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A new type of three-dimensional framework constructed from dodecanuclear cadmium(II) macrocycles†‡

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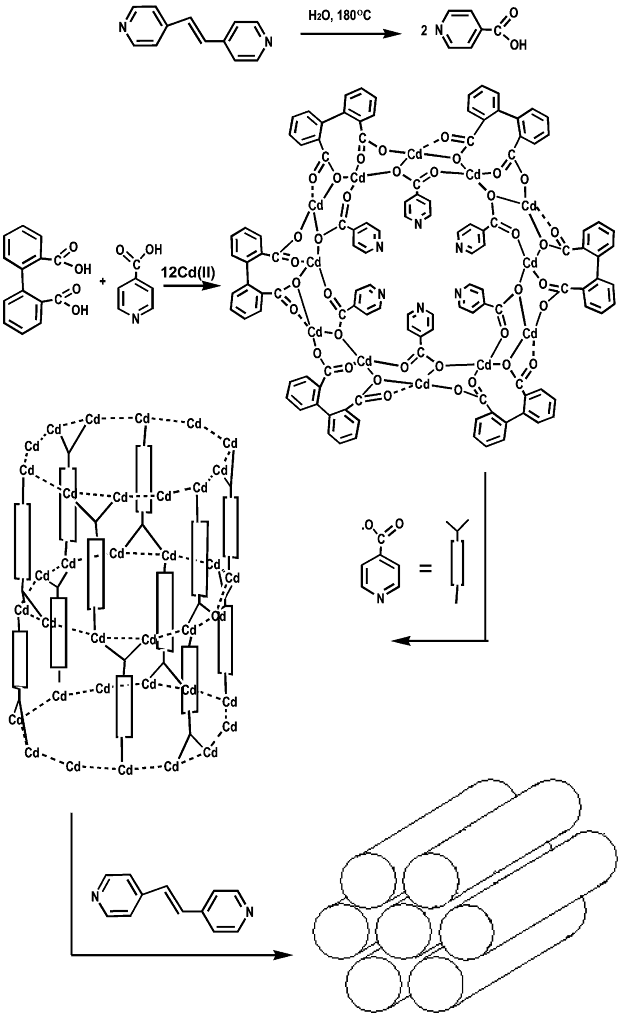
A new type of three-dimensional framework based on dodecanuclear Cd(II) macrocycles $[\{Cd_2(dpa)(pya)\}_6(pya)_6(dpe)_3]_n$ (1) (H_2dpa = diphenic acid; Hpya = isonicotinic acid, dpe = 1,2-di(4-pyridyl)ethylene) was prepared by the hydrothermal reaction and *in situ* synthesis of pya from dpe precursor.

Metal-organic extended structures have attracted considerable interest in coordination chemistry and material science because of their intriguing structural diversities and potential applications in functional materials, nanotechnology and biological recognition.[1–5] Many such examples constructed from small molecular units have been reported,[3–5] however, those built from nanoscale molecular units are less common.

The nanoscale metal ring complexes, including dodecanuclear copper(I),[6a] nickel(II) [6b] and iron(III),[6c,d] octanuclear cobalt(II) and nickel(II)[7] as well as hexanuclear cadmium(II),[8a] and iron(III)[8b,c] ring complexes, situated at the boundary of molecular and condensed matter have been developed. Herein, we report the synthesis and characterization of a novel three-dimensional framework $[\{Cd_2(dpa)(pya)\}_6(pya)_6(dpe)_3]_n$ (**1**) (H_2dpa = diphenic acid; Hpya = isonicotinic acid, dpe = 1,2-di(4-pyridyl)ethylene) constructed from dodecanuclear cadmium(II) macrocycles (Scheme 1).

When the directed reaction of cadmium(II), H_2dpa, Hpya and dpe was carried out in the conventional solution or hydrothermal methods, unfortunately, uncharacterized precipitate insoluble in any common solvents was obtained. However, the hydrothermal reaction of H_2dpa, dpe, $Cd(NO_3)_2\cdot 4H_2O$, NaOH and H_2O in a molar ratio of 1 : 1 : 1 : 1.5 : 1500 (pH = 5 ~ 6) at 180 °C for 3 days afforded a large amount of colorless prismatic crystals of **1**.† Isonicotinate was formed *in situ* in this case from dpe precursor. Thus, *in situ* synthesis of isonicotinate is crucial for the formation of the complex. Complex **1** is insoluble in water and common organic solvents, such as methanol, acetone, acetonitrile, dichloromethane, tetrahydrofuran, *N*,*N*″-dimethylformamide and dimethyl sulfoxide. The elementary analysis and IR spectrum confirmed the formula of **1**. The thermogravimetric analysis (TGA) studies of the polycrystalline sample showed no weight loss up to 390 °C and the first weight loss of 60% from 400 °C to 530 °C, but differential thermal analysis (DTA) studies illustrated a small phase change from 280 to 350 and an absorption heat reaction taking place at 400 °C, which indicate that the compound is stable up to 280 °C. X-ray powder diffraction (XRPD) patterns confirm that the compound is thermally stable below 280 °C and decomposes from 300 °C.

The single-crystal X-ray analysis§ reveals that crystal structure of complex **1** is a three-dimensional pillared framework containing the basic nanoscale dodecanuclear cadmium(II) macrocycle units $[Cd_{12}(dpa)_6(pya)_6]$. As shown in Fig. 1, there are two crystallographically independent Cd(II) centers in the structure. Cd(1) is in a distorted octahedral geometry, being coordinated by a nitrogen atom and three oxygen atoms from four different isonicotinate as well as two oxygen atoms from different carboxylate group in a dpa. Cd(2) is coordinated by a nitrogen atom from dpe, two oxygen atoms from two independent isonicotinate as well as one oxygen atom and a semi-chelating carboxylate oxygen atom from different dpa [Cd(2)–O(22A) = 2.893Å], thus, the coordination geometry of Cd(2) may be described as a highly distorted octahedral geometry. Isonicotinate has two types of distinctly different bridging modes: one acts as a tridentate ligand through a μ_3, η^1, η^2-carboxylate bridge (Scheme 2a) which has not so far been reported in isonicotinate complexes; the other adopts an *exo*-tridentate bridging mode through pyridyl nitrogen atom and a μ_2, η^2-carboxylate group (Scheme 2b). The ligands dpa (Scheme 2c) and isonicotinate with a μ_3, η^1, η^2-carboxylate



Scheme 1 Reaction of dpa, pya and cadmium(II) resulted in a $[Cd_{12}(dpa)_6(pya)_6]$ macrocycle which was pillared by pya and linked by dpe to form a three-dimensional framework.

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† Electronic supplementary information (ESI) available: Synthesis of **1** and Figures S1–S4. See http://www.rsc.org/suppdata/cc/b2/b212425d/

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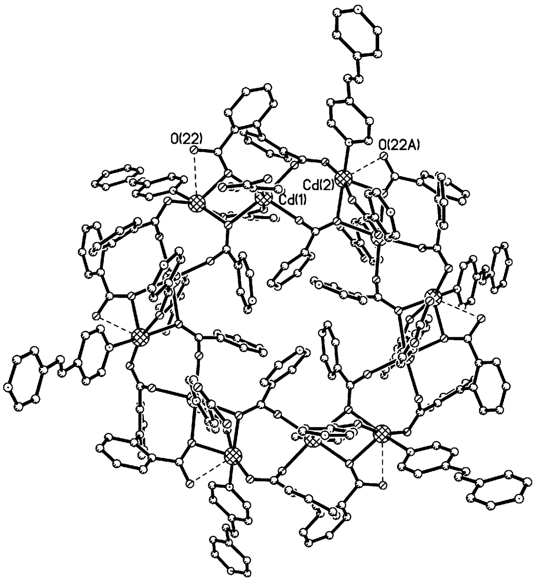
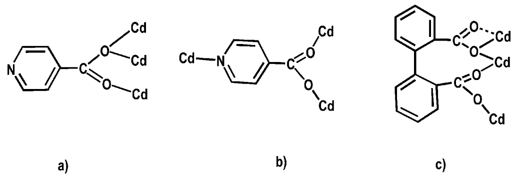


Fig. 1 A view of dodecanuclear Cd(II) macrocycle in **1**.

bridging mode link twelve Cd(II) centers to form a dodecanuclear Cd(II) macrocycle with a crystallographic C_3 symmetry passing through the center of the macrocycle. The pyridyl groups of six isonicotinate ligands do not participate in coordination and lie inside the macrocycle to fill effectively the cavity of the macrocycle. Six dpa ligands lie in the exterior of the macrocycle in a twisted mode, the dihedral angle of two phenyl rings in dpa is 114.1°, this might be regarded as a result of orientation adjust to achieve the macrocycle.



Scheme 2 Coordination modes of pya and dpa in **1**.

The dodecanuclear Cd(II) macrocycles are cross-linked by *exo*-tridentate isonicotinate ligands in their perpendicular direction to form a one-dimensional pillared framework. Isonicotinate ligands serve as pillars linking the adjacent macrocycles along the *z*-axis through carboxylate oxygen atoms bridging between Cd(II) centers of four-membered Cd_2O_2 ring in one macrocycle and pyridyl nitrogen atom binding to the non-semi-chelating Cd(II) in the other macrocycle. The closest distance of two cyclic planes separated by isonicotinate is 9.60 Å.

The distinguishing feature of **1** is that one-dimensional pillars are connected by dpe ligands through binding between the semi-chelating Cd(II) centers from different pillars to form a three-dimensional structure, as shown in Fig. 2. The longer spacer in dpe might play an important role in the construction of the three-dimensional framework. To the best of our knowledge, this is the first example of three-dimensional frameworks based on macrocycles and organic pillars and greatly different from reported three-dimensional layered-pillar structures,[3–5] as well as three-dimensional frameworks constructed by carboxylate and pyridyl group mixed ligands.[9]

In summary, the present work has shown that three-dimensional pillared frameworks can be constructed from nanoscale metal ring complexes through using mixed ligands and a precursor of a pillared molecule. Further studies, such as synthesis of gradually separated structures and related pillared complexes as well as their nature are in progress and will be reported later.

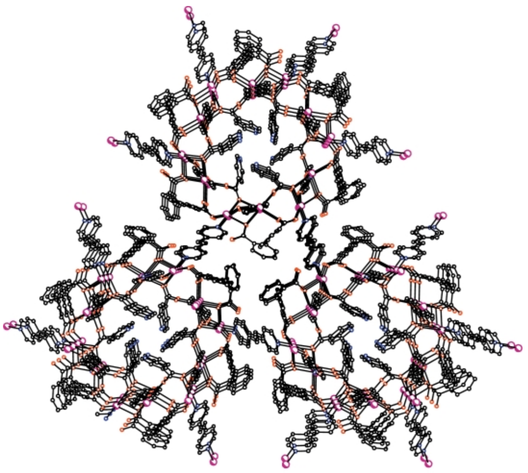


Fig. 2 A view of three-dimensional framework in **1** along *c* axis.

Notes and references

§ *Crystal data*: Crystal dimensions 0.38 × 0.16 × 0.14 mm, $C_{32}H_{21}Cd_2N_3O_8$, M_r = 800.32, trigonal, space group *R*-3, $a = b$ = 39.6981(4), c = 9.5923(2) Å, V = 13091.6(3) Å^{-3}, Z = 18, D_c = 1.827 g·cm^{-3}, T = 293(2) K, λ = 0.7107 Å, μ = 1.521 mm^{-1}, 15398 reflections were collected, of which 5136 were unique (R_{int} = 0.0380, $1.03 \leq \theta \leq 25.01$), R_1 = 0.0463, wR_2 = 0.0947, GOF = 1.273 for 429 parameters. The positions of H atoms were generated geometrically (C–H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. One of the pyridyl rings (C(52), C(53), C(54), N(51), C(55), C(56)) was treated as disorder and refined with rigid ring. CCDC 185306. For crystallographic files in CIF or other format see http://www.rsc.org/suppdata/cc/b2/b212425d/.

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