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Cadmium Metal–Organic Frameworks Based on Ditopic Triazamacrocyclic Linkers: Unusual Structural Features and Selective CO₂ Capture

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Two assemblies involving Cd²⁺ ions and 1,4,7-triazacyclononane (TACN) Nfunctionalized by different arylcarboxylic acids were envisioned for constructing metalorganic frameworks with general formula $[Cd_2(L^1)(H_2O)_3](NO_3)_{0.7}(HCOO)_{0.2}Br_{0.1}$ $(Cd_2L^1)_{0.7}(HCOO)_{0.2}Br_{0.1}$ $L^1 = 1,4,7$ -tris(4-(carboxybenzyl)-1,4,7-triazacyclononane) and Cd(HL²)(H₂O)₂ (CdL², L²) = 1,4,7-tris(3-(4-benzoate)prop-2-yn-1-yl)-1,4,7-triazacyclononane). Materials were prepared under solvothermal conditions and characterized by single crystal X-ray analysis and porosity measurements. The two crystal structures show an open-framework. Cd_2L^1 reveals a cationic net with nodes constituted by dinuclear cadmium complexes in which each cadmium atom adopts a hexacoordinated environment involving both the carboxylate and the cyclic amine. In contrast, CdL^2 displays a two-fold interpenetrated structure with a pcu topology. In this net, the node is a mononuclear complex in which the Cd atom exhibits a seven-coordination geometry. Both materials show a high permanent porosity and interesting CO_2 adsorption properties with a high selectivity over N_2 and CH_4 . The adsorption capacities and selectivities for CO2 were calculated from a multisite Langmuir isotherm model and IAST theory, which gave insight into the nature of solid-gas interactions and evidenced the influence of interpenetration or polarity of the charged framework on their adsorption properties.



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Cadmium Metal–Organic Frameworks Based on Ditopic Triazamacrocyclic Linkers: Unusual Structural Features and Selective CO₂ Capture

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ABSTRACT: Two 3D cadmium metal-organic frameworks with general formula $[Cd_2(L^1)(H_2O)_3](NO_3)_{0.7}(HCOO)_{0.2}Br_{0.1}$ (Cd₂L¹, L¹ = 1,4,7-tris(4-(carboxybenzyl)-1,4,7triazacyclononane) and Cd(HL²)(H₂O)₂ (CdL², L² = 1,4,7-tris(3-(4-benzoate)prop-2-yn-1yl)-1,4,7-triazacyclononane) based on 1,4,7-triazacyclononane (TACN) N-functionalized by different arylcarboxylic acids were prepared under solvothermal conditions and characterized by single crystal X-ray analysis and porosity measurements. Crystal structure of Cd_2L^1 reveals a cationic net with a *bcs* topology, and nodes are constituted by dinuclear cadmium complexes, in which each cadmium atom adopts a hexacoordinated environment involving both the carboxylate and the cyclic amine. In contrast, CdL² displays a two-fold interpenetrated structure with a *pcu* topology. In this net, the node is a mononuclear complex in which the Cd atom exhibits a seven-coordination geometry. Both materials show a high permanent porosity and good CO_2 adsorption properties with a high selectivity over N_2 and CH₄. The adsorption capacity and selectivity for CO₂ were calculated from a multisite Langmuir isotherm model and the ideal adsorbed solution theory (IAST), which gave insights into the nature of solid-gas interactions and evidenced the influence of interpenetration or polarity of the charged framework on their adsorption properties.

INTRODUCTION

Microporous solids are among the most studied materials by chemists and physicists in recent years. Many of them are essential in different biomimetic and industrial processes, and are for this reason considered as multifunctional materials. Besides inorganic porous solids such as zeolites, Metal-Organic Frameworks (MOFs) have been considered as a new class of porous molecular materials and have been widely utilized over the last two decades.^{1,2} MOFs are crystalline materials constituted of metallic ions or polynuclear clusters coordinated to organic linkers to form porous 2D or 3D structures. The organic linkers, metal ions and supramolecular assembly can be tuned to control the chemical functionalities, the porosity, the topology and the nanoscale morphology of the crystalline structure, allowing a systematic and fine tailoring of their porous architecture and reactivity, which represents a fundamental advance in the field of materials science. The versatility of MOFs is based on the large choice of organic linkers and inorganic components that resulted in more than 20,000 MOFs structures with single topologies.³ Most of them are porous with nanometer size of the pores,³⁻¹⁰ which makes such materials attractive for many applications such as hydrogen storage,^{11,12} selective adsorption and gas separation,¹³⁻¹⁶ heterogeneous catalysis,¹⁷ chemical sensors¹⁸ and nanomedicine.¹⁹

In particular, MOFs are regarded as promising candidates for the capture of greenhouse gases and especially carbon dioxide, which is becoming a growing source of concern nowadays.^{15,16,20-23} The use of MOFs as sorbents has received great attention, because such materials are able to outperform other benchmark porous solids like zeolites or activated carbon. It is well-known that the postcombustion flue gas from coal-fired power plants contains about 15% CO₂ and 85% N₂, whereas the contents of CO₂ in natural and landfill gas (mixture of CO₂ and CH₄) used for the precombustion process are about 5% and 50%, respectively. The separation of CO₂ from CH₄ is then required in order to increase the

 energy density of the fuel gases and reduce pipeline corrosion concerns induced by the acidity of CO_2 .^{15,20} In these contexts, cutting edge selective adsorption processes with porous materials are awaited to achieve efficient capture and recovery of CO_2 from N₂ and CH₄. Therefore, MOFs hold promise to address this challenging issue benefiting from their modular synthesis and their tunable porosity and functionality.

Economically viable MOFs for CO_2 capture require to present a high selectivity and gas uptake, as well as a moderate enthalpy of adsorption for recovering and recycling them with a low energy consumption.²¹ Although a high surface area is a prerequisite to ensure a high accessibility of the adsorption sites, the strength of CO_2 interactions with the framework is also a key factor associated with uptake, selectivity and regeneration ability. Thus, many efforts have been devoted to enhance the CO_2 affinity and selectivity using different strategies, including the introduction of Lewis basic sites into the framework, ^{15,21,24-33} the generation of coordinatively unsaturated metal sites exposed to gas molecules binding,³⁴⁻³⁸ or addition of cationic or anionic charges.³⁹ Ligand shortening^{40,41} or framework interpenetration control⁴⁰⁻⁴³ are also good alternatives for a fine control of the pore size because of the presence of microcavities that endows a better performance for selective CO_2 capture. One interesting approach to develop innovative sorbents is then to combine several of these structural features to provide a careful tuning of gas adsorption properties.

Till now, most of porous coordination polymers were prepared from polydentate linkers functionalized by only one type of coordination sites such as carboxylate, nitrogen or phosphonate donors. An appealing strategy that implies the assembly of polytopic organic ligands bearing at least two distinct coordinating groups was developed in the last years. Actually, considerable research efforts were devoted to the preparation of materials containing strong chelating agents such as dipyrrins,⁴⁴⁻⁴⁷ salens,^{48,49} porphyrins,⁵⁰⁻⁵⁴

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bipyridine⁵⁵⁻⁵⁹ or phenanthroline ligands.⁶⁰ The use of such metalloligands was explored in order to bring multifunctionality to the framework and offered the opportunity to enhance gas binding properties and to introduce catalytic sites in the resulting MOFs.^{38,48,49,51,59,61-66} Such an approach can be used for the subsequent chemical transformation of CO_2 .^{67,68}

However, the design and preparation of porous and crystalline materials based on metalloligands still remain challenging. A fine control of their assembly can be gained by systematically adjusting the denticity and the size of the linkers, while the overall connectivity is determined by both the topology of the ligand and the nature of the metal ion.

Our strategy implies the utilization of azamacrocycles as strong chelators for supramolecular assembling since their polydentate and cyclic features allow a rational control of the coordination sphere around metal ions. Azamacrocylic ligands are still scarce in the field of MOFs despite their original geometries, which can give rise to unusual structures and topologies.⁶⁷⁻⁷³ The presence of *N*-donor atoms enables the complexation of metal ions, allowing the preparation of metalloligands prior to the formation of a network.⁷⁴ Actually, the assembly relies on the fact that the coordination sphere of the metal ion is not saturated when using non-functionalized polyazamacrocycles like 1,4,7-triazacyclononane (TACN), 1,4,8,11-tetraazacyclotetradecane (cyclam) or 1,4,7,10-tetraazacyclodecane (cyclen). Consequently, the supramolecular assembly requires the utilization of a second ligand capable of coordinating unoccupied sites of the metal ion.⁷⁵⁻⁷⁹

However, a more straightforward assembling of macrocycles is favored when additional donor atoms from carboxylate are anchored in a divergent manner on a polyazamacrocyclic scaffold. Such polytopic and polydentate ligands can be simply obtained by functionalization of the nitrogen atoms by carboxylate pendent arms.^{67,68,70,73,78} Only rare examples of permanently porous MOFs constructed from such *N*-functionalized polyazamacrocycles have already been reported,^{67,70,78,80,81} because of the flexibility of the cyclic chelate and the wide

 diversity of coordination geometries adopted by transition metals. Nevertheless, this synthetic strategy provided MOFs with new functionalities, giving rise to various applications such as selective gas adsorption,^{67,70} separation of isomers,⁷³ catalysis⁶⁸ or biomedical imaging.⁸²

Ligands that possess a *C*₃ geometry like TACN and its *N*-functionalized derivatives are ideally suited to generate mono- and polynuclear metal complexes for the construction of MOFs since TACN is a tridentate ligand that coordinates facially to a metal ion, leaving two or three free coordination sites.⁷⁰ Such derivatives are of interest in the field of selective metal ions or anions sensors,⁸³ therapy,⁸⁴ medical imaging diagnosis⁸⁵⁻⁸⁸ and hybrid materials,^{89,90} and to our knowledge only two coordination polymers based on *N*-functionalized TACN were reported so far.^{70,80}

Our group has previously described a stable crystalline material obtained with Zn^{2+} ions and this scaffold, and the material has shown high porosity with selective capture of CO₂ over N₂.⁷⁰ This work paves a way to prepare a new family of porous materials using the isoreticular paradigm developed along the last two decades.⁹¹ This strategy enables the successful synthesis of a large diversity of MOFs with a fine tuning of their pore size and an improvement of their specific surface area and gas storage properties.^{3,91-93} In this work we address the question as to whether the isoreticular concept can be a useful tool for the construction of new porous structures with a TACN platform. In addition, the role of the spacers length anchored on the TACN has been investigated to provide diversity both in structures and adsorption properties.

In the pursuit of new high-performance CO_2 gas separation materials, we have selected two TACN macrocycles *N*-functionalized by benzylcarboxylate (L^1) or propynylbenzoate (L^2) arms possessing different lengths, and porous materials were prepared by assembling of these ligands with Cd^{2+} ions. Herein we describe the synthesis of the ligands and corresponding Cd-MOFs. Structures and adsorption properties of two Cd-MOFs, Cd_2L^1 and

 CdL^2 , have been thoroughly analyzed based on XRD data on single crystals and powders, FTIR, TGA and porosity measurements as well as selective CO₂ capture and separation towards N₂, CH₄ and CO. The materials Cd_2L^1 and CdL^2 represent rare examples of permanently porous MOFs belonging to the family of polyazamacrocycles that demonstrates interesting properties for the selective adsorption of CO₂.

EXPERIMENTAL SECTION

The experimental section associated to ligand, material synthesis and their characterizations are reported in the Supporting Information.

RESULTS AND DISCUSSION

Two linkers presenting a high flexibility ($\mathbf{H}_{3}\mathbf{L}^{1}$ and $\mathbf{H}_{3}\mathbf{L}^{1}$, Figure 1), were used for the preparation of porous architectures thanks to coordination of metallic centers: *i*) inside the cavity of the macrocycle, thus providing a metalloligand,⁷⁰ and *ii*) by the carboxylate groups allowing 3D polymer expansion and binding on the coordinatively unsaturated metallic ions of the metalloligand.

Ligand synthesis. Polytopic H_3L^1 linker was prepared as previously described by our group.⁷⁰ The five-steps synthetic approach to polyazamacrocycle H_3L^2 bearing longer carboxylate-functionalized pendent arms is summarized in Scheme 1 (see Supporting Information for details). Commercially available 4-bromobenzoic acid was protected as methyl ester (1) and was introduced in the Sonogashira reaction with propargylic alcohol to afford methyl 3-(4-benzoate)-1-hydroxyprop-2-yn-1-yl (2) in 57 % overall yield. This alcohol was converted in good yield (67%) to the corresponding bromide 3 using CBr₄ as a brominating agent. *N*-alkylation of TACN by bromide 3 was achieved in DMF in the presence

of K_2CO_3 as a base to give the expected triester **4** in 63% yield. In the final step, the saponification of **4** was performed using NaOH in a THF/MeOH mixture. H_3L^2 was isolated in its protonated form after acidification of the reaction mixture with hydrobromic acid.



Figure 1. Structure of polytopic ligands H_3L^1 and H_3L^2 studied in this work.



Scheme 1. Synthesis of H_3L^2 .

 Synthesis and preliminary characterization of the materials. The choice of Cd^{2+} was guided by its chemical analogy with Zn^{2+} ions and its propensity to adopt hexa- to octacoordinated environments in view to promote the growth of 3D frameworks. Crystals of Cd materials were obtained in solvothermal conditions using $Cd(NO_3)_2$ ·4H₂O as a metal salt and

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a 0.015 M solution of H_3L^1 or H_3L^2 linkers in a 10:1:1 mixture ratio of DMF, ethanol and water at 80 °C or 100 °C, respectively, for 24 hours in a sealed Pyrex tube. Octahedral and rectangular parallelepiped-shaped crystals were obtained in 62% and 49% yield for H_3L^1 and H_3L^2 , respectively. The composition of the solids was inferred from ICP-AES, elemental analyses, bromide titration with silver nitrate, SEM and ¹H NMR spectroscopy. The material based on H_3L^1 gave a metal: ligand ratio equal to 2. SEM/EDS analysis revealed the presence of bromine atoms in the solid. ¹H NMR analysis of the digested solid in DMSO- d_6 /DCl also showed the presence of a formate anion resulting from the degradation of DMF in solvothermal conditions. The presence of bromide, formate and nitrate in the solid pointed out formation framework. the of а cationic Overall, а general formula of $[Cd_2(L^1)(H_2O)_3](NO_3)_{0.7}(HCOO)_{0.2}Br_{0.1} (= Cd_2L^1)$ was inferred. For material prepared from H_3L^2 , the analyses gave a metal: ligand ratio equal to 1 and revealed the absence of bromide and formate anions in the solid. This result unveiled the neutral charge of the framework and therefore the monoprotonation of the ligand in order to satisfy the charge balance. A general formula of $[Cd(HL^2)(H_2O)_2]$ (= CdL²) was then inferred. Moreover, the FTIR spectra present signatures of different carboxylate vibrations for both materials (Figure S2), thus indicating several coordination modes of this donor group. Therefore, the analytical data demonstrate that CdL^2 and Cd_2L^1 do not display the expected isoreticular structures.

Structural studies of Cd_2L^1 . According to single-crystal X-ray diffraction studies, Cd_2L^1 crystallizes in a cubic crystal system with a $I\bar{4}3d$ space group, a cell parameter a = 26.7228(8) Å and a unit cell volume of 19083.0(17) Å³. This compound is isostructural to the zinc(II) analogue Zn_2L^1 described in our previous work.⁷⁰ The asymmetric unit contains two crystallographically independent Cd^{2+} ions (Figure 2a), both adopting a hexacoordinated geometry. The azamacrocycle acts as a tridentate *N*-donor ligand for one Cd atom. The two

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Cd are located in close proximity to each other (Cd1^{...}Cd2: 3.790(9) Å) and are interconnected through three bridging benzenecarboxylate linkers coming from three different ligands. Three oxygen atoms from the carboxylate groups and the $fac-N_3$ donor atoms surround the Cd1 atom, which then displays a distorted octahedral geometry. The deviation from the ideal geometry is caused by steric constraints imposed by the macrocycle as evidenced by the values of 2.417(5) Å for the Cd1–N1 bond and 76.3(2)° for the N1–Cd1–N1 angle. The distortion of the coordination polyhedron can be assigned to a large displacement of Cd1 from the N₃-mean plane. As a matter of fact, the distances between Cd1 atom and centroids of the two planes, defined by the three nitrogen atoms and the three $O_3(2)$ atoms, are 1.701 Å and 0.953 Å respectively. It has to be noticed that Cd1–N1 and Cd1^{...}Cd2 distances are significantly higher than those observed for the isostructural $\mathbf{Zn_2L^1}$ (2.201 and 3.517 Å. respectively),⁷⁰ which is in accordance with the larger ionic radius of $Cd^{2+} vs Zn^{2+}$. Cd2 atom adopts a slightly distorted trigonal prism geometry and is coordinated to three oxygen atoms from the bridging carboxylate and three water molecules, the latter having an individual occupancy of 1/3. Overall, the stability of the architecture is supported by the rigidity of this dinuclear cadmium cluster.

Thus, a secondary building unit (SBU) for $\mathbf{Cd_2L^1}$ is composed of two cadmium ions, one N₃-cyclic chelate unit, three carboxylates and three water molecules, giving the formula $[Cd_2(COO)_3(fac-N_3)(H_2O)_3]$. Each SBU can be seen as a 6-connected node and the framework can be described as a *bcs* net according to a topological approach (Figure 2b).⁹⁴ The view along the unit cell axis reveals the presence of regular voids due to the presence of square-shaped channel apertures of 7.5 Å (Figure 2c,d). Owing to the cubic symmetry of the framework, the voids are connected to each other to form a 3D network of channels. According to calculation with the SOLV PLATON program,^{95,96} the structure has an overall

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solvent accessible void volume of 46.1% (8797 Å³), and the pore volume was estimated to $0.380 \text{ cm}^3 \text{ g}^{-1}$.

Owing to the charge of the cation (+2) and that of the ligand (-3), $[Cd_2(L^1)(H_2O)_3]$ framework is monocationic and charge-balancing anions are expected to be situated in the channels, but cannot be located by X-ray crystallography because they don't occupy specific coordination sites. As mentioned above, the cavities of Cd_2L^1 are filled with solvent molecules and HCOO⁻, NO₃⁻ and Br⁻ anions, which are present in the reaction mixture.



Figure 2. (a) Representation of the SBU $[Cd_2(L^1)(H_2O)_3]$, (b) view of the *bcs* net adopted by Cd_2L^1 , (c) view of the open channels along the c axis showing the coordination polyhedra of Cd nodes (solvent molecules and hydrogen atoms are omitted for clarity), (d) space-filling model of Cd_2L^1 shown along the c axis (Cd: yellow, O: red, C: brown).

Structural studies of CdL². Following the isoreticular approach, H_3L^2 was designed by insertion of alkyne spacers between the aryl moieties and the TACN scaffold. This new ligand was expected to behave similarly to H_3L^1 and to form isoreticular nets with larger pore apertures and a higher porosity. To our surprise, a new material presenting a different topology and possessing metallic nodes with an original coordination scheme was obtained. Single-crystal X-ray diffraction analysis of CdL² revealed that this MOF crystallizes in a monoclinic crystal system with space group C2/c and cell parameters of a = 20.9966(15) Å, b= 18.9165(14) Å, c = 29.059(2) Å and $\beta = 92.303(3)^\circ$. Only one ligand molecule and one cadmium atom form the asymmetric unit. The overall structure can be described as a pair of identical nets, which are mutually interwoven to form a doubly interpenetrated framework (Figure 3b,c).

The Cd atom (Figure 3a and S7b) is heptacoordinated and exhibits an unusual CdN₃O₄ coordination scheme. These structural moieties constitute the primary building unit (PBU) of the framework. Each metal ion is linked to three *fac*-nitrogen atoms from one TACN macrocycle in a κ^3 -fashion and three oxygen atoms belonging to two carboxylate and one oxygen atom from a carboxyl group, each of them belonging to three vicinal ligands. The Cd–N(1,2,3) bond lengths (2.383, 2.422, 2.417 Å) are slightly longer compared with those found for MMCF-1 based on cyclen (2.349 Å).⁶⁷ These values are quite similar to those determined for Cd₂L¹ (2.417(5) Å) and other TACN derivatives (Cd–N = 2.414(9) Å).⁸⁰ despite the structural difference of the coordination environment around Cd.

One carboxylate anion acts as a monodentate donor (Cd–O6: 2.237(3) Å) whereas the second anion coordinates the metal center in bidentate fashion with Cd–O(3,4) bond lengths of 2.519(3) and 2.276(4) Å. Surprisingly, the third carboxylate group is protonated and coordinates to Cd atom through the carbonyl group, and exhibits a longer Cd–O2 bond length

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(2.497(3) Å). The protonation is clearly evidenced by the short carbonyl C1–O2 (1.217 Å) and longer C1–O1 (1.305 Å) bond lengths compared to the C–O bonds from two carboxylate groups. This unusual coordination seems to stem from the formation of the O1–H1^{...}O6 hydrogen bond between this carboxyl group and the adjacent monodentate carboxylate (Figure 3a and S7b), which is evidenced by the short H1^{...}O6 distance (1.676 Å) and a large angle O1–H1^{...}O6 (170°). This hydrogen bond is suspected to improve the stability of the supramolecular assembly.

FTIR analysis of the activated CdL^2 (dried in vacuum) provides additional data to point out the coordination modes of O-donor ligands (Figure S2). In the spectrum, the C=O stretching band for the carboxylic group was observed at 1676 cm⁻¹, and two additional vibrations at 1583 and 1538 cm⁻¹ were assigned to the carboxylate group coordinated in a bidentate fashion. Two other bands at 1652 and 1404 cm⁻¹ were attributed to the monodentate carboxylate.⁹⁷

Bond lengths for Cd–N(1,2,3) and those of Cd–oxygen atoms reflect a distorted geometry of the CdN₃O₄ coordination polyhedron. This distortion is clearly indicated by the difference in the distances between the Cd atom and two centroids defined for the N₃ and O₄ mean planes (1.727 Å and 1.367 Å, respectively). This distorted geometry is similar to that observed in Cd₂L¹ and is mainly due to the shift of the metal atom above the mean plane of the macrocycle, thus lying closer to oxygen donors. The geometry around Cd atom was assessed using the method of the continuous shape measure (CShM).^{98,99} A pentagonal bipyramid (PBPY-7) and a capped trigonal prism (CTPR-7) geometry were assumed as the most representative polyhedra. The calculations were in favour of a distorted PBPY-7 environment (S_Q (PBPY-7) = 2.68 (D_{5h}) and S_Q (CTPR-7) = 4.06 (C_{2v})). In such a geometry, the equatorial plane is defined by two nitrogen atoms (N2, N3) of the macrocycle and three

oxygen atoms (O2, O3, O4) while N1 and O6 constitute the two apical donor atoms (Figure S7b).

Cadmium atoms can be described as 6-connecting nodes adopting a near octahedral geometry. These nodes are linked to the closest cadmium atom through carboxylates and the TACN macrocycle to produce a *pcu* net (Figure 3b). The network exhibits a slight distortion as indicated by the difference in edge lengths of the parallelogram (14.131 and 14.585 Å) and the deviation of the inside angle (89.0°) from a right angle.



Figure 3. View of the CdL^2 structures: (a) Representation of the 6-connected Cd node, (b) view of the interpenetrated *pcu* topology, (c) view along the c axis showing the interpenetrated framework and the coordination polyhedral of the Cd nodes (solvent

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molecules and hydrogen atoms are omitted for clarity, (d) space-filled model of CdL^2 shown along the c axis (Cd: yellow, O: red, C: black).

The network is twofold interpenetrated and the closest distance between two adjacent aryles from two different nets is 3.8 Å (Figure S7c,d). Interestingly, these interpenetrated networks exhibit multiple π - π interactions (Figures S8 and S9) between two adjacent alkynes (C8^{...}C19 = 3.39(1) Å, C8^{...}C18 = 3.46(1) Å), one alkyne and one aromatic ring (C20^{...}C4 = 3.64(1) Å, C19^{...}C5 = 3.44(1) Å, C6^{...}C18 = 3.65(1) Å, C5^{...}C18 = 3.61(1) Å) and two phenylene moieties (C4^{...}C22 = 3.72(1) Å). We can assume that the two fold interpenetrated framework is thermodynamically more stable than the expected isoreticular non-interpenetrated one due to enhanced stabilization by multiple weak stacking interactions. These results provide further evidence of the importance of controlling such interactions to design interpenetrated assemblies^{23,42,100-104} and show limitations of the isoreticular approach.

Despite interpenetration, \mathbf{CdL}^2 is highly porous and displays a solvent accessible volume of 54.7% (6308 Å³) and an accessible pore volume estimated to 0.633 cm³ g⁻¹. These values outperform those of the non-interpenetrated $\mathbf{Cd}_2\mathbf{L}^1$. The view along the *c* axis reveals square open channels with an aperture between 8.0 and 11.5 Å for the smallest and largest one, respectively (Figure 3b,c and S8). Furthermore, the space-filling model clearly shows that the pore accessibility is not restricted (Figure 3d).

It has to be noted that all attempts to obtain a non-interpenetrated analogue of CdL^2 using solvothermal synthetic conditions by varying the temperature and the concentration of the reagents were unsuccessful.

Powder X-ray diffraction

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Powder X-Ray diffraction (PXRD) measurements were carried out to further investigate the crystallinity of the two materials and their phase purity (Figures S10 and S11). The positions of the sharp peaks in the experimental PXRD patterns for the as-synthesized solids are in good agreement with the simulated diffractograms calculated from single-crystal data, thus demonstrating the high phase purity and homogeneity of both solids. The structural robustness of both frameworks was also evaluated after immersing the as-synthesized solids in common solvents such as methanol, THF, dichloromethane (CH₂Cl₂) and acetone. Crystals of Cd_2L^1 show good stability in methanol, THF and acetone. However, the material does not retain its crystallinity after immersion in CH₂Cl₂ since the structure partially collapses. Compound CdL^2 exhibits small structural deformations after solvent exchange with methanol, THF, CH₂Cl₂ and acetone but retains its crystallinity. Cell parameters calculated in each solvent condition according to the Lebail refinement are reported in Table S18. A slight flexibility of the interpenetrated CdL^2 framework can be rationalized by the displacement of the two networks with respect to each other, triggered by the introduction of solvent molecules inside the pores and between the interwoven nets.

Special attention was made to analyse the crystallinity of Cd_2L^1 and CdL^2 after complete removal of the solvent molecules. At least 3 exchanges with THF were performed before drying the solids under vacuum at 298 K. For Cd_2L^1 , PXRD patterns of the desolvated framework match well with those of the as-synthesized compound and indicate that this material retained its crystallinity (Figure S11 and Table S19). However, Cd_2L^1 becomes amorphous after heating at 80 °C for 1 h. Interestingly, the structure can be totally recovered after soaking the activated material in DMF. This behavior can be viewed as intermediate between the 1st and the 3rd generation of porous coordination polymer according to Kitagawa's classification.¹⁰⁵ After THF exchange and activation of CdL^2 under vacuum at 298 K, a broadening of the diffraction peaks was observed, which suggests some structural

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modifications or a partial collapse of the framework during desolvation. The lower structural stability of CdL^2 compared with Cd_2L^1 is quite unexpected since interpenetrated frameworks often provide materials with higher structural stability.¹⁰⁶⁻¹⁰⁸ This result can probably be assigned to the presence of a mononuclear primary building unit (uninode) for CdL^2 in contrast to Cd_2L^1 that is built from dinuclear SBUs.

TGA analysis

Thermal stabilities of the two materials were studied by TGA between 25 and 1000 °C (Figure S4). Values of the weight loss and those of the residues enable us to confirm the composition of the solids suggested from the elemental analysis, ICP-AES and X-ray data. Crystals of Cd_2L^1 and CdL^2 were analyzed after thorough exchange of the solvent used for their synthesis (DMF) by THF and drying under vacuum at room temperature for 48 h. Thermal behavior of both compounds shows a small weight loss (3%) around 400 – 420 K, which can be due to the loss of residual solvent or water molecules adsorbed in the pores. After a plateau until 570 K, a dramatic weight loss is observed between 600 and 780 K that corresponds to decomposition of the networks leading to the formation of CdO. The residual weights of each sample (Cd_2L^1 : 30.5%; CdL^2 : 17.5%) are in good agreement with the expected values (Cd_2L^1 : 29.8%; CdL^2 : 17.1%). Therefore, the frameworks show a similar thermal stability despite their different structures.

Adsorption properties

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The porosity of the two materials was evaluated by recording N_2 adsorption isotherms at 77 K (Figure S12). Before analysis, DMF-soaked samples were activated under reduced pressure as described above. The absence of residual solvent trapped in the pores was checked by ¹H NMR spectroscopy after the decomposition of both samples in acidic media (Figure S3). The permanent porosity of the solids was confirmed by the typical type-I shape of adsorption isotherms, characteristic of microporous solids¹⁰⁹ with a nitrogen uptake of 163 and 97 cm³ g⁻¹ at saturation, respectively for Cd_2L^1 and CdL^2 . The BET surface areas were calculated to 625 and 343 m² g⁻¹, and the Langmuir surface areas were 730 and 414 m² g⁻¹, respectively. Since the materials are exclusively microporous, the single data point at relative pressure close to 0.95 gave microporous volumes equal to 0.253 and 0.150 cm³ g⁻¹. The higher porosity of Cd_2L^1 compared with CdL^2 shows a discrepancy with the solvent accessible volume calculated from the single crystal X-ray data and gives evidence of a partial collapse of the framework during desolvation for the interpenetrated CdL^2 as shown by PXRD analyses (see *supra*). Hence, Cd_2L^1 is a more opened framework than CdL^2 . These values are in the same range $(350-800 \text{ m}^2 \text{ g}^{-1})$ as those obtained with other MOFs based on cyclam, cyclen or other polyazacycloalkane,^{67,69,78,110} but significantly smaller than those of the previously described $\mathbf{Zn}_{2}\mathbf{L}^{1}$ (1100 m² g⁻¹) which is isostructural to $\mathbf{Cd}_{2}\mathbf{L}^{1,70}$ A mean pore size diameter was calculated using the Horvath-Kawazoe method that gave a value around 8 Å for both solids (Figure S13) in agreement with the two crystal structures.

The permanent porosity was also studied by CO_2 adsorption measurements at 195 K. Actually, pore accessibility or re-opening can be promoted by CO_2 at low temperature. As shown in Figure S14, both materials show no gate phenomenon, usually characterized by an inflection point disclosing a delayed adsorption induced by a structurally dynamic behavior.¹¹¹⁻¹¹³ Such behaviour is in agreement with the rigidity of both frameworks.

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For \mathbf{CdL}^2 , the isotherm displays a type-I morphology and the progressive pore-filling is observed with saturation profile nearly reached for 1 atm pressure. In addition, the CO₂ isotherm displays a small hysteresis loop. The adsorption capacity at 1 atm (99 cm³ g⁻¹) and the calculated Langmuir surface area (408 m² g⁻¹) are very close to values found from N₂ uptake (97 cm³ g⁻¹ and 414 m² g⁻¹, respectively). Cd₂L¹ exhibits a similar isotherm of CO₂ at 195 K but the gas uptake at 1 atm is significantly lower (66 cm³ g⁻¹) and the Langmuir surface is only 348 m² g⁻¹. It has to be noted that the initial slope in the low-pressure range is more pronounced, indicating a higher affinity for CO₂ than CdL².

Overall, the CO₂ capacities at 195 K for both materials are in the same order than for MIL-96(Al),¹¹⁴ MIL-102(Cr)¹¹⁵ or MOFs formed by the assembly of polyazamacrocycles^{67,70,75,110} but for the latter, most of them are flexible and show gate-opening or breathing effects upon CO₂ adsorption.^{76,77,79} Therefore, Cd_2L^1 and CdL^2 represent one of the first example of permanently porous MOFs based upon a *N*-functionalized and flexible polyazamacrocyclic ligand and only few reports have described porous structures constructed from platforms like di-,¹¹⁶⁻¹¹⁹ tri-,^{70,80} or tetra-azamacrocycles.^{67,73,78}

 CO_2 adsorption in non-condensing conditions (273 – 298 K) was also explored in order to study the selective binding of CO_2 and its interactions with the surface of the materials. First, gas adsorption isotherms for CO_2 , CO, N_2 , and CH_4 at 298 K were recorded.

As shown in Figure 4, both materials show a significant CO₂ and moderate CH₄ uptake, and an overall low affinity for CO and N₂, with values of N₂ adsorption equal to 1.6 cm³ g⁻¹ and 1.0 cm³ g⁻¹ and CO uptake close to 1.0 cm³ g⁻¹ and 3.0 cm³ g⁻¹ for Cd₂L¹ and CdL² respectively. CdL² adsorbs 26.7 cm³ g⁻¹ (5.2 % w/w) of CO₂ at 1 atm, whereas the uptake for Cd₂L¹ is 42.9 cm³ g⁻¹ (8.4 % w/w). No distinct plateau was observed for both isotherms in the 0 – 1 atm pressure range, indicating that the samples can adsorb a greater volume of CO₂ at higher pressure or lower temperatures. The difference in CO₂ capacity at 1 atm between these materials is in part ascribed to a pore blocking effect a partial collapse of the framework of the desolvated CdL^2 that limits the accessibility of the porosity.



Figure 4. Adsorption isotherms of CO₂ (298 K: blue filled circles, 285 K: blue hollow circles, 273 K: blue filled squares), CO (pink square), CH₄ (green triangle) and N₂ (brown square) recorded at 298 K for (a) Cd_2L^1 and (b) CdL^2 . Solid (298 K), dashed (285 K) and dotted (273 K) lines represent the CO₂-fitting curves using a single or a dual-site Langmuir model for Cd_2L^1 and CdL^2 respectively (see Tables S20, S21 and S22).

CH₄ uptake is significantly lower than CO₂ but still higher than N₂ under the same conditions for both materials. The higher adsorption of CH₄ over N₂ is expected and is ascribed to the higher polarizability of CH₄ (26 x 10^{-25} cm³) *vs.* N₂ (17.6 x 10^{-25} cm³) and CO (19.5 x 10^{-25} cm³).¹²⁰ Consequently, CH₄ is preferentially adsorbed than N₂ and CO in most of reported sorbents.

At ambient conditions, the CO₂ capture for Cd_2L^1 and CdL^2 are in the same range than other Cd-MOFs^{67,121} and are also comparable to well-known IRMOF-1, IRMOF-3, MOF-177,¹²² imidazolate frameworks ZIF-8,¹²² ZIF-20,¹²³ ZIF-69,¹²⁴ ZIF-78¹²⁵ and other MOFs presenting a high porosity (see Table S23 for additional details). Nevertheless, CO₂ adsorption is lower than the one we have obtained in our previous work for Zn_2L^1 (88.0 cm³ g⁻¹).⁷⁰

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The porous nature of the interpenetrated (CdL^2) or the charged frameworks (Cd_2L^1) prompted us to explore their CO₂ capture at lower temperatures than 298 K to get more information on gas-surface interactions. CO₂ uptakes at 1 atm for Cd_2L^1 are 52.3 and 62.5 cm³ g⁻¹ at 285 and 273 K, respectively (Figure 4). For CdL^2 , these values are significantly lower, 34.9 and 42.9 cm³ g⁻¹, respectively. Accordingly, Cd_2L^1 presents higher uptakes whatever the temperature, which can be explained by its higher porosity and polarity induced by the charged framework. The isotherm curves for Cd_2L^1 show a steeper slope for CO₂ uptake in the initial stage, which demonstrates more favorable interactions between CO₂ molecules and the host framework. In other words, Cd_2L^1 offers a higher affinity for CO₂ than CdL^2 .

The isosteric heats of adsorption ($IQ_{st}I = -\Delta H$) were then determined to estimate solid–gas interactions, since the coverage dependent enthalpies allows a better understanding of the adsorption selectivity for CO₂ over other components in a mixed gas stream, in particular CO₂/N₂ and CO₂/CH₄. As a result, a high magnitude of $|Q_{st}|$ for CO₂ contributes to an improvement of such selectivities. The $|Q_{st}|$ values less than 30 kJ mol⁻¹ are indicative of nonselective physisorption interactions, values between 30 and 50 kJ mol⁻¹ are typical of moderately strong gas-sorbent interactions involving polar functional groups, and values above 50 kJ mol⁻¹ arise from stronger interactions. Moreover, isosteric heats at zero coverage provide a quantifiable estimation of binding strengths with the most energetic sites.

The isosteric heats of adsorption were calculated from CO_2 isotherms at three different temperatures (273, 285 and 298 K, Figure S19) using the Clausius-Clapeyron equation. The heat of adsorption for Cd_2L^1 lies in the range of 25.1 to 28.0 kJ mol⁻¹ whatever the volume adsorbed. This result is consistent with the single-site Langmuir model used to fit the isotherms (see below and Table S21). The porous solid CdL^2 displays more heterogeneous adsorption energy sites because the enthalpy for CdL^2 is higher at low gas loadings and decreases from 30.7 to 24.3 kJ mol⁻¹ for a 30 cm³ g⁻¹ uptake. The higher heat of adsorption for CdL² probably originates from the interpenetration of the net, which gives rise to smaller pore size and stronger interactions between the network and CO₂ molecules in the low coverage domain. Nevertheless, the values of the adsorption heats are characteristic of CO₂ physisorption for both materials, and low $|Q_{st}|$ values enable their total recovery with a low energy consumption.

These enthalpy values are similar to those of benchmark porous materials with polar functional moieties such as HKUST-1 (35 kJ mol⁻¹),¹²⁶ bio-MOF-1 (35 kJ mol⁻¹),¹²⁷ PCN-6 (35 kJ mol⁻¹)¹²⁸ and the two-fold interpenetrating Cd-MOF based on a cyclen macrocycle (MMCF-1, 26 kJ mol⁻¹).⁶⁷ Overall, Cd_2L^1 and CdL^2 show a significant porosity and CO₂ uptake, despite the difference of porosity and topology between the two structures.

CO₂ adsorption selectivity calculations

The relatively high CO₂ and marginal N₂ and CH₄ uptakes at 298 K and 1 atm prompted us to calculate the selectively for CO₂ to evaluate the CO₂/N₂ and CO₂/CH₄ separation performance. In a first glance, the adsorption selectivity for CO₂/CH₄ and CO₂/N₂ was estimated according to Henry's law by the ratio of the initial slope for both isotherms (Table S22). These calculations gave CO₂/CH₄ selectivities for Cd₂L¹ and CdL² equal to 12.0 and 6.6 at 298 K, respectively. These values compete with those of the well-studied Cu₃(BTC)₂ (7.7)¹²⁹ or with other nitrogen linker-based MOFs including ZIF-204 (4.6), ZIF-68 (5.5), and ZIF-78 (10.5).^{22,130} In addition, the CO₂/N₂ selectivities at low coverage are close to 19.5 and 109, respectively for Cd₂L¹ and CdL², and these values make these materials promising for applications in gas separation.

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More reliable information is required to evaluate the efficiency of the two materials for gas separation. In terms of prediction, the ideal adsorbed solution theory (IAST) is a powerful method¹³¹ to give a close approximation of the selectivity in a binary gas mixtures from the experimental single-component isotherms.^{15,22,40,132-136} The calculations were run assuming a CO_2/N_2 binary mixture at a molar ratio of 15:85 to mimic the composition of the flue gas in postcombustion processes, and with a 50:50 molar ratio for CO_2/CH_4 mixtures typical of general feed compositions of landfill gas. For such calculations, a deeper insight into adsorption process is required, using equilibrium isotherm models based on the Langmuir isotherm. While all isotherm data for Cd_2L^1 can be adequately fitted by a single-site Langmuir equation, the CO_2 isotherms for CdL^2 required a dual-site Langmuir model that indicates the presence of adsorption sites with different energies (Tables S21 and S22). These data were then used in order to give reliable IAST calculations and the results are shown in Figures S20 to S23.

The results demonstrate high selectivities for the studied CO_2/N_2 and CO_2/CH_4 mixtures at 298 K whatever the pressure. The CO_2/N_2 selectivities are equal to 286.0 and 88.4 at 1 atm for Cd_2L^1 and CdL^2 , respectively. In the same way, the CO_2/CH_4 selectivity is equal to 19.9 and 4.7 at 1 atm. Interestingly, the CO_2/N_2 and CO_2/CH_4 selectivities increase with rising pressure for Cd_2L^1 while they decrease smoothly for CdL^2 . The most pronounced change (14-fold increase) in the pressure range of 0–1 atm was observed for Cd_2L^1 and the CO_2/N_2 mixture (Figure S23). Generally, the host-guest interactions decrease with rising pressure. The unusual behavior for Cd_2L^1 is assigned to enhanced CO_2-CO_2 interactions with increasing pressure.

Both materials compare favourably or even outperform many neutral, charged, aminefunctionalized or coordinatively unsaturated MOFs reported previously (Table S23 and S24). Actually, the selectivities for the majority of MOFs lie mainly in the ranges of 5–30 and 10– 75 for CO_2/CH_4 and CO_2/N_2 at 298 K, respectively.²² It turns out that only few of them have

shown selectivities higher than 20 for CO_2/CH_4 and 200 for CO_2/N_2 at room temperature.^{15,40,132} Thus, the two present materials gave interesting CO_2 adsorption properties for separation purposes despite the absence of open metal sites or free basic amine lying in the pores of the framework. However, Cd_2L^1 and CdL^2 show moderated CO_2 uptake at 1 atm due to their rather small surface area compared with benchmark MOFs^{15,16} that possess high affinities for CO_2 in low pressure such as Mg-MOF-74 (190 cm³ g⁻¹, CO_2/N_2 at 298 K: 182), $Cu_3(BTC)_2$ (117 cm³ g⁻¹, CO_2/N_2 at 298 K: 22) and UTSA-16 (96 cm³ g⁻¹, CO_2/N_2 at 298 K: 300).^{16,34,132}

The selective capture of CO₂ at 298 K for CdL² is ascribed to the decrease of the channel size due to network interpenetration, which is well known to enhance the affinity for CO₂,^{40,137} rather than a size-exclusion effect of the framework through a molecular sieving process since the pore size shown by X-ray single crystals analysis and HK calculation gave pore size significantly larger than the guest size (CO₂, 3.3 Å over N₂, 3.64 Å, O₂, 3.46 Å and CO, 3.76 Å). In addition, there is some evidence in the literature that interpenetration allows to increase gas uptake at low pressure or low temperature due to smaller pore size and the presence of microdomains that do not exist in the non-interpenetrated analogues.^{40,42} In fact, the contraction of the pores allows a better overlap of the attractive potential fields between the opposite walls and endows a significant enhancement for the adsorption of polarizable gas molecule like CO₂ (CO₂: 29.1 x 10^{-25} cm⁻³; N₂: 17.4 x 10^{-25} cm⁻³).^{40,41,138}

In the case of $\mathbf{Cd_2L^1}$, the origin of the preference for $\mathbf{CO_2}$ over N_2 and $\mathbf{CH_4}$ is ascribed to the existence of a cationic framework that enables quite strong interactions with $\mathbf{CO_2}$, thanks to its high quadrupole moment (-1.4 x 10^{-35} C.m). Actually, charged frameworks have received increasing attention and are well recognized to enhance adsorbent-adsorbate interactions in the material, owing to the strong induced electrostatic field occurring in the cavity.^{13,22,137,139}

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It is also evident that Cd_2L^1 gives better separation properties than CdL^2 as a result of the existence of a cationic framework and a higher porosity. Accordingly, both materials demonstrated a considerable interest for separation process such as natural gas purification or CO_2 capture applications. To the best of our knowledge, the CO_2 selectivity over N₂ and CH_4 estimated from IAST calculations at 1 atm for Cd_2L^1 is one of the highest already reported for MOFs based on polyazamacrocyclic ligands.^{67,70,76,78} These outcomes also point out that our strategy of employing a flexible polyazamacrocycle-based ligand as a platform represents an appealing way to construct functional porous MOFs for various applications.

CONCLUSION

Two rare examples of Cd-MOFs based on the 1,4,7-triazacyclononane platform were designed and synthesized. The isoreticular strategy was applied using two TACN linkers H_3L^1 and H_3L^2 bearing 4-carboxybenzyl and 3-(4-carboxyphenyl)-prop-2-ynyl pendant arms that were reacted with Cd^{2+} ions in solvothermal conditions with the aim to prepare isostructural MOFs with different porosities. Two 3D coordination polymers Cd_2L^1 and CdL^2 were obtained and characterized using single crystal X-ray analysis. Unexpectedly, the solids exhibited different topologies and crystalline organizations, indicating that the isoreticular concept was not fulfilled with this triazamacrocyclic platform despite the small structural differences of their carboxylate-functionalized arms. CdL^2 presents an interpenetrated framework with uninodal 6-connected node assembled into two interpenetrated *pcu* networks, while a non-interpenetrated Cd_2L^1 material with a *bcs* net is built from 6-connected dinuclear clusters as SBU. The difference in topology and porosity for these two materials was assigned to the stabilization of interpenetrated CdL^2 network by multiple π - π bonds between two adjacent nets. Despite its interpenetrated structure, CdL^2 is highly porous and the solvent

accessible volume is about 55 %. Importantly, Cd_2L^1 is positively charged and chargebalancing anions are located in the channels that presents about 46% of porosity. Both materials offered a good CO₂ uptake capacity as well as separation abilities over N₂, CO and CH₄ at 298 K. However, Cd_2L^1 displayed a higher porosity and a significant enhancement of the CO₂ capture and selectivity when compared with CdL^2 (42.9 *vs* 26.7 cm³ g⁻¹), which was assigned to the polarity of the cationic framework, yielding stronger electrostatic interactions between CO₂ molecules and the surface, and a better stability of the framework. Accordingly, these materials are of interest for CO₂ separation processes in the context of flue gas streams from coal-fired power and steel plants (CO₂–N₂ and CO₂–CO). This work also highlights the interest of polyazamacrocycles for MOF elaboration. Being strong chelators of metal ions, these compounds can be regarded as unusual metallolinkers to yield functional materials. The diversity of carboxy-functionalized pendent arms that can be anchored to the cyclic amine provides an excellent opportunity for preparing novel building blocks for MOFs construction with well-designed and promising applications not only for gas adsorption, but also for medical imaging and catalysis.

ASSOCIATED CONTENT

Supporting Information

The Supplementary Information is available free of charge on the ACS Publication website. Details of synthesis and analyses of the organic linkers L^1 and L^2 , and their respective materials Cd_2L^1 and CdL^2 were given, as well as TGA, single crystal and powder

diffraction data, FTIR spectra, gas adsorption measurements with multi-site Langmuir fits and parameters used for IAST calculations.

Accession Codes

CCDC-1529941 (Cd_2L^1) and 1529942 (CdL^2) information contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>

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Notes

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Cadmium Metal–Organic Frameworks Based on Ditopic Triazamacrocyclic Linkers: Unusual Structural Features and Selective CO₂ Capture

Hervé Feuchter, Guillaume Ortiz, Yoann Rousselin, Alla Lemeune, Stéphane Brandès



Two assemblies involving Cd²⁺ ions and 1,4,7-triazacyclononane N-functionalized by 4-carboxybenzyl or 3-(4carboxyphenyl)-prop-2-ynyl pendant arms were envisioned for constructing metalorganic frameworks. A cationic and an interpenetrated open-frame-works were obtained depending on the length of the side arms. Both materials show permanent porosity and selective adsorption properties of CO₂ over N₂, CO and CH₄.