Three-dimensional metal-intercalated covalent organic frameworks for near-ambient energy storage

Fei Gao, Zijing Ding & Sheng Meng

Beijing National Laboratory for Condensed Matter Physics, and Institute of Physics, Chinese Academy of Sciences, 100190 Beijing, China.

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Correspondence and
requests for materials
should be addressed to
S.M. (smeng@iphy.ac.
cn)

A new form of nanoporous material, metal intercalated covalent organic framework (MCOF) is proposed and its energy storage property revealed. Employing density functional and thermodynamical analysis, we find that stable, chemically active, porous materials could form by stacking covalent organic framework (COF) layers with metals as a gluing agent. Metal acts as active sites, while its aggregation is suppressed by a binding energy significantly larger than the corresponding cohesive energy of bulk metals. Two important parameters, metal binding and metal-metal separation, are tuned by selecting suitable building blocks and linkers when constructing COF layers. Systematic searches among a variety of elements and organic molecules identify Ca-intercalated COF with diphenylethyne units as optimal material for H₂ storage, reaching a striking gravimetric density ~ 5 wt% at near-ambient conditions (300 K, 20 bar), in comparison to < 0.1 wt% for bare COF-1 under the same condition.

Finding low cost, safe, and efficient energy storage materials has been a major challenge to develop renewable-energy based economy. Hydrogen is considered as an appealing energy carrier alternative to fossil fuels in many applications, because it is abundant, energy intensive, and pollution-free^{1–3}. U.S. Department of Energy (DOE) set a target for practical H storage materials to have a gravimetric capacity of 5.5 wt% by 2017⁴. The challenge is to dramatically increase storage capacity and reversibility at ambient conditions⁵. Carbon-based nanostructures and porous materials including fullerene, nanotube, and carbyne networks, have been proposed as potential H₂ storage media, thanks to their high surface-to-weight ratios, good reversibility and fast kinetics^{6–10}. However, most of them failed at room temperature and ambient pressure due to improper binding to H₂.

To reach high and retrievable H storage at ambient conditions, a light three-dimensional (3D) material with H₂ binding energies in the range of 0.2–0.6 eV/H₂ is required^{11,12}. This implies porous materials must have dense active sites for H₂ binding, to which two approaches have been adopted. One is to substitute carbon by other elements such as boron/nitrogen^{11,13}; however, it shows little effect and is difficult to apply. The other is to dope light metals including alkali, alkali earth or transition metals, into porous materials^{14,15}. Improving metal binding by using nanostructure curvature^{16,17} or incorporation of sp-carbons^{18,19} has been also explored. It was found alkali metals have too weak interaction with the substrate and H₂²⁰; whereas transition metals tend to cluster on material surface, reducing substantially H₂ storage capacity²¹. Upon compromise, calcium is recognized as a superior coating element thanks to its delicate balance of binding strengths to base materials and H₂^{18,22–24}. Ca-coated fullerene, Ca₃₂C₆₀, yields strong local electric fields on C₆₀ and reaches a H₂ uptake up to ~ 8.4 wt%²². Ca-doped carbyne networks maintain a small distance ~ 10 Å between metal adsorbates and a high H₂ density of ~ 8 wt%¹⁸. However, both materials have their own flaws: their 3D assembly without affecting H₂ density is either not achievable or not experimentally demonstrated; and it is difficult to control the position and stability of dopant Ca atoms^{18,22}. Similar problems emerge in Ca-doped nanotube, graphite and graphene^{14,23,24}.

Covalent organic framework (COF) has been recently synthesized as an important extension of carbon porous materials^{25,26}. A variety of experimental studies^{27,28} show that small planar organic molecules form two-dimensional (2D) or 3D supramolecular architectures including COFs, through self-assembly of end linker groups, as schematically shown in Figure 1. Due to their adjustable porous structure and unparalleled strength, COFs are very promising for H₂ storage. At low temperature 77 K and high pressure 100 bar, 2D or 3D COFs can currently store 3–7 wt% H₂²⁷. Stunning H₂ uptake of ~ 20 wt% at 77 K and 100 bar has been predicted in theoretical simulations for COF-108 and COF-102-3; but it deteriorates quickly to a value below 1–2 wt% at near ambient condition, for instance, at 300 K and 20 bar^{29–31}. Similar trends were observed for COF-1, a simple layered

Figure 1 | Formation of COFs. (a) Schematic diagram of COF building block composed by two ending linkers and an organic unit, (b) An example of real building blocks: benzene diboronic acid (BDDBA), (c) 2D COF formed by BDDBA self-assembly, named COF-1. Crosses mark positions tested for metal binding.

COF with the phenyl group as organic unit and boronic acid as the linker (see Fig. 1), shows a H_2 density of 1.28 wt% at 77 K but it decreases to ~ 0.08 wt% at 298 K and 20 bar in experiment^{27,32}. Suitable metal doping also improves H_2 storage in COFs^{33–38}. Grand canonical Monte Carlo simulations reveal that H storage capacity in Li-coated COF-202 can reach 4.39 wt% at 298 K and 100 bar, which is three times higher than in undoped COF-202³⁴. However, with the increase of Li concentration, Li atoms form clusters and H storage density reduces³⁵. Using density functional theory (DFT) calculations, Wu et al. found that both Li and Ca forms clusters on COF-10, which are 0.17 and 0.20 eV/atom more stable than scattered atoms, respectively. This reduces storage density from 3 to 1.5 H_2 per metal atom. Ca dopants provide a stronger bonding to H_2 (energy ~ 0.21 eV) compared with Li dopants (0.12 eV), due to more charge transfer from Ca to the substrate³⁵. As a remedy, two-step doping, namely, metal decoration on B-substituted COF fragments, was also proposed³⁶. On all these successful 3D reference materials, H_2 density is below 1–2 wt% at near ambient conditions^{30,31}. New methods and concepts for further improvement without metal aggregation are key to develop next generation H storage media.

Here we present a radically different approach to improve H storage in COFs. We explore the feasibility of using a new class of 3D network—metal-intercalated COF (MCOF), for near ambient H_2 storage. Metal binding in such new class of 3D materials (see the inset of Fig. 2a) has a binding energy significantly larger than that in bulk metals, thus intrinsically blocking metal segregation. Quantum mechanical calculations and thermodynamical analysis reveal that optimized MCOF material stores 4.87 wt% of H_2 at 300 K and 20 bar, greatly enhanced from the value of < 0.1 wt% for the bare COF-1 in the same condition³².

The paper is organized as follows. After this introduction section, we first expound the idea and important considerations in constructing MCOF in the “Results” section. The feasibility of various light metal elements intercalating in model COF layers, COF-1, is tested. Ca is identified to be the most suitable gluing metal element. To further improve H storage performance, we start COF structural optimization through the selection of organic building blocks and linkers. In optimizing organic blocks, small organic molecules as well as polycyclic aromatic hydrocarbons (PAHs) are considered and compared to the reference molecule, benzene. We also investigate the effects of linker groups, where we find $\text{B}(\text{OH})_2$ linkers preserve H_2 binding properties of doped organic units. Ca intercalated COF layers with diphenylethyne organic units (CaCOF-d) are identified as an outstanding H storage material. After discussing H_2 storage properties in 3D CaCOF-d layers at saturation and near ambient conditions, we give a brief discussion on how MCOF can be synthesized experimentally, and present a summary on our major findings.

Results

It seems natural to combine light metals and extended COF layers for near ambient H_2 storage. The two are both light and stable, and can potentially form new framework with dense active sites. In early experiments the newly synthesized COF materials are found to interact weakly with H_2 molecules, leading to low storage density at ambient conditions. In the meantime, various theoretical efforts

Figure 2 | Partial density of states (PDOS) projected onto the COF component (black lines) and the d -orbitals of Ca (red lines) in (a) CaCOF-1 and (b) CaCOF-1 after H_2 adsorption. The PDOS projected onto H_2 (blue line, multiplied by 20 times) is also shown in (b). The inset in (a) shows the side view of CaCOF-1, and the inset in (b) shows the charge density associated with the states in the shaded region.

demonstrated that metal doping cannot effectively improve H_2 storage due to metal clustering problem on single COF layers. We start a new approach to explore that whether metal atoms could be intercalated between COF layers to form stable 3D stacks without metal segregation. The choice of workable metal elements and COF materials should be tested to satisfy the requirements of being stable, light, and active for H_2 storage.

Constructing metal intercalated COF for H_2 storage. We first take one of the simplest COF materials, COF-1, whose organic unit is a benzene ring and linker boronic acid, as our representative model substrate and investigate its interaction with various metal elements. A range of light metals including Li, Na, Mg, K, Ca, and Ti are considered, since they are most commonly adopted to decorate porous nanomaterials serving as active sites for H_2 binding. We first test the adsorption site of metal atoms on a single layer COF-1. We find metal atoms prefer to adsorb onto the center of the organic unit, a phenyl ring, rather than on top of B, O, or B_3O_3 rings. For instance, the binding energy of Ca (E_{Ca}) on all sites falls in the range of 0.001–0.008 eV, except on the center of phenyl ring, which is 0.77 eV. This site preference is a result of Ca interacting with the π orbital of phenyl ring, which is absent from the electron rich boroxine ring. As shown later, the energy for Ca binding to the phenyl group in COF is an order of magnitude larger than that on isolated benzene (0.07 eV), because the π orbitals are extended onto neighboring B atoms connected to phenyl rings in COF and Ca binding is thus enhanced by delocalized π electrons, as clearly displayed in Fig. 2b inset.

Most importantly, the Ca binding energy increases to 2.83 eV when Ca and COF-1 layers assemble into multilayered metal intercalation structure, the MCOF. The interlayer distance increases from 3.35 Å to 4.40 Å upon metal intercalation and the stacking manner might also be changed. Ca binding on boroxine rings is ~ 1 eV less stable than on phenyl rings in intercalated 3D COF layers. We expect metal intercalation takes place simultaneously or with a small barrier through the pores of a diameter of ~ 10 Å present in COF-1. The Ca binding energy is 3.37 eV if Van der Waals density functional (VDW-DF)^{39,40} is used to incorporate van der Waals (VDW) interactions; the additional 0.54 eV is attributed to the VDW interactions between adjacent COF layers. For comparison, the cohesive energy in bulk Ca is 1.88 eV/Ca in our calculation and the experimental value is 1.86 eV/Ca⁴⁰, much smaller than Ca binding energy in COFs. The energy for a second Ca binding around the Ca on the phenyl ring center is 1.81 eV with a Ca–Ca distance of 3.28 Å; the energy is smaller than the binding energy of first Ca and the cohesive energy of Ca bulk, showing straightforwardly that Ca clustering is not favored. Vibrational analysis also confirms that no major negative frequencies occur in the vibrational spectrum of CaCOF-1. Therefore, Ca and COF-1 forms stable 3D materials (referred to as CaCOF-1) via metal intercalation.

Some other metals also work in the same way as Ca to form MCOFs. In Table 1, we list the calculated parameters including the interlayer distance (L) and metal binding energy (E_M) for metal intercalation COF-1. Metal insertion into the COF layers significantly expands the equilibrium interlayer distances, from $L = 3.4$ Å for bare COFs²⁵ to $L = 5.4$ Å for KCOF-1. The binding energies of metals to COFs vary from metal to metal, with E_M for Mg being smallest (≤ 0.2 eV) and E_M for Ti being largest (≥ 5.0 eV) in our calculations. This is in accord with the rather inert (active) nature of Mg (Ti) metals. However, both cases have the metal binding energy, E_M , smaller than the cohesive energy in bulk metals, E_C , as is the case for most metal doped nanostructures previously studied²². Surprisingly, on the other hand, Li, Na, K and Ca metals have E_M significantly larger than the corresponding E_C (see Table 1). This behavior renders metal segregation in such MCOFs thermodynamically unstable. Consequently, 3D network formed in this way is a new class of stable materials without any metal clustering problems.

Table 1 | Metal binding energies (E_M) and interlayer distances (L) for 3D stacked MCOFs. The cohesive energies (E_C) for bulk metals are also listed for comparison

	MCOF-1		MCOF-d		Bulk metal
	L (Å)	E_M (eV)	L (Å)	E_M (eV)	E_C (eV)
Li	3.7	2.289	3.9	2.231	1.605
Na	4.6	1.408	4.7	1.490	1.048
Mg	4.3	0.057	3.7	0.202	1.296
K	5.4	1.596	5.4	1.708	0.798
Ca	4.4	2.830	4.4	2.786	1.877
Ti	3.6	5.058	3.6	4.993	5.207

The new MCOF material can be approximately viewed as reduced intercalation compounds with metal dopants in cation states. Our Bader charge analysis shows that there are about 1.42 electrons transferred from Ca to COF-1 during CaCOF-1 formation, and 0.84 electrons transferred from Li to COF-1. This new class of materials contains porous structures with stable, active metal sites, which provide extraordinary advantages for molecular adsorption and storage, in particular, for H_2 storage. In this aspect, MCOF as the new class of 3D material is significantly different from earlier proposals including those employing $Ca_{32}C_{60}$ and other metal-doped materials, in that:

i) It is an extended three-dimensional framework that can be readily exploited in practical applications; while $Ca_{32}C_{60}$ is finite whose 3D assembly is not feasible without significantly reducing H_2 density.

ii) MCOF is thermodynamically stable with metal binding energies greater than that in bulk metals; while on C_{60} , Ca has a binding energy of 1.3 eV, significantly smaller than that in bulk Ca (1.88 eV)^{18,22}, therefore metal segregation is a severe problem during 3D assembly.

iii) MCOFs have intrinsic well-ordered pores freely available for H_2 diffusion during charge/discharge processes; while $Ca_{32}C_{60}$ material does not have this advantage.

The porous MCOF-1 structures with stable, active metal sites are ideal candidates for H_2 storage. We employ first-principles DFT to study the interaction between MCOF and H_2 molecules, to eliminate uncertainties in H_2 binding configuration and energies in empirical calculations. Structure optimization with a full coverage of four intact H_2 per metal atom was performed for CaCOF-1 and LiCOF-1. We found that LiCOF-1 fails to bind H_2 strongly. The H_2 binding energy (E_b) varies from ~ 0.05 eV/ H_2 to 0.02 eV/ H_2 for a single H_2 and for 4 H_2 adsorption per Li, due to the fact that Li is strongly bound to the upper and lower COF-1 layers and the interlayer spacing is rather limited (3.7 Å). On the other hand, CaCOF-1 can serve as an excellent H_2 storage material with the H_2 binding energy of 0.13 eV/ H_2 with generalized gradient approximation (GGA) exchange-correlation functional and 0.42 eV/ H_2 with local density approximation (LDA), corresponding to a gravimetric storage capacity of 4.54 wt% and volumetric density of 35.2 g/L at 0 K, very close to the 2017 DOE target. Using VDW-DF the H_2 binding energy to CaCOF-1 is 0.18 eV/ H_2 , a reasonable value lying between GGA and LDA numbers, which are known to underestimate and overestimate E_b , respectively¹¹. Simpler Grimme's DFT+dispersion approach also gives reasonable values for VDW interaction energies between H_2 and metal sites in metal organic frameworks⁴¹. In high-level MP2 and quantum Monte Carlo calculations a binding energy of ~ 0.2 eV was obtained for H_2 binding to partially charged Ca, with basis-sets extrapolated to complete basis limit^{42,43}. This number is close to our results. Based on the calculated H_2 binding energy, it is shown later the high H density persists at near-ambient conditions. For comparison, H_2 storage capacity of the COF-1 without metal intercalation was found only 1.28 wt% at 77 K and ambient pressure, and 0.08 wt% at 298 K and 20 bar in experiment³².

The nearly sixty times increase in storage density under near ambient conditions in COF-1 upon Ca intercalation is attributed to the presence of dense, active metal sites and the ideal binding energy to H_2 . In CaCOF-1 framework, the empty Ca $3d$ orbitals interact strongly with the p orbitals of COF-1, presenting large density of states (DOS) around the Fermi level, see Fig. 2. These states are saturated upon H_2 binding. The energy distribution of H_2 orbitals is highly overlapped with Ca $3d$ orbitals, suggesting H_2 binding onto CaCOF-1 via a Kubas mechanism, namely, hybridization between the antibonding σ^* orbital of H_2 and the d -orbital of Ca^{3,22}.

Optimizing MCOFs: the organic building blocks. Although CaCOF-1 has shown outstanding property and great promise for H_2 storage, it is unclear whether this approach can be extended to other systems, or can be further improved to produce new materials satisfying DOE target of a 5.5 wt% density. We then explore a range of possible alternatives of organic building units and illuminate the systematic trends in H_2 binding behaviors, in the hope to optimize MCOF building blocks for enhanced H_2 storage capacity and to identify important parameters for MCOF design.

Benzene as the reference organic unit. To seek an optimal organic building block, the organic unit of COF-1, a benzene ring, was first studied as a standard reference. Ca binding to C_6H_6 produces a small energy, 0.07 eV/Ca, less than the binding energy of Ca to the single layer COF-1, due to limited electron conjugation in isolated benzene molecules. The first H_2 adsorbs onto CaC_6H_6 in intact form, with H-H bond length (d_{HH}) expanding from 0.749 to 0.785 Å. With the increase of the number of adsorbed H_2 molecules (n), H_2 binding energy and H-H bond length both first increase, then decrease, shown in Fig. 3. The maximum averaged H_2 binding energy $E_b = 0.34$ eV/ H_2 is reached when $n = 4$; and the maximum d_{HH} reaches 0.804 Å at $n = 3$. The maximum is not for $n = 1$ because of the competition between electron polarization and Pauli repulsion. We note that there is a strong correlation between average E_b and d_{HH} , which might be used to steer optimal design of H_2 storage material. PDOS analysis for 1-5 H_2 adsorption onto CaC_6H_6 clearly indicates there is a largest mixing between H_2 states and Ca d -orbitals and a high occupation of H_2 antibonding states and Ca d -orbitals for $n = 3$ and 4. The sixth H_2 , initially placed close to Ca, is repelled to a

distance larger than 6 Å, suggesting the system with five H_2 to be saturated. The maximum of five H_2 molecules offer 10 electrons, together with 2 electrons from Ca and 6 π -electrons from benzene, the 18-electron rule is nicely satisfied as proposed for H_2 storage on transition metal complexes¹⁵. The average binding energy is ~ 0.29 eV/ H_2 . For comparison, on Ca-decorated terephthalic acid, H_2 binding energy was calculated to be 0.20 eV in GGA and 0.24 eV in MP2 with completed basis set⁴². Among the adsorbed H_2 molecules, we observe that H_2 prefers to adsorb in the neighborhood of Ca- C_6H_6 , than on the top site of Ca. This is also indicated by the difference in binding energies (0.11 vs 0.06 eV) and H-H lengths (0.785 vs 0.752 Å) on the two sites, respectively. It is because the neighboring four molecules interact with Ca via the Kubas mechanism, as shown in Fig. 4; while the top H_2 is bound via the long-ranged electrostatic attraction since no overlap between H_2 bound state and Ca d -orbital was observed in PDOS¹². Notice that in the case of Ca coated fullerene²², the maximal number of adsorbed H_2 molecules per Ca is five with the same trend for E_b . The Ca binding energy increases to 0.73 eV/Ca with two Ca bound on both sides of benzene, perhaps due to the more polarized π orbitals of benzene than the case of single Ca adsorption. Detailed analysis shows that upon two Ca adsorption, there are +0.99 electrons transferred from each Ca to benzene, larger than that for a single Ca adsorption (+0.88 electrons). The H_2 can be adsorbed in total, leading to H storage capacity of 11.2 wt% (0 K), with $d_{HH} = 0.785$ Å; the E_b of 0.23 eV/ H_2 falls in the ideal range of 0.2–0.6 eV/ H_2 .

Comparison to other small molecules. Then a series of Ca-decorated small organic molecules including C_2H_m ($m = 2,4,6$) and ring structures are investigated. Although some molecules are not yet directly used as COF building blocks, exploring their potential performance yields valuable information for comparison to currently available materials and provides new insights for future applications. Compared with C_6H_6 , we find Ca binding to the first three molecules is very weak, with $E_{Ca} \leq 0.01$ eV, making them unstable for hosting H_2 . The binding energy of Ca to neutral C_5H_5 is 3.24 eV, showing a strong interaction between them. This is a result of electron deficiency in C_5H_5 : to form a stable aromatic system⁴⁴, 6 π electrons are required; where C_5H_5 supplies only 5, with another electron from Ca. Therefore the CaC_5H_5 complex formed is a

Figure 3 | (a) Average H_2 binding energy (E_b) and H-H bond length (d_{HH}) as a function of the number of adsorbed H_2 on $Ca-C_6H_6$. (b) Optimized geometry of ten adsorbed H_2 on $Ca_2C_6H_6$.

Figure 4 | (a) Side and (b) top view of charge density difference after Ca binding onto benzene. Isosurfaces with values of $\pm 0.005 e/\text{\AA}^3$ are shown. Red and blue clouds correspond to electron depletion and accumulation, respectively. (c) Same as (b) but for both two Ca and 10 H₂ binding to benzene. (d), (e) Same as (a) and (b) but for Ca binding on five-membered C₅H₅. (f) The H₂ binding energy as a function of distance (*z*) between Ca and H₂ on C₅H₅.

product of reduction-oxidation chemical reaction, namely, C₅H₅ is reduced by an electron from Ca to form a stable compound. Very surprisingly, the Ca-C₅H₅ seems to be saturated and does not bind any H₂. No matter where the H₂ molecule is initially placed, it is repelled to a distance $> 4 \text{ \AA}$ from Ca with negligible binding energies ($\leq 0.005 \text{ eV/H}_2$), shown in Fig. 4(f). It implies the electrostatic force is dominant. This behavior is in contrast to that for Ca-C₆H₆, suggesting that strong interaction between Ca and the organic component does not necessarily introduce a strong binding to H₂; instead, the metal-organic complexes get saturated and become inert to H₂ binding. Therefore organic systems with too strong or too weak Ca binding fail to bind H₂ well. A good balance between stability (Ca-binding) and reactivity (Ca-H₂ interaction) is required for optimal H₂ storage.

Next, we substitute carbon atoms in benzene by boron or nitrogen, to check whether H storage properties are affected. Typical structures considered and results are shown in Fig. 5 (first row) and Table 2. We found substitutional structures with more than three B deform and are unstable, thus are not listed. Ca-doped C₄H₆B₂ and C₄H₄N₂ show much enhancement for the first H₂ adsorption, so we study multiple H₂ adsorption on them. The two can both host up to five H₂. The corresponding $E_b = 0.22 \text{ eV}$ and $d_{HH} = 0.771 \text{ \AA}$ for H₂ on CaC₄H₆B₂, and $E_b = 0.14 \text{ eV}$ and $d_{HH} = 0.784 \text{ \AA}$ for CaC₄H₄N₂. While they retain similar H₂ binding properties as that for Ca-C₆H₆, the Ca-binding is significantly improved, leading to more stabilized material and benign thermodynamical properties without metal clustering. This is due to the fact that the Ca-C₄H₆B₂ complex is

formed by chemical redox reaction, where Ca electrons are transferred to two-electron deficient C₄H₆B₂ molecule. If we dope two Ca to C₄H₆B₂ on both sides, ten H₂ are adsorbed, with $E_{Ca} = 2.56 \text{ eV/Ca}$, $d_{HH} = 0.771 \text{ \AA}$, and $E_b = 0.17 \text{ eV/H}_2$, corresponding to H₂ storage density of 11.5 wt% (0 K). The experimental route for B-substitution

Figure 5 | A variety of organic molecules serving as COF building units studied in this work. Cross symbols indicate stable positions for Ca binding.

Table 2 | Ca binding energy (E_{Ca}), adsorbed H-H bond length (d_{HH}) and energy (E_b) for H_2 on six- and five- membered rings

	C_6H_6	$C_4H_4N_2$	C_5H_6B	$C_4H_6B_2$	$C_3H_6B_3$	C_4H_4O	C_4H_4S	C_4H_5N
E_{Ca} (eV)	0.07	0.73	3.02	3.13	4.80	0.19	0.11	0.25
E_b (eV)	0.11	0.15	0.01	0.35	0.02	0.20	0.27	0.35
d_{HH} (Å)	0.785	0.774	0.753	0.805	0.755	3.778	3.846	3.680

might be complicated and their stability requires further investigation. Similar results^{36,45,46} were observed for Ca doping in B-substituted metal-organic framework MOF-5 and COF.

We also consider substitution of C in the five membered rings. Three existing heterocycles, furan (C_4H_4O), tetrahydrothiophene (C_4H_4S) and pyrrole (C_4H_5N) are tested. Ca binding energies are 0.10–0.25 eV on these structures, and the first H_2 is dissociatively adsorbed on the top of Ca, with $d_{HH} \geq 3.680$ Å (Table 2). Less than two more H_2 molecules can be adsorbed further, with the binding energy of 0.1–0.2 eV/ H_2 . They are not suitable for H_2 storage.

Large polycyclic aromatic hydrocarbons. Polycyclic aromatic hydrocarbons are formed when two or more benzene rings are connected in the same aromatic plane. The interaction energy between Ca and the isolated compounds increases to around 1.1 eV, shown in Table 3. In this case, the distance between adjacent Ca atoms, d_{Ca-Ca} , is an important parameter. If the distance is too small, it could lead to metal clustering or H_2 bound to two Ca atoms, both reducing H storage capacity. We found on p-terphenyl ($C_{18}H_{14}$) $d_{Ca-Ca} = 4.105$ Å, and four H_2 molecules between adjacent Ca dissociate by the strong reaction to Ca. With the distance extends to 6.847 Å on diphenylethyne, dissociation of H_2 molecules disappears and all H_2 are kept intact with $d_{HH} \approx 0.782$ Å. As a result, the total number of twenty H_2 are adsorbed on Ca-doped diphenylethyne (five per Ca), with a capacity of 10.6 wt% (0 K). However, for these isolated molecules, Ca binding energy is smaller than its cohesive energy in bulk, the metal clustering problem might occur if using these isolated compounds for H_2 storage.

Optimizing MCOFs: effects of the linker groups. Besides the organic units, linker groups play an essential role in forming COFs via connecting organic units studied above. Two common covalent linkers, $-COOH$ and $-B(OH)_2$, are usually employed. The carboxylic acid groups form hydrogen-bonded assemblies²⁸, while $-B(OH)_2$ groups produce a six-membered ring (B_3O_3) after sublimation of three water molecules²⁷. Five-membered BO_2C_2 ring could also form if hydroxyl groups ($-OH$) are readily available during COF synthesis²⁷.

To investigate the effect of linking groups on H storage, we add $-COOH$ and $-B(OH)_2$ to four Ca-decorated compounds, including benzene, biphenyl, p-terphenyl and diphenylethyne. Similar to Ca-coated benzene, ten H_2 molecules can be stably adsorbed on $Ca_2C_6H_4(B(OH)_2)_2$. Slight changes in binding energy of H_2 from 0.23 to 0.21 eV, and in d_{HH} from 0.785 to 0.787 Å are observed. Ca binding is also improved by 0.203 eV, due to π electron delocalization from phenyl rings to more electron-negative linker groups. For Ca-coated biphenyl, we compare H_2 adsorption on compounds with

$-B(OH)_2$ and $-COOH$ linkers, shown in Table 4. While the former shows little difference from $C_{12}H_{10}$ in every respect, the latter enlarges Ca-Ca distance from 3.658 to 4.155 Å, leading to the number of adsorbed H_2 increasing from 12 to 16. This is attributed to a stronger interaction between Ca and phenyl rings when $-COOH$ linkers are connected to phenyl rings. Therefore, the presence of $-B(OH)_2$ linkers preserves H storage properties of the original compound, while the $-COOH$ groups increase the H_2 capacity by elongating Ca-Ca distances.

We adopt this principle to select linker groups for Ca-decorated PAHs. The Ca-Ca separation on $C_{18}H_{10}(COOH)_4$ is only a little larger than that on $C_{18}H_{14}$ (from 4.105 to 4.244 Å), but H_2 capacity increases greatly, from 18 to 24 H_2 molecules per unit, shown in Fig. 6(a,b). On the other hand, since the Ca-Ca separation is already too large on diphenylethyne (6.8 Å), we use $-B(OH)_2$ linkers to preserve its H_2 storage property. As expected, all parameters such as $E_{Ca} = 0.87$ eV, $E_b = 0.17$ eV, $d_{Ca-Ca} = 6.9$ Å, and $d_{HH} = 0.783$ Å are very close to the original complex. The same number of H_2 molecules is adsorbed. Importantly, both systems have a desirable H_2 binding energy of ~ 0.17 eV/ H_2 . So the $Ca_4C_{14}H_8(B(OH)_2)_2$ unit could potentially serve as an optimal building block promising for constructing MCOF to store H_2 .

Properties of three-dimensional CaCOF-d. The optimization procedures described above identify Ca intercalated COF structure with diphenylethyne organic unit and B_3O_3 linkers, named as COF-d hereafter, as most promising for H_2 storage. Similar to COF-1, COF-d also forms 3D MCOF structures upon intercalation with metal elements such as Ca and Li, which preserves the ideal H_2 storage property in low-dimension materials. We then calculate the equilibrium structure and energy storage properties of the 3D intercalated CaCOF-d material in a rhombic unit cell with in-plane dimensions of $27.24 \text{ Å} \times 27.24 \text{ Å}$ and vary its interlayer distance. The unit cell contains three branches of diphenylethyne connected to the center boroxine ring, namely, it consists of 42 carbon atoms, 24 hydrogen atoms, 6 oxygen atoms, 6 boron atoms and 6 calcium atoms before H_2 adsorption (see Fig. 7). The optimized interlayer spacing is found to be 4.4 Å for the minimum energy configuration, adopting an eclipsed stacking manner to maximize interlayer interactions. We note the eclipsed stacking is chosen for all COFs with relatively large organic building blocks, with or without metal intercalation²⁵. The Ca binding energy in CaCOF-d, with respect to isolated COF-d layer and free Ca atoms as a reference, is calculated to be 2.79 eV/Ca (see Table 1), largely exceeding the cohesive energy of 1.88 eV for bulk Ca. This indicates Ca atoms in this assembly cannot form metal clusters, similar to the case of CaCOF-1. Compared to CaCOF-1, the Ca binding energy is only slightly decreased by

Table 3 | Number of adsorbed Ca atoms (N_{Ca}), average binding energies per Ca (E_{Ca}) and distances between adjacent Ca (d_{Ca-Ca}) on representative PAHs. n is the number of adsorbed intact H_2 molecules

	Naphthalene	Anthracene	Biphenyl	p-Terphenyl	Diphenylethyne
	$C_{10}H_8$	$C_{14}H_{10}$	$C_{12}H_{10}$	$C_{18}H_{14}$	$C_{14}H_{10}$
N_{Ca}	4	4	4	6	4
E_{Ca} (eV)	1.14	1.06	1.16	1.13	0.80
d_{Ca-Ca} (Å)	3.326	3.859	3.658	4.105	6.847
n	8	11	12	18	20

Table 4 | Average binding energy per Ca (E_{Ca}) and the distance between adjacent Ca (d_{Ca-Ca}) on biphenyl with or without linker groups. Also shown are total number of adsorbed H_2 molecules (n), and their bond lengths (d_{HH}) and binding energies per H_2 (E_b)

	$C_{12}H_{10}$	$C_{12}H_8(B(OH)_2)_2$	$C_{12}H_6(COOH)_4$
E_{Ca} (eV)	1.16	1.25	1.46
d_{Ca-Ca} (Å)	3.658	3.695	4.155
n	12	12	16
E_b (eV)	0.13	0.15	0.16
d_{HH} (Å)	0.765	0.765	0.776

0.04 eV/Ca. Interestingly, Li binding energy in LiCOF-d is also 0.06 eV/Li smaller than that in LiCOF-1, indicating the diphenylethyne unit is slightly less reactive than single phenyl groups during MCOF formation. Both CaCOF-d and LiCOF-d intercalation are stable 3D materials.

Three-dimensional stacking in CaCOF-d does not reduce much H_2 storage capacity in low-dimensioned clusters and overlayers. In CaCOF-d, a single Ca can adsorb four intact H_2 , all parallel to the

Figure 6 | Optimized geometry of (a) 22 H_2 on $Ca_6C_{18}H_{14}$, (b) 24 H_2 on $Ca_6C_{18}H_{10}(COOH)_4$, (c) 20 H_2 on $Ca_4C_{14}H_8(B(OH)_2)_2$.

Figure 7 | (a) H_2 storage on two-dimensional Ca-decorated COF-d layer. There are five H_2 molecules per Ca adsorbed in 2D CaCOF-d. The hexagonal unit is blown up on the right panel for clarity. (b) Three-dimensional CaCOF-d structure in two views. There are four H_2 molecules per Ca adsorbed in 3D CaCOF-d. For clarity H_2 molecules are omitted in the left panel.

plane of the COF-d layer, as shown in Fig. 7b, with the average binding energy ~ 0.15 eV/ H_2 in GGA form of exchange-correlation energy and 0.42 eV/ H_2 in LDA. We believe the exact binding energy

Figure 8 | (a) H_2 storage density of 3D CaCOF-d as a function of pressure at 77 K, 298 K, and 400 K. H_2 binding energy around 0.29 eV is used. (b) Comparison of storage density in CaCOF-d (excluding free-volume storage) and bare COF-1 (data from experiments in Ref.27) at 77 K.

lies between the two values, close to the averaged value at 0.29 eV/H₂, based on an empirical guideline that the binding energy averaged from LDA and GGA values is close to the precise Quantum Monte Carlo result for H₂ on B-doped fullerene¹¹. A storage capacity of 4.94 wt% at 0 K is calculated. The distance between two adjacent COF-d layers is 5.0 Å upon H₂ binding, enlarged by 0.6 Å compared to H₂ free materials. The estimation of H₂ density excludes the free volume storage of H₂ in the pores of CaCOF-d, which has a diameter of ~ 20 Å. If all possible adsorption sites are considered, this porous 3D network satisfies the 2017 DOE target for H₂ storage.

To unveil its practical advantage as a new class of ideal H storage material, Figure 8 shows the storage capacity of CaCOF-d as a function of pressure and temperature at near ambient conditions. The H₂ capacity at a given temperature T and pressure P is evaluated via the relation $f(\text{occupation number of adsorbed H}_2 \text{ molecules}) = kT\partial Z/\partial\mu$, where k is Boltzmann constant, Z is the grand partition function, and μ is the H₂ chemical potential^{47,48}. The grand partition function follows,

$$Z = \sum_{g_l} \prod_l \exp\{-g_l(\varepsilon_l - \mu)/kT\},$$

where ε_l is the adsorption energy per H₂ molecule when the number of adsorbed molecules is l , and g_l is the multiplicity (degeneracy) of the configuration for a given l . The chemical potential of H₂, μ , is given by

$$\mu(P, T) = \mu^0(T) - kT \ln \frac{P}{P^0},$$

where $\mu^0(T)$ is standard chemical potential and P^0 is standard state pressure. Here, μ and ε_l are negative values. The gravimetric density ρ of hydrogen storage is then obtained as,

$$\rho(P, T) = \frac{l_{\max} - f(P, T)}{l_{\max}} \times \rho_{\max}.$$

We adopt ambient pressure μ values in the literature⁴⁸. At 298 K and 20 bar, we obtain 4.87 wt% storage capacity (excluding H₂ storage in the free volume), which is substantially large than experimental values for un-doped COF-1 (0.1 wt%)³². The storage capacity is higher if H₂ adsorption onto B₃O₃ rings and in free volume is considered. Most of the stored H₂ (3.2 wt%) will be released at 298 K and 1 bar (by solely decreasing the pressure), or at 400 K and 20 bar (by solely increasing the temperature), where about 1.7 wt% H₂ retains. This favors near-ambient condition operation for H₂ storage and release, with impressive accessible H₂ uptake. Without Ca, the storage capacity is very low (see Fig. 8b), and near-ambient condition operation is not possible due to too small H₂ binding energies (~ 40 meV/H₂). The bulk MCOFs formed by Ca intercalation have advantages of being intrinsically three-dimensional, thermodynamically stable, and with well-ordered and adjustable pores, in contrast to previously proposed Ca₃₂C₆₀ and other Ca-doped nanomaterials^{22–24}.

Discussion

The 3D network based on Ca-decorated carbyne was recently proposed as stable H₂ storage media, where Ca binding energy ranges from 1.4 to 2.0 eV/Ca depending on Ca-Ca separation¹⁸. The E_{Ca} 's are close to bulk Ca cohesive energy. However, the base material, the 3D carbyne network has yet to be synthesized in experiment. Its existence and room temperature stability (in particular chemical reactivity) remain questionable. On the other hand, crystalline 3D networks formed by stacking COFs via van der Waals forces have been explicitly demonstrated²⁵; we expect Ca-decorated COF-1 to be readily fabricated in experiment, by Ca intercalation between weakly bound COF-1 layers at high temperatures (600 K) in Ar gases. Based on existing materials (graphite and metals), a similar approach has resulted the discovery of CaC₆, a superconducting material with

highest transition temperature of 11.5 K among metal-intercalated carbon materials⁴⁹. Hydrogen storage on metal intercalated graphite was also explored recently^{50–53}. Once formed, the new Ca-intercalated 3D COF material is thermodynamically stable (characterized by large Ca binding energy), and would be quite inert, except for Ca active sites. The metal sites in MCOF might be sensitive to water vapor contamination, as is the case for all other H₂ storage materials with active sites; in real applications water concentration must be carefully controlled during H₂ charging and discharging processes. Overall, these novel properties would favor MCOF synthesis and H₂ storage applications.

In conclusion, we have designed a new class of 3D networks based on first-principles: metal-intercalated COFs, which have well-defined crystal structures and are chemically active for molecular adsorption. Metal atoms prefer to bind to aromatic organic units rather than B₃O₃ connecting rings in MCOFs. Li, Na, K and Ca could be intercalated into COF-1 and COF-d layers and form thermodynamically stable materials, with metal binding stronger in MCOF than in bulk metals. For H₂ storage, Ca is the most suitable metal to be intercalated in the stacking structures. Important parameters, such as Ca-binding and separation, and trends on 5,6-membered rings and larger PAHs are identified. The covalent linker –B(OH)₂ preserves nicely H₂ storage properties, while –COOH linkers adjust Ca separation and in turn H₂ store capacity. Systematic optimization of organic building units and linker groups identifies CaCOF-d as most promising for near-ambient H₂ storage. The porous 3D material, CaCOF-d, reaches ~ 5 wt% H₂ storage capacity under near-ambient conditions without metal clustering problems. Routes for experimental synthesis are discussed. We envisage that this new class of MCOF porous materials, with a high density of active metal sites, would prove useful in a variety of applications including gas adsorption, sensors, and air cleaning.

Methods

Our first-principles calculations were performed within the framework of density functional theory (DFT) using Vienna ab initio simulation package (VASP)⁵⁴. The ultrasoft pseudopotentials⁵⁵ and general gradient approximation (GGA) in Perdew-Wang form for exchange-correlation energy⁵⁶ are used. For the cases of hydrogen adsorption in MCOFs, we also use local density approximation (LDA) for comparison⁵⁷. Although GGA tends to underestimate H₂ binding energies and LDA overestimates them, the trends for comparing relative energy differences are reliable^{42,58}. Recently developed van der Waals density functional (VDW-DF) by Langreth et al.³⁹ and parameterized by Klimes et al.⁴⁰ is also employed to check the energies in some critical cases. The binding energies and lengths reported throughout the manuscript are based on GGA exchange-correlation functional unless otherwise specified explicitly. Spin polarization is invoked whenever necessary. We found local magnetic moments are zero for CaCOF systems and very small (< 0.3 μ_B) for Li-COFs and variations in total energy are negligible. The supercells usually contain a vacuum layer of > 10 Å and have cell dimensions of 15 Å × 15 Å × 15 Å and 30 Å × 15 Å × 20 Å for small and large finite systems, respectively. A plane wave cutoff of 400 eV and single Gamma for k -point sampling are employed for isolated systems. For periodic systems, a rhombic 15.20 Å × 15.20 Å unit cell for COF-1 and 27.24 Å × 27.24 Å for COF-d is used within the COF plane, and the interlayer distance is carefully optimized. K -point mesh of 1 × 1 × 5 is used for calculating metal and H₂ binding properties of MCOFs. All atoms are allowed to relax until the forces on each atom have magnitudes less than 0.01 eV/Å.

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Author contributions

S.M. conceived the idea and carried out theoretical analysis. F.G. performed most of the numerical simulations. Z.D. carried out some numerical simulations and theoretical analysis. S.M. and F.G. analyzed the data and wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information

Competing financial interests: The authors declare no competing financial interests.

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