

Designing novel organic–inorganic frameworks*

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Abstract: Crystal engineering of coordination frameworks is a topical and rapidly advancing field, and a variety of entirely new solid materials have been synthesized. We describe the main challenges involved in the hydrothermal approach to these materials using, as an example, cadmium- and zinc-based coordination frameworks. We discuss the unusual crystal architectures of the products, and show that the kind and quality of the resulting crystals are directly controlled by the composition of the ternary reactive mixture and the temperature regime used in the hydrothermal synthesis.

Keywords: crystal engineering; coordination polymers; MOF; metal-organic frameworks; synthesis.

INTRODUCTION

The aim of the field of “crystal engineering”, a term coined by Schmidt [1], is the construction of large molecular networks, with predictable and controllable topologies and properties. The most topical area of research in this field nowadays is the isolation of novel metal–organic frameworks (commonly known as MOFs), coordination polymers, or coordination frameworks [2–9].

Ever since the publication of the pioneering 1990 paper by Hoskins and Robson [10], the synthesis and structural characterization of coordination frameworks have attracted growing interest [2–9,11–13]. The number of papers published on the subject has been increasing very rapidly, and the total now stands at over 3000 (Fig. 1). Research is being driven by the large variety of fascinating architectures, the promising properties of the products (high porosity, host–guest exchange, catalysis, gas storage, photoluminescence, nonlinear optical properties, chirality, clathration, photochromism, and magnetic properties) and their consequent potential applications as functional materials.

Early advances in the field are associated with the work of Desiraju [6] and Etter [14] on organic crystals assembled via hydrogen bonds. Hoskins and Robson [10] expanded the field to include multi-dimensional coordination frameworks assembled by much stronger and highly directional coordinative interactions (several hundreds of kJ mol^{-1}) between metal centers and multi-topic organic ligands (with one or more donor atoms), thus combining the properties of organic and inorganic compounds. The design and synthesis of MOFs relies on the use of multi-topic organic ligands capable of forming bridges with metal centers with one or more vacant coordinative sites. Depending on the combined properties of the ligands and metallic cations, discrete (“0D”) or infinite 1D, 2D, or 3D structures with large voids have been obtained.

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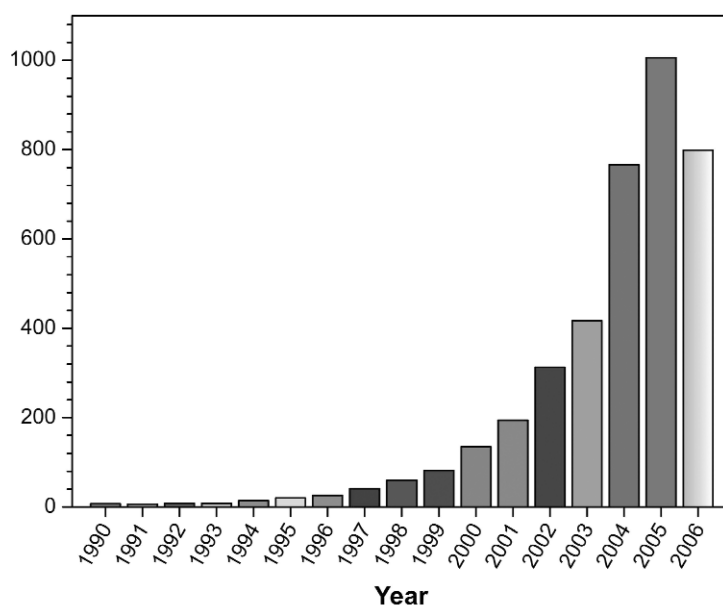


Fig. 1 Scientific papers on coordination polymers published annually and cited by the ISI Web of Science (as of 20 October 2006).

Various synthetic approaches have been used to isolate highly crystalline samples suitable for structural characterization using X-ray diffraction, in particular that of single crystals. Among these, solvothermal approaches have attracted much interest over the last few years, as they allow for the synthesis of complex metastable phases in relatively large quantities and for the elimination of the solubility problems of heavy organic molecules in aqueous media. However, since these reactions are usually irreversible, with fast kinetics of nucleation and crystal growth, powdered materials are generally obtained. Even though quite recently some interesting, though rather simple, networks have been unveiled through the use of systematic X-ray powder studies, to isolate large single crystals special experimental conditions must be used, such as close control of the temperature program. Unfortunately, very little effort has been devoted so far to understanding factors which, for a given reactive system, control the isolation of different products when the molar ratios of the components are varied.

The construction of novel MOFs requires the presence in the reactive mixture of multi-topic organic ligands capable of forming one or more bridges and of metal centers with one or more vacant coordinative sites [15–37]. There are a number of challenges to be faced. We must carefully choose the solvent, the synthetic regime, the ligand, the counterion, and the chemical composition of the reactive mixture, and we must deal with effects such as supramolecular isomerism [2]. To illustrate the problems involved, we use as an example the synthesis of several cadmium- and zinc-based coordination frameworks containing the organic ligands shown in Fig. 2 [23,24,26].

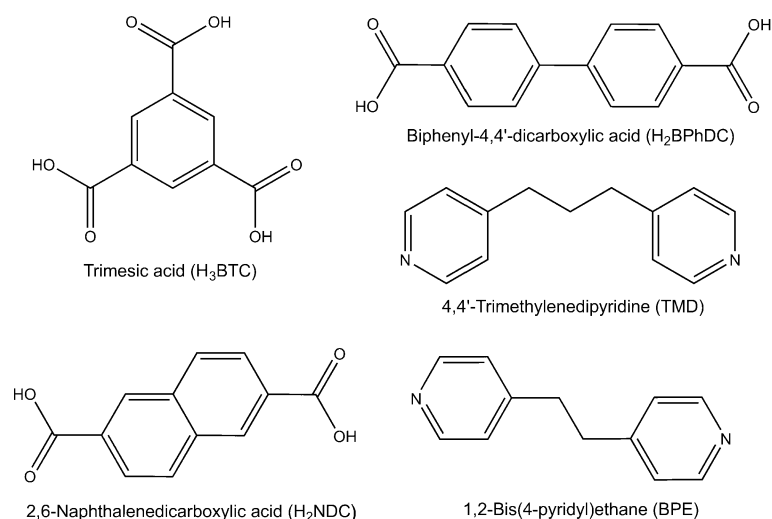


Fig. 2 Multi-topic organic ligands employed in the preparation of the n -dimensional coordination polymers discussed in this paper.

RESULTS

Cd^{2+} —2,6-naphthalenedicarboxylic acid—triethylamine (TEA) system [26]

According to Pearson's classification [38], Cd^{2+} cations are acids of weak-to-medium strength, able to coordinate simultaneously in solution to both "hard" (e.g., oxygen-containing) and "soft" (e.g., nitrogen-containing) organic bases. Consider a ternary reactive mixture composed of Cd^{2+} , 2,6-naphthalenedicarboxylic acid (H_2NDC), and TEA [26]. To investigate the importance of the chemical composition of the starting mixture in the final products, 12 different compositions with variable amounts of the three components were selected (among many). The nature, structure, and degree of crystallinity of the products was carefully monitored using powder X-ray diffraction, and by morphological studies using electron microscopy, infrared, thermal, and elemental composition analyses. Figure 3 shows a simplified ternary diagram with the different molar compositions, along with scanning electron microscopy (SEM) pictures of selected products. The phase diagram is composed of four regions corresponding to: (1) a layered material formulated as $[Cd_2(NDC)(OH)_2]$, for which a structural model is still unknown; (2) a new 3D compound formulated as $[Cd(NDC)(H_2O)]$ (**I**) (microcrystalline); (3) **I** isolated as a single-crystalline phase; (4) a mixture of compounds **I** and $[Cd_2(NDC)(OH)_2]$. Large single crystals of **I** were found to form in high yield (>95 %) for $[Cd^{2+}] < 0.6$ and $[H_2NDC] > 0.25$; layered $[Cd_2(NDC)(OH)_2]$ was isolated for $[TEA] > 0.7$ (greater than the stoichiometric amount required for complete deprotonation of H_2NDC). Square brackets signify molar fractions.

Compound **I** has a compact 3D structure and contains only one crystallographically unique Cd^{2+} site with a distorted square-pyramidal coordination environment, composed of four oxygen donor atoms from four symmetry-related NDC^{2-} ligands and a water molecule occupying the apical position. Zigzag metallic chains running along the [001] direction of the unit cell are formed by the bridging carboxylate groups. These chains are interconnected via NDC^{2-} bridges, spaced by small rectangular channels with a cross-section of ca. $2.0 \times 3.5 \text{ \AA}$ (Fig. 4). The coordinated water molecules point toward these channels and are further engaged in two identical hydrogen-bonding interactions. Taking the geometrical center between each two consecutive Cd^{2+} cations within the metallic chains as nodes for the framework, each node is thus connected to another four, with the smallest closed circuits enclosing a total of six nodes. Compound **I** can thus be regarded as a distorted (6,4) diamond net [39].

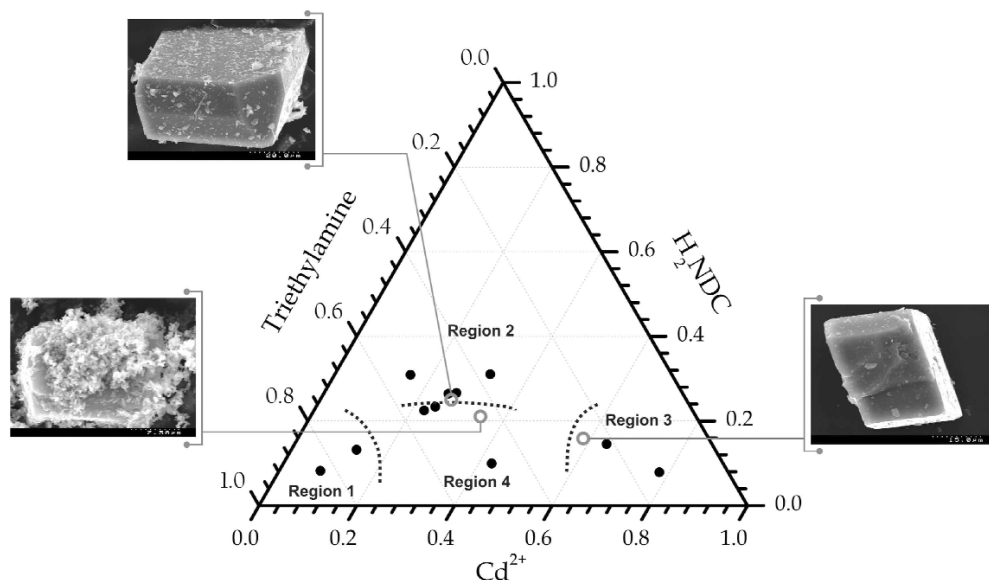


Fig. 3 Ternary diagram for the synthesis of $[\text{Cd}(\text{NDC})(\text{H}_2\text{O})]$, showing SEM pictures for selected compounds/mixtures. Region 1: layered $[\text{Cd}_2(\text{NDC})(\text{OH})_2]$; region 2: microcrystalline $[\text{Cd}(\text{NDC})(\text{H}_2\text{O})]$ (powder product); region 3: $[\text{Cd}(\text{NDC})(\text{H}_2\text{O})]$ as large crystals; region 4: mixture of crystalline $[\text{Cd}(\text{NDC})(\text{H}_2\text{O})]$ with layered $[\text{Cd}_2(\text{NDC})(\text{OH})_2]$.

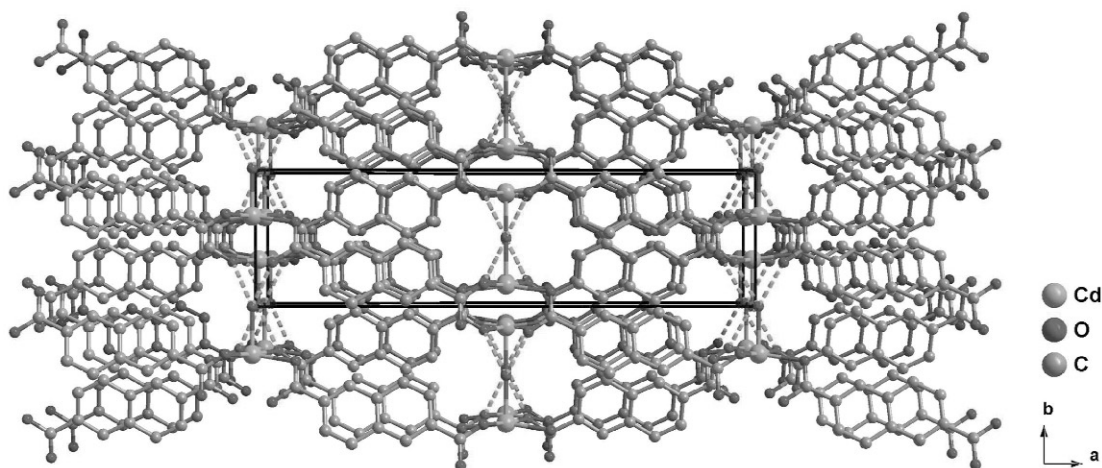


Fig. 4 Crystal packing of $[\text{Cd}(\text{NDC})(\text{H}_2\text{O})]$ as seen along the $[001]$ direction of the unit cell. Hydrogen bonds are represented as dashed lines. H-atoms have been omitted for clarity.

The temperature regime was systematically varied to find an optimal profile (Fig. 5) [26]. The conclusions from the many experiments are as follows: (1) temperatures above $145\text{ }^\circ\text{C}$ tend to lead to a mixture of microcrystalline compounds (probably containing metal oxides); (2) postsynthesis quenching of the reaction vessel, a procedure usually employed in zeolite synthesis, systematically leads to microcrystalline powders; (3) step-by-step cooling after the reaction at the higher temperature improves the crystallinity of the product, usually giving high-quality single crystals.

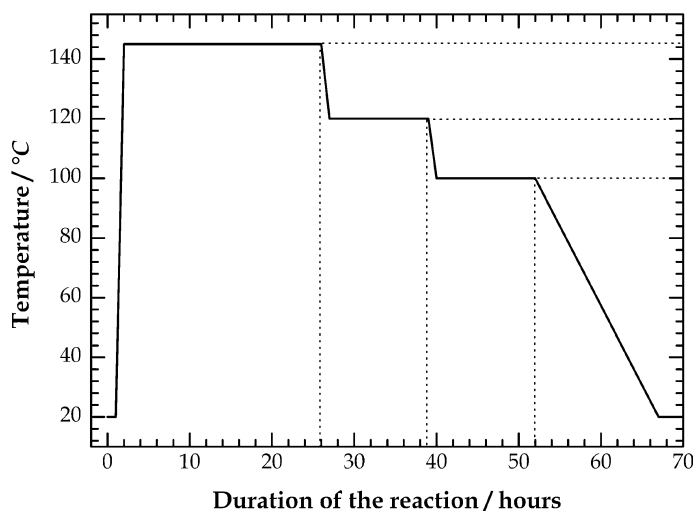


Fig. 5 Optimal temperature regime for the hydrothermal synthesis of $[\text{Cd}(\text{NDC})(\text{H}_2\text{O})]$, $[\text{Zn}(\text{BPhDC})(\text{H}_2\text{O})]$, and $[\text{Cd}(\text{BPhDC})(\text{BPE})(\text{H}_2\text{O})]$ (see text for details).

Zn^{2+} —biphenyl-4,4'-dicarboxylic acid (H_2BPhDC)—TEA system

$[\text{Zn}(\text{BPhDC})(\text{H}_2\text{O})]$ (**II**) is another 3D diamondoid-type compact coordination polymer which was first reported by Liang et al. [40]. Using a slightly different synthetic method, very similar to that employed for $[\text{Cd}(\text{NDC})(\text{H}_2\text{O})]$, we isolated the same compound as a highly crystalline phase (large crystal plates, see Fig. 6) from reactive ternary mixtures containing Zn^{2+} , H_2BPhDC , and TEA, and redetermined its crystal structure at the low temperature of 180 K (see Experimental Section). Even though the products were highly crystalline, the powder X-ray diffraction patterns and elemental analysis revealed the exist-

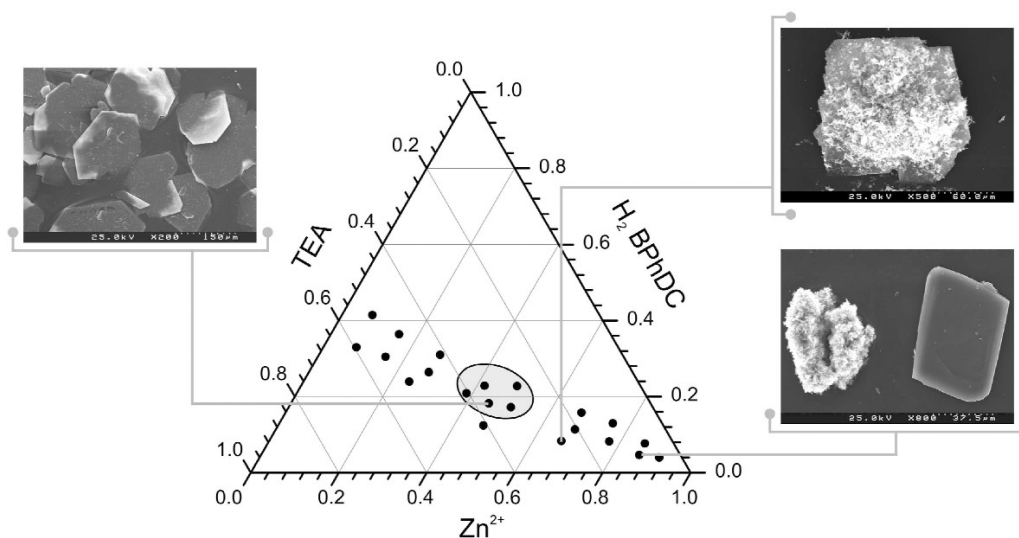


Fig. 6 Ternary diagram of the variation in the composition of the reactive mixture which can lead to $[\text{Zn}(\text{BPhDC})(\text{H}_2\text{O})]$. Black dots represent sampled mixtures (for a typical synthetic method, see Experimental Section), and a rough estimate of the region from which the material can be isolated as a pure phase is highlighted in grey. SEM pictures for selected compounds/mixtures are also provided.

tence of a persistent unknown crystalline phase. The presence of $[\text{Zn}(\text{BPhDC})(\text{H}_2\text{O})]$ was unequivocally verified by manually harvesting crystals from the contents of several reaction vessels, which were then indexed using the single-crystal diffractometer (see Experimental Section). This unknown phase could only be completely eliminated for a particular region of the ternary diagram (Fig. 6). The synthesis of this compound is another good example of the need to optimize the conditions for a typical hydrothermal approach.

Cd^{2+} — H_2BPhDC —1,2-bis(4-pyridyl)ethane (BPE) system [15]

This system leads to a remarkable extended 3D structure with the empirical molecular formula $[\text{Cd}(\text{BPhDC})(\text{BPE})(\text{H}_2\text{O})]$ (**III**). The framework is assembled by only one crystallographically unique metal center coordinated to two BPE and three BPhDC^{2-} ligands, with coordination geometry resembling that of a highly distorted octahedron (Fig. 7). BPhDC^{2-} acts as a bridging ligand (with a distinct coordination system for each of its carboxylate groups) thus exhibiting rod-like properties despite the internal rotations about the C2 axis. In one of the modes, the carboxylate group is coordinated to only one metal center. The second mode has the carboxylate forming a *syn-syn* bidentate bridge between two neighboring cadmium centers, thus leading to the formation of a binuclear secondary building unit (SBU) with a paddlewheel-like structure, with the two bridging BPhDC^{2-} ligands occupying the equatorial positions (Fig. 7).

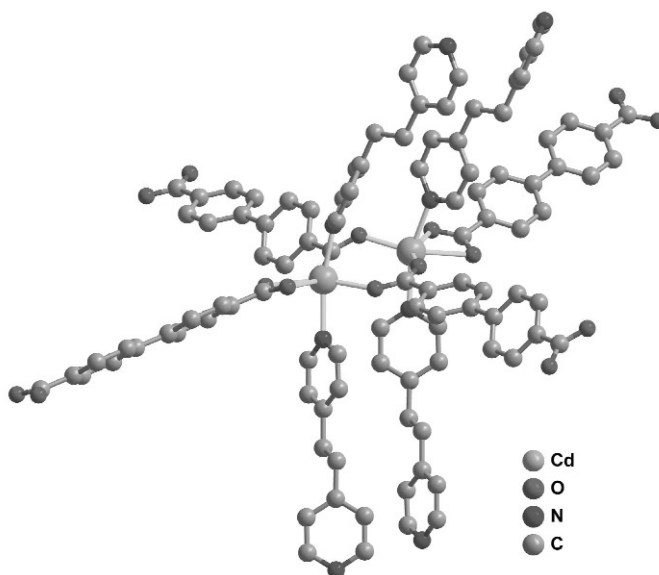


Fig. 7 Binuclear secondary building block of $[\text{Cd}(\text{BPhDC})(\text{BPE})(\text{H}_2\text{O})]$ (**III**) [15].

The self-assembly of this SBU in 3D space leads to the formation of a remarkable open framework, with large channels running along the three directions of the unit cell (Fig. 8). From a topological perspective, this single framework can be envisaged as being built from highly distorted cuboidal $[\text{Cd}_{16}(\text{BPhDC})_8(\text{BPE})_6]$ units, which ultimately describe a rather unusual 6-coordinated network, with $4^8.5^4.6^3$ topology. As usually occurs with crystalline hybrid materials containing large channels, in **III** these are filled by other identical frameworks, thus producing a rather dense material. In particular, two identical single frameworks fill the voids of a third, leading to a three-fold interpenetration (Fig. 9).

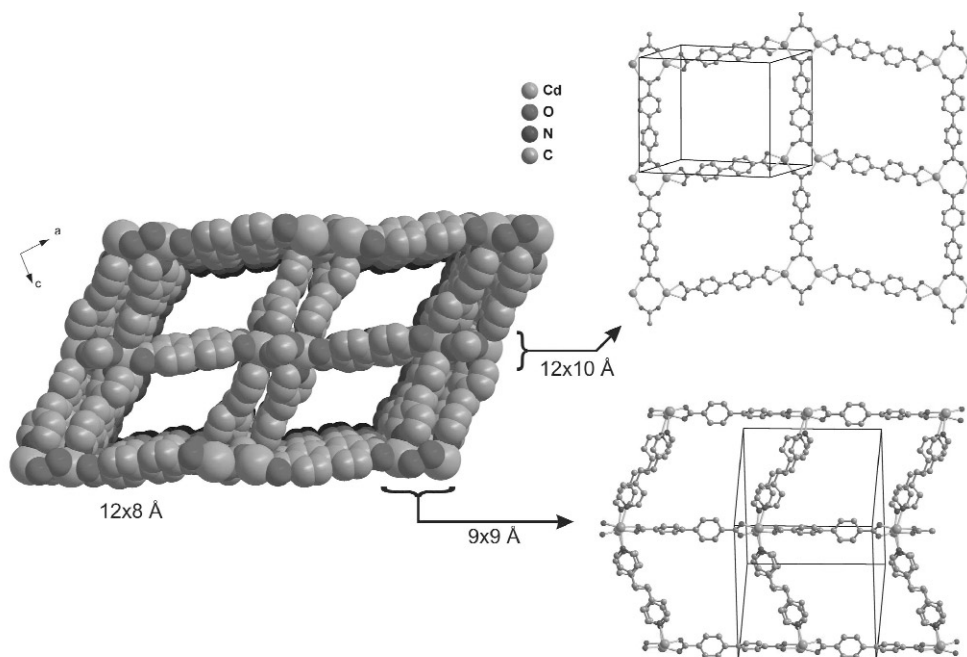


Fig. 8 Overhead view along the crystallographic [010] direction of the single framework of $[\text{Cd}(\text{BPhDC})(\text{BPE})(\text{H}_2\text{O})]$ (represented in space-filling mode) constructed by the self-assembly of the SBU depicted in Fig. 7. The single framework contains a 3D channel system whose approximate dimensions (based on van der Waals radii for the elements) are depicted in the figure.

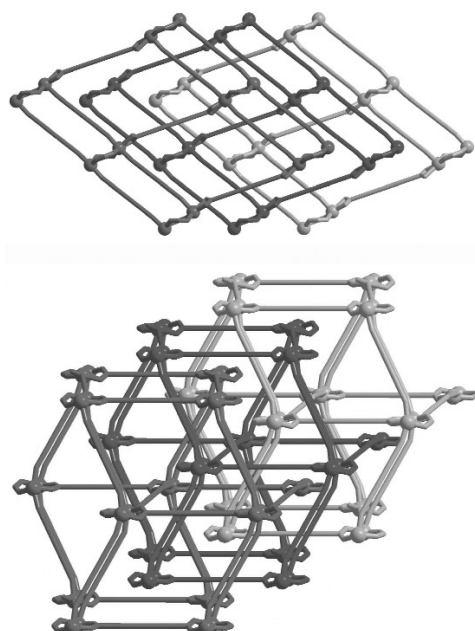


Fig. 9 Three-fold interpenetration of identical $[\text{Cd}(\text{BPhDC})(\text{BPE})(\text{H}_2\text{O})]$ single frameworks composing the crystal structure of **III**. Each framework has been simplified for clarity: the aromatic rings of BPhDC^{2-} and BPE have been removed and direct connections between the C-carboxylic acid groups (for the BPhDC^{2-}) and N-donor atoms (for BPE) have been placed there instead.

Cd^{2+} —trimesic acid (H_3BTC)—BPE system [24]

1,3,5-Benzenetricarboxylic acid (H_3BTC , also known as trimesic acid) is a rigid planar molecule soluble in a number of solvents, in particular water. The three *exo*-carboxylic acid groups are arranged symmetrically around the benzene ring, forming a flat trigonal molecule which, in many cases, acts as a three-connected node for the topological representation of the frameworks. Even though the carboxylate groups can freely rotate around the C–C bond, which ultimately is the main thing responsible for the structural diversity inherent in the use of this ligand with either transition-metal centers or lanthanides, the molecule is rather rigid, which also makes it an interesting primary building block. Having in mind that structural diversity and, thus, peculiar topologies can arise when flexibility is also introduced in the primary building blocks employed, we have decided to use, along with H_3BTC , a second molecule derived from the commonly used 4,4'-bipyridine (4,4'-bpy) spacer. Indeed, when chemical functional groups, such as $-\text{CH}_2-$, are selectively included between the two 4-pyridyl rings, a new family of organic ligands with variable flexibility and functionality arises. Thus, these flexible bridges can direct particular properties to the frameworks, such as variable dimensionality, void space, degree of interpenetration, and topological features. BPE turns out to be a good starting candidate for this study as, usually, this ligand adopts two conformations: the *gauche* and *anti* [41].

The reaction between H_3BTC and BPE under hydrothermal conditions gives rise to a highly crystalline product formulated as $[\text{Cd}_{1.5}(\text{BTC})(\text{BPE})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (**IV**). The structure contains two distinct repeating structural motifs, each containing a crystallographically unique Cd^{2+} center in a distorted octahedral coordination geometry: one center is coordinated to two BTC^{3-} and two BPE ligands, while the second has two water molecules occupying the apical positions, with two BTC^{3-} and one BPE ligand forming the equatorial plane. As expected, the BPE ligand acts as an effective inter-metallic bridge, always connecting the same types of metal centers. The assembly of the previously described metallic repeating structural motifs leads to the formation of a single framework, $[\text{Cd}_{1.5}(\text{BTC})(\text{BPE})(\text{H}_2\text{O})_2]$, exhibiting triple metallic layers pillared by disordered BPE bridges. Interestingly, such inter-layer connections lead to the formation of cavities with average cross-section of ca. $5.2 \times 8.5 \text{ \AA}$ (Fig. 10).

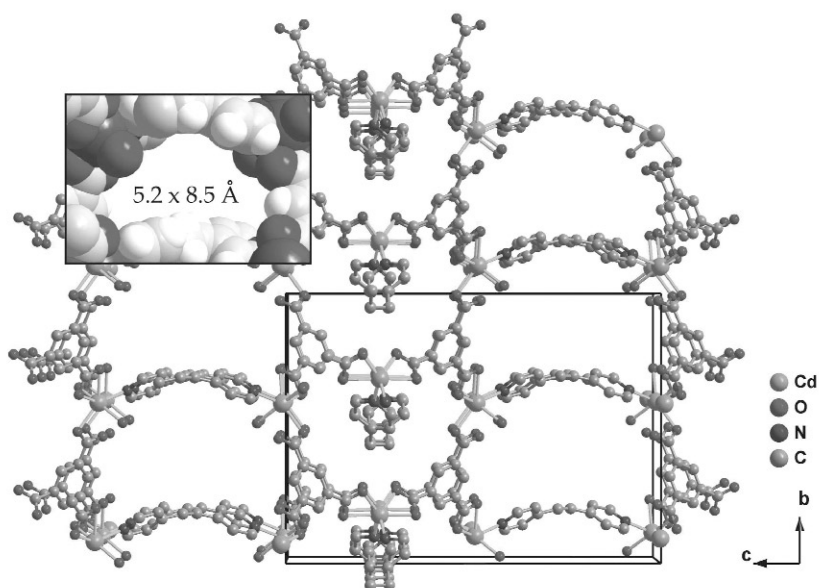


Fig. 10 Projection along the [100] direction of the unit cell of the single $[\text{Cd}_{1.5}(\text{BTC})(\text{BPE})(\text{H}_2\text{O})_2]$ framework, which contains a 1D channel system with average cross-section of ca. $5.2 \times 8.5 \text{ \AA}$.

It is noteworthy that other, less prominent, channels exist for this single framework. As observed for material **III**, the voids of the single $[\text{Cd}_{1.5}(\text{BTC})(\text{BPE})(\text{H}_2\text{O})_2]$ framework are too large only to be filled by solvent molecules. Consequently, **IV** exhibits two-fold interpenetration, in which the two identical $[\text{Cd}_{1.5}(\text{BTC})(\text{BPE})(\text{H}_2\text{O})_2]$ frameworks are related by a two-fold rotation (Fig. 11). Another common feature with the previously described structure is that connections between interpenetrated frameworks are assured by hydrogen bonds involving water molecules.

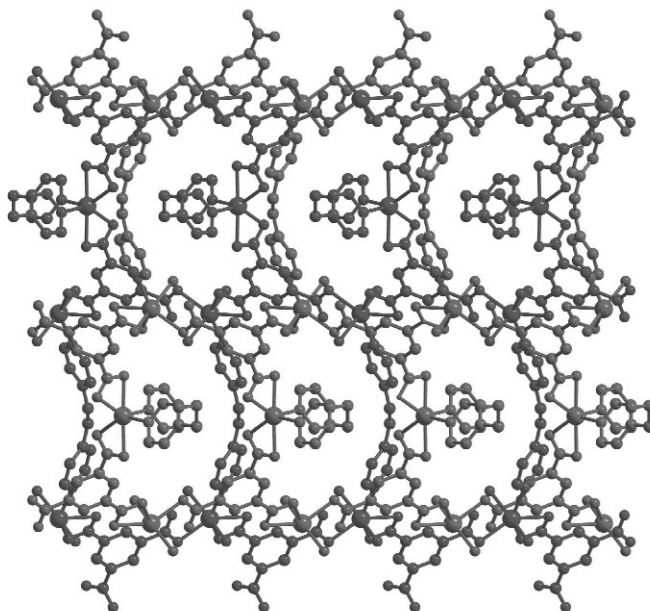


Fig. 11 Schematic representation of the two-fold interpenetration of single $[\text{Cd}_{1.5}(\text{BTC})(\text{BPE})(\text{H}_2\text{O})_2]$ frameworks in the structure of **IV**.

Cd^{2+} —trimesic acid (H_3BTC)—4,4'-trimethylenedipyridine (TMD) system [23]

The inclusion of an extra $-\text{CH}_2-$ group in the structure of BPE provides a new organic ligand, TMD, with significantly increased structural flexibility, between the two coordinating 4-pyridyl groups. Indeed, when combined with Cd^{2+} cations and H_3BTC under typical hydrothermal synthetic conditions, three novel materials could be isolated (in some cases, not even individually): $[\text{Cd}(\text{HBTC})(\text{TMD})_2] \cdot 8.5\text{H}_2\text{O}$ (**V**), $[\text{Cd}(\text{HBTC})(\text{TMD})(\text{H}_2\text{O})] \cdot 4.5\text{H}_2\text{O}$ (**VI**), and $[\text{Cd}_2(\text{BTC})(\text{TMD})_2(\text{NO}_3)] \cdot 3\text{H}_2\text{O}$ (**VII**), with structures **V** and **VI** being isolated as a mixture of crystals.

Compound **V** (Fig. 12) is formed by an undulating 2D $[\text{Cd}(\text{HBTC})(\text{TMD})_2]$ plane net, with typical (4,4) topology. The network is perforated by rectangular windows, ca. $3.4 \times 11.0 \text{ \AA}$ in cross-section, distributed in a herringbone pattern and containing several water molecules of crystallization involved in hydrogen bonds. The crystal structure of **V** is obtained by parallel packing of this 2D network in an [ABAB...] fashion.

Compound **VI** is best described as a porous 3D diamondoid framework with channels running in several directions in the unit cell. The most prominent channels are distributed in a brick-wall fashion along the [001] direction and have a cross-section of ca. $3 \times 13 \text{ \AA}$ (Fig. 13). The void space of the single $[\text{Cd}(\text{HBTC})(\text{TMD})(\text{H}_2\text{O})]$ framework is enough to allow two-fold interpenetration, as shown in Fig. 14.

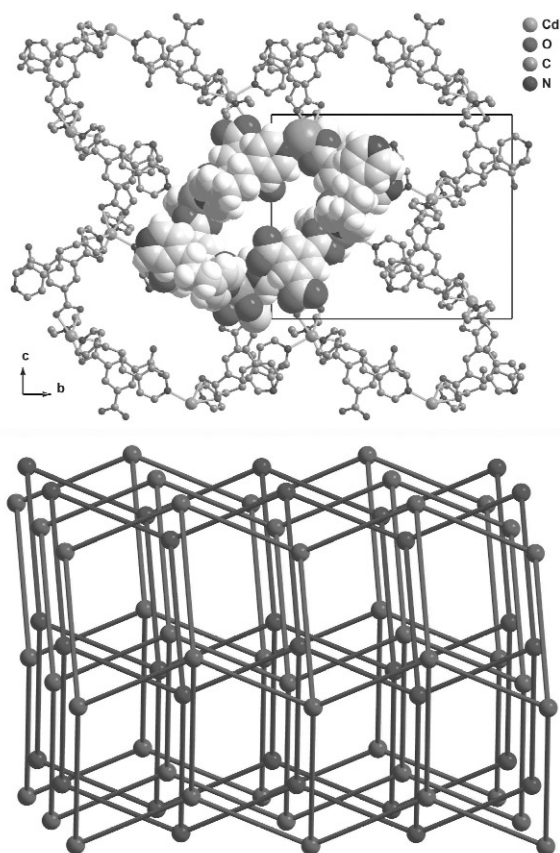


Fig. 12 Top: 2D [Cd(HBTC)(TMD)₂] plane net emphasizing the pores with cross-section ca. 3.4×11.0 Å (based on van der Waals radii), which are distributed in a distorted herringbone manner containing the various water molecules of crystallization. Bottom: Topological representation of the [Cd(HBTC)(TMD)₂] plane nets. Circles (nodes of the framework) are Cd²⁺ cations. The 4-gons have dimensions of 9.9710(2) Å and 13.0496(3) Å, which represent the HBTC²⁻ (“short–horizontal” connections) and TMD (“long–vertical” connections) bridging ligands.

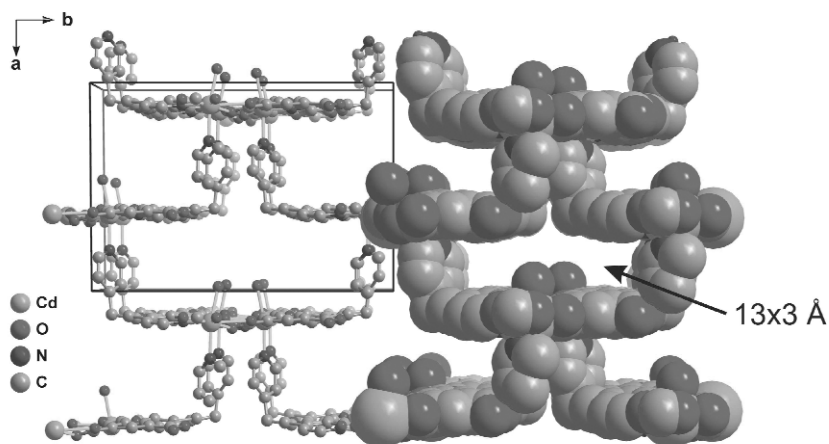


Fig. 13 View in perspective along the [001] direction of the unit cell of the 3D [Cd(HBTC)(TMD)(H₂O)] diamondoid single framework in VI. On the right, the space-filling representation (van der Waals radii) is overlaid to emphasize the rectangular channels running along the same direction.

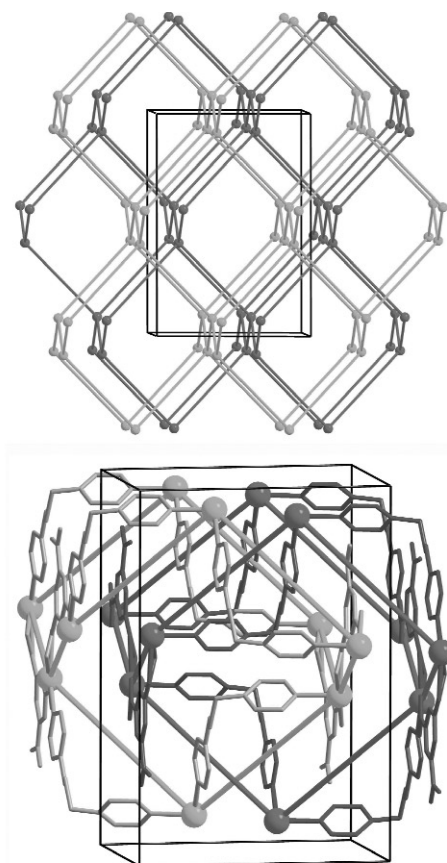


Fig. 14 Top: Topological representation of **VI** showing the two-fold interpenetration of irregular (6,4) diamond nets. Cd^{2+} centers are the nodes of the single $[\text{Cd}(\text{HBTC})(\text{TMD})(\text{H}_2\text{O})]$ framework; “long” connections between metal centers correspond to TMD bridges, while “short” connections represent the HBTC^{2-} bridges. Bottom: Topological connections overlapped with crystal packing.

Structure **VII** (not shown) is formed by the 3D assembly of a binuclear SBU (composed of two crystallographically independent Cd^{2+} cations) which leads to a compact, neutral, and coordinately bonded 8-connected framework, $[\text{Cd}_2(\text{BTC})(\text{TMD})_2(\text{NO}_3)]$, exhibiting unusual $3^6.4^{22}$ topology.

It is straightforward to conclude that the increased flexibility of the second ligand employed is the main cause of the structural diversity registered for this type of reactive mixture. Moreover, the simultaneous isolation in the same batch of more than one type of framework is an indication that, even though the frameworks are topologically rather different, they should share common thermodynamic features.

EXPERIMENTAL SECTION

Reagents were purchased from commercial sources and used as received without further purification. Syntheses were carried out in a PTFE-lined stainless steel reaction vessel (ca. 21 cm³, filling rate 70 %) purchased from Parr Instruments, under autogeneous pressure and static conditions using the temperature profile depicted in Fig. 5. $[\text{Zn}(\text{BPhDC})(\text{H}_2\text{O})]$ proved to be air- and light-stable, and insoluble in water and common organic solvents.

Typical synthesis of [Zn(BPhDC)(H₂O)]

To a solution of Zn(NO₃)₂·6H₂O (1.116 g, Aldrich) in distilled water (ca. 12.5 g), H₂BPhDC (0.493 g, Fluka), and TEA (0.399 g, Avocado) were added, and the mixture was stirred thoroughly for 1 h at ambient temperature. The suspension, with a molar composition of 1.00 H₂BPhDC:1.84 Zn²⁺:1.94 TEA:340 H₂O, was transferred to the reaction vessel and put in the oven. After reacting, a slightly yellow and extremely crystalline product was isolated by vacuum filtering. Crystals suitable for single-crystal X-ray diffraction were manually harvested and preserved in a portion of the autoclave aqueous solution. The remaining microcrystalline powder was washed with ca. 50 cm³ of distilled water and ca. 3 × 50 cm³ of absolute ethanol, and then air-dried at 70 °C. Calculated elemental composition (based on single-crystal data; in %): C 51.96, H 3.11. Found (%): C 52.01, H 3.08.

INSTRUMENTATION

Elemental analyses for carbon, hydrogen, and nitrogen were performed on an Exeter Analytical CE-440 Elemental Analyser. Samples were combusted under an oxygen atmosphere at 975 °C for 1 min, with helium as the purge gas. SEM images were obtained at the University of Aveiro using a FEGSEM Hitachi S4100 microscope operating at 25 kV. Samples were prepared by deposition on aluminum sample holders and carbon coating.

Single-crystal X-ray diffraction

Suitable single crystals of [Zn(BPhDC)(H₂O)] were mounted on a glass fiber using perfluoropolyether oil [42]. Data were collected at 180 K on a Nonius Kappa charge-coupled device (CCD) area-detector diffractometer (Mo K_α graphite-monochromated radiation, λ = 0.7107 Å), equipped with an Oxford Cryosystems cryostream and controlled by the Collect software package [43]. Images were processed using the software packages Denzo and Scalepack [44], and the data were corrected for absorption by the empirical method employed in Sortav. The structure was solved by the direct methods of SHELXS-97 [45], and refined by full-matrix least squares on F² using SHELXL-97 [46].

Non-hydrogen atoms were directly located from difference Fourier maps and refined with anisotropic displacement parameters. Hydrogen atoms associated with coordinated water molecules were directly located from successive difference Fourier maps, and refined with the O–H and H...H distances restrained to 0.92(5) Å and 1.50(5) Å, respectively, to ensure a chemically reasonable geometry for these molecules. Hydrogen atoms attached to carbon were located at their idealized positions using the *HFIX 43* instructions in SHELXL [46], and included in the refinement in riding-motion approximation with an isotropic thermal displacement parameter fixed at 1.2 times U_{eq} of the carbon atom to which they are attached. The last difference Fourier map synthesis showed the highest peak (0.407 eÅ⁻³) located at 1.48 Å from Zn(1), and the deepest hole (–0.596 eÅ⁻³) at 0.97 Å from Zn(1). The Flack parameter [47], refined to 0.00(2), assuring a valid absolute-structure determination from the single-crystal data.

Crystal data for [Zn(BPhDC)(H₂O)]: C₁₄H₁₀O₅Zn, *M* = 323.59, orthorhombic, space group *P*2₁2₁2₁, *Z* = 4, *a* = 6.5207(5) Å, *b* = 7.5365(8) Å, *c* = 24.735(3) Å, *V* = 1215.6(2) Å³, μ(Mo-Kα) = 2.037 mm⁻¹, *D*_c = 1.768 g cm⁻³, *T* = 180(2) K, *F*(000) = 656, crystal size = 0.23 × 0.16 × 0.02 mm³, θ range = 3.53 to 24.96°, data completeness = 96.3 %. Of a total of 5090 reflections collected, 1984 were independent (*R*_{int} = 0.0697). Final *R*1 = 0.0460 [*I* > 2σ(*I*)] and *wR*2 = 0.0777 (all data).

Crystallographic data (excluding structure factors) for the low-temperature redetermination of [Zn(BPhDC)(H₂O)] have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-270971. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, UK [Fax: (+44) 1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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