

<https://doi.org/10.1038/s44456-026-00019-z>

Ferrocene-functionalized covalent organic framework exceeding the ultimate hydrogen storage targets: a first-principles multiscale computational study

Marcus Djokic¹ & Jose L. Mendoza-Cortes^{1,2}✉

The development of efficient hydrogen storage materials is crucial for advancing the hydrogen economy and meeting the U.S. Department of Energy's targets of 6.5 wt% and 50 g L⁻¹ for automotive applications. We present a computational study of ferrocene-functionalized covalent organic frameworks (COFs) for hydrogen storage. Following the **Multi-binding Sites United in Covalent-Organic Framework** (MSUCOF) approach, we introduce MSUCOF-4-FeCp, designed by incorporating ferrocene (FeCp₂) moieties into IRCOF-102. Notably, it achieves exceptional performance with total gravimetric and volumetric uptakes of 18.0 wt% and 72.6 g L⁻¹ at 298 K and 700 bar. The material exhibits optimal binding energies (15–20 kJ·mol⁻¹) ensuring both high total uptake and a high working capacity. This work establishes ferrocene functionalization as a cost-effective alternative to precious metal incorporation in COFs.

The urgent need for sustainable energy solutions positions hydrogen as a promising clean energy carrier, capable of addressing both energy security and environmental concerns associated with the dependence on fossil fuels. However, the widespread adoption of hydrogen as a transportation fuel faces significant challenges, particularly in developing safe, efficient, and cost-effective storage systems. The U.S. Department of Energy (DOE) has established ambitious targets for hydrogen storage in light-duty vehicles: 6.5 wt% gravimetric capacity and 50 g L⁻¹ volumetric capacity, with the overarching goal of reducing clean hydrogen costs to \$1 per kilogram by 2031^{1,2}.

Covalent organic frameworks (COFs) have emerged as particularly promising candidates for hydrogen storage applications due to their high surface areas, tunable pore structures, and composition primarily of light elements³. Unlike their metal-organic framework (MOF) counterparts, COFs offer the advantage of lower framework density while maintaining structural integrity and thermal stability. The crystalline nature of COFs allows for precise control over the size and functionality of pores, allowing rational design approaches to optimize their hydrogen uptake properties^{4,5}.

Recent advances in COF chemistry have demonstrated that hydrogen storage performance can be significantly enhanced through strategic incorporation of functional groups and heteroatoms^{6,7}. The introduction of open metal sites and polarizing groups has been shown to strengthen van der Waals (VdW) interactions with hydrogen molecules, thus improving binding

enthalpies and storage capacities^{8,9}. First-principles studies have likewise shown that functionalizing nanoporous frameworks with light or transition metals, for example Li-functionalized MOFs and metal-cluster frameworks, markedly enhances reversible hydrogen uptake^{10–12}. However, achieving the optimal balance between gravimetric and volumetric performance remains a central challenge, as strategies to increase volumetric uptake often lead to increased framework density and reduced gravimetric capacity¹³.

Metallocenes represent a unique class of organometallic compounds characterized by their distinctive “sandwich” structure, where a central metal atom is coordinated to two cyclic organic ligands. The discovery of ferrocene in 1951 by Kealy and Pauson¹⁴ revolutionized organometallic chemistry and earned its structural elucidators, Geoffrey Wilkinson¹⁵ and Ernst Otto Fischer¹⁶, the 1973 Nobel Prize in Chemistry¹⁷. Ferrocene (Fe(η⁵–C₅H₅)₂) exhibits remarkable thermal stability (stable to 400 °C), chemical inertness, and well-defined electrochemical properties with a reversible Fe²⁺/Fe³⁺ redox couple at +0.4 V vs. SCE¹⁸. In ferrocene, the iron center is sandwiched between two cyclopentadienyl (Cp) rings: aromatic, planar five-membered carbocyclic anions (C₅H₅⁻) that each bind the metal in a pentahapto (η⁵) fashion through all five carbon atoms, an arrangement responsible for the complex's well-defined geometry and exceptional stability.

The electronic structure of ferrocene, governed by the 18-electron rule, provides multiple potential binding sites for small molecules; these binding

¹Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI, USA. ²Department of Physics and Astronomy, Michigan State University, East Lansing, MI, USA. ✉e-mail: jmendoza@msu.edu

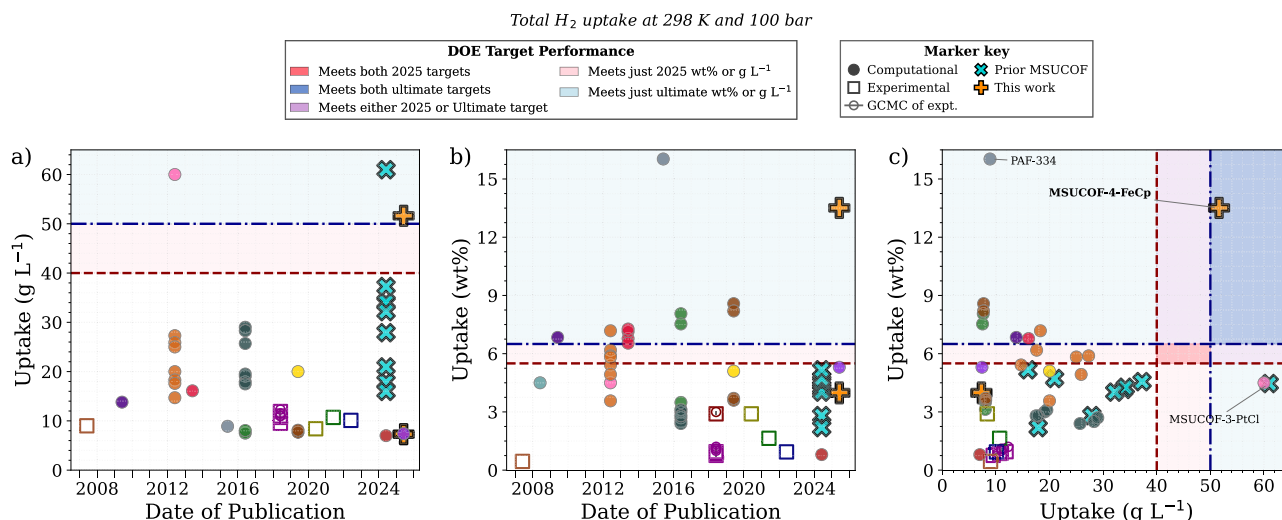


Fig. 1 | Leading porous-material hydrogen-storage performance benchmarked against the U.S. Department of Energy (DOE) light-duty-vehicle targets². All points are total H₂ uptake at 298 K and 100 bar; only room-temperature (293–298 K) data are included, and the 100 bar ceiling matches the literature, which overwhelmingly reports isotherms up to ≤100 bar. **a** Volumetric and **b** gravimetric uptake versus publication year, and **c** volumetric versus gravimetric uptake (the storage-density trade-off). Marker shape encodes data type (filled circles,

computational GCMC/DFT; open squares, experimental); a light blue cross marks our prior MSUCOF study³¹ and an orange plus marks the present work. Gray tie-lines link each experimental point to an independent GCMC simulation of the same material, and identical colors denote a common source; all plotted values and references are listed in SI Table S4^{25,27,28,57–71}. At 298 K and 100 bar, MSUCOF-4-FeCp reaches 51.6 g L^{−1} and 13.5 wt%, the only material here to exceed both DOE Ultimate targets (50 g L^{−1} and 6.5 wt%) simultaneously.

sites have been exploited across various porous materials. Ferrocene-functionalized MOFs have already been synthesized, utilizing the redox-active iron center to enable photocatalytic reduction of CO₂ with enhanced electron transfer capabilities¹⁹. Similarly, microporous polymers containing ferrocene demonstrate improved storage of CO₂ through the synergistic effects of microporosity and metal-ligand interactions²⁰. Analogously, superior hydrogen storage performance has also been reported for ferrocene-derived porous carbons²¹.

The versatility of ferrocene extends beyond simple gas adsorption: it fundamentally alters electronic density distributions, spatial arrangements, and coordination environments within composite materials, thereby modulating catalytic activity for HER/OER reactions²². In hypercrosslinked polymers, ferrocene incorporation achieves enhanced H₂ adsorption through a dual mechanism; the abundant micropores provide high surface area, while Fe centers offer strong binding sites via Coulombic Fe–H₂ interactions and favorable spin states²³. Theoretical studies reveal that low-spin Fe²⁺ centers, as found in ferrocene, can achieve up to a fourfold enhancement in H₂ loading compared to high-spin configurations²⁴.

The iron center can engage in direct coordination interactions, while the cyclopentadienyl rings contribute π -electron density for additional binding modes. This dual-site accessibility makes ferrocene an attractive candidate for gas storage applications because it can potentially interact with multiple hydrogen molecules simultaneously without compromising structural integrity.

Previous studies have shown that iron-containing binding sites can achieve hydrogen binding energies in the optimal range of 15–25 kJ·mol^{−1}, sufficient for room-temperature storage while allowing facile desorption²⁴. The key advantage of ferrocene over other iron-containing species lies in its exceptional stability and well-defined coordination environment, which should maintain consistent binding properties throughout storage-desorption cycles.

The incorporation of transition metals into COF structures has been demonstrated to enhance hydrogen storage performance through enhanced adsorbate-framework interactions⁹. However, most successful approaches have relied on expensive precious metals, such as platinum and palladium, limiting practical implementation²⁵. Iron-based systems offer a compelling alternative that combines favorable electronic properties with abundant availability and low cost. Iron costs on the order of \$0.1 per kilogram, several

orders of magnitude less than platinum (tens of thousands of dollars per kilogram) at the time of writing²⁶.

In the search for a room temperature storage material, researchers often report gravimetric uptake (wt%) up to 100 bar, as this metric prioritizes maximum energy density with minimal added weight. The evolution of this field is exemplified in Fig. 1. Early efforts produced materials with exceptional volumetric capacity (Fig. 1a). The subsequent shift toward prioritizing gravimetric performance has driven exponential improvements among leading MOFs and COFs (Fig. 1b), yet this optimization often comes at the expense of volumetric performance. This inherent trade-off is illustrated in Fig. 1c: the most successful materials to date approach either the DOE volumetric or gravimetric target, but not simultaneously both. For example, both taps-COF-1²⁷ and tapa-COF-1²⁸ successfully exceed the 6.5 wt% (ultimate gravimetric target) yet achieve less than 20% of the DOE ultimate volumetric target of 50 g L^{−1}.

Strong binding sites that enhance volumetric capacity typically require heavy metal centers or dense framework designs that penalize gravimetric metrics. Our ferrocene functionalization strategy circumvents this limitation by introducing highly effective binding sites with minimal mass contribution, enabling MSUCOF-4-FeCp to achieve both volumetric and gravimetric targets; a milestone that, to the best of our knowledge, no other porous framework has been reported to reach at room temperature without cryogenic cooling or a temperature swing (Fig. 1).

IRCOF-102 was selected as the baseline framework for ferrocene functionalization due to its robust three-dimensional boroxine-linked topology. As an isorecticular (IR) extension²⁹ of COF-102,³⁰ IRCOF-102 maintains the same tetrahedral node geometry and boroxine chemistry while incorporating extended biphenyl linkers in place of single phenyl units. The framework, constructed from tetrakis(4'-borono-[1,1'-biphenyl]-4-yl)methane (Linker 1), provides larger pores and higher surface area than the parent structure while preserving the synthetic accessibility and stability of COF-102.

Our design strategy employs tetrakis(4-(4-boroninden-7-yl)phenyl)methane (Linker 2), where the fused cyclopentadienyl ring provides the coordination environment for the formation of ferrocene while the boronic acid at the 4-position enables the condensation of boroxine. This 4,7-substitution maintains a para relationship preserving the linear geometry critical for framework assembly. The framework is designated MSUCOF-4-

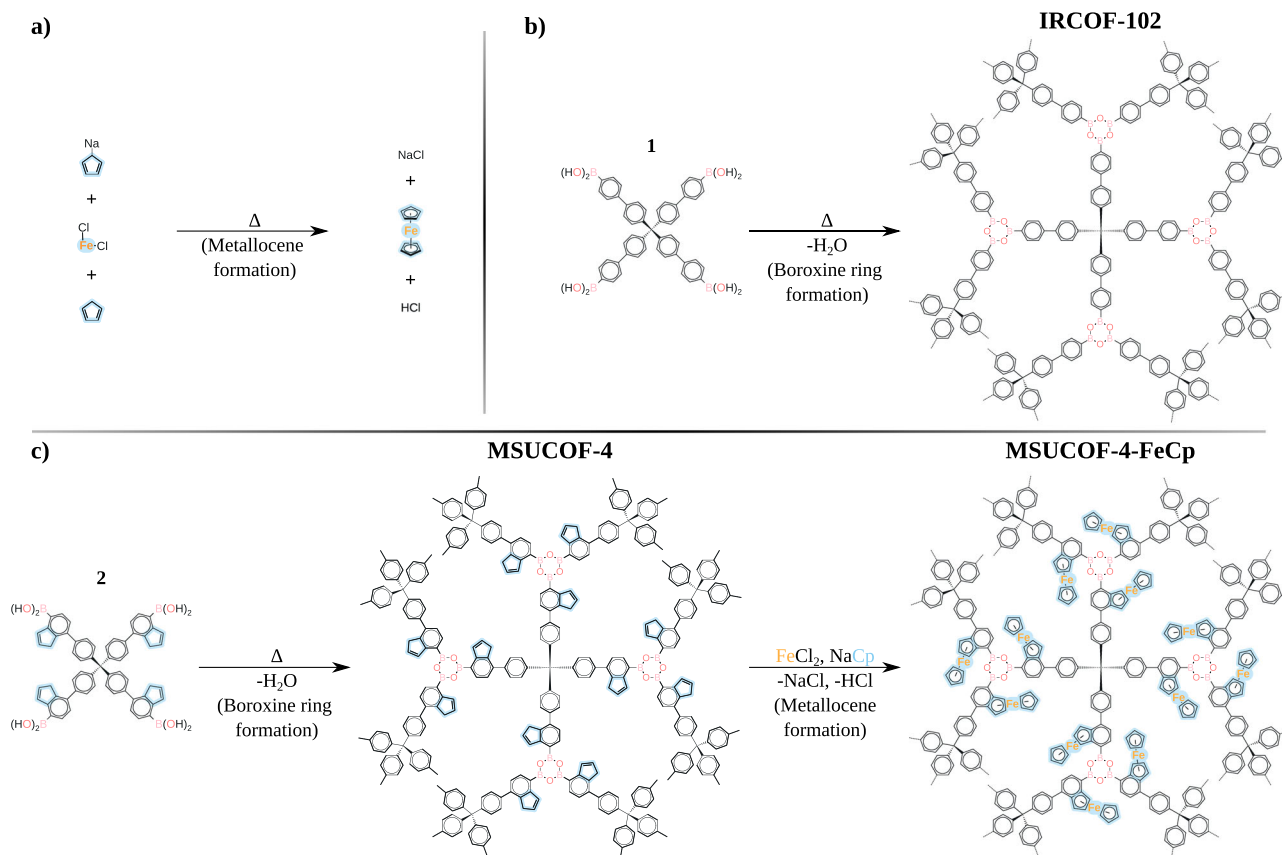


Fig. 2 | Schematic illustration of framework synthesis and post-synthetic metallation. **a** (Top left) Representative metalloocene formation reaction, $\text{FeCl}_2 + \text{Cp} + \text{NaCp} \rightarrow \text{NaCl} + \text{FeCp} + \text{HCl}$. **b** (Top right) Boroxine condensation of tetrakis(4'-borono-[1,1'-biphenyl]-4-yl)methane (Linker 1) to form IRCOF-102. **c** (Bottom) Boroxine ring formation of tetrakis(4-(4-boroninden-7-yl)phenyl)

methane (Linker 2) to yield MSUCOF-4, a modified variant of IRCOF-102 in which biphenyl units are replaced by indene moieties; the cyclopentadienyl (Cp) portion of the indene linker is highlighted in light blue. Subsequent post-synthetic metalloocene formation affords the metallated framework MSUCOF-4-FeCp. Atom colors: Fe (orange), B (pink), O (red), and C (black).

FeCp instead of MSUCOF-4-FeCp₂ as a Cp ring is integrated within Linker 2, with only the second Cp ring and the Fe center added post-synthetically.

Ferrocene units are located within tritopic pore regions, where three framework struts converge around each boroxine linkage (Fig. 2). These tritopic arrangements create cooperative binding environments that enhance binding energies without reaching chemisorption,³¹ with ferrocene moieties providing multiple binding sites (Fe centers and Cp rings) for complementary hydrogen interactions.

The preferred synthetic route involves the condensation of Linker 2 to form MSUCOF-4, followed by post-synthetic metallation with FeCl_2 and NaCp to produce MSUCOF-4-FeCp. This approach enables comprehensive characterization before metallation and avoids the potential coordination of iron with boroxine-forming groups during synthesis. The transformation proceeds through the deprotonation of the cyclopentadiene ring already in MSUCOF-4 to generate Cp^- , which coordinates with Fe^{2+} and an additional Cp^- (from NaCp) to form the ferrocene unit without sterically hindering pore accessibility. The post-synthetic strategy offers superior control over framework formation and metal incorporation³².

Because the metalation reagents (FeCl_2 and NaCp) are themselves moisture-sensitive and are handled under the strictly anhydrous, inert conditions standard for metalloocene formation, the hydrolytically labile boroxine network is not exposed to the aqueous conditions that drive its degradation, and post-synthetic metallation is by now a well-established route for both metal-organic and COFs^{33–35}. Should the boroxine framework nonetheless prove insufficiently robust to the metalation conditions, the ferrocene functionalization is transferable to hydrolytically more stable isorecticular linkages, since the Fe-H_2 interaction responsible for the enhanced uptake does not depend on the linkage chemistry.

Results and discussion

Structural properties and design validation

Incorporation of ferrocene into the IRCOF-102 framework results in MSUCOF-4-FeCp, which has well-defined structural properties that support high hydrogen storage performance. As shown in Table 1, MSUCOF-4-FeCp maintains a high surface area of $4780 \text{ m}^2 \text{ g}^{-1}$ while achieving a balanced pore volume of $2.55 \text{ cm}^3 \text{ g}^{-1}$ and a void fraction of 0.84. The framework density of 0.33 g cm^{-3} is significantly lower than the precious metal-functionalized variants, contributing to enhanced gravimetric performance. For comparison, structural and uptake results for MSUCOF-(1–3) from our previous work³¹ are included. Surface areas and pore volumes were determined using a hydrogen-sized probe rolling across the VdW surface of each framework (Fig. S1; see Supplementary Note 1 for details).

Pristine COFs often suffer from poor binding energies at room-temperature. Strategies to address this limitation include functionalization, such as incorporating ferrocene onto the ligands. Not only does this strategy inject strong binding sites throughout the pore, it does so without an excessive binding strength that can compromise the working capacity (see the “Binding energy analysis and mechanisms” section).

It is important to note that MSUCOF-4 incorporates one cyclopentadienyl ring as an extended variant of the linkers present in IRCOF-102, yet it lacks the complete $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ moiety found in MSUCOF-4-FeCp. This partial functionalization accounts for the intermediate geometric properties observed: MSUCOF-4 shows reduced surface area (4840 vs $5680 \text{ m}^2 \text{ g}^{-1}$), pore volume (4.14 vs $5.11 \text{ cm}^3 \text{ g}^{-1}$), and void fraction (0.88 vs 0.90) compared to pristine IRCOF-102. However, as shown in subsequent sections, MSUCOF-4 still exhibits hydrogen storage performance comparable to IRCOF-102 despite these geometric differences. This indicates

that the exceptional performance of MSUCOF-4-FeCp is primarily due to the ferrocene complex-hydrogen interactions rather than purely geometric factors.

Electronic structure calculations

The electronic properties of the pristine IRCOF-102 and functionalized MSUCOF-4-FeCp were studied and visualized by calculating the band structure and the density of states (Fig. 3). For these calculations, we follow the methods described for the periodic framework calculations in the Methods. These calculations were performed using spin unrestricted DFT, allowing α and β orbitals to vary to capture any potential magnetic ordering. These MSUCOF-4 and IRCOF-102 families of materials follow the $I\bar{4}3d$ space group (No. 220); accordingly the reciprocal space was sampled in the high symmetry path $\Gamma\text{--H--N--}\Gamma\text{--P--H}|\text{P--N}$ as determined by SeeKPath to capture the relevant band dispersion³⁶. The atom-projected density of states will reveal the atomic contributions at frontier bands.

Table 1 | Comparison of geometric properties of selected MSUCOFs

COF name	Surface area (m ² g ^{−1})	Pore volume (cm ³ g ^{−1})	Void fraction	Density (g cm ^{−3})
MSUCOF-1	5060	5.06	0.91	0.18
MSUCOF-1-PtCl ₂	2890	2.09	0.88	0.42
MSUCOF-3-CoCl	3770	0.94	0.73	0.78
MSUCOF-3-PtCl	2190	0.55	0.72	1.31
IRCOF-102	5680	5.11	0.90	0.18
MSUCOF-4	4840	4.14	0.88	0.22
MSUCOF-4-FeCp	4780	2.55	0.84	0.33

These results show expected trends for porous materials. In both materials, many of the bands exhibit minimal band dispersion (flat bands with no spin asymmetry); the valence-band edge of MSUCOF-4-FeCp, for instance, disperses by only about 3 meV across the Brillouin zone. This flatness is a real-space localization effect rather than a signature of an engineered flat-band lattice: the boroxine nodes and aromatic struts are joined by long covalent bridges spanning the large pores, so the orbital overlap between neighboring building units, and hence the inter-unit transfer integral that sets the band width, is negligible, leaving the frontier states essentially molecular and fragment-localized. The large cubic $I\bar{4}3d$ cell folds many of these molecular-like levels into closely spaced bands, increasing their number without flattening them, while ferrocene functionalization adds a second, sharper localization at the valence-band edge, where the mutually isolated metallocene units provide no Fe-Fe pathway across the cell.

Additionally, IRCOF-102 displays a band gap large enough to classify it as an insulator ($E_g = 4.10$ eV), which is consistent with its composition of light main-group elements (C, B, O) engaged in saturated covalent bonding. MSUCOF-4-FeCp acts as a functionalized variant with $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ additions in tritopic regions within the pore. By adding this moiety, MSUCOF-4-FeCp experiences a more narrow band gap of $E_g = 3.02$ eV (notably 410 nm in the visible light range), enhancing its potential for electronic and catalytic applications.

Analysis of the HOMO and LUMO character of MSUCOF-4-FeCp reveals that the valence band edge is predominantly Fe-centered, with contributions from Fe(d) and C(p) orbitals of the cyclopentadienyl rings. Meanwhile, the conduction band edge is localized on an organic framework, primarily C(p,d), with minor contributions from B(p), Fe(d), and H(p). This spatial separation of frontier orbitals is indicative of metal-to-ligand charge transfer, suggesting that photoexcitation would generate oxidized Fe centers and reduced organic sites. These charge-separated states are favorable for both photocatalysis and electrocatalysis, as is common with ferrocene-based systems. These localized redox-active sites are typical of molecular catalysts embedded in porous frameworks and do not preclude efficient catalysis, where electron transfer occurs at discrete metal centers rather than through band-like transport.

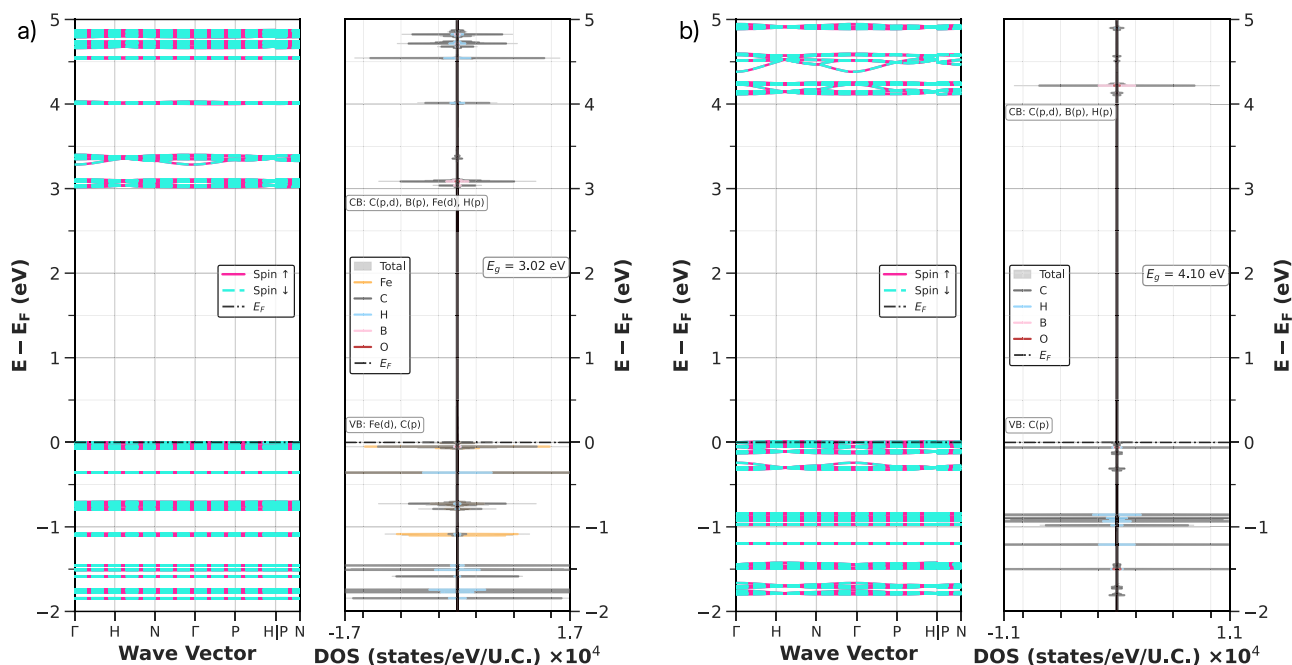


Fig. 3 | Electronic structure of MSUCOF-4-FeCp and IRCOF-102. Band structure (left) and density of states (right) are shown for **a** MSUCOF-4-FeCp and **b** IRCOF-102. Both materials exhibit flat bands typical of porous materials. Functionalization in MSUCOF-4-FeCp narrows the band gap, enhancing the potential for electronic or catalytic applications.

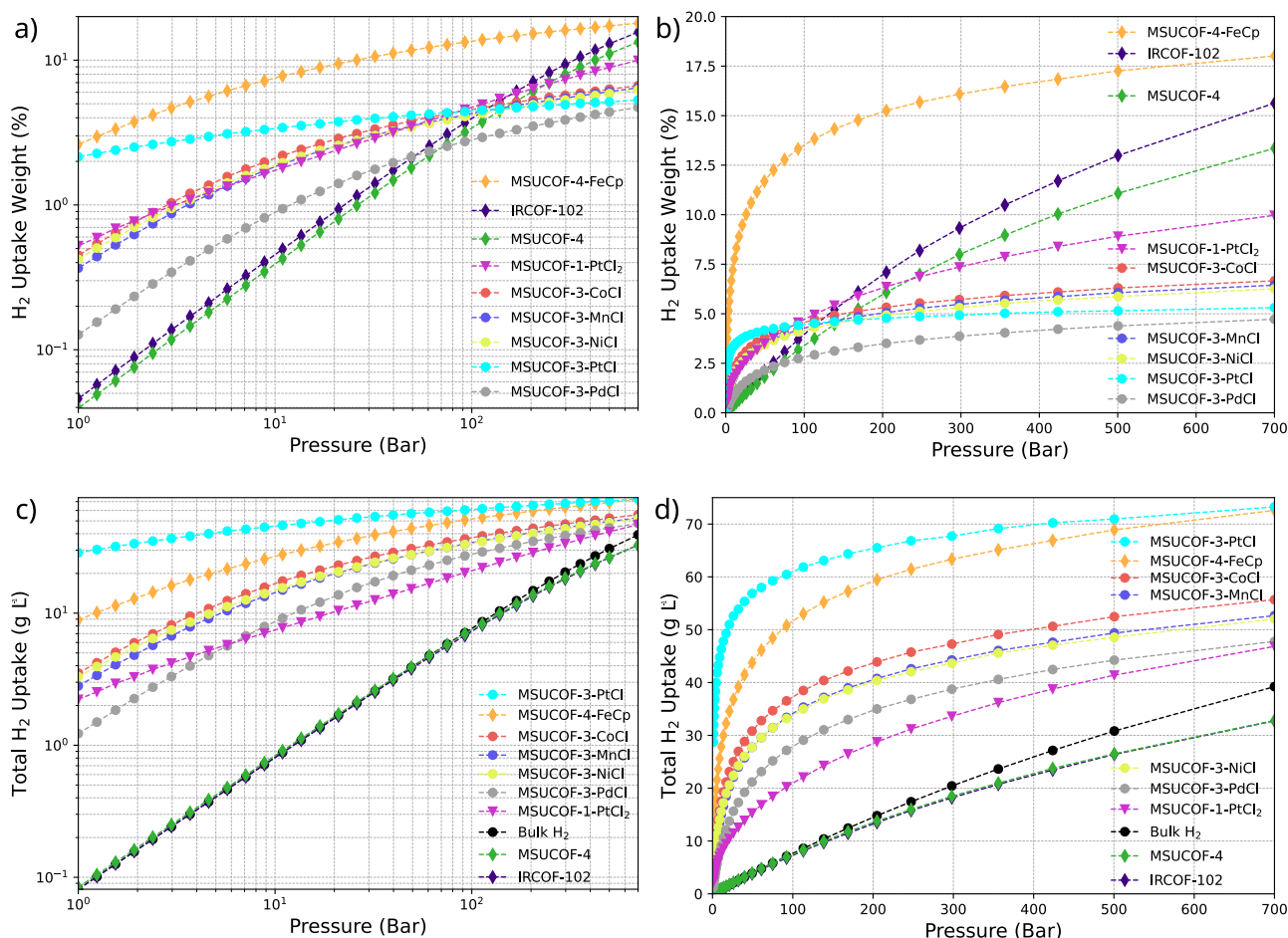


Fig. 4 | Comparison of total gravimetric and volumetric hydrogen uptake at 298 K for the MSUCOF-4 family against top-performing MSUCOF variants. Gravimetric uptake is shown in (a, b) and volumetric uptake in (c, d). Log-log plots

(a, c) provide detail in the low-pressure region, while linear plots (b, d) show high-pressure behavior. MSUCOF-4-FeCp demonstrates superior performance across all pressure ranges.

Hydrogen storage performance

The hydrogen storage performance of MSUCOF-4-FeCp demonstrates exceptional promise in meeting DOE targets. Figure 4 presents both gravimetric and volumetric uptake isotherms at 298 K, showing that MSUCOF-4-FeCp achieves a total hydrogen uptake of 18.0 wt% and 72.6 g L⁻¹ at 700 bar. This performance represents a significant improvement over the parent IRCOF-102, and the gravimetric uptake is approximately 3.5 times higher than that of the denser MSUCOF-3-PtCl variant. We chose to measure up to these pressures because 700 bar (70 MPa) is the established commercial standard for onboard hydrogen storage: the Toyota Mirai stores 5.6 kg H₂ in three 70 MPa carbon-fiber-reinforced tanks (EPA range up to 402 mi, 647 km) and the Hyundai NEXO stores 6.3 kg H₂ in three 70 MPa tanks (up to 380 mi, 611 km), both fueled to the SAE J2601 70 MPa protocol³⁷.

Three complementary uptake metrics are reported throughout this work. *Total* (absolute) uptake, n^{abs} , counts all H₂ molecules held within the framework. *Excess* uptake subtracts the amount of bulk H₂ that would occupy the accessible pore volume at the same temperature and pressure, $n^{\text{exc}} = n^{\text{abs}} - V_{\text{pore}} \rho_{\text{H}_2}^{\text{bulk}}$, and most closely reflects what gravimetric adsorption experiments measure; the accessible volume is computed with a 1.445 Å probe (half the H₂ kinetic diameter), with inaccessible pore regions excluded (see “Methods” and Supplementary Note 1). *Net* uptake applies the stricter correction of the full unit-cell volume, $n^{\text{net}} = n^{\text{abs}} - V_{\text{cell}} \rho_{\text{H}_2}^{\text{bulk}}$, so that a positive value indicates a storage advantage, at the material level, over an empty pressure vessel of identical volume. Bulk H₂ densities $\rho_{\text{H}_2}^{\text{bulk}}$ are taken from the NIST Chemistry WebBook³⁸.

Total uptake therefore sets an upper bound, excess an intermediate (pore-referenced) measure, and net the most conservative material-level benchmark (it still references the crystallographic unit cell, not a packed storage system); we report all three to avoid the ambiguity that arises when only one is quoted (see Supplementary Note 4).

Working capacity (WC)—defined as the amount of hydrogen that can be practically delivered between high storage pressure (700 bar) and rough delivery pressure (5 bar)—is a critical heuristic to approximate realistic delivery that can be obtained in a reasonable time frame. Unlike MSUCOF-3-PtCl, which detrimentally locks hydrogen even at low pressures, MSUCOF-4-FeCp maintains a balanced adsorption profile that ensures a higher WC.

The log-log total uptake plots (Fig. 4a, c) best capture low pressure adsorption behavior, where the linear response reflects the Henry regime in which uptake scales proportionally with pressure. Sub-linear behavior develops as saturation effects emerge, ultimately reaching a plateau that is characteristic of Langmuir-like saturation. In contrast, the linear plots (Fig. 4b, d) better resolve high pressure behavior. These complementary representations reveal distinct material characteristics: strong adsorbents such as MSUCOF-3-PtCl dominate at low pressure, but also saturate earlier.

In terms of volumetric uptake (Fig. 4b), MSUCOF-4-FeCp retains less H₂ at low pressures than MSUCOF-3-PtCl, but still more than the first-row transition metal (TM) chelation complexes of MSUCOF-3-TMCl. However, the linear volumetric uptake plot (Fig. 4d) reveals that MSUCOF-4-FeCp approaches the energy density of MSUCOF-3-PtCl at high pressures. This balance is critical for volumetric working capacities (WC_v): MSUCOF-4-FeCp achieves 52.2 g L⁻¹, surpassing all previous variants of MSUCOF-

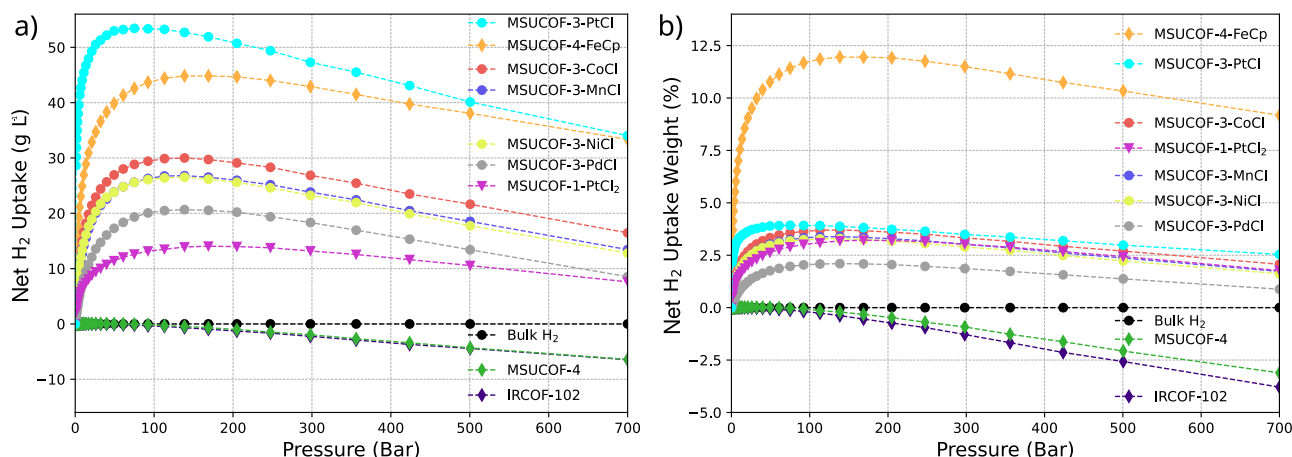


Fig. 5 | Comparison of net volumetric and gravimetric uptake at 298 K for the MSUCOF-4 family against top-performing MSUCOF variants. a Net volumetric and **b** net gravimetric uptake versus pressure; each curve peaks at its optimal storage

pressure, and the bare frameworks (MSUCOF-4 and IRCOF-102) fall below zero at high pressure. MSUCOF-4-FeCp achieves the highest net gravimetric uptake, and a net volumetric uptake second only to the denser MSUCOF-3-PtCl.

Table 2 | Working capacity performance metrics for select MSUCOF variants at 298 K

Material	P_{opt} (bar)	WC_g (wt%)	WC_v (g L ⁻¹)
MSUCOF-1-PtCl ₂	169	8.71	41.4
MSUCOF-3-CoCl	139	5.22	44.3
MSUCOF-3-MnCl	139	5.20	43.1
MSUCOF-3-NiCl	130	4.95	41.7
MSUCOF-3-PdCl	139	4.20	42.7
MSUCOF-3-PtCl	75	2.29	32.6
IRCOF-102	3	15.4	32.4
MSUCOF-4-FeCp	145	12.2	52.2
DOE Targets			
2025	—	5.5	40.0
Ultimate	—	6.5	50.0

P_{opt} denotes the optimal pressure at which net uptake is maximized, WC_g and WC_v represent gravimetric and volumetric working capacities (700 bar to 5 bar), respectively. Bold indicates MSUCOF-4-FeCp, the framework introduced in this work.

1–3 (32.6–44.3 g L⁻¹) by accumulating substantial H₂ at high pressures without detrimentally locking it in low pressures. Despite its exceptional total volumetric uptake, MSUCOF-3-PtCl hinders its own WC_v to 32.6 g L⁻¹ precisely for this reason.

The spacious unit cell inherited from IRCOF-102 (roughly 4× the volume of MSUCOF-3) reduces the density of the framework, allowing MSUCOF-4-FeCp to achieve its high volumetric performance without sacrificing its gravimetric uptake. Gravimetric uptake increases from 5.8 wt % at 5 bar to 18.0 wt% at 700 bar, yielding a gravimetric working capacity (WC_g) of 12.2 wt%. The low-density MSUCOF-2 family achieves 11.4–18.9 wt% WC_g but suffers from poor volumetric performance (33.2–38.7 g L⁻¹), while the pristine IRCOF-102 (15.4 wt%, 32.4 g L⁻¹) closely matches the pristine MSUCOF-1 (15.2 wt%, 32.4 g L⁻¹). Thus, among porous frameworks reported at room temperature, MSUCOF-4-FeCp uniquely satisfies both DOE ultimate targets (6.5 wt% and 50 g L⁻¹) at room temperature.

The net uptake metric provides another crucial performance indicator by comparing the porous material with compressed bulk hydrogen under identical conditions. Positive net uptake values indicate that the

incorporation of the porous material provides a storage advantage over simple compression, while negative values suggest that the added weight and volume of the material actually reduce overall storage efficiency. Excess uptake isotherms, which apply a less stringent correction using only the accessible pore volume, are provided in Fig. S3.

The net uptake plot (Fig. 5) reveals peaks at optimal pressures (P_{opt}) that reflect the interplay between binding strength and saturation behavior. MSUCOF-4-FeCp achieves $P_{\text{opt}} = 145$ bar; substantially higher than MSUCOF-3-PtCl ($P_{\text{opt}} = 75$ bar), which saturates prematurely due to its stronger binding and smaller pores, yet comparable to the dense first-row TM variants of MSUCOF-3 ($P_{\text{opt}} \approx 130$ –139 bar). Crucially, MSUCOF-4-FeCp maintains positive net uptake across a broad pressure range, validating that the enhanced ferrocene binding interactions more than compensate for the framework's mass and volume even at 700 bar. These metrics are summarized in Table 2. Based on this WC, several variants of MSUCOF achieve either the 2025 DOE gravimetric or volumetric target, but among them MSUCOF-4-FeCp remains the only reported framework to satisfy both ultimate targets (6.5 wt% and 50 g L⁻¹).

Binding energy analysis and mechanisms

Analysis of isosteric heat of adsorption (Q_{st}) shows that MSUCOF-4-FeCp has a heterogeneous, loading-dependent binding-energy distribution centered in the intermediate physisorption regime (Fig. 6), a range well-suited for room-temperature storage that balances adsorption strength against release at the delivery pressure rather than representing a single optimal value. Interestingly, the binding energy profile is similar to that of MSUCOF-3-CoCl, a material that we previously recognized for its superior WC. Moderate binding strengths (7–20 kJ·mol⁻¹) allow efficient hydrogen adsorption at high pressures without locking hydrogen into the structure. The physisorption-to-chemisorption transition is gradual; the 20 kJ·mol⁻¹ line marks the onset of chemisorption rather than full dissociative chemisorption, which requires substantially higher binding energies.

From the GCMC simulations, we can derive a probability distribution $P(E)$ that illustrates the proportions of adsorbed H₂ molecules experiencing interaction energy E at thermodynamic equilibrium. This distribution satisfies the normalization condition:

$$\int_{-\infty}^{\infty} P(E) dE = 1 \quad (1)$$

In Eq. (1), the negative integration limits are associated with energies that correspond to attractive interactions, while any interaction greater than zero is repulsive. The isosteric heat of adsorption is directly tied to the

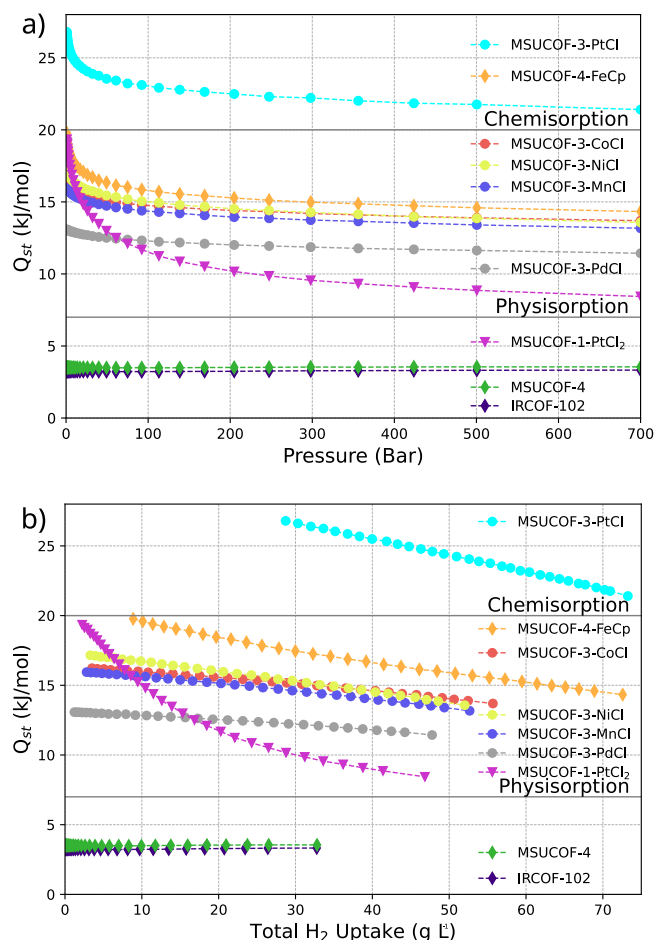


Fig. 6 | High-pressure H₂ isosteric heat of adsorption at 298 K. Q_{st} is plotted versus **a** pressure and **b** total H₂ uptake, showing optimal binding-energy characteristics for MSUCOF-4-FeCp, which lies entirely between chemi- and physisorption for H₂.

ensemble-averaged interaction energy through:

$$Q_{st} = -\langle E \rangle = - \int_{-\infty}^{\infty} E \cdot P(E) dE \quad (2)$$

This relationship (Eq. (2)) shows that Q_{st} represents the mean of the energy distribution. Note the negative sign that converts the interaction energy to a positive heat of adsorption, following the standard reporting convention. Then it follows that the variance of the distribution can be calculated with the following.

$$\sigma^2 = \int_{-\infty}^{\infty} (E - \langle E \rangle)^2 \cdot P(E) dE \quad (3)$$

Equation (3) quantifies the diversity of binding sites within the framework. A larger variance indicates a broader range of binding environments, which can be advantageous for maintaining adsorption across various pressure levels.

The analysis of the energy distribution shed light on the binding mechanisms within select MSUCOFs (Fig. 7). At 1 bar, the distribution shows a primary broad peak with a long tail towards 0, indicating that the majority of initial interactions occur at favorable primary binding sites, while few stragglers permeate the pore and interact at weaker sites. At higher pressures, there is a clear right shift of both the overall average binding strength (Q_{st}) and the average of each individual site (μ_i) as they begin to saturate. When secondary peaks appear as shoulders on the primary distribution, accurate quantification requires a method to de-convolute the

isolated individual contributions. Each peak i is fitted with an asymmetric (skewed) Gaussian function:

$$P_i(E) = \begin{cases} A_i \exp\left(-\frac{(E-\mu_i)^2}{2\sigma_{L,i}^2}\right) & \text{for } E \leq \mu_i \\ A_i \exp\left(-\frac{(E-\mu_i)^2}{2\sigma_{R,i}^2}\right) & \text{for } E > \mu_i \end{cases} \quad (4)$$

where A_i is the amplitude, μ_i is the center (mean energy), and $\sigma_{L,i}$ and $\sigma_{R,i}$ are the widths left and right, respectively. This asymmetric form captures the characteristic skewness of the interaction energy distributions. All peaks are fitted simultaneously using a composite model to avoid double-counting in overlapping regions while preserving an accurate determination of individual binding site energies. In Eq. (5), N is the number of peaks.

$$P(E) = \sum_{i=1}^N P_i(E) \quad (5)$$

The average energy for each de-convoluted peak is given by its fitted Gaussian mean μ_i :

$$\langle E \rangle_{\text{peak},i} = \mu_i \quad (6)$$

This approach provides site-specific energies that are more accurate than simple numerical integration over peak boundaries, which can be biased by overlapping contributions from adjacent peaks. The fraction of H₂ molecules that experience energies within the peak i is shown in Eq. (7). The individual Gaussian component $P_i(E)$ is integrated throughout the energy range and normalized by the total area under $P(E)$ to determine the fraction of molecules that experience that particular binding mode.

$$f_{\text{peak},i} = \frac{\int_{-\infty}^{\infty} P_i(E) dE}{\int_{-\infty}^{\infty} P(E) dE} \quad (7)$$

At 1 bar, the main peak for MSUCOF-4-FeCp, which is centered around $-18.8 \text{ kJ}\cdot\text{mol}^{-1}$ ($-4.5 \text{ kcal}\cdot\text{mol}^{-1}$), highlights the dominant Fe-H₂ interaction. Any unusual features at weaker binding energies likely stem from any of the following: geometries that are sterically constrained; shielded H₂-H₂ interactions; compounded effects at key overlapped regimes amongst tritopic regions; or interactions with the cyclopentadienyl rings.

When pressure increases to 700 bar, the distribution shows two distinct peaks at -13.2 and $-7.7 \text{ kJ}\cdot\text{mol}^{-1}$ (-3.2 and $-1.8 \text{ kcal}\cdot\text{mol}^{-1}$), which relate to different binding environments within the ferrocene coordination sphere. The predominant broad peak at $-13.2 \text{ kJ}\cdot\text{mol}^{-1}$ likely corresponds to coordination with the low-spin Fe²⁺ center in ferrocene, which theoretical studies have shown provides enhanced H₂ binding compared to high-spin configurations²⁴. Likewise, the sharp peak at $-7.7 \text{ kJ}\cdot\text{mol}^{-1}$ can be partially attributed to previously mentioned weaker binding regimes that serve as a backup when the primary binding modes saturate.

As pressure evolves, $P(E)$ shows a sequential occupation of binding sites based on their relative affinities. At low pressures, mainly the strongest sites (leftmost region of $P(E)$) are populated, resulting in higher average binding energies. As pressure increases and strong sites saturate, weaker sites begin to dominate, shifting the distribution toward less negative energies and reducing the ensemble-averaged Q_{st} .

This sequential picture, previously inferred from the binding energies alone, is substantiated directly. By decomposing the real GCMC snapshots into the first and second ferrocene solvation shells, the non-ferrocene framework motifs, and the open pore (Supplementary Note 7, Figs. S6–S8), we find that the first shell supplies the dominant strong-binding population at every pressure ($\langle E \rangle \approx -16$ to $-18 \text{ kJ}\cdot\text{mol}^{-1}$; 78% of adsorbed H₂ at 1 bar and still 47% at 700 bar), while the growth of the weaker feature reflects the progressive filling of the second shell and the open pore as the first shell saturates. The second ferrocene shell remains more strongly bound than the

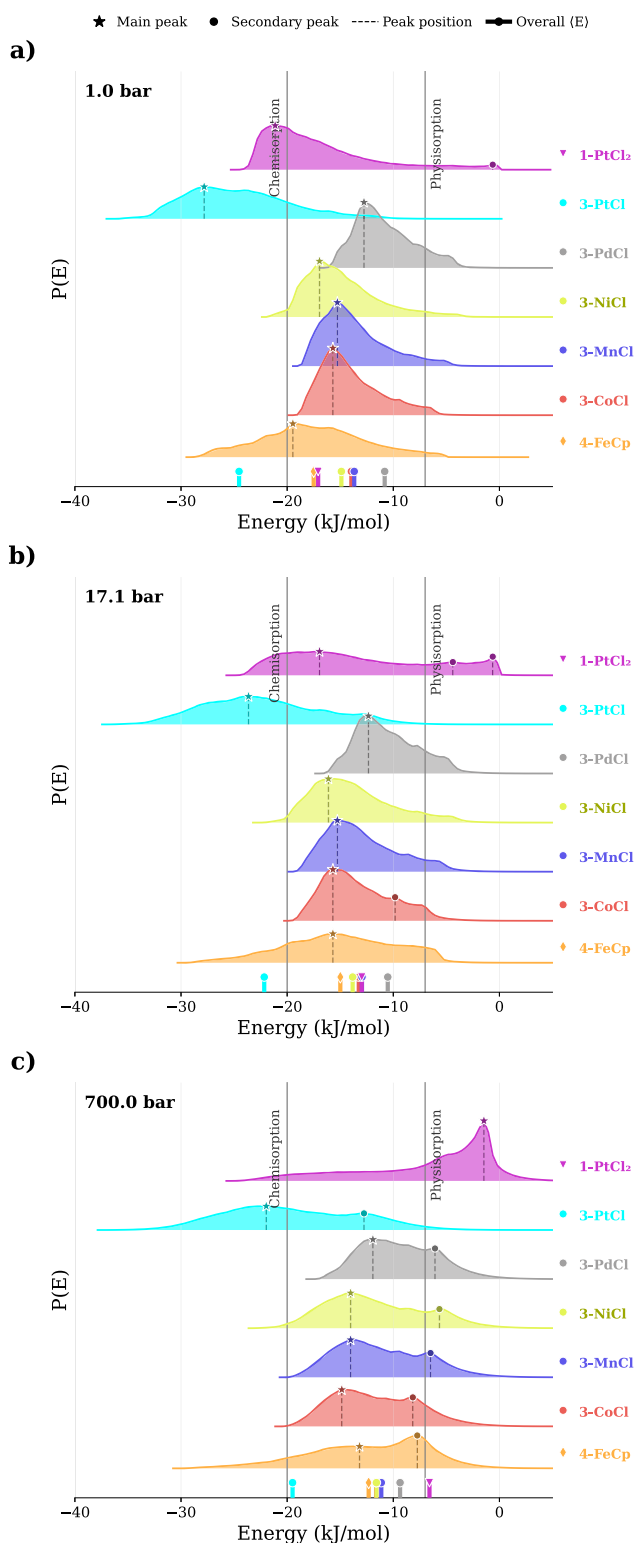


Fig. 7 | Ridge plot of H_2 interaction energy distributions at 1, 17.1, and 700 bar. Distributions $P(E)$ are shown at **a**, **b** 17.1, and **c** 700 bar; curves are vertically offset for clarity. Solid stars and open circles mark primary and secondary Q_{st} peaks, respectively. Colored ticks indicate ensemble-averaged energies $\langle E \rangle$; vertical dashed lines delineate chemisorption ($>20 \text{ kJ mol}^{-1}$) and physisorption ($<7 \text{ kJ mol}^{-1}$) regimes.

bulk-like pore population throughout, whereas the few non-ferrocene framework sites contribute only a few percent of the population at comparably weak energies ($\approx -9 \text{ kJ mol}^{-1}$); both the adsorbed density and the binding strength therefore remain dominated by the iron centers rather than the linkers across the full pressure range.

From the definition of $Q_{st} = -\langle E \rangle$ in Eq. (2), the response of the binding energy upon loading follows directly:

$$\frac{\partial Q_{st}}{\partial n} = -\frac{\partial \langle E \rangle}{\partial n} \quad (8)$$

where n represents the hydrogen load. For heterogeneous adsorbents possessing a distribution of binding site energies, adsorption should proceed sequentially: the strongest sites populate first, followed by progressively weaker sites as loading increases. Consequently, $\langle E \rangle$ shifts towards less negative values with increasing n . In contrast, homogeneous adsorbents with uniform binding sites remain constant regardless of loading.

$$\frac{\partial Q_{st}}{\partial n} \begin{cases} < 0 & (\text{heterogeneous}) \\ \approx 0 & (\text{homogeneous}) \end{cases} \quad (9)$$

This negative slope is characteristic of heterogeneous adsorbents and is observed for the most promising MSUCOF materials in Fig. 6b. MSUCOF-4-FeCp maintains a constant negative slope across a wide range of uptakes/loading, which indicates that it maintains a distribution of binding sites rather than uniform interactions. In contrast, MSUCOF-4 and IRCOF-102 are flat, suggesting that H_2 is mainly bulk filling within the pores. MSUCOF-1-PtCl₂ is an interesting case where beyond 15 g L^{-1} it quickly flattens as it approaches saturation.

A summary breakdown of the values and statistics in Fig. 7 is shown in Table 3 (a more detailed breakdown can be found in Table S6). The dual-peak behavior at high pressures supports the idea of a multi-binding site mechanism, which is key to the exceptional storage capacity of MSUCOF-4-FeCp. Integration of individual peaks reveals that the majority (83%) of adsorbed H_2 still interact with Fe centers at 700 bar, while the remaining fraction (17%) engages with weaker framework sites. Hydrogen density fields visualizing the spatial distribution of adsorbed H_2 at 1, 10, and 30 bar confirm that ferrocene sites serve as primary adsorption centers (Fig. S5). This strong preference for metal coordination demonstrates the critical role of ferrocene centers in achieving high storage densities. In the case of MSUCOF-1-PtCl₂, up to three peaks are observed: one, primary binding site; two, secondary or shielded binding sites; and three, a bulk filled interaction near 0 kJ mol^{-1} as the previous two saturate.

Practical considerations

Beyond the cost advantages mentioned earlier in the Introduction, ferrocene functionalization brings additional practical benefits for large-scale implementation. Iron is among the most abundant elements in the Earth's crust, with global reserves exceeding 800 billion metric tonnes of crude ore, while platinum-group metals are scarce and geographically concentrated, with production dominated by South Africa and Russia²⁶. This abundance makes iron-based systems less susceptible to supply chain disruptions and price volatility that affect precious metal-dependent technologies.

MSUCOF-4-FeCp outperforms both pristine COFs and other metal-functionalized variants, while offering significant economic and strategic benefits. The total gravimetric uptake of 18.0 wt% significantly exceeds the DOE target of 6.5 wt%, while the total volumetric uptake of 72.6 g L^{-1} exceeds the target of 50 g L^{-1} . More importantly, balanced performance metrics ensure a high WC at the material level.

The stable and well-defined nature of ferrocene, along with its demonstrated thermal stability up to 400°C , suggests excellent cycling stability for pressure swing adsorption applications. It should be noted that these computational results represent idealized conditions: perfect crystallinity without defects, vacancies, or residual solvent molecules; experimental performance may deviate accordingly.

To probe the principal material engineering concerns, we performed NPT molecular dynamics simulations. Under uniform external pressure in vacuum the empty framework buckles reversibly above approximately 375 to 400 bar; with H_2 present, however, the adsorbed gas pressurizes the pore walls from within and braces the lattice, so that

Table 3 | Energy distribution statistics for hydrogen adsorption derived from GCMC simulations at 298 K

Material	P bar	$\langle E \rangle$ kJ·mol ⁻¹	Q_{st} kJ·mol ⁻¹	σ kJ·mol ⁻¹	Peaks N
<i>Low pressure</i>					
MSUCOF-1-PtCl ₂	1	-17.08	17.08	5.18	2
MSUCOF-3-CoCl	1	-13.96	13.96	2.89	1
MSUCOF-3-MnCl	1	-13.68	13.68	3.02	1
MSUCOF-3-NiCl	1	-14.89	14.89	3.36	1
MSUCOF-3-PdCl	1	-10.81	10.81	2.74	1
MSUCOF-3-PtCl	1	-24.53	24.53	4.81	1
MSUCOF-4-FeCp	1	-17.51	17.51	4.79	1
<i>Intermediate pressure</i>					
MSUCOF-1-PtCl ₂	17.1	-12.97	12.97	6.68	3
MSUCOF-3-CoCl	17.1	-13.25	13.25	3.28	2
MSUCOF-3-MnCl	17.1	-12.95	12.95	3.39	1
MSUCOF-3-NiCl	17.1	-13.83	13.83	3.78	1
MSUCOF-3-PdCl	17.1	-10.52	10.52	2.91	1
MSUCOF-3-PtCl	17.1	-22.16	22.16	5.58	1
MSUCOF-4-FeCp	17.1	-14.99	14.99	5.20	1
<i>High pressure</i>					
MSUCOF-1-PtCl ₂	700	-6.59	6.59	6.15	1
MSUCOF-3-CoCl	700	-11.62	11.62	3.98	2
MSUCOF-3-MnCl	700	-11.13	11.13	4.13	2
MSUCOF-3-NiCl	700	-11.60	11.60	4.63	2
MSUCOF-3-PdCl	700	-9.36	9.36	3.55	2
MSUCOF-3-PtCl	700	-19.49	19.49	6.16	2
MSUCOF-4-FeCp	700	-12.32	12.32	5.52	2

N denotes the number of resolved peaks.

the loaded framework remains mechanically stable through 700 bar, with no collapse and a cell volume that drifts by less than 1.5% over the trajectory (Fig. 8 and Supplementary Note 9). Upon loading, the framework expands by about 4% relative to its unloaded 1 bar volume; a rigid-framework GCMC holds the cell fixed and so does not capture this modest swelling, slightly and conservatively underestimating uptake by at most this amount.

Fast refueling also releases the heat of adsorption: the worst-case adiabatic excursion, with zero heat removal, is about +267 K, but at realistic automotive fill rates the projected rise falls to roughly 140 K for a 3-min fill and 100 K for a 5-min fill, and lower still with active cooling, remaining within the framework's verified-stable range (to at least 600 K, Supplementary Note 10).

Equally important, the DOE targets are defined at the system level, whereas the capacities reported here are material-level (single-crystal) upper bounds: bed packing density, binder and container mass, dead and void volume, and the balance-of-plant for high-pressure operation will lower the deployed system capacity below these crystallographic values. Repeated adsorption-desorption and thermal cycling were not simulated explicitly; framework cycling durability is inferred from the single-load stability above and the reversibility of the empty-framework deformation, while repeated fast-fill thermal cycling is itself a separate fatigue consideration for the tank liner and composite overwrap. A full system-level evaluation, including packing, thermal-management hardware, and cycling qualification, lies beyond the scope of this material-screening study. Thus, experimental synthesis, optimization, and long-term performance validation are essential for future work.

We have demonstrated through comprehensive first-principles multiscale computational simulations that ferrocene-functionalized COFs represent a promising new class of hydrogen storage materials. MSUCOF-4-FeCp achieves exceptional performance metrics with total gravimetric and volumetric hydrogen uptakes of 18.0 wt% and 72.6 g L⁻¹ at 298 K and 700 bar, substantially exceeding DOE targets. More critically, the working capacities of 12.2 wt% (WC_g) and 52.2 g L⁻¹ (WC_v) demonstrate that MSUCOF-4-FeCp is the only porous crystalline framework reported, to our knowledge, to meet both DOE ultimate targets at room temperature, without cryogenic cooling or a temperature swing (Fig. 1).

These remain material-level results obtained under idealized, defect-free conditions, and realizing them in a deployed system raises the system-level requirements detailed above.

Energy distribution analysis from GCMC simulations reveals that iron coordination, the cyclopentadienyl ring, and tritopic region compounded interactions provide multiple hydrogen binding sites while maintaining moderate binding energies. This approach offers significant economic advantages over precious metal alternatives. The stable and well-defined nature of ferrocene suggests excellent cycling stability.

Beyond hydrogen storage, the ferrocene-narrowed band gap and its metal-to-ligand charge-transfer character suggest applications in photocatalysis and electrocatalysis.

This work establishes ferrocene functionalization as a viable strategy for enhancing the hydrogen storage performance in COFs and provides a foundation for future experimental validation. The computational framework developed here can be extended to explore other metallocene systems and optimize material properties for specific applications.

Methods

Quantum mechanical calculations

Density functional theory (DFT) calculations were performed to determine the electronic structure, binding properties, and optimal geometries of ferrocene-functionalized fragments and the complete MSUCOF-4-FeCp framework. Workflow automation for CRYSTAL23 calculations was managed using our MACE (Mendoza Automated CRYSTAL Engine) python package,³⁹ an open-source framework for automating CRYSTAL quantum chemistry workflows that include input generation, queue management, and error recovery. MACE is freely available to enable other researchers to easily adopt and extend these computational workflows.

Fragment calculations were performed using CRYSTAL23^{40,41} with the M06 functional⁴² and the pob-TZVP-rev2 basis set⁴³ employing spin-polarized treatment with an extra-large integration grid⁴⁴. The M06 functional was selected for its balanced performance in reproducing thermochemistry and non-covalent interactions⁴⁵. Geometry optimizations employed convergence criteria of 2.72×10^{-11} eV for SCF energy, 1.54×10^{-3} eV Å⁻¹ for RMS forces, and 6.35×10^{-5} Å for RMS atomic displacements, with Γ -point only Monkhorst-Pack sampling of the 500 Å supercell. These thresholds are round values in the program's native atomic units (an SCF energy of 10^{-12} Hartree, an RMS gradient of 3×10^{-5} Hartree/Bohr, and an RMS displacement of 1.2×10^{-4} Bohr), an order of magnitude tighter than the CRYSTAL23 defaults.

Full periodic calculations used CRYSTAL23 with HSE06-D3^{46–48} providing accurate treatment of electronic properties such as band gap, band structure, and density of states⁴⁹. Comprehensive geometric optimizations for atomic positions and lattice parameters used identical convergence criteria as for the fragment calculations described above with Monkhorst-Pack Γ -centered grids. Notably, ferrocene units adopt eclipsed Cp conformations within the framework, contrary to the staggered preference of isolated molecules, because of spatial constraints and electronic interactions with neighboring struts. The framework-imposed eclipsed conformation was used for the periodic calculations, while the fragment force-field training set included both the eclipsed and staggered conformers to ensure transferability. The optimized fractional coordinates and lattice parameters for IRCOF-102, MSUCOF-4, and MSUCOF-4-FeCp are reported in Supplementary Note 2.

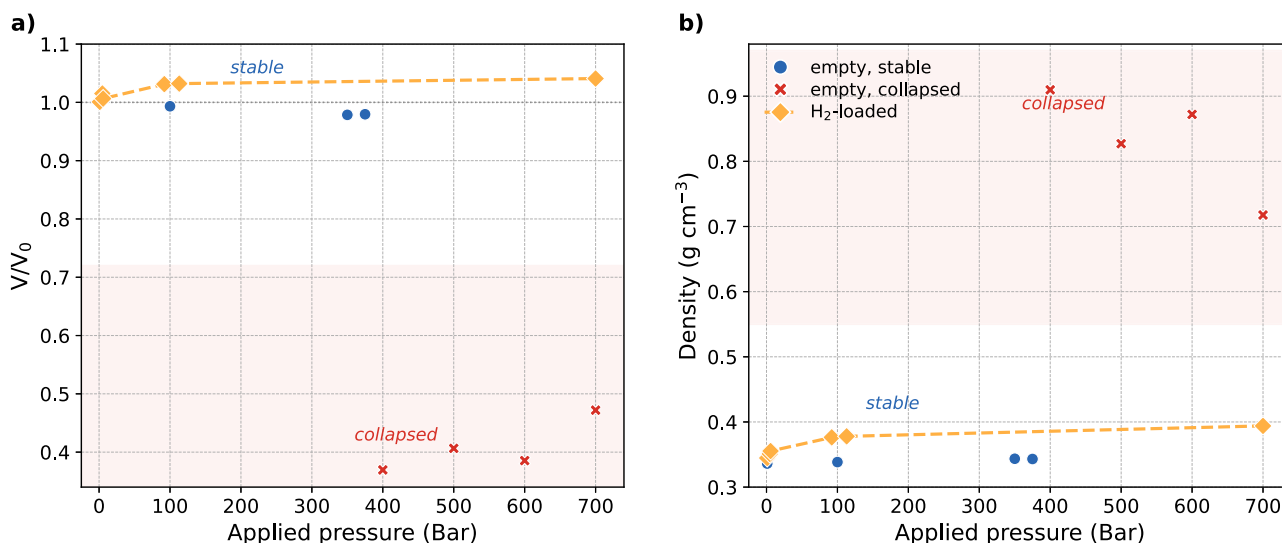


Fig. 8 | Mechanical stability of MSUCOF-4-FeCp under applied pressure from NPT molecular dynamics (UFF4MOF, 298 K). **a** Relative unit-cell volume V/V_0 , where V_0 is the MD-equilibrated empty framework at 1 bar, and **b** framework density versus applied pressure for the empty (vacuum) framework and the H₂-loaded framework. The empty framework is stable up to approximately 375 bar (blue

circles) but buckles reversibly at higher pressures, contracting to roughly half its volume (red crosses, collapsed branch). With H₂ present, the adsorbed gas braces the pores from within, and the loaded framework remains stable through 700 bar (orange diamonds), expanding by only about 4%. Shaded bands mark the collapsed regime; values are last-50-ps trajectory averages.

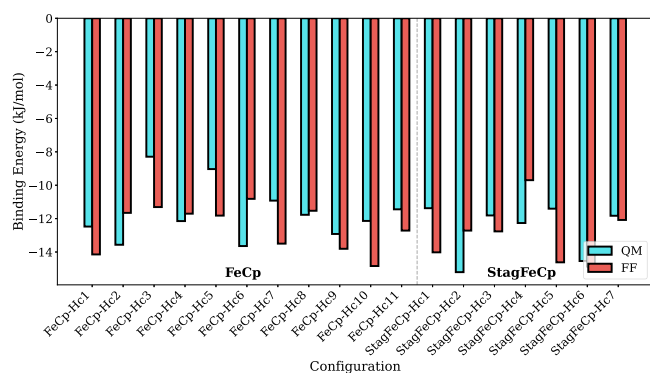


Fig. 9 | Validation of the QM-fitted force field for ferrocene-H₂ interactions. Hc denotes hydrogen configuration number. FeCp labels correspond to eclipsed ferrocene (as observed in MSUCOF-4-FeCp), while stagFeCp denotes staggered conformers.

Surface area and pore volume

Surface areas and pore volumes were calculated using the Atom Volumes & Surfaces tool in Materials Studio⁵⁰. The VdW surface is constructed by rolling a spherical probe across the framework atoms, where the probe radius is defined by the adsorbate of interest. For hydrogen storage applications, a probe radius of 1.445 Å was used, corresponding to half the kinetic diameter of H₂ (2.89 Å). This approach provides a consistent basis for comparing geometric properties across the IRCOF-102, MSUCOF-4, and MSUCOF-4-FeCp frameworks.

Force field development and validation

Quantum mechanics-derived force fields were developed following our previous methodology³¹ employing a Morse potential (Eq. (10))^{51–53} for H₂-ferrocene interactions:

$$U_{ij}^{\text{Morse}}(r_{ij}) = D_0[(1 - e^{-\alpha(r_{ij}-r_0)})^2 - 1] \quad (10)$$

The initial H₂ binding configurations were identified using the Adsorption Locator tool in Materials Studio,⁵⁰ which uses Monte Carlo sampling to locate energetically favorable adsorption sites; a random

selection spanning various H₂ distances and orientations relative to the ferrocene center was extracted for quantum-mechanical refinement. Fragment calculations for these configurations followed the quantum-mechanical protocol described above, with vibrational frequency analysis confirming the absence of imaginary frequencies and providing zero-point energy (ZPE) and vibrational enthalpy (ΔH_{vib}^0) corrections. Binding enthalpies were computed as

$$\Delta H_{\text{bind}}^0 = \Delta H_{\text{Linker}+\text{H}_2}^0 - \Delta H_{\text{Linker}}^0 - \Delta H_{\text{H}_2}^0, \quad (11)$$

where each ΔH^0 is the sum of the electronic energy, the ZPE, and the vibrational-enthalpy correction. The parameters (D_0 , α , r_0) were fitted to DFT binding energy curves using GULP,⁵⁴ sampling multiple Hydrogen configurations (Hc) around eclipsed and staggered variants of ferrocene. Representative training configurations are shown in Fig. S2. A least-squares fitting procedure achieved a mean absolute error of 1.82 kJ·mol⁻¹ and a mean bias error of -0.66 kJ·mol⁻¹ across the test configurations, both below the thermal energy ($RT = 2.48$ kJ·mol⁻¹) at 298 K (Fig. 9). A sensitivity analysis shows that this residual error does not affect the conclusions: even after propagating the worst-case over-binding through the full isotherm, the WC of MSUCOF-4-FeCp still exceeds both DOE ultimate targets with 99.999% confidence, as the systematic bias would have to exceed 3.5 kJ·mol⁻¹, roughly five times the observed 0.66 kJ·mol⁻¹, before this result is in doubt (Supplementary Note 3).

The optimized parameters shown in Table 4 reveal distinctive binding characteristics for the ferrocene iron center. The H₂-Fe interaction exhibits a notably deep potential well ($D_0 = 1.987$ kcal·mol⁻¹) combined with a small width parameter ($\alpha = 0.466$ Å⁻¹), indicating diffuse and extended interaction. This combination produces a broad, attractive potential that facilitates hydrogen capture while maintaining reversibility. In contrast, the chelation complex FeCl₂ of our prior study exhibited drastically different electronic environment ($D_0 = 1.092$ kcal·mol⁻¹, $\alpha = 1.180$ Å⁻¹, $r_0 = 3.155$ Å), with weaker, shorter-range binding despite greater metal accessibility³¹. Notably, the cyclopentadienyl rings geometrically constrain the Fe center of ferrocene, yet donate substantial π -electron density which, in addition to its low spin electronic configuration, creates an electron-rich environment that strengthens Coulombic interaction with the H₂ quadrupole moment.

Table 4 | Morse potential parameters for H₂-ferrocene interactions derived from DFT calculations

Interaction	<i>D</i> ₀ (kcal·mol ^{−1})	<i>a</i> (Å ^{−1})	<i>r</i> ₀ (Å)
H ₂ -C	0.101	1.924	3.120
H ₂ -H	0.001	1.849	3.247
H ₂ -Fe	1.987	0.466	2.476

Grand Canonical Monte Carlo simulations

Hydrogen storage isotherms were calculated using Grand Canonical Monte Carlo (GCMC) simulations implemented in Materials Studio⁵⁰ at 298 K and 1–700 bar. The Metropolis algorithm used translation, rotation, insertion, deletion, and regrowth moves in a 2:1:1:1:0.1 ratio. Equilibrium was achieved after 1,000,000 steps, followed by 3,000,000 production steps to average uptake and isosteric heat of the ensemble (*Q*_{st}).

Equation of state

To convert between fugacity (used in GCMC simulations) and pressure (for experimental comparison), the VdW equation of state was employed:⁵⁵

$$\ln \frac{f}{P} = \left(b - \frac{a}{RT} \right) \frac{P}{RT} \quad (12)$$

where *f* is the fugacity, *P* is the pressure, *T* is the temperature (298 K), *R* is the gas constant, and *a* = 0.2476 L² bar mol^{−2} and *b* = 0.02661 L mol^{−1} are empirical parameters for hydrogen. In our previous work, we showed that this formulation showed only 0.735% difference from Peng-Robinson at 700 bar³¹.

Molecular dynamics

Framework stability was assessed with constant-stress, constant-temperature (NPT) molecular-dynamics simulations using the UFF4-MOF force field⁵⁶ (Nosé thermostat, Parrinello-Rahman barostat, 1 fs timestep, 10⁶ steps, 1 ns). For the mechanical-stability tests at 298 K, two scenarios were compared: the empty framework under a uniform external hydrostatic pressure imposed in vacuum, and the H₂-loaded framework, initialized from GCMC-equilibrated snapshots so that the H₂ pressure is exerted from within and around the pores, as in real operation. Each pressure is an independent NPT run initialized from the relaxed (zero-pressure) framework rather than a decompressed high-pressure structure. Because GCMC-equilibrated H₂ configurations were generated only at discrete pressures, the loaded runs use the nearest available snapshots (the 4.6 and 5.7 bar runs bracket the nominal 5 bar delivery pressure, and the 92 and 113 bar runs represent the intermediate ~100 bar point). Thermal stability was probed with NPT-MD temperature ladders for the empty framework (1 bar, 298 to 600 K) and the H₂-loaded framework (700 bar, 250 to 600 K), with the 250 and 600 K loaded runs extended to 7 ns. All structural comparisons are referenced to the MD-equilibrated framework at 1 bar.

Hydrogen density and binding-site analysis

Hydrogen density fields were generated using the Sorption module in Materials Studio,⁵⁰ in which the local H₂ density at each grid point is calculated by averaging the count of sorbates over the associated volume element during the GCMC sampling. To resolve where hydrogen binds relative to the ferrocene units, the adsorbed H₂ configurations from the 298 K GCMC ensembles were folded into the local frame of a single ferrocene using its molecular symmetry, and each adsorbed molecule was assigned to the first or second ferrocene solvation shell, to the non-ferrocene framework motifs (boroxine nodes, tetrahedral carbon centers, and phenyl rings), or to the open pore.

Energy distribution analysis

The interaction-energy distributions from the GCMC ensembles were deconvoluted into binding-mode contributions by fitting asymmetric Gaussian functions, and the population fraction of each peak was obtained by numerical integration of the distribution within its energy boundaries.

Data availability

The optimized crystal structures of IRCOF-102, MSUCOF-4, and MSUCOF-4-FeCp are provided as crystallographic files in the Supplementary Information, and the GCMC uptake isotherms, energy-distribution statistics, and fitted force-field parameters are reported in the main text and Supplementary Information. Any additional data that support the findings of this study are available from the corresponding author on reasonable request.

Code availability

The custom post-processing and analysis scripts used to produce the figures and derived quantities reported here are available from the corresponding author on reasonable request. The simulation software used (BIOVIA Materials Studio, CRYSTAL, and GULP) is described in the Methods. Additionally, the MACE (Mendoza Automated CRYSTAL Engine) package used to automate the DFT calculations is openly available³⁹.

Received: 2 March 2026; Accepted: 6 August 2026;

Published online: 01 October 2026

References

1. U.S. Department of Energy. Hydrogen shot. <https://www.energy.gov/eere/fuelcells/hydrogen-shot-summit> (2021).
2. U.S. Department of Energy. Technical targets for onboard hydrogen storage for light-duty vehicles. <https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles> (2020).
3. Yaghi, O. M. Reticular chemistry-construction, properties, and precision reactions of frameworks. *J. Am. Chem. Soc.* **138**, 15507–15509 (2016).
4. Wu, H., Simmons, J. M., Srinivas, G., Zhou, W. & Yildirim, T. Adsorption sites and binding nature of CO₂ in prototypical metal-organic frameworks: a combined neutron diffraction and first-principles study. *J. Phys. Chem. Lett.* **1**, 1946–1951 (2010).
5. Mendoza-Cortes, J. L., Han, S. S., Furukawa, H., Yaghi, O. M. & Goddard III, W. A. Adsorption mechanism and uptake of methane in covalent organic frameworks: theory and experiment. *J. Phys. Chem. A* **114**, 10824–10833 (2010).
6. Fan, W. et al. Multivariate polycrystalline metal-organic framework membranes for CO₂/CH₄ separation. *J. Am. Chem. Soc.* **143**, 17716–17723 (2021).
7. Humby, J. D. et al. Host-guest selectivity in a series of isorecticular metal-organic frameworks: observation of acetylene-to-alkyne and carbon dioxide-to-amide interactions. *Chem. Sci.* **10**, 1098–1106 (2019).
8. Al-Rowaili, F. N. et al. A review for Metal-Organic Frameworks (MOFs) utilization in capture and conversion of carbon dioxide into valuable products. *J. CO₂ Util.* **53**, 101715 (2021).
9. Han, S. S., Mendoza-Cortes, J. L. & Goddard III, W. A. Recent advances on simulation and theory of hydrogen storage in metal-organic frameworks and covalent organic frameworks. *Chem. Soc. Rev.* **38**, 1460–1476 (2009).
10. Sathe, R. Y., Dhillip Kumar, T. J. & Ahuja, R. Furtherance of the material-based hydrogen storage based on theory and experiments. *Int. J. Hydrog. Energy* **48**, 12767–12795 (2023).
11. Sathe, R. Y., Ussama, M., Bae, H., Lee, H. & Dhillip Kumar, T. J. Density functional theory study of Li-functionalized nanoporous R-graphyne-metal-organic frameworks for reversible hydrogen storage. *ACS Appl. Nano Mater.* **4**, 3949–3957 (2021).

12. Sathe, R. Y. & Dhillip Kumar, T. J. Electronic structure calculations of reversible hydrogen storage in nanoporous Ti cluster frameworks. *ACS Appl. Nano Mater.* **3**, 5575–5582 (2020).
13. Caskey, S. R., Wong-Foy, A. G. & Matzger, A. J. Dramatic tuning of carbon dioxide uptake via metal substitution in a coordination polymer with cylindrical pores. *J. Am. Chem. Soc.* **130**, 10870–10871 (2008).
14. Kealy, T. J. & Pauson, P. L. A new type of organo-iron compound. *Nature* **168**, 1039–1040 (1951).
15. Wilkinson, G., Rosenblum, M., Whiting, M. C. & Woodward, R. B. The structure of iron bis-cyclopentadienyl. *J. Am. Chem. Soc.* **74**, 2125–2126 (1952).
16. Fischer, E. O. & Pfab, W. Cyclopentadien-metallkomplexe ein neuer Typ metallorganischer verbindungen. *Z. Naturforsch. B* **7**, 377–379 (1952).
17. Laszlo, P. & Hoffmann, R. Ferrocene: Ironclad history or Rashomon tale? *Angew. Chem. Int. Ed.* **39**, 123–124 (2000).
18. Roy, G. et al. Ferrocene as an iconic redox marker: from solution chemistry to molecular electronic devices. *Coord. Chem. Rev.* **473**, 214816 (2022).
19. Lai, G.-Q., Li, N., He, J. & Lan, Y.-Q. A ferrocene-modified stable metal-organic framework for efficient CO₂ photoreduction reaction. *Chem. Commun.* **59**, 12471–12474 (2023).
20. Samy, M. M. et al. Conjugated microporous polymers containing ferrocene units for high carbon dioxide uptake and energy storage. *Mater. Chem. Phys.* **287**, 126177 (2022).
21. Chen, Y., Cao, X., Zhu, H. & Liu, Y. Preparation of a porous carbon from ferrocene-loaded polyaniline and its use in hydrogen adsorption. *Int. J. Hydrog. Energy* **37**, 7629–7637 (2012).
22. Sariga & Varghese, A. The renaissance of ferrocene-based electrocatalysts: properties, synthesis strategies, and applications. *Top. Curr. Chem.* **381**, 1–93 (2023).
23. Peng, Q. et al. Ferrocene-based hypercrosslinked polymers derived from phenolic polycondensation with unexpected H₂ adsorption capacity. *Mater. Today Chem.* **24**, 100854 (2022).
24. Cha, M. H., Nguyen, M. C., Lee, Y. L., Im, J. & Ihm, J. Iron-decorated, functionalized metal organic framework for high-capacity hydrogen storage: first-principles calculations. *J. Phys. Chem. C* **114**, 14276–14280 (2010).
25. Mendoza-Cortes, J. L., Goddard III, W. A., Furukawa, H. & Yaghi, O. M. A covalent organic framework that exceeds the DOE 2015 volumetric target for H₂ uptake at 298 K. *J. Phys. Chem. Lett.* **3**, 2671–2675 (2012).
26. U.S. Geological Survey. *Mineral Commodity Summaries 2025*. Technical Report, U.S. Geological Survey (2025).
27. Li, X.-D., Zhang, Y., Guo, J.-H., Yu, S.-Q. & Du, D.-W. Computer-aided prediction of structure and hydrogen storage properties of tetrakis (4-aminophenyl) silsesquioxane based covalent-organic frameworks. *Int. J. Hydrog. Energy* **44**, 8357–8364 (2019).
28. Li, X.-D. et al. Predicting 1,3,5,7-tetrakis (4-aminophenyl) adamantane based covalent-organic frameworks as hydrogen storage materials. *RSC Adv.* **6**, 21517–21525 (2016).
29. Nguyen, H. L. Reticular design and crystal structure determination of covalent organic frameworks. *Chem. Sci.* **12**, 8632–8647 (2021).
30. El-Kaderi, H. M. et al. Designed synthesis of 3D covalent organic frameworks. *Science* **316**, 268–272 (2007).
31. Djokic, M. & Mendoza-Cortes, J. L. Multi-binding sites united in covalent-organic frameworks (MSUCOF) for H₂ storage and delivery at room temperature. *Energy Fuels* **38**, 4711–4720 (2024).
32. Guan, Q., Zhou, L.-L. & Dong, Y.-B. Metalated covalent organic frameworks: from synthetic strategies to diverse applications. *Chem. Soc. Rev.* **51**, 6307 (2022).
33. Evans, J. D., Sumbly, C. J. & Doonan, C. J. Post-synthetic metalation of metal-organic frameworks. *Chem. Soc. Rev.* **43**, 5933–5951 (2014).
34. Singh, V., Jang, S., Vishwakarma, N. K. & Kim, D.-P. Intensified synthesis and post-synthetic modification of covalent organic frameworks using a continuous flow of microdroplets technique. *NPG Asia Mater.* **10**, e456 (2018).
35. Liu, M. et al. Post-synthetic modification of covalent organic frameworks for CO₂ electroreduction. *Nat. Commun.* **14**, 3800 (2023).
36. Hinuma, Y., Pizzi, G., Kumagai, Y., Oba, F. & Tanaka, I. Band structure diagram paths based on crystallography. *Comput. Mater. Sci.* **128**, 140–184 (2017).
37. SAE International. *Fueling Protocols for Light Duty Gaseous Hydrogen Surface Vehicles* Standard J2601 (SAE International, 2020).
38. Linstrom, P. J. & Mallard, W. G. The NIST chemistry WebBook: a chemical data resource on the internet. *J. Chem. Eng. Data* **46**, 1059–1063 (2001).
39. Djokic, M., Maldonado-Lopez, D., Lewis, B., Comaskey, W. P. & Mendoza-Cortes, J. L. *Mendoza Automated CRYSTAL Engine (MACE)*. <https://doi.org/10.5281/zenodo.18635426> (2026).
40. Erba, A. et al. CRYSTAL23: a program for computational solid state physics and chemistry. *J. Chem. Theory Comput.* **19**, 6891–6932 (2023).
41. Dovesi, R. et al. *CRYSTAL23 User's Manual* (University of Torino, 2023).
42. Zhao, Y. & Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **120**, 215–241 (2008).
43. Vilela Oliveira, D., Laun, J., Peintinger, M. F. & Bredow, T. BSSE-correction scheme for consistent Gaussian basis sets of double- and triple-zeta valence with polarization quality for solid-state calculations. *J. Comput. Chem.* **40**, 2364–2376 (2019).
44. Laun, J. & Bredow, T. BSSE-corrected consistent gaussian basis sets of triple-zeta valence with polarization quality of the fifth period for solid-state calculations. *J. Comput. Chem.* **43**, 839–846 (2022).
45. Mardirossian, N. & Head-Gordon, M. Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals. *Mol. Phys.* **115**, 2315–2372 (2017).
46. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *J. Chem. Phys.* **118**, 8207–8215 (2003).
47. Krukau, A. V., Vydrov, O. A., Izmaylov, A. F. & Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *J. Chem. Phys.* **125**, 224106 (2006).
48. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132**, 154104 (2010).
49. Borlido, P. et al. Exchange-correlation functionals for band gaps of solids: benchmark, reparametrization and machine learning. *npj Comput. Mater.* **6**, 1–17 (2020).
50. BIOVIA, Dassault Systèmes. *Materials Studio 2022* (Dassault Systèmes, 2022).
51. Morse, P. M. Diatomic molecules according to the wave mechanics. II. vibrational levels. *Phys. Rev.* **34**, 57–64 (1929).
52. Yang, L., Sun, L. & Deng, W.-Q. Combination rules for Morse-based van der Waals force fields. *J. Phys. Chem. A* **122**, 1672–1677 (2018).
53. Koh, H. S., Rana, M. K., Wong-Foy, A. G. & Siegel, D. J. Predicting methane storage in open-metal-site metal-organic frameworks. *J. Phys. Chem. C* **119**, 13451–13458 (2015).
54. Gale, J. D. & Rohl, A. L. The general utility lattice program (GULP). *Mol. Simul.* **29**, 291–341 (2003).
55. Winn, J. S. The fugacity of a van der Waals gas. *J. Chem. Educ.* **65**, 772 (1988).
56. Coupry, D. E., Addicoat, M. A. & Heine, T. Extension of the universal force field for metal-organic frameworks. *J. Chem. Theory Comput.* **12**, 5215–5225 (2016).
57. Guo, J.-H., Zhang, H., Gong, M. & Cheng, X.-L. Ca²⁺- and Mg²⁺-doped covalent organic frameworks exhibiting high hydrogen and acetylene storage. *Struct. Chem.* **24**, 691–703 (2013).

58. Ghosh, S. & Singh, J. K. Hydrogen adsorption in pyridine bridged porphyrin-covalent organic framework. *Int. J. Hydrog. Energy* **44**, 1782–1796 (2019).
59. Cao, D., Lan, J., Wang, W. & Smit, B. Lithium-doped 3D covalent organic frameworks: high-capacity hydrogen storage materials. *Angew. Chem. Int. Ed.* **48**, 4730–4733 (2009).
60. Pramudya, Y. & Mendoza-Cortes, J. L. Design principles for high H₂ storage using chelation of abundant transition metals in covalent organic frameworks for 0–700 bar at 298 K. *J. Am. Chem. Soc.* **138**, 15204–15213 (2016).
61. Mendoza-Cortes, J. L., Han, S. S. & Goddard, W. A. High H₂ uptake in Li-, Na-, K-metalated covalent organic frameworks and metal organic frameworks at 298 K. *J. Phys. Chem. A* **116**, 1621–1631 (2012).
62. Kapelewski, M. T. et al. Record high hydrogen storage capacity in the metal-organic framework Ni₂(m-dobdc) at near-ambient temperatures. *Chem. Mater.* **30**, 8179–8189 (2018).
63. Jaramillo, D. E. et al. Ambient-temperature hydrogen storage via vanadium(II)-dihydrogen complexation in a metal-organic framework. *J. Am. Chem. Soc.* **143**, 6248–6256 (2021).
64. García-Holley, P. et al. Benchmark study of hydrogen storage in metal-organic frameworks under temperature and pressure swing conditions. *ACS Energy Lett.* **3**, 748–754 (2018).
65. Madden, D. G. et al. Densified HKUST-1 monoliths as a route to high volumetric and gravimetric hydrogen storage capacity. *J. Am. Chem. Soc.* **144**, 13729–13739 (2022).
66. Chen, Z. et al. Balancing volumetric and gravimetric uptake in highly porous materials for clean energy. *Science* **368**, 297–303 (2020).
67. Kaye, S. S., Dailly, A., Yaghi, O. M. & Long, J. R. Impact of preparation and handling on the hydrogen storage properties of Zn₄O(1,4-benzenedicarboxylate)₃ (MOF-5). *J. Am. Chem. Soc.* **129**, 14176–14177 (2007).
68. Wu, X. et al. Ultrahigh hydrogen storage capacity of novel porous aromatic frameworks. *J. Mater. Chem. A* **3**, 10724–10737 (2015).
69. Oliveira, J. C. A., Gonçalves, D. V., Montenegro, D. L. & Lucena, S. M. P. Predicting hydrogen storage at 298 K in activated carbons. *Adsorption* **30**, 403–413 (2024).
70. Anbumani, P., Duvvuri, R., Radhika, S., Azeez, A. A. & Sujith, R. A multi-objective optimization-driven screening approach for maximizing hydrogen storage capacities in MOFs. *Sci. Rep.* **16**, 242 (2026).
71. Klontzas, E., Tylianakis, E. & Froudakis, G. E. Hydrogen storage in 3D covalent organic frameworks. A multiscale theoretical investigation. *J. Phys. Chem. C* **112**, 9095–9098 (2008).

Acknowledgements

This study received no direct funding. M.D. acknowledges Michigan State University's College of Engineering for support through the Graduate Office Fellowship and the Dissertation Completion Fellowship, and thanks Daniel

Maldonado-Lopez for helpful discussions. J.L.M.-C. acknowledges Michigan State University's College of Engineering for support through startup funds. Computational resources and services were provided by the Institute for Cyber-Enabled Research at Michigan State University.

Author contributions

M.D. performed the DFT calculations, validated the force field parameters, performed the GCMC simulations, analyzed the data, created all figures, and wrote the manuscript. J.L.M.-C. conceived the material design, developed the initial methodology and results, supervised the project, co-wrote and revised the manuscript. Both authors discussed the results and approved the final version.

Competing interests

The authors declare the following competing interests: M.D. and J.L.M.-C. are inventors on a pending U.S. provisional patent application (applicant, Michigan State University) relating to the metallocene-functionalized covalent organic frameworks for hydrogen storage described in this work. The authors declare no other competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s44456-026-00019-z>.

Correspondence and requests for materials should be addressed to Jose L. Mendoza-Cortes.

Reprints and permissions information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2026