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ARTICLE TYPE

Porous materials based on metal-nucleobase systems sustained by coordination bonds and base pairing interactions

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The present work summarizes the different approaches that can be applied to reach porous materials based on metal-nucleobase systems. The rigidity and the multiple donor sites of the nucleobases make them suitable linkers to provide coordination bond sustained Metal-Organic Frameworks (MOFs). Furthermore, the ability of the nucleobases to establish complementary hydrogen bonding interactions allows achieving similar metal-nucleobase porous materials but sustained by hydrogen bond pairing interactions between the nucleobases (Supramolecular Metal-Organic Frameworks, SMOFs).

Introduction

Metal-Organic Frameworks (MOFs), also known as porous coordination polymers (PCPs), are microporous crystalline materials, which have become a very substantial field of research over the last 15 years.¹ Structure of MOFs consists essentially of inorganic nodes, isolated metal atoms or metal clusters, which are linked by organic molecules. Although the combination of inorganic nodes and linkers provides endless possibilities, the crystal engineering principles to afford these materials are relatively well settled.² Basis arises from the elementary idea concerning that the packing of rigid building units with rigid linkers leads to an inefficient occupation of the space, thus providing accessible voids within the crystal structure. This statement does not preclude other options, and although there are MOFs based on flexible linkers,³ most reported are based on the above described idea.⁴

In this sense, a subclass of MOFs where biomolecules act as bridging ligands has emerged since this kind of ubiquitous and versatile molecules are suitable to build up a new generation of porous materials called MBioFs.⁵ Among the bridging biomolecules, nucleobases appear as appealing alternatives since they provide a rigid molecular linker outfitted with many positions able to coordinate to metal centers, but also to establish complementary hydrogen bonding interactions.⁶ Nucleobases are classified in double-ringed purines (adenine and guanine) and pyrimidines (cytosine, thymine and uracil). The greater heteroatom number of the purine nucleobases makes them better bridging ligands than the pyrimidinic ones, as it can be derived from the results for bridging purine (adenine: 63 hits, and guanine: 5 hits) and pyrimidinic (thymine: 2 hits, uracil: 17 hits, and cytosine: 15 hits) nucleobases get in the CSD database.⁷ The low number of guanine bridged complexes is not due to an inappropriate geometry disposition of the coordination donor atoms but to its great insolubility in common solvents. Additionally, hydrogen bonding donor/acceptor positions of the

purine nucleobases surpass that of the pyrimidinic ones, and make them more appropriate for interacting with other entities.

On the other hand, the chances to achieve this type of porous materials increase with the coordination mode rigidity of the bridging ligand. In particular, the capacity of the nucleobase to anchor to the metal centers through several positions at the same time assists for this purpose, since the rigidity of the building unit is reinforced and, therefore, the opportunities of obtaining a porous material increase. The multiple anchorage can involve multiple coordination bonds but it can be also envisaged as a less exploited combination of coordination and hydrogen bonds.

Recently, a new class of porous materials has emerged in which the coordination bonds are released from guiding the crystal structure and supramolecular interactions occupy this role (Figure 1). Particularly, up to day reported examples of 3D Supramolecular Metal-Organic Frameworks (SMOFs) rely on π - π stacking interactions⁸ and/or hydrogen bonding interactions^{9,10,11}.

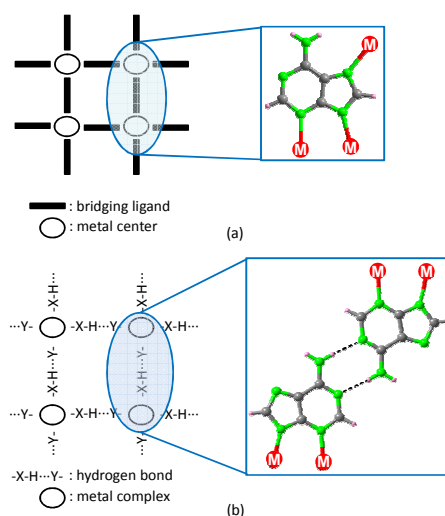


Fig. 1 Metal-nucleobase coordination-bond sustained MOFs (a) and base pairing assembled SMOFs (b).

The aim of this report is to provide an overview of opportunities that simple, cheap, ubiquitous and versatile nucleobases offer to the emerging area of extended porous materials. This contribution has been arbitrarily restricted to those examples in which the nucleobases play a key role sustaining the 3D framework as crucial linkers and not only as mere terminal ligands or tethered substituents. The manuscript is divided into more common coordination bond based MOFs and the emerging hydrogen-bond sustained SMOFs. Potential applications and properties that arise from the biological functionality of the nucleobases, such as sensing¹² and gene regulation,¹³ are beyond the scope of this work.

Metal-nucleobase coordination-bond sustained MOFs

Although during long time nucleobases were evaluated as suitable ligands for the construction of biomimetic compounds¹⁴ there has been a substantial increase in their use as they can be appropriate pillars for the building up of porous materials.^{5,6}

The first porous polymeric compound of this type was reported by our research group in 2004.¹⁵ It consists of a 3D coordination polymer with formula $[\text{Cu}_4(\mu_3\text{-adeninato-}\kappa\text{N3:}\kappa\text{N7:}\kappa\text{N9})(\text{ox})_2(\text{H}_2\text{O})_4]_n$ containing the adenine nucleobase as an anionic N3,N7,N9 -bridging ligand. The deprotonation of the adenine at the reaction media promotes the polymerization of the framework by sequentially bridging $[\text{Cu}_2(\mu\text{-adeninato})_4(\text{H}_2\text{O})_2]$ paddle-wheel entities through $[\text{Cu}(\text{ox})(\text{H}_2\text{O})]$ units (Figure 2). The resulting structure, with **nbo** topology,¹⁶ contains one-dimensional (1D) tubular channels with a diameter of about 13 Å that represent around a 40% of the total volume.

In 2009, Rosi et al. reported a porous network of formula $(\text{Me}_2\text{NH}_2)_2[\text{Zn}_8(\mu_4\text{-adeninato-}\kappa\text{N1:}\kappa\text{N3:}\kappa\text{N7:}\kappa\text{N9})_4(\mu\text{-BPDC-}\kappa\text{O:}\kappa\text{O}')_4(\mu\text{-BPDC-}\kappa^2\text{O:}\kappa^2\text{O':}\kappa^2\text{O'':}\kappa^2\text{O'''})_2(\mu_4\text{-O})] \cdot 8\text{DMF} \cdot 11\text{H}_2\text{O}$ (BPDC: biphenyldicarboxylate) obtained under solvothermal conditions at 130°C.¹⁷ It consists of infinite zinc-adeninate columnar secondary building units (SBUs) composed of apex-sharing zinc-adeninate octahedral cages with a **pcu** topology (Figure 3a). The zinc-adeninate columns are interconnected via multiple BPDC linkers giving rise to an anionic network that allows the exchange of the cationic counterions. The authors proved that this compound presents permanent porosity with a BET surface area of 1700 m²/g, and additionally, it is able to storage and release cationic drug molecules. Later, in 2012, they published $(\text{Me}_2\text{NH}_2)_4[\text{Zn}_8(\mu_4\text{-adeninato-}\kappa\text{N1:}\kappa\text{N3:}\kappa\text{N7:}\kappa\text{N9})_4(\mu\text{-BPDC-}\kappa\text{O:}\kappa\text{O}')_6(\mu\text{-O})] \cdot 49\text{DMF} \cdot 31\text{H}_2\text{O}$ compound with the same building blocks but lowering the solvothermal reaction temperature to 85°C to afford an augmented **lcs** net (Figure 3b). The same components are arranged in such a way that they build up a mesoporous material with a high surface area (4300 m²g⁻¹) and one of the largest, reported to date, pore volume (4.3 cm³g⁻¹) for Metal-Organic Frameworks.¹⁸

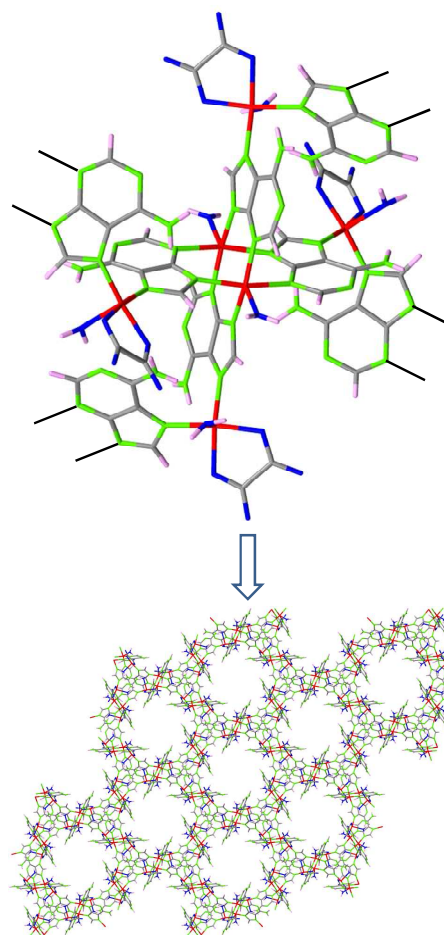


Fig. 2 Crystal structure of $\{[\text{Cu}_2(\mu\text{-adeninato})_4(\text{H}_2\text{O})_2][\text{Cu}(\text{ox})(\text{H}_2\text{O})]_2\}_n$ compound.

Another family of metal-adenine-carboxylate compounds that has attracted great interest is that of formula $[\text{M}_2(\mu_3\text{-adeninato-}\kappa\text{N3:}\kappa\text{N7:}\kappa\text{N9})_2(\mu\text{-OOC}(\text{CH}_2)_x\text{CH}_3\text{-}\kappa\text{O:}\kappa\text{O}')_2]_n$.¹⁹⁻²¹ The crystal structure consists of paddle-wheel shaped centrosymmetric dimeric units in which two metal(II) atoms are bridged by two adenine ligands coordinated by their N3 and N9 nitrogen atoms and two carboxylic ligands with a $\mu\text{-O,O'}$ coordination mode. These units are cross-linked through the apical coordination of the imidazole N7 atom of the adeninato ligands in such a way that each paddle-wheel shaped unit is linked to four adjacent entities (Figure 4). This self-assembling process generates a 4-connected uninodal net (**lvt** topology) that exhibits a three-dimensional system of intersecting cavities. The accessible effective volume is directly related to the length of the aliphatic chain, which is pointing toward the inner portion of the channels with free-volume that ranges from *ca.* 40% for the acetate analogues and negligible values for pentanoate and longer carboxylates. It is worth mentioning that the synthetic conditions play a relevant role in obtaining the different members of this last family of compounds. In fact, cobalt(II) analogues are obtained under solvothermal conditions,¹⁹ the copper(II) ones using room conditions aqueous synthesis,²⁰ and the nickel(II) and zinc(II) ones employing a less common solvent free approach under conventional oven or microwave assisted heating.²¹ The presence of the highly polar amino groups of the adenines in the pore walls

makes these compounds to present a great adsorption selectivity towards CO₂, especially those with narrower pores.²² Related to this great adsorption selectivity and taking advantage of the retention of the crystal structure even when the carboxylic ligand is changed, core-shell frameworks comprising a porous mixed core (acetato/pentanoato) and a less porous shell (pentanoato) were performed. Thus, the resulting material exhibited 30% higher CO₂ uptake than the pentanoato analogue and low N₂ uptake in comparison to the core.²³ On the other hand, making use of the templating effect that exert butyric acid microemulsions, a simple synthetic route that doubled the adsorption capacity of the butanoato analogue was achieved.²⁴ Moreover, this last 3D crystal structure seems to be so robust that it is obtained even when using long chain aliphatic dicarboxylic acids: HOOC(CH₂)_nCOOH [n from 3 to 5].²⁵ Surprisingly, only one of the two carboxylic groups is deprotonated and coordinated to the metal centers, μ - $\kappa O1:\kappa O2$, while the other remains protonated inside the channels of the crystal structure in such a way that the dicarboxylic ligands do not join the dimeric fragments as it could, initially, be expected. Only when short chain dicarboxylic acids are employed a different crystal structure is obtained. In this last case the great tendency of these acids to chelate metal ions hinders the paddle-wheel shaped SBUs providing crystal structures based on discrete complex entities.²⁶

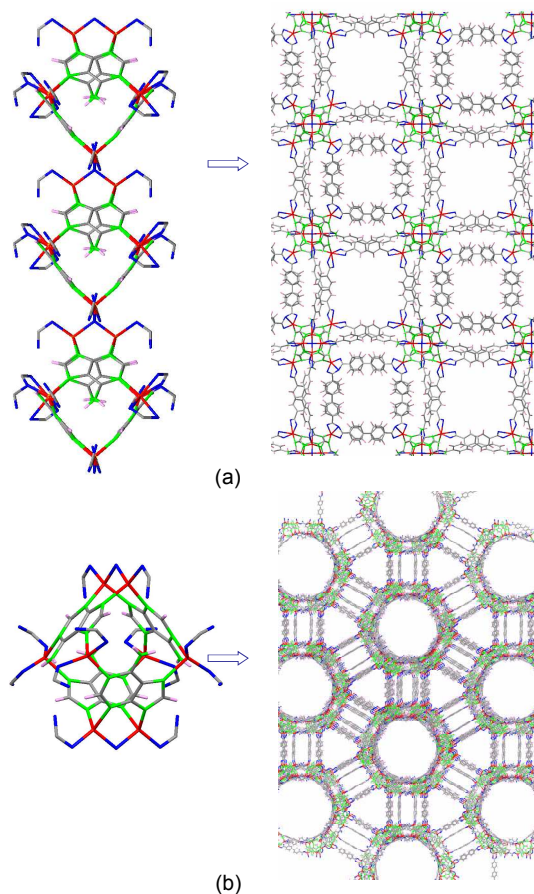


Fig. 3 SBUs and the resulting crystal structures of compounds (a) (Me₂NH₂)₂[Zn₈(μ₄-adeninato)₄(μ-BPDC)₆(μ₄-O)]·8DMF·11H₂O, and (b) (Me₂NH₂)₄[Zn₈(μ₄-adeninato)₄(μ-BPDC)₆(μ-O)]·49DMF·31H₂O.

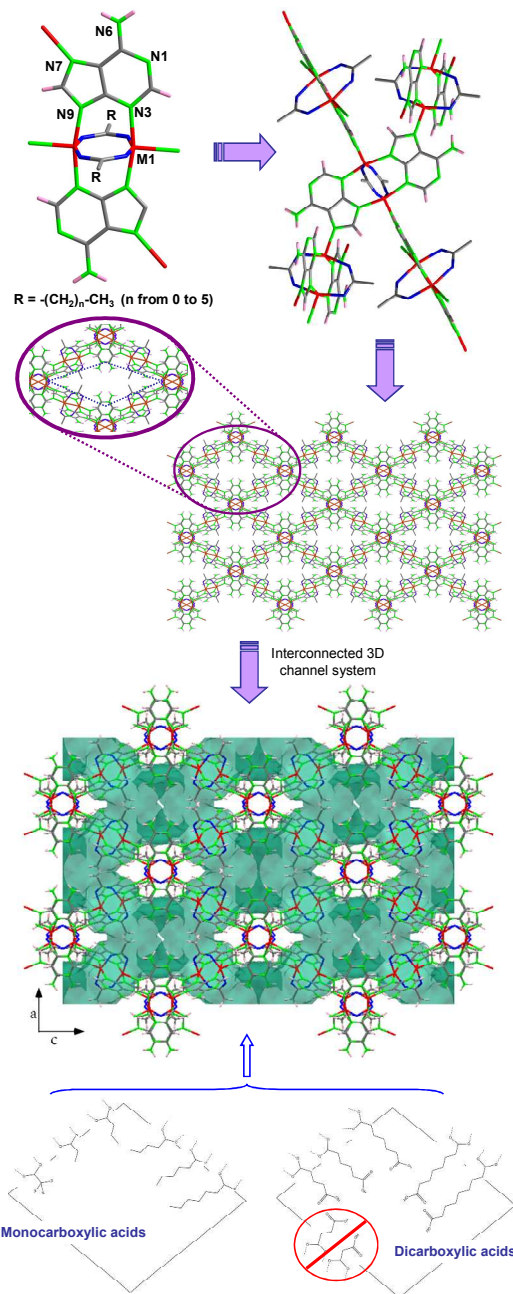


Fig. 4 Porous crystal structure of [M(μ₃-adeninato)(μ₂-carboxylato)]_n compounds (M being Co²⁺, Ni²⁺, Cu²⁺ or Zn²⁺).

There are other examples of MOFs sustained by collaborative nucleobase/non-nucleobase bridging ligands, such as [Co₃(μ-OH)₄(μ₅-hypoxanthinato-κN3:κN7:κN9:κO6:κO6)₂]_n, with the hypoxanthinato ligand (**umr** topology), that shows spin canting, metamagnetism, and heterogeneous catalytic ability for the selectivity oxidation of cis-cyclooctene,²⁷ and the anionic [Cd₄(μ-Cl)(μ₄-adeninato-κN1:κN3:κN7:κN9)₂Cl₆]_n⁻ network counterbalanced by the presence of H⁺/H₃O⁺ cations in the channels.²⁸ All the above examples share in common that the purine nucleobase employs at least N3, N7 and N9 positions to join the metal centers, providing in this way a rigid linker that favors the presence of voids in the resulting structures. Both of them present permanent porosity upon activation but whereas

cobalt compound is able to adsorb both N_2 ($237 \text{ cm}^3 \text{ g}^{-1}$ at 77 K) and CO_2 ($160 \text{ cm}^3 \text{ g}^{-1}$ at 195 K), the small opening of the 1D channels (diameter: $\sim 4 \text{ \AA}$) in cadmium compound only allows the adsorption of CO_2 ($10.5 \text{ cm}^3 \text{ g}^{-1}$ at 273 K).

Among nucleobase based MOFs we can also underline zeolitic type frameworks in which the purine adopts a $\mu\text{-}\kappa\text{N7}:\kappa\text{N9}$ coordination mode (Figure 5a). $[\text{M}(\mu\text{-purinato-}\kappa\text{N7}:\kappa\text{N9})_2]_n$ was the first example of a MOF based on this purine nucleobase coordination mode, in which cobalt(II) or zinc(II) tetrahedral nodes are connected through N7,N9 -purinate bridging ligands (**lta** topology).²⁹ Adsorption measurements upon zinc compound (Langmuir surface area of $800 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $0.27 \text{ cm}^3 \text{ g}^{-1}$), in which large cavities are surrounded by smaller pore apertures, indicate a strong interaction between the framework and H_2 and CO_2 molecules. Similarly, a 2-nitroimidazole and purine mixed ligand zinc(II) ZIF, $[\text{Zn}(\mu\text{-nitroimidazolato-}\kappa\text{N1}:\kappa\text{N3})(\mu\text{-purinato-}\kappa\text{N7}:\kappa\text{N9})_n]$, was later reported (**gme** topology) with BET surface area of $813 \text{ m}^2 \text{ g}^{-1}$, a pore volume of $0.34 \text{ cm}^3 \text{ g}^{-1}$, and a maximum N_2 uptake of 9.8 mmol g^{-1} .³⁰

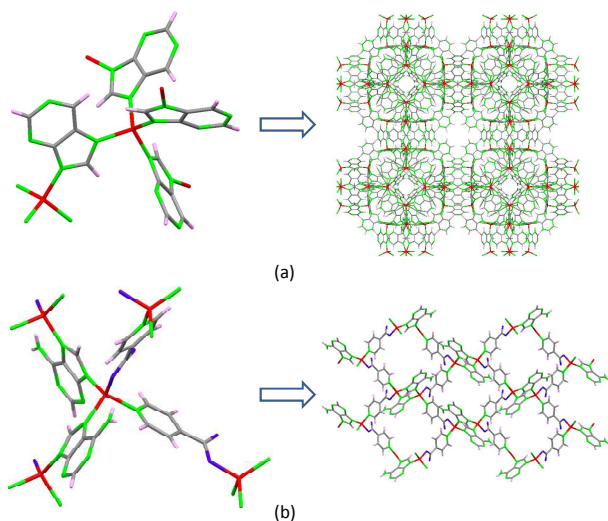


Fig. 5 Metal coordination environment and final crystal structures of compounds (a) $[\text{Zn}(\mu\text{-purinato-}\kappa\text{N7}:\kappa\text{N9})_2]_n$, and (b) $[\text{Zn}(\mu\text{-adeninato-}\kappa\text{N7}:\kappa\text{N9})(\mu\text{-isonicotinato-}\kappa\text{N}:\kappa\text{O})]_n$.

Furthermore, the use of pyridinecarboxylate ligands together with adenine gave rise as well to zeolitic type metal-organic frameworks (Figure 5b). In fact, two compounds, showing the same **dmp** topology, were achieved with isonicotinato, $[\text{Zn}(\mu\text{-adeninato-}\kappa\text{N7}:\kappa\text{N9})(\mu\text{-isonicotinato-}\kappa\text{N}:\kappa\text{O})]_n$,³¹ and 2-aminoisonicotinato, $[\text{Zn}(\mu\text{-adeninato-}\kappa\text{N7}:\kappa\text{N9})(\mu\text{-2-aminoisonicotinato-}\kappa\text{N}:\kappa\text{O})]_n$.³² The functionalization of the isonicotinato ligand with an amino group resulted in a significant enhance of the adsorption selectivity towards CO_2 . Finally, $[\text{Zn}_{1.33}(\text{O}_2\text{H})_{0.33}(\mu\text{-nitroimidazolato-}\kappa\text{N1}:\kappa\text{N3})_{1.167}(\mu_3\text{-purinato-}\kappa\text{N1}:\kappa\text{N7}:\kappa\text{N9})_n]$ represents another example of this family in which the usual $\mu\text{-}\kappa\text{N7}:\kappa\text{N9}$ coordination mode is reinforced by the coordination through N1 position.³⁰ This compound presents a BET surface area of $578 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $0.23 \text{ cm}^3 \text{ g}^{-1}$. As a result of the change of symmetry in comparison with other ZIFs, this framework with **rho** topology exhibits wider windows of 9 \AA .

All above mentioned results underline the suitability of purine nucleobases as framework component of MOFs due to their many

available coordination positions and the stiffness of their molecular structure. In fact, the lower coordination positions of the pyrimidinic nucleobases did not yet allow the isolation of a MOF based on these ligands as linkers.

Metal-nucleobase base pairing assembled SMOFs

These new materials replace the coordination bonds, as builders of the final crystal architecture, by hydrogen bonds which are also directional and predictable interactions (Figure 1). Although such kind of alternative materials can arise an alike fascination to that of MOFs, the crystal engineering principles and the synthetic approach are not yet settled, and examples of this kind of materials are rather scarce. Recently we have reported a successful synthetic approach to achieve this goal based on the following key factors: (i) the use of rigid building units, (ii) the establishment of predictable and rigid synthons between the building units, and (iii) the non-coplanarity of functional groups involved in the predictable synthons. The rigidity of the building units (discrete complexes) can be achieved using rigid ligands bonded through multiple positions. It means, in most common cases, a double anchoring of the ligand by means of two simultaneous coordination bonds or the combination of a coordination bond and an intramolecular hydrogen bond. The predictability and rigidity of the synthons requires the presence of adjacent functional groups, incorporated into the rigid ligands, able to establish complementary hydrogen bonding interactions. Finally, the requisite of non-coplanar arrangement of the synthons comes from our objective of obtaining three-dimensional extended systems that is achieved by the presence of at least three non-coplanar synthons. The use of complexes with non-planar coordination geometries makes this last condition easy to be accomplished.

A suitable system that would fulfil all the above described requirements for obtaining SMOFs are discrete metal-nucleobase systems, especially, once again, those based on purine nucleobases. These ligands provide, at one hand, the advantage of the increased rigidity of the supramolecular building block due to the coordination through multiple positions, and, at the other hand, they present many edges capable of establishing complementary hydrogen bonding interactions that provide rigid and predictable synthons (Figure 6).

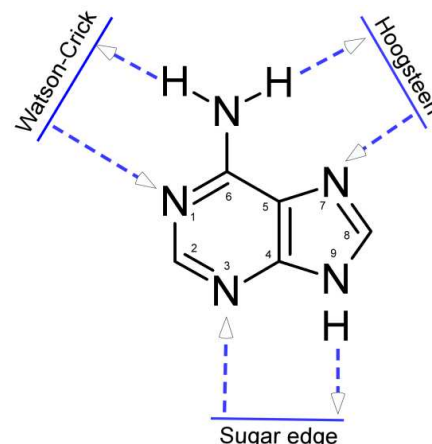


Fig. 6 Adenine edges capable of establishing rigid complementary double hydrogen bonding synthons.

[Zn₆(μ-adeninato-κN7:κN9)₆(pyridine)₆(dimethylcarbamate)₆]
 ·10.5DMF compound is representative of these compounds since
 it consists of hexameric Zn-adeninate macrocycles that are
 connected through the Watson-Crick faces of the nucleobases
 giving rise to a three-dimensional supramolecular framework in
 which the macrocyclic cavities are ordered into one-dimensional
 channels (Figure 7).¹¹ The entrance to each cavity is occluded by
 pyridine rings. Therefore, the activation of this compound was
 made in conditions in which a fraction of the coordinated
 pyridine molecules are removed to widen the cavity aperture. In
 this way, this compound was able to uptake N₂ (77 K and 1 bar:
 ~90 cm³g⁻¹), H₂ (77 K and 1 bar: ~1wt%) and CO₂ (273 K and 1
 bar: ~3.5 mmol/g).

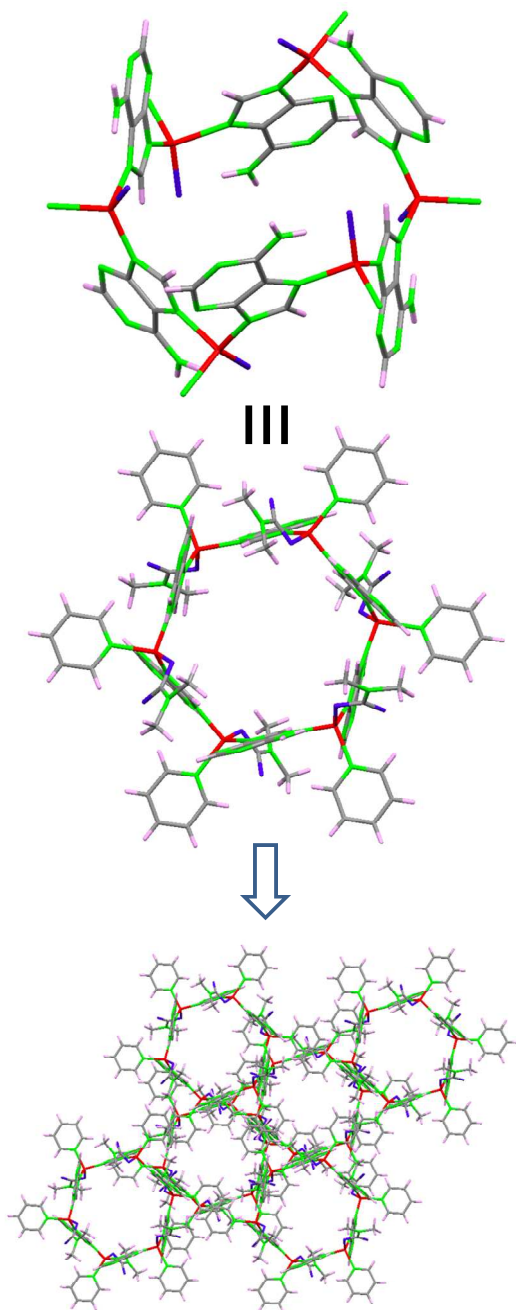


Fig. 7 Hexameric macrocycle and three-dimensional packing [Zn₆(μ-adeninato-κN7:κN9)(pyridine)₆(dimethylcarbamate)₆].

Apart from the previous compound, the first examples that
 allowed us to settle the synthetic approach to render SMOFs are
 the ones based on [Cu₂(μ-adenine)₄(X)₂]²⁺ (X=Cl⁻, Br⁻)
 supramolecular building blocks in which two or more
 nucleobases are tightly anchored to the metal centers by two
 donor positions (N3 and N9 sites), imposing a rigid building
 unit.⁹ Moreover, this coordination motif imposes a rigid
 geometrical restraint among the nucleobases providing a set of
 non-coplanar synthons. As many hydrogen donor/acceptor
 positions of the nucleobase remain free, these discrete entities are
 able to self-assemble among them by means of double hydrogen
 bonds to provide extended supramolecular solids with **reo**
 topology in which great channels are present (Figure 8). These
 compounds present a surface instability that creates a diffusion
 barrier permeated only by strong interacting adsorbate molecules
 such as CO₂ but not N₂, H₂, and CH₄, what makes them attractive
 for selective gas adsorption and separation technologies.
 Zaworotko et al. reported an analogous compound, based in the
 [Cu₂(μ-adenine)₄(X)₂]²⁺ dinuclear entity, replacing the halides by
 bulkier TiF₆²⁻ anions that improve the chemical stability of the
 supramolecular network toward humidity, thus avoiding the
 surface instability, and therefore, being able to adsorb CO₂, CH₄
 and N₂.³³ These studies also pointed out the relevance of the
 solvent selection because strong hydrogen bond donor and
 acceptor solvents such as water molecules could disrupt the direct
 hydrogen bonding interactions between the nucleobases that is
 one of the key factors to achieve this type of compounds.

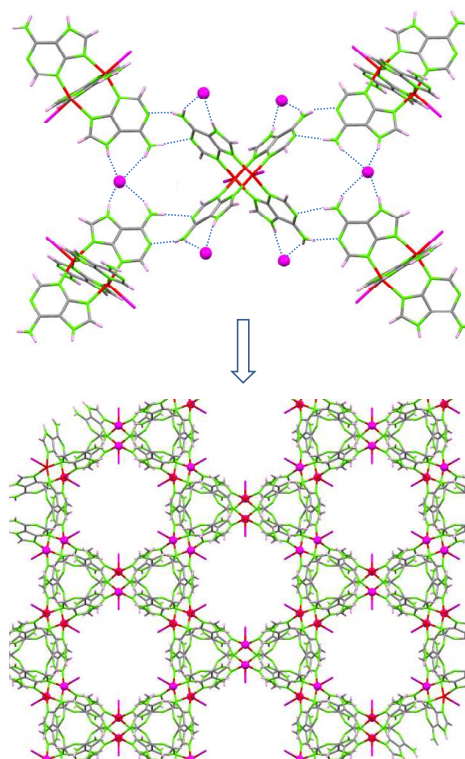


Fig. 8 Details of the adenine base pairing interaction and 3D framework of [Cu₂(μ-adenine)₄Cl₂]Cl₂.

Another example is provided by the self-assembly of
 trischelate [Co(6-thioguaninato-κN7,κS6)₃] entities.¹⁰ The
 coordination mode of the nucleobase renders a rigid metal-

complex and, at the same time, exposes its Watson-Crick (N1, N2) and sugar edges (N3, N9) providing a set of non-coplanar synthons (Figure 9). The sugar edge of the nucleobases establish a double hydrogen bonding interaction with the nucleobases of three neighboring entities to give a $R_2^2(8)$ ring. This rigid synthon, based on direct thioguaninato...thioguaninato pairing interactions, leads to layers in the *ab* plane in which Δ and Λ isomers of the trischelate complex are sequentially arranged. The interactions among the three-connected uninodal 2D nets are linked via weaker hydrogen bonds (N2-H...S6 and C8-H...S6) and reinforced with π - π interactions, leading to 3D structure (**acs** topology) containing 1D channels with diameter of 8.2–9.4 Å. According to N_2 (77 K) and CO_2 (273 K) adsorption studies this compound is highly selective towards CO_2 adsorption. It does not adsorb N_2 but shows a significant CO_2 uptake with a non-saturating curve reaching a value of 1.4 mmol/g at 1 bar.

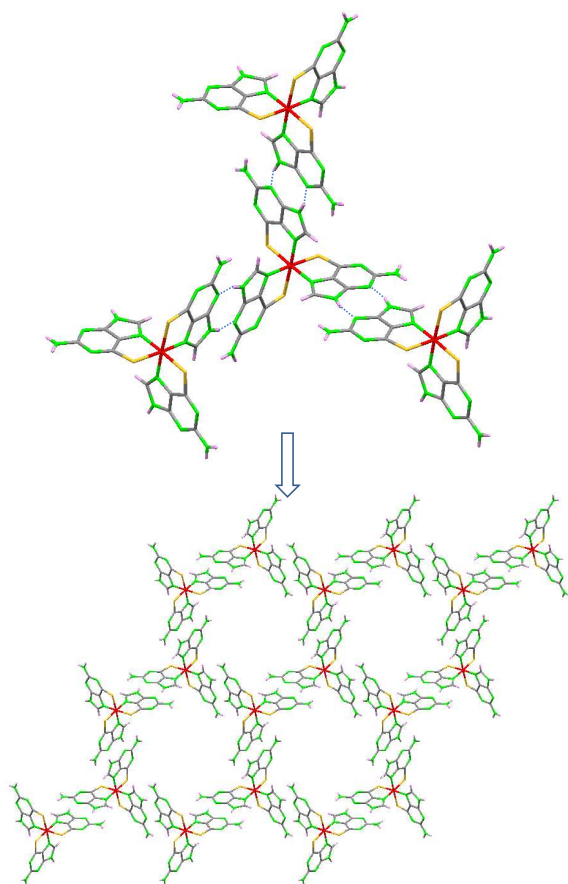


Fig. 9 Details of the adenine base pairing interaction and 3D framework of $[Co(6\text{-thioguaninato-}\kappa N7,\kappa S6)_3]$.

20

There exists an example in which $[Cu_8(\mu_4-OH)_4(\mu_3-OH)_4(adeninato-\kappa N9)_4(\mu\text{-adeninato-}\kappa N3:\kappa N9)_4(\mu\text{-adenine-}\kappa N3:\kappa N9)_2]$ octameric clusters are formed by the stacking of four $Cu_2(\mu-OH)_2$ dimers that are 90° rotated and linked by a semicoordination to the neighboring Cu(II) atoms through the hydroxide bridges (Figure 10).¹⁰ The resulting aggregate can be described as the stacking of three cubanes (cubes with the vertices alternatively occupied by the metal and the bridging hydroxide ligand). The surface of each octamer is occupied by

eight adeninato (four $\mu\text{-}\kappa N3:\kappa N9$ bridging ligands, and four terminal) and two neutral adenine ligands ($\mu\text{-}\kappa N3:\kappa N9$). All the adenines, adeninatos and hydroxides are rigidly anchored to the octameric entity because of their multiple coordination bond (OH/adenine/adeninato) or the combination of a coordination bond and an intramolecular hydrogen bond (terminal adeninato). The interaction of each octamer with the adjacent ones gives rise to bidimensional networks which are further connected via complementary hydrogen bonding interactions of the adeninato ligands with neighboring tectons. The combination of the above described interactions leads to a 3D supramolecular net with **sqc3** topology, where the geometrical requirements imposed by the rigidity of the octameric unit and the hydrogen bonding interactions avoid the full occupancy of the space. This is reflected in the presence of large monodimensional channels of ca. 4.9 Å that occupy a 30% of the unit cell volume.

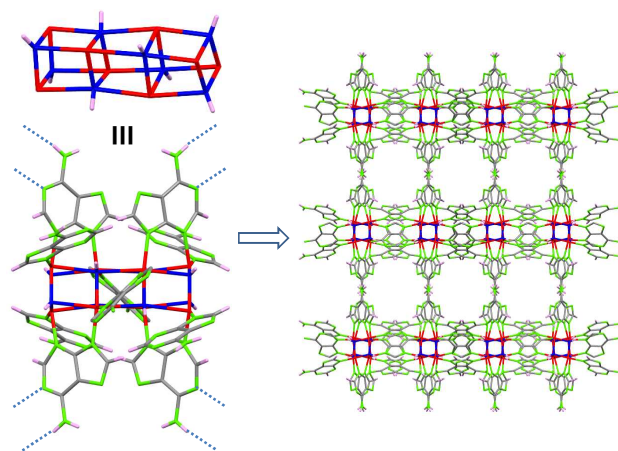


Fig. 10 Octameric unit and three-dimensional packing of $[Cu_8(\mu_4-OH)_4(\mu_3-OH)_4(adeninato-\kappa N9)_4(\mu\text{-adeninato-}\kappa N3:\kappa N9)_4(\mu\text{-adenine-}\kappa N3:\kappa N9)_2]$.

The last example corresponds to a supramolecular structure containing neutral monomeric $[Co(adenine-\kappa N7)_2Cl_2]$ units. 9H-adenine acts as a monodentate ligand and it is coordinated to the Co(II) metal centre through the N7 position, but it requires a second anchoring position of the nucleobase to be stiff enough to generate a supramolecular porous structure.¹⁰ Such stiffness is achieved by the presence of intramolecular hydrogen bonding interactions between the amino hydrogen atom and the chloride one. The adenine also exposes its Watson-Crick and sugar-edges to establish intermolecular complementary hydrogen bonding interactions with adjacent adenine molecules (Figure 11). These interactions build up a four-connected uninodal 3D supramolecular net with **dia** topology that would represent a new porous material with a 67 % of void space. Nevertheless, the real crystal structure involves three interpenetrated networks that occupy all the available space providing a non-porous material. This entanglement problem is also common in MOFs.³⁴ Moreover, it is worth mentioning that diamondoid nets tend to exhibit interpenetration, so gas adsorption studies in this kind of compounds are scarce. Although this problem can be surpassed in some coordination bond based interpenetrated MOF, it still remains a challenge for SMOFs.³⁵

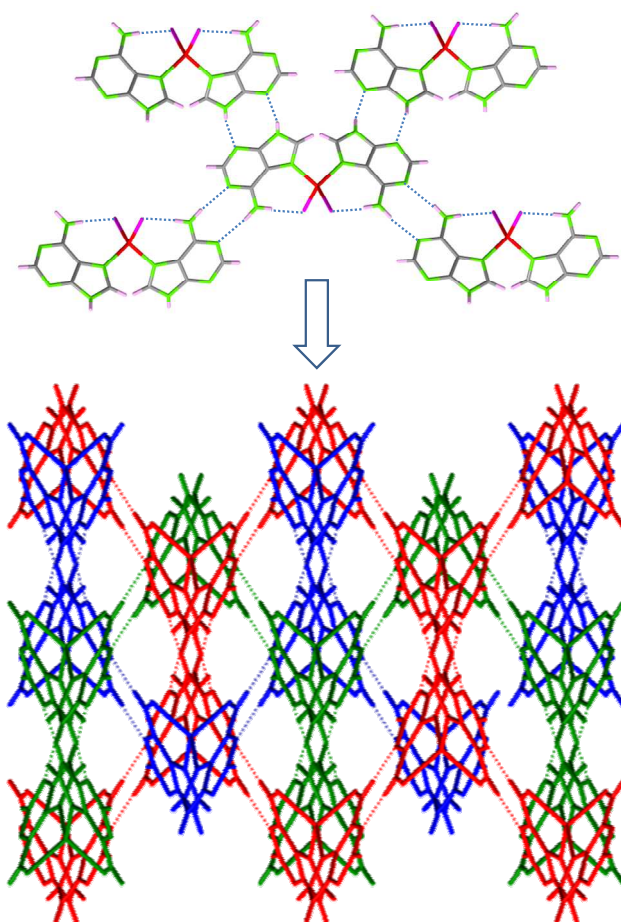


Fig. 11 Hydrogen bonding interactions and triple interpenetrated crystal structure of $[\text{Co}(\text{adenine-}\kappa\text{N7})_2\text{Cl}_2]$. Each subnet is represented using a different color.

5 Metal-nucleobase coordination-bond and base pairing sustained porous materials

The goal to achieve metal-nucleobase porous materials can be also achieved by a simultaneous and collaborative polymerization through both coordination bond and complementary hydrogen bonding interactions. This is the case of compound $[\text{Cu}_2(\mu\text{-adeninato-}\kappa\text{N3}:\kappa\text{N9})_2(\mu\text{-adeninato-}\kappa\text{N7}:\kappa\text{N9})(\mu\text{-OH})(\text{H}_2\text{O})(\text{CH}_3\text{OH})]_n$.¹⁰ It consists of 1D infinite coordination polymers held together by complementary hydrogen bonding interactions in a 3D supramolecular porous structure (Figure 12).

The coordination polymer can be described as non-centrosymmetric dinuclear units in which two Cu(II) atoms are bridged with two adeninate moieties by the N3 and N9 atoms and also by one hydroxyl group. These dinuclear units are connected by additional bridging adeninates that are coordinated to the Cu(II) centers by the N7 and N9 atoms to provide a 1D coordination chain. The bridging adeninates inside the dinuclear units are tilted 22° but they present wider tilt angle with respect to those connecting the dimeric units (56 and 78° , respectively) in the polymeric chain. This fact together with the complementary double hydrogen bonding interactions of the nucleobases promotes a three-dimensional propagation of the supramolecular structure. The $\mu\text{-}\kappa\text{N3}:\kappa\text{N9}$ -adeninates are able to establish double base pairing synthons through Watson-Crick and Hoogsteen faces

leading to $\text{R}_2^2(8)$ and $\text{R}_2^2(10)$ hydrogen bonding rings, respectively. On the other hand, the $\mu\text{-}\kappa\text{N7}:\kappa\text{N9}$ -adeninates are hydrogen bonded to the bridging hydroxide and the coordinated water molecule of an adjacent polymeric chain through N1 and N6 positions of the Watson-Crick face. The resulting supramolecular crystal structure shows the presence of 1D channels that represent a 44% of unit cell volume.

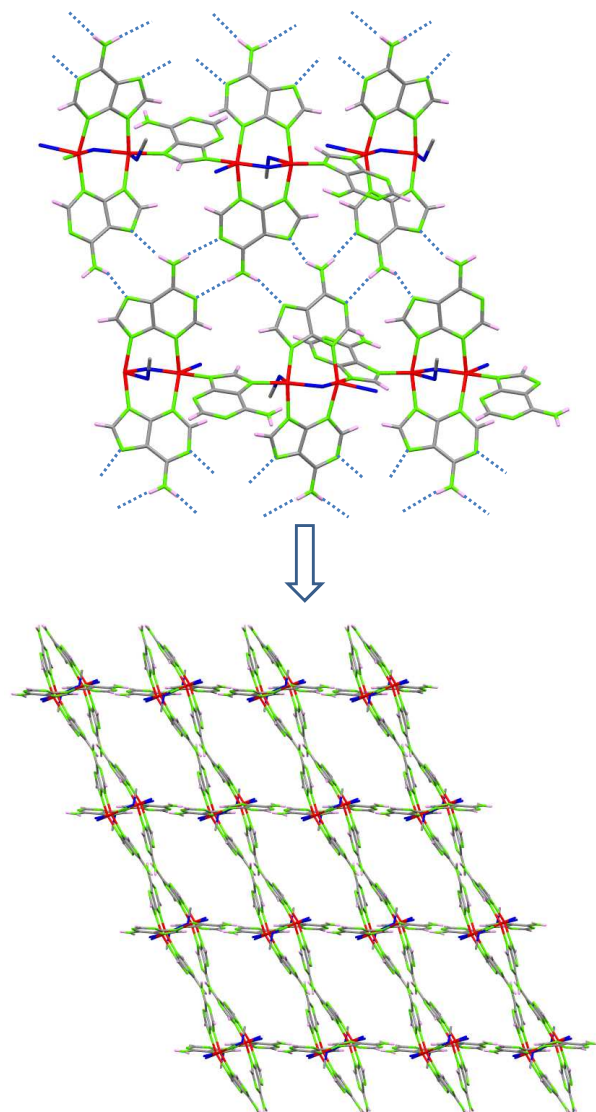


Fig. 12 Supramolecular complementary base pairing interactions among the coordination polymeric chains and porous supramolecular architecture of $[\text{Cu}_2(\mu\text{-adeninato-}\kappa\text{N3}:\kappa\text{N9})_2(\mu\text{-adeninato-}\kappa\text{N7}:\kappa\text{N9})(\mu\text{-OH})(\text{H}_2\text{O})(\text{CH}_3\text{OH})]_n$.

Conclusions

In this highlight article we have paid attention to the suitability of the metal-nucleobase systems to provide porous materials. The molecular stiffness and the multiple coordinating positions of the purine nucleobases make them appropriate building blocks to build up 3D porous structures based on the polymerization through coordination bonds (MOFs). Additionally, the well known ability of the nucleobases to establish complementary

hydrogen bond interactions allows generating a new type of porous materials, Supramolecular Metal-Organic Frameworks (SMOFs), in which the base pairing interactions replace the coordination bonds in the role of sustaining the 3D architecture. However, all discrete metal-nucleobase systems are not well suited to provide supramolecular porous materials. They should meet the following requirements: (i) rigid discrete entity, achievable if the nucleobase is anchored to the building unit through multiple positions, usually by two coordination bonds or the combination of a coordination bond and an intramolecular hydrogen bond, (ii) rigid and predictable synthons, as those provided by complementary hydrogen bonding interactions taking place between nucleobases, and (iii) a metal coordination geometry that imposes a non-coplanar arrangement of several nucleobases allowing a three-dimensional propagation of the base pairing interactions.

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Notes and references

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TABLE OF CONTENTS

Two approaches to metal-nucleobase porous materials: coordination bond sustained MOFs and hydrogen bond pairing based SMOFs.

