Rationally-designed nitrogen-rich MOC material: An efficient CO₂ adsorbent and H₂ confiner

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ABSTRACT. MOFs have been postulated for years as industrially achievable materials for CO₂ capture and H₂ storage. However, a great leap forwards their real applications is still pending. This article details the design of a MOF material, including the reasoned choices of metal ion, organic linker and even the structural subunits, as efficient adsorbent of both CO₂ and H₂. In particular, it was planned (i) to raise the polarizability of the framework by using a highly N-riched organic linker, and (ii) to favour the formation of nanocavities with suitable size to confine small molecules. The resultant tetrazole-imidazole-based ITF-1 material containing nanocubes, certainly achieved all these aimed premises. Nevertheless, such structural and compositional distinctiveness was reflected in some noteworthy adsorption features. CO₂ adsorption was highly remarkable and it was characterized by a wide hysteresis loop along the whole studied range of pressures. H₂ molecules totally filled the nanocavities under only 0.1 bar at 77 K, and at 273 K, H₂ uptake became tens of times higher than expected according to their textural properties. These unique adsorption results, together with the discussed relationship between structure/composition of ITF-1 and their adsorption features, underline the importance of a reasoned design of MOF materials for particular applications.

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ABSTRACT. MOFs have been postulated for years as industrially achievable materials for CO₂ capture and H₂ storage. However, a great leap forwards their real applications is still pending. This article details the design of a MOF material, including the reasoned choices of metal ion, organic linker and even the structural subunits, as efficient adsorbent of both CO₂ and H₂. In particular, it was planned (i) to raise the polarizability of the framework by using a highly N-riched organic linker, and (ii) to favour the formation of nanocavities with suitable size to confine small molecules. The resultant tetrazole-imidazole-based ITF-1 material containing

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29 MOC sub-units, carbon dioxide, hydrogen, hysteresis loop, adsorption.
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1. INTRODUCTION

Nowadays, two of the biggest scientific challenges in environmental and energetic fields are CO₂ capture and H₂ storage. In both fields, Metal-Organic Framework materials (MOFs) have been postulated as potential alternatives, but they are still far from reaching the imposed requirements^{1, 2}. The rush to get most open MOFs is sometimes justified in terms of improving their capacity for adsorbing highly demanded gases. However, CO₂ capture is a more complex phenomenon than a simple adsorption process, as this molecule is generally emitted accompanied by a variety of gases. Therefore, not only the global capacity of the adsorbent but also a high selectivity to CO₂ is valuable, if not compulsorily required. It is well-known the enhancement of the CO₂ affinity by porous adsorbents when they exhibit small pores, able to confine the molecules by increasing the van der Waals forces³, and when they are functionalized with N-containing groups such as amines⁴ or imines⁵. MOFs are not an exception and thus similar behavior has been described in amino-functionalized MOFs^{6, 7} compared to their non-functionalized homologues. Similarly, tetrazole-based MOFs exhibit ones of the highest values of CO₂ adsorption capacity amongst the known MOFs and, not least important a remarkable CO₂ selectivity at 273 K and 1 bar in mixtures CO₂/CH₄, due to the multipointed interactions between CO₂ molecules and MOF structure^{8, 9}. Moreover, metal azolate frameworks are characterized by possessing strong and directional coordination ability in bridging metal ions^{10, 11}, and thus they generally show good thermal and chemical stabilities, sometimes higher than those of the carboxylate-based MOF homologues¹². Therefore, a coherent design of a MOF material for CO₂ capture purposes could include organic linker based on imidazoles, triazoles or, even better, tetrazoles.

Regarding H₂ storage by MOFs, it is quite common to find a linear correlation between their H₂ uptakes and their surface areas,^{1, 13} evidencing a poor chemical affinity of these materials for efficiently retaining H₂. Breaking that linearity becomes really difficult because of the hardly-compressible character of H₂.¹ However, it is widely assumed that achievement of MOFs of either lower framework density or possessing larger pores is not enough to reach the adsorption industry needs.¹ Instead, it must be combined with some other features of MOFs that increase the interaction to H₂ molecules. Fortunately, the exceptional versatility of MOFs has allowed developing very different strategies for making MOF materials better adsorbents of H₂, such as the increase of free volume of the framework by discovering new opener structures¹⁴, the presence of unsaturated and exposed metal sites¹⁵, the possibility of functionalizing the organic linker¹⁶, the partial doping of framework metal^{17, 18}, the incorporation of extraframework noble metal species to favor spillover effects^{19, 20} or the ion exchange in MOF having charged frameworks²¹⁻²³. Although all these strategies were successful to a greater or lesser extent, the results of none of these approaches have been promising enough to guarantee that any of them is the right way to go. However, there is another potential structural feature in MOFs that has been theoretically pointed out^{23, 24} but scarcely studied^{25, 26} as augment of H₂ adsorption efficiency: the confinement of H₂ within tailored nanocavities, what would increase the isosteric heat of H₂ adsorption by favoring the dispersive (van der Waals) H₂-MOF surface interaction²⁷. A confinement of H₂ molecule will be ideal within pores whose walls are separated by two times the kinetic diameter of H₂ (2.9 Å)²⁷, so that quantum effects becomes noteworthy in pores with diameters below 6 Å²⁴. In the same way, other authors have suggested that MOFs with pore diameters slightly larger than kinetic diameter of hydrogen molecule (4.5-5.0 Å)²⁸ are desirable for H₂ adsorption, even sacrificing part of their pore volume. Additionally, it is foreseeable that

confinement effects become more pronounced when cavities with diameters close to 6 Å in the three spatial dimensions (rather than simple pores, windows or free volume delimited by network catenation) constitutes the MOF framework. All these premises match very well with MOF materials containing the so-called metal-organic cubes (MOCs), forming nanocavities²⁹ of the desired dimensions. Those subunits MOCs are formed by isolated metal ions and imidazole-based linkers, which gives Me-imidazole-Me angles of $\sim 145^\circ$, just like the average angle of zeolite nets. In fact, MOC-based materials usually adopt zeolite-like topologies, like other zeolite-related MOFs (either ZIF³⁰ or ZMOF^{31, 32} materials), which have also organic linkers based on imidazole. Some zeolite nets share eight tetrahedral subunits in a cube-like arrangement, commonly called double 4-ring D4R³³. Accordingly, the metal-organic cubes can be considered as D4R building subunits able to generate zeolite-like frameworks^{29, 34, 35} with different topologies such as **lta**, **aco**, **ast** or **asv**. The imidazole-based D4R cube subunits have dimensions close to those ideals for H₂ confinement^{24, 27, 28}, as the distance between two contiguous metal atoms, which are in the cube corner, are of *ca.* 6.3 Å not considering their atomic neither van de Waals radius³⁴.

Therefore, the choice of a MOC-based material in this work seems reasonable because it would have nanocavities of a predesigned size and also because it would be an imidazole-tetrazole-based MOF with high N-content that would favor H₂³⁶ and CO₂ molecule polarization. In other words, both CO₂ and H₂ adsorption could be favored by different reasons in that still-theoretical MOF. To make the linker even richer in N, a non-commercially available linker will be prepared in our laboratory by introducing two tetrazole groups over the two consecutive C atoms of the imidazole (Figure 1). Presumably, the metal ion would continue preferring to be

linked to the N atoms of the imidazole groups, which are prone to direct D4R MOCs sub-units³⁵ and would be not necessarily hindered by tetrazole substitution.

Figure 1. Organic linker 1H- imidazol-4,5-tetrazole (HIT).

Moreover, the choice of metal ion should be based on controlling its coordination number, and the size and the geometry of its inorganic units in order to generate predesigned finite metal-organic units. In this context, indium has been chosen as the structural metal for other MOFs exhibiting zeolite-like topology or MOC structures³⁸, in which inorganic moiety is composed by isolated metal atoms instead of metal clusters³⁴, favouring the formation of cavities with smaller sizes. More importantly, some MOCs have been also described with In^{3+} as isolated metal ion²⁹. Therefore, the choice of In as metal atom and imidazole as the linking point within the organic ligand should make easier our aim, taking MOC-2 and MOC-3 materials as inspiration³⁵.

2. EXPERIMENTAL SECTION

2.1. Organic ligand preparation. The organic linker 4,4'-(1H-imidazole-4,5-diyl)bis(1H-tetrazol-4-ium) (HIT, Figure 1) is not commercially available. It was prepared following a modified recipe given by Demko et al.³⁷ in which tetrazole groups substitutes cyano ones, shown in Scheme 1. 1H-imizole-4,5-dicarbonitrile (20 mmol), sodium azide (1.43 g, 22 mmol), zinc

bromide (4.50 g, 20 mmol), and 40 mL of water were mixture in a round-bottom flask. The reaction mixture was refluxed for 24 h under vigorous stirring. The white solid was filtered and washed 5 times with 20 mL of deionized water. 3 mL of nitric acid was added to the last suspension, until reaching a pH value of 1, and vigorous stirring was continued during 1 h at 80-90 °C. Finally, tetrazole-based product was filtered and again washed another 5 times with 20 mL of deionized water, and dried in an oven at 110 °C during 6 h.

Scheme 1. Synthesis of HIT organic ligand.

2.2. Metal-organic framework material preparation. ITF-1 (Imidazole- and Tetrazole-based Framework number 1) material was prepared from a mixture of HIT and In(NO₃)₃·xH₂O in a N,N'-dimethylformamide (DMF) / acetonitrile (CH₃CN) mixture middle acidified, also containing hexamethylenetetramine (HMTA) as an structure directing agent (SDA), having the following molar composition: 1 In : 2 HIT : 500 DMF : 574 CH₃CN: 4 HTMA : 18 HNO₃. This mixture was heated at 1 °C/min up to 85 °C, and this temperature was maintained during 42 hours. After decanting the mother liquor, the solid product was washed and kept submerged in a DMF:CH₃CN mixture (1:1 vol.).

2.3. Characterization of the samples. Single-crystal X-Ray Diffraction (XRD) data for ITF-1 were collected using Bruker-AXS SMART-APEX CCD diffractometer using MoK α (λ = 0.71073 Å). Indexing was performed using APEX2³⁸ (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01³⁹. Absorption correction was

performed by multi-scan method implemented in SADABS⁴⁰. Space groups were determined using XPREP implemented in APEX2³⁸. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F^2) contained in APEX2³⁸, WinGX v1.70.01⁴⁰⁻⁴⁴ and OLEX2 programs packages⁴⁵. Atoms of the ligand and metal cations have been refined anisotropically. Disordered counterions and solvent have been refined isotropically and using restraints. Counterions and solvent molecules are heavily disordered. In some cases it was possible to tentatively locate dimethyl ammonium cations and acetonitrile molecules. The rest of disordered solvent have been modeled as O atoms. Cations (N31 and N41) form hydrogen bonds with MOC nitrogen atoms. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: $U_{iso}(H) = 1.2U_{eq}(-CH)$. The relatively large electron density peak (3.972 e.Å^{-3}) is located 0.94 Å from In cations. Crystal data and refinement conditions are shown in Table S1. Powder X-Ray Diffraction (PXRD) patterns were obtained in a Philips XPERT PRO using $\text{CuK}\alpha$ ($\lambda = 1.542 \text{ Å}$) radiation. In order to avoid the effects of preferred crystal orientation, the samples were grounded.

Scanning electron microscopy (SEM) images and micro-elemental analysis (EDS) were obtained on a Philips XL-30 ESEM operated at 200 kV. Fourier transform-infrared spectra (FT-IR) were recorded for powder samples in a Mattson Infinity Series spectrophotometer with a coupled catalytic chamber and a resolution of 4 cm^{-1} . Elemental analyses were carried out using an analyzer type ELEMENTAR VARIO EL III, equipped with a thermal conductivity detector, being the oven temperature and the reduction coil temperature of 1423 K and 1123 K, respectively. N_2 adsorption–desorption isotherms were measured at 77 K on an AutoSorb equipment (Quantachrome Instruments). Samples of about 20–40 mg were previously in situ evacuated under high vacuum ($<10^{-7} \text{ bar}$) for 24 h at 40 °C .

CO_2 and H_2 (99.999 %) isotherms at 273 K (and also at 77 K in the case of H_2 isotherms) were carried out on a Hiden Analytical Intelligent Gravimetric Analyzer equipped with an ultra-high

vacuum system. The microbalance showed a long-term stability of $\pm 1 \mu\text{g}$ with a weight resolution of $0.2 \mu\text{g}$. The approach to equilibrium was measured real time using a computer algorithm. The pressure was monitored by two pressure transducers in the ranges 0–1 bar and 0–20 bar. The buoyancy effects were corrected as a function of temperature taking into account the void volume of the cell determined with He gas at 77 K, and assuming that the amount of He adsorbed is negligible.

3. RESULTS AND DISCUSSION

Once the pure organic ligand was obtained (NMR and FTIR spectra are shown in Supporting Information), a systematic study of crystallization variables of the new MOF material was carried out by modifying: organic ligand/metal ratio, nature of solvent, presence / absence of different structure directing agents, basic-acidic media or crystallization conditions. Finally, optimized conditions were found for crystallizing the new ITF-1 material, as described in Experimental part.

The crystalline structure of this material was solved by single crystal X-ray diffraction technique (Figure 2). At first glance, the most relevant features of the structure are that: (i) a 3-D N-rich zeolite-like MOF composed by indium and a linker with exposed tetrazole groups and, (ii) D4R MOC-based nanocavities of the desired dimensions. Therefore, the main objectives of the new structure have been somehow achieved. In the negative part, the concentration of these nanocavities within the framework is rather low, compared to some other MOC-n materials described by Eddaoudi and coworkers.^{34, 35} Such low concentration is related to the arrangement and the steric hindrances of tetrazole groups, as they must necessarily point out away from the MOC, what makes difficult any condensation between MOC units, even by sharing vertexes. Nevertheless, these handicaps could somehow become advantageous, since it could allow the

evaluation of both H₂ and CO₂ confinement and adsorption efficiency regarding its isolated MOC D4R units and the influence of a high exposing degree of N atoms from the tetrazole groups.

The as-synthesized ITF-1 material has a molar composition of C₉₆H₁₆₁In₈N₁₃₈O_{16.76} or [In₈(C₅H₁N₁₀)₁₂]¹²⁻·12[NH₂(CH₃)₂]⁺·6CH₃CN·16.76H₂O. As predesigned and unlike so many porous MOFs, this structure does not contain metal clusters, what partially explain their relatively small pores. Each In³⁺ ion has a quite symmetrical octahedral coordination to six nitrogen atoms, InN₆, belonging to one of three different HIT linkers connected to the In metal by both the imidazole and a tetrazole groups. The bis(bidentate) ligand 4,4'-(1H-imidazole-4,5-diyl)bis(1H-tetrazol-4-ium) (HIT) favors the coordination of the both N atoms of the imidazole group to two different indium atoms, leading to the construction of a metal–organic cube, in such a way that imidazole rings form the cube edges and single indium atoms form the cube vertexes. This is exactly what we expected from the original design, based on the precedents found in other MOCs.^{29, 34} Therefore, the metal–nitrogen bonds from imidazole rings rather than these from tetrazole groups are indeed the driving force of the achieved structure. In – In – In angle is strictly 90°, making clear the exactness of the MOCs cube units, whereas the In – In distances along the edges are 6.543 Å, a bit longer than Ni-Ni distances (6.29-6.33 Å) in a similar MOC subunit³⁴, as a consequence of different ionic radii of Ni²⁺ (83 pm in octahedral coordination) and In³⁺ (94 pm in the same coordination). Taking into account that atoms are not points but have a not-negligible size (whose magnitude depends on the considered radius), the size of the cavity is close to the estimated optimum size for H₂ confinement.

Crystal data of ITF-1 material were: C₉₆ H₁₆₁ In₈ N₁₃₈ O_{16.76}; Mr = 4435.29, Trigonal, *R*-3, *a* = *b* = 29.475(2), *c* = 22.140(2), *V* = 16657.7(18) Å³, *Z* = 3, *D_c* = 1.326 g/cm³. These results agreed

very well with that from elemental analysis, 29.5 % C, 39.0 % H, 33.2% N. The spatial arrangement of linkages between MOC units gives ITF-1 material with a known zeolitic topology, whose three-letter IZA code is AST,³³ (Figure 2, bottom) coinciding with the topology of MOC-3³⁵. Although strictly speaking AST materials with zeolitic composition are not porous, as its largest pore is of the 6-MR, in the case of ITF-1 the pores are very much larger since the HIT linker substitutes an oxygen atom of its homologous zeolite framework. The theoretical accessible volume was 46 %, estimated through Connolly software⁴⁶.

Figure 2. a) Unit cell of ITF-1, as solved by single-crystal data. In: light brown, C:grey, N: blue. b) Cube arrangements in AST topology. c) Representation of MOC cube with In metal as light brown polyhedron.

In order to confirm the purity of the sample and the goodness of single-crystal resolution, the experimental and the simulated (from crystallographic data) powder X-ray diffraction patterns are compared in Figure 3. Both patterns match very well in position and relative intensity of the reflections, ratifying that the only phase present in the sample corresponds to the solved structure.

Figure 3. Powder XRD patterns of experimental and simulated from single-crystal data of ITF-1 material.

SEM images of ITF-1 sample at different magnifications are shown in Figure 4. The sample is basically formed by well-defined polyhedral crystals of uniform size (of ca. 20 μm) and shape, which suggests again the high purity of the sample.

Figure 4. SEM micrographs of as-synthesized ITF-1 material.

The porosity of these materials was measured by carbon dioxide adsorption at 273 K (Figure 5, red line), since the adsorbed volume of N₂ at 77 K was practically negligible (Figure 5, black line). Like in other microporous materials unable to adsorb N₂ in a substantial part of their porosity, the micropore specific surface area of the ITF-1 material was estimated by applying Dubinin-Radushkevich⁴⁷ and Stoeckli⁴⁸ methods to the experimental CO₂ adsorption data registered at 273 K. The so-estimated surface area was 213 m²/g, evidencing the microporous character of the ITF-1 material. Although the estimated surface area seems to be rather low compared to those of some other MOFs, it must be noted that: (i) its homologue MOC-3, which has an **ast** topology too and very similar D4R cubes, also gave relatively low surface area (450 m²/g)³⁵; (ii) unlike MOC-3, ITF-1 was practically unable to adsorb N₂ at 77 K (Figure 5), giving an idea that it has more hindered / inaccessible porosity; and (iii) there is no guarantee that the pores are wholly accessible for CO₂ at 273 K, being possible, for instance, that the detected adsorbed CO₂ is retained basically by the polarizing tetrazole groups. The reason why N₂ is scarcely adsorbed in an evacuated samples (otherwise, it is difficult to explain the substantial CO₂ adsorption) are not clear at this point, and it was unexpected from the structure solved from X-ray crystallographic data. This a priori anomalous behavior suggests N₂ molecules cannot enter the pores at 77 K due to diffusional resistances. Similar behavior has been reported for other porous materials, including MOF-^{49, 50} and carbon-based^{51, 52} ones, all of them having small pores as a common feature. At higher temperatures (for instance, at 273 K, at which CO₂ isotherm was registered) thermal energy allows the molecules to overcome these resistances. In addition, CO₂ adsorption should be favored against the N₂ one due to the smaller size (3.30 vs. 3.64 Å, respectively) and the higher quadrupolar moment / polarizability of the former⁵³. The

difference in polarizability will be highlighted below, and attributed to the high N content of the tetrazole-based MOF material. Therefore, although both isotherms from Figure 5 could not be strictly comparable, it is presumable that this MOF could have a relevant behavior as CO₂/N₂ separator, in good agreement with what has been described for some other N-rich MOFs⁵⁴.

Figure 5. N₂ and CO₂ isotherms of the ITF-1 sample at 77 and 273 K, respectively.

Figure 6 shows the CO₂ adsorption / desorption isotherms of the sample ITF-1 at 273 K in the pressure range of 0-10 bar. CO₂ adsorption is outstanding for a MOF material with a surface area of only 213 m²/g. Such CO₂ uptake (18.6 wt.% at 10 bar) is about one third of the one given by a MOF-5 material (59.3 wt.%) under the same conditions¹⁷, which has a notable CO₂ capacity amongst some other materials². However, an analysis of those data considering the specific surface area of both compared MOF materials (213 m²/g for ITF-1 and 2450 m²/g¹⁷ for MOF-5)

indicates a CO₂ uptake almost four times more effective in the case of the ITF-1 sample (0.087 vs. 0.024 g CO₂/m² adsorbent). On the other hand, another noteworthy feature of the isotherm from Figure 6 is a prominent hysteresis loop between the adsorption and desorption branches. Its origin is probably related to the constrained pores that avoided an appropriate estimation of surface area by N₂ adsorption isotherms at 77 K (Figure 5); if so, physical rather than chemical interaction could differentiate adsorption and desorption processes. A second possibility would be related to the interaction between N-rich framework and CO₂; during the adsorption process, CO₂ could be fixed on any center with mild affinity for it, and even this CO₂ adsorption could contribute to hinder other potential stronger adsorption centers, also facilitated by the diffusional problems in so narrow cavities; the longer time spent until desorption starts would allow CO₂ to find the centers that retains it more strongly, and the desorption is consequently produced more orderly according to the centers affinity for CO₂. In both possibilities, the presence of the hysteresis loop suggests that the CO₂ isotherm is not under equilibrium conditions but somehow influenced by kinetics. The hysteresis loop only closes at pressures very near 0 bar (below 0.02 bar). Some other MOF materials have been reported to have similar behavior, like the so-called NOTT-202a⁵⁵. In other reported hysteresis loop in a CO₂ isotherm, this phenomenon was explained based on the flexibility of the MOF structure⁵⁶. The latter explanation cannot be discarded in the ITF-1 material, as the relatively weak links between D4R cubes, together with the presumably high affinity of the N-rich organic linker for CO₂, could lead to a reversible deformation of the framework (The stability of the framework after CO₂ adsorption was made clear by powder X-ray diffraction in Figure S3 of Supporting Information, so any deformation, if exists, has necessarily to be reversible). Nevertheless, the hysteresis loop of the so-called YO-MOF⁵⁵ almost closes at pressures of 0.4 atm, whereas that of the isotherm of the ITF-1 material

at the same temperature only closes at practically 0 bar. It suggests that the reversible framework flexibility, if present, seems not to be the only factor responsible of the observed hysteresis loop

in Figure 6.

Figure 6. CO₂ adsorption (full circles) / desorption (empty circles) isotherm at 273 K of the ITF-1 sample.

It has been already established that the structural part of the design of the ITF-1 material led to a reasonable achievement (Figure 2). Moreover, one of the pursued applied aims, consisting on efficiently adsorbing CO₂, has been also relatively successful (Figure 6). The remaining objective, trying to find a MOF able to strongly confining H₂ molecules, was probably the most ambitious challenge because of the difficultness of storing a so hardly-compressible gas molecule and having so low critical temperature (32.97 K). Nevertheless, the structure of ITF-1 contains nanocavities a priori following the designed requirements (Figure 2), what increases the expectancy. The most extended test to evaluate the capacity of porous materials as H₂ physisorbents is their adsorption isotherm at 77 K. Figure 7 shows the corresponding isotherm

for ITF-1 material (black line, full circles) at moderate pressures, in the range of 0-10 bar. At 10 bar, the H_2 uptake reached by this MOF is of 0.52 wt.% (0.88 wt.% was reached at 20 bar), which is quite lower than the H_2 uptake values reported for some MOFs with higher surface areas¹. Like in the CO_2 isotherm, if the amount of adsorbed H_2 is expressed per unit of surface area of the adsorbent, the H_2 uptake of ITF-1 is again competitive with these given for open MOF materials. In this sense, it is convenient to have in mind the already mentioned relationship between the surface area of MOF materials and their H_2 uptake. That relationship is only disrupted by MOF materials that possess any property (exposed metal centers, supported noble metals inducing spillover, etc.) able to introduce an extra contribution in the otherwise simple and weak interaction H_2 -framework, generally independent on the MOF nature. Therefore, the better relative position of ITF-1 along the series of MOFs as H_2 adsorbents when H_2 uptake is divided by the surface area of the adsorbent ($1.8 \text{ g H}_2/\text{m}^2$ for MOF-5 vs. $4.2 \text{ g H}_2/\text{m}^2$ for ITF-1),

again suggests that ITF-1 effectively possesses a special singularity for attracting / retaining H_2 .

Figure 7. H₂ adsorption isotherms at 77 K (full circles) and 273 K (empty triangles) of the sample ITF-1. The inset shows a schematic picture of a MOC cavity filled by 4 H₂ molecules.

Furthermore, the H₂ isotherm at 77 K rarely has two very different slopes. To the best of our knowledge, no isotherm has been reported with so marked different regions. Even the isotherm of the material known as MOC-3, which has the same **ast** topology, which contains very similar D4R nanocavities and whose H₂ uptake is also higher than that expected from their surface area, showed a typical shape of a H₂ isotherm without any evident inflexion point or any sudden changes in adsorption behavior³⁸. In contrast, an abrupt slope change at pressure as low as *ca.* 0.05 bar is observed in the H₂ isotherm at 77 K of the ITF-1 material (Figure 7). Before such pressure is introduced, the slope of the isotherm is surprisingly high, as if some concrete adsorption centers have extraordinary affinity for H₂. More interestingly, there is an extremely good matching between the amount of adsorbed H₂ before the inflexion point (up to 0.05 bar) and the number of H₂ molecules fitted into the nanocavities of ITF-1, as estimated from the crystallographic-solved structure, both being 4 H₂ molecules per D4R cube. Detailed calculation of this matching can be found in Supporting Information. It means that the cube-shaped nanocavities of ITF-1 are exceptional confiners of H₂, even better than expected when they were designed. Indeed, these cavities are wholly filled up with H₂ at 77 K under very low pressures (below 0.05 bar). Once the nanocavities are filled of H₂, the capacity of the material ITF-1 for adsorbing H₂ is rather limited, as predicted by the low surface area of the material. Nevertheless, the shape of the H₂ isotherm at 77 K at higher pressures is also unusual compared to conventional H₂ isotherms of some other porous adsorbents under similar conditions. The typical plateau of the conventional (type I) isotherms when micropores are filled, is not reached for ITF-

1 materials up to 10 bar. It indicates that the real adsorption capacity of these materials has not
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7 been achieved, probably due to a poor connectivity between cages with void space.

8 The H₂ isotherm registered at 273 K (Figure 7, empty red triangles) is not less impressive. If
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10 only a few modifications in some particular MOFs get to slightly improve the H₂ adsorption
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12 dictated by their surface area at 77 K, this aim is extraordinarily much harder at room
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14 temperature^{1, 57}. In this context, the 0.174 wt.% of adsorbed H₂ at 10 bar and 273 K is not a
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17 minor result for a MOF with low surface area. It means that at that pressure (which is very low
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19 for H₂ storage purposes), practically all nanocavities are full of H₂ at room temperature. In order
20
21 to contextualize this result, a MOF-5 material, which has a surface area of more than one order
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23 of magnitude higher than that of ITF-1, only adsorbs 0.05 wt.% of H₂ at room temperature^{20, 58-60}.
24
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26 It means that the linearity between H₂ uptake and surface area of MOFs, in principle so hard to
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28 break, is however easily broken by the ITF-1 material, since it adsorbs several tens of times more
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30 amount of H₂ than that dictated by that rule. The relevance of this result is made clear when
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32 compared to the higher reported enhancement of H₂ uptake at room temperature induced by
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34 spillover effect over some MOFs, which implies multiplying by a factor of 3 the H₂ uptake of the
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36 bare MOF²⁰.
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43 4. CONCLUSIONS

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45 This work describes in detail the design and the according preparation of a MOF material
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47 containing, a N-rich linker and nanocavities to improve, on one hand, the affinity for CO₂ and
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49 H₂, and on the other, the confining effect of these small molecules. Such design entails, firstly,
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51 the synthesis of the non-commercialized tetrazole- and imidazole-based organic linker and,
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53 subsequently, the optimization of the synthesis conditions with indium as the strategically chosen
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metal. The resultant so-called ITF-1 material made up by metal-organic cubes arrangement with **ast** topology, showed the main structural and compositional designed premises. Thanks to this, it was able to adsorb much more amount of both CO₂ and H₂ than expected from its relatively low surface area. In addition, the corresponding isotherms had unusual and exciting singularities, which were explained according to its structure. Thus, the CO₂ isotherm at 273 K has a prominent hysteresis loop along the whole studied range of pressures (0-10 bar), presumably due to the high polarizability of its N-rich organic linker and/or the nanosize of the cavities of ITF-1. H₂ isotherm at 77 K indicated a hierarchical filling up, in such a way that each nanocavity is wholly occupied (by four H₂ molecules) at very low H₂ pressure, and the subsequent adsorption is rather discreet. Finally, the H₂ isotherms registered at nearly room temperature (273 K) showed the possibility of completely filling up the nanocavities at pressure as low as 10 bar. In spite of the absolute values of adsorption of either CO₂ or H₂ are far from being the best amongst MOFs, this study provides key insights into the design of new MOFs for efficiently adsorbing these gases of high energetic and environmental interest. Additionally, we expect that the detailed rational design behind this noteworthy and successful adsorption results encourages and inspires the MOFs scientific community to dedicate enough effort in the design materials of particular physical-chemical properties for reaching concrete objectives in detriment of simply using trial-and-error strategies just trying to get new structures with scarce practical interest. Of course, the goal continues being to achieve a particular MOF material uniting highly porosity and high physical-chemical retention for a particular gas (mainly H₂ or CO₂).

ASSOCIATED CONTENT

Supporting Information. Crystallographic data and some other extra characterization of the material ITF-1.

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REFERENCES

- (1) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D. W., Hydrogen storage in metal-organic frameworks. *Chem Rev* **2012**, 112, (2), 782-835.
- (2) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T. H.; Long, J. R., Carbon dioxide capture in metal-organic frameworks. *Chem Rev* **2012**, 112, (2), 724-81.
- (3) Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J., Porous materials with optimal adsorption thermodynamics and kinetics for CO₂ separation. *Nature* **2013**, 495, (7439), 80-4.
- (4) Srivastava, R.; Srinivas, D.; Ratnasamy, P., Sites for CO₂ activation over amine-functionalized mesoporous Ti(Al)-SBA-15 catalysts. *Microporous Mesoporous Mater.* **2006**, 90, (1-3), 314-326.
- (5) Sanz, R.; Calleja, G.; Arencibia, A.; Sanz-Perez, E. S., CO₂ adsorption on branched polyethyleneimine-impregnated mesoporous silica SBA-15. *Appl. Surf. Sci.* **2010**, 256, (17), 5323-5328.
- (6) Karra, J. R.; Walton, K. S., Molecular Simulations and Experimental Studies of CO₂, CO, and N₂ Adsorption in Metal-Organic Frameworks. *J. Phys. Chem. C* **2010**, 114, (37), 15735-15740.
- (7) Stavitski, E.; Pidko, E. A.; Couck, S.; Remy, T.; Hensen, E. J. M.; Weckhuysen, B. M.; Denayer, J.; Gascon, J.; Kapteijn, F., Complexity behind CO₂ Capture on NH₂-MIL-53(Al). *Langmuir* **2011**, 27, (7), 3970-3976.
- (8) Cui, P.; Ma, Y. G.; Li, H. H.; Zhao, B.; Li, J. R.; Cheng, P.; Balbuena, P. B.; Zhou, H. C., Multipoint Interactions Enhanced CO₂ Uptake: A Zeolite-like Zinc-Tetrazole Framework with 24-Nuclear Zinc Cages. *J. Am. Chem. Soc.* **2012**, 134, (46), 18892-18895.
- (9) Tseng, T. W.; Luo, T. T.; Chen, S. Y.; Su, C. C.; Chi, K. M.; Lu, K. L., Porous Metal-Organic Frameworks with Multiple Cages Based on Tetrazolate Ligands: Synthesis, Structures, Photoluminescence, and Gas Adsorption Properties. *Cryst. Growth Des.* **2013**, 13, (2), 510-517.
- (10) Natarajan, S.; Mahata, P., Non-carboxylate based metal-organic frameworks (MOFs) and related aspects. *Curr. Opin. Solid State Mat. Sci.* **2009**, 13, (3-4), 46-53.
- (11) Aromi, G.; Barrios, L. A.; Roubeau, O.; Gamez, P., Triazoles and tetrazoles: Prime ligands to generate remarkable coordination materials. *Coord. Chem. Rev.* **2011**, 255, (5-6), 485-546.
- (12) Catalan, J.; Abboud, J. L. M.; Elguero, J., BASICITY AND ACIDITY OF AZOLES. *Adv. Heterocycl. Chem.* **1987**, 41, 187-274.
- (13) Poirier, E.; Dailly, A., On the Nature of the Adsorbed Hydrogen Phase in Microporous Metal-Organic Frameworks at Supercritical Temperatures. *Langmuir* **2009**, 25, (20), 12169-12176.

- (14) Furukawa, H.; Ko, N.; Go, Y. B.; Aratani, N.; Choi, S. B.; Choi, E.; Yazaydin, A. O.; Snurr, R. Q.; O'Keeffe, M.; Kim, J.; Yaghi, O. M., Ultrahigh porosity in metal-organic frameworks. *Science* **2010**, 329, (5990), 424-8.
- (15) Dinca, M.; Long, J. R., Hydrogen storage in microporous metal-organic frameworks with exposed metal sites. *Angew Chem Int Ed Engl* **2008**, 47, (36), 6766-79.
- (16) Mavrandonakis, A.; Klontzas, E.; Tylianakis, E.; Froudakis, G. E., Enhancement of Hydrogen Adsorption in Metal-Organic Frameworks by the Incorporation of the Sulfonate Group and Li Cations. A Multiscale Computational Study. *J. Am. Chem. Soc.* **2009**, 131, (37), 13410-13414.
- (17) Botas, J. A.; Calleja, G.; Sanchez-Sanchez, M.; Orcajo, M. G., Cobalt Doping of the MOF-5 Framework and Its Effect on Gas-Adsorption Properties. *Langmuir* **2010**, 26, (8), 5300-5303.
- (18) Botas, J. A.; Calleja, G.; Sanchez-Sanchez, M.; Orcajo, M. G., Effect of Zn/Co ratio in MOF-74 type materials containing exposed metal sites on their hydrogen adsorption behaviour and on their band gap energy. *Int. J. Hydrogen Energy* **2011**, 36, (17), 10834-10844.
- (19) Sabo, M.; Henschel, A.; Froede, H.; Klemm, E.; Kaskel, S., Solution infiltration of palladium into MOF-5: synthesis, physisorption and catalytic properties. *J. Mater. Chem.* **2007**, 17, (36), 3827-3832.
- (20) Li, Y. W.; Yang, R. T., Significantly enhanced hydrogen storage in metal-organic frameworks via spillover. *J. Am. Chem. Soc.* **2006**, 128, (3), 726-727.
- (21) Calleja, G.; Botas, J. A.; Sanchez-Sanchez, M.; Orcajo, M. G., Hydrogen adsorption over Zeolite-like MOF materials modified by ion exchange. *Int. J. Hydrogen Energy* **2010**, 35, (18), 9916-9923.
- (22) Nouar, F.; Eckert, J.; Eubank, J. F.; Forster, P.; Eddaoudi, M., Zeolite-like Metal-Organic Frameworks (ZMOFs) as Hydrogen Storage Platform: Lithium and Magnesium Ion-Exchange and H-2-(rho-ZMOF) Interaction Studies. *J. Am. Chem. Soc.* **2009**, 131, (8), 2864-2870.
- (23) Reguera, L.; Krap, C. P.; Balmaseda, J.; Reguera, E., Hydrogen storage in copper Prussian blue analogues: Evidence of H-2 coordination to the copper atom. *J. Phys. Chem. C* **2008**, 112, (40), 15893-15899.
- (24) Thomas, K. M., Hydrogen adsorption and storage on porous materials. *Catal. Today* **2007**, 120, (3-4), 389-398.
- (25) Chen, B. L.; Zhao, X.; Putkham, A.; Hong, K.; Lobkovsky, E. B.; Hurtado, E. J.; Fletcher, A. J.; Thomas, K. M., Surface interactions and quantum kinetic molecular sieving for H-2 and D-2 adsorption on a mixed metal-organic framework material. *J. Am. Chem. Soc.* **2008**, 130, (20), 6411-6423.
- (26) Zhao, X. B.; Xiao, B.; Fletcher, A. J.; Thomas, K. M.; Bradshaw, D.; Rosseinsky, M. J., Hysteretic adsorption and desorption of hydrogen by nanoporous metal-organic frameworks. *Science* **2004**, 306, (5698), 1012-1015.
- (27) Reguera, E., Materials for Hydrogen Storage in Nanocavities: Design criteria. *Int. J. Hydrogen Energy* **2009**, 34, (22), 9163-9167.
- (28) Han, S. S.; Kim, H. S.; Han, K. S.; Lee, J. Y.; Lee, H. M.; Kang, J. K.; Woo, S. I.; van Duin, A. C. T.; Goddard, W. A., Nanopores of carbon nanotubes as practical hydrogen storage media. *Appl. Phys. Lett.* **2005**, 87, (21).
- (29) Alkordi, M. H.; Brant, J. A.; Wojtas, L.; Kravtsov, V. C.; Cairns, A. J.; Eddaoudi, M., Zeolite-like Metal-Organic Frameworks (ZMOFs) Based on the Directed Assembly of Finite Metal-Organic Cubes (MOCs). *J. Am. Chem. Soc.* **2009**, 131, (49), 17753-17755.

- (30) Park, K. S.; Ni, Z.; Cote, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M., Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, 103, (27), 10186-91.
- (31) Liu, Y.; Kravtsov, V.; Larsen, R.; Eddaoudi, M., Molecular building blocks approach to the assembly of zeolite-like metal-organic frameworks (ZMOFs) with extra-large cavities. *Chem Commun (Camb)* **2006**, (14), 1488-90.
- (32) Nouar, F.; Eubank, J. F.; Bousquet, T.; Wojtas, L.; Zaworotko, M. J.; Eddaoudi, M., Supramolecular building blocks (SBBs) for the design and synthesis of highly porous metal-organic frameworks. *J. Am. Chem. Soc.* **2008**, 130, (6), 1833-+.
- (33) Baerlocher, C.; Meier, W. M.; Olson, D. H., *Atlas of Zeolite Framework Types*. ed.; Elsevier: Amsterdam, 2007; Vol. 6th edition.
- (34) Liu, Y. L.; Kravtsov, V.; Walsh, R. D.; Poddar, P.; Srikanth, H.; Eddaoudi, M., Directed assembly of metal-organic cubes from deliberately predesigned molecular building blocks. *Chem. Commun. (Cambridge, U. K.)* **2004**, (24), 2806-2807.
- (35) Sava, D. F.; Kravtsov, V. C.; Eckert, J.; Eubank, J. F.; Nouar, F.; Eddaoudi, M., Exceptional Stability and High Hydrogen Uptake in Hydrogen-Bonded Metal-Organic Cubes Possessing ACO and AST Zeolite-like Topologies. *J. Am. Chem. Soc.* **2009**, 131, (30), 10394-+.
- (36) Belof, J. L.; Stern, A. C.; Eddaoudi, M.; Space, B., On the mechanism of hydrogen storage in a metal-organic framework material. *J. Am. Chem. Soc.* **2007**, 129, (49), 15202-15210.
- (37) Demko, Z. P.; Sharpless, K. B., Preparation of 5-substituted 1H-tetrazoles from nitriles in water. *J. Org. Chem.* **2001**, 66, (24), 7945-7950.
- (38) *Bruker APEX2. Bruker AXS Inc.* ed.; , Madison, Wisconsin, USA, 2010, 2010.
- (39) *Bruker SAINT. Data Reduction Software. Bruker AXS Inc.* ed.; Madison, Wisconsin, USA, 2010.
- (40) Sheldrick, G. M., *SADABS. Program for Empirical Absorption Correction*. ed.; University of Gottingen, Germany, 2008.
- (41) Farrugia, L. J., WinGX suite for small-molecule single-crystal crystallography. *Applied Crystallography* **1999**, 32, 837-838.
- (42) Sheldrick, G. M., PHASE ANNEALING IN SHELX-90 - DIRECT METHODS FOR LARGER STRUCTURES. *Acta Crystallogr. Sect. A* **1990**, 46, 467-473.
- (43) Sheldrick, G. M., A short history of SHELX. *Acta Crystallogr. Sect. A* **2008**, 64, 112-122.
- (44) Sheldrick, G. M.; Schneider, T. R., SHELXL: High-resolution refinement. In *Macromolecular Crystallography, Pt B*, Carter, C. W.; Sweet, R. M., Eds. 1997; Vol. 277, pp 319-343.
- (45) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, 42, 339-341.
- (46) Connolly, M. L., COMPUTATION OF MOLECULAR VOLUME. *J. Am. Chem. Soc.* **1985**, 107, (5), 1118-1124.
- (47) Dubinin, M. M., In *Chem. Phys. Carbon*, Walker, P. L., Ed. Marcel Dekker Inc.: New York, 1966; Vol. 2, pp 51-69.
- (48) Stoeckli, F.; Ballerini, L., EVOLUTION OF MICROPOROSITY DURING ACTIVATION OF CARBON. *Fuel* **1991**, 70, (4), 557-559.

- (49) Bae, Y. S.; Farha, O. K.; Hupp, J. T.; Snurr, R. Q., Enhancement of CO₂/N₂ selectivity in a metal-organic framework by cavity modification. *J. Mater. Chem.* **2009**, 19, (15), 2131-2134.
- (50) Bae, Y. S.; Mulfort, K. L.; Frost, H.; Ryan, P.; Punnnathanam, S.; Broadbelt, L. J.; Hupp, J. T.; Snurr, R. Q., Separation of CO(2) from CH(4) using mixed-ligand metal-organic frameworks. *Langmuir* **2008**, 24, (16), 8592-8598.
- (51) Lozano-Castello, D.; Cazorla-Amoros, D.; Linares-Solano, A., Usefulness of CO₂ adsorption at 273 K for the characterization of porous carbons. *Carbon* **2004**, 42, (7), 1233-1242.
- (52) Nguyen, T. X.; Bhatia, S. K., Determination of pore accessibility in disordered nanoporous materials. *J. Phys. Chem. C* **2007**, 111, (5), 2212-2222.
- (53) Bourrelly, S.; Llewellyn, P. L.; Serre, C.; Millange, F.; Loiseau, T.; Ferey, G., Different adsorption behaviors of methane and carbon dioxide in the isotopic nanoporous metal terephthalates MIL-53 and MIL-47. *J. Am. Chem. Soc.* **2005**, 127, (39), 13519-13521.
- (54) Lin, Q. P.; Wu, T.; Zheng, S. T.; Bu, X. H.; Feng, P. Y., Single-Walled Polytetrazolate Metal-Organic Channels with High Density of Open Nitrogen-Donor Sites and Gas Uptake. *J. Am. Chem. Soc.* **2012**, 134, (2), 784-787.
- (55) Yang, S. H.; Lin, X.; Lewis, W.; Suyetin, M.; Bichoutskaia, E.; Parker, J. E.; Tang, C. C.; Allan, D. R.; Rizkallah, P. J.; Hubberstey, P.; Champness, N. R.; Thomas, K. M.; Blake, A. J.; Schroder, M., A partially interpenetrated metal-organic framework for selective hysteretic sorption of carbon dioxide. *Nat. Mater.* **2012**, 11, (8), 710-716.
- (56) Mulfort, K. L.; Farha, O. K.; Malliakas, C. D.; Kanatzidis, M. G.; Hupp, J. T., An Interpenetrated Framework Material with Hysteretic CO₂ Uptake. *Chem.-Eur. J.* **2010**, 16, (1), 276-281.
- (57) Frost, H.; Snurr, R. Q., Design requirements for metal-organic frameworks as hydrogen storage materials. *J. Phys. Chem. C* **2007**, 111, (50), 18794-18803.
- (58) Li, Y. W.; Yang, R. T., Hydrogen storage in metal-organic frameworks by bridged hydrogen spillover. *J. Am. Chem. Soc.* **2006**, 128, (25), 8136-8137.
- (59) Panella, B.; Hirscher, M.; Putter, H.; Muller, U., Hydrogen adsorption in metal-organic frameworks: Cu-MOFs and Zn-MOFs compared. *Adv. Funct. Mater.* **2006**, 16, (4), 520-524.
- (60) Rowsell, J. L. C.; Millward, A. R.; Park, K. S.; Yaghi, O. M., Hydrogen sorption in functionalized metal-organic frameworks. *J. Am. Chem. Soc.* **2004**, 126, (18), 5666-5667.

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A new porous MOF-based adsorbent (ITF-1) has been prepared following a series of rationally designed structural and compositional features. ITF-1 resulted very rich in N atoms and possesses MOC cavities of ideal dimensions to confine H_2 and/or CO_2 . It showed singular behavior in adsorption: MOC cavities become full of H_2 at 0.1 bar and high CO_2 capacity per surface area.