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Assembly of an eight connected porous Cd(II) framework with octahedral and cubo-octahedral cages: Sorption and luminescent properties

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ABSTRACT

An eight connected 3D porous coordination polymer, $\{[Cd(BTC)_{0.66}(BPz)_2] \cdot 6H_2O\}_n$ (**1**) (BTC = benzene-1,3,5-tricarboxylic acid, BPz = 3,3′,5,5′-tetramethyl-4,4′-bipyrazole) has been synthesized from hydrothermal reaction of $Cd(NO_3)_2 \cdot 4H_2O$ with BPz and BTC. Complex **1** is a thermally stable microporous MOF having cubo-octahedral and octahedral cages as the Supermolecular Building Block (SBB) with an eight connected *reo* topology. It shows moderate N_2 sorption (101 $cm^3\ g^{-1}$) at 77 K with a BET surface area of 330 $m^2\ g^{-1}$. Complex **1** also exhibits photoluminescent property in solid state with λ_{max} at 397 nm.

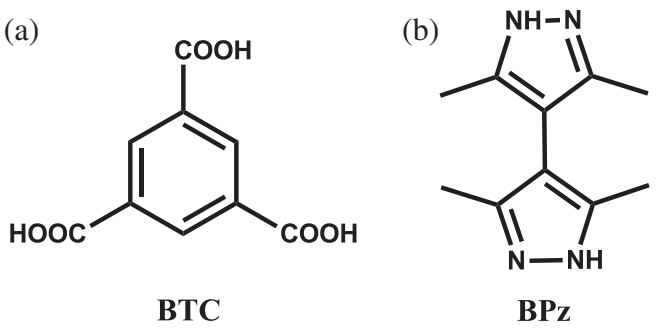
Porous metal–organic frameworks (MOFs) have attracted great attention because of their intriguing structural architectures and potential applications in storage, separation, sensing, catalysis and more recently biomedicine [1]. Porous nature is the most important character of MOFs, therefore tuning the pore size and shape remains the key factor in the design and fabrication of these materials [2]. One of the main obstacles in acquiring high porosity is the possibility of interpenetration of the porous framework. To prevent this, one powerful strategy uses metal organic polyhedral cages as Molecular Building Blocks (MBBs) and later Supermolecular Building Blocks (SBBs) for the construction of highly porous MOFs [3]. Comparing with the open channels of conventional MOFs, polyhedral based MOFs have large voids which are interconnected through relatively small windows. This makes them perfect for the storage of small guest molecules [4]. In the recent years, several groups have reported highly porous MOFs in which octahedral, cubo-octahedral, truncated tetrahedral and many other polyhedra cages are present as SBBs [5]. Out of the various polyhedra, the cubo-octahedral cage has gained considerable attention which is constituted by eight triangular and six square faces and forms the vertex figure of the *fcu* net [6].

In this work, an easier way to construct polyhedral based MOF has been presented using low level self assembly starting from metal ions and simple ligands whose coordination modes are well-known. Herein, we have reported the synthesis and structure of a three-dimensional (3D) microporous Cd(II) MOF based on benzene-1,3,5-tricarboxylic acid (BTC) and 3,3′,5,5′-tetramethyl-4,4′-bipyrazole (BPz) as linkers (Scheme 1). The obtained MOF revealed an uncommon eight connected *reo* topology from the assembly of octahedral and cubo-octahedral cages as SBBs which exhibited gas adsorption property at 77 K.

The hydrothermal reaction of $Cd(NO_3)_2 \cdot 4H_2O$ with BTC and BPz afforded colorless crystals of $\{[Cd(BTC)_{0.66}(BPz)_2] \cdot 6H_2O\}_n$ (**1**) which was structurally characterized by single-crystal X-ray diffraction (detailed experimental procedure is given in ESI).

Complex **1** crystallizes in trigonal space group, R-*3c*. In the asymmetric unit, there is one Cd(II) ion and one third of BTC which lies on three fold rotation axis and one complete BPz molecule (Fig. S1). Cd(II) ion acquired six coordinated octahedral geometry from nitrogen atoms of four BPz moieties and oxygen atoms of two carboxylate groups of BTC (N_4O_2) (Fig. 1).

The equatorial plane consists of four nitrogen atoms from the BPz (N1, $N1^i$ (symmetry code for i = x, 1 + x–y, 0.5 + z), N4 and $N4^{ii}$ (symmetry code for ii = 0.33 + x, 0.66 + x–y, 1.16 + z)) while the two oxygen atoms from the carboxylate groups of BTC moiety occupy the axial



Scheme 1. Symbolic representation of the ligands used.

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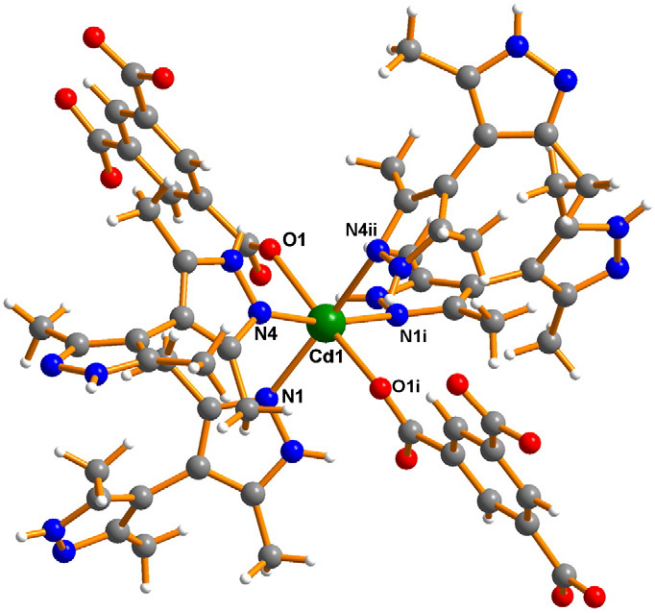

Fig. 1. Coordination environment of Cd(II) in **1** (symmetry code of i = x, 1 + x–y, 0.5 + z; ii = 0.33 + x, 0.66 + x–y, 1.16 + z).

positions (O1, $O1^{i}$ (symmetry code for i = x, 1 + x–y, 0.5 + z)) with bond distances, Cd1–N1, 2.329 (4) Å, Cd1–N4, 2.367 (4) Å, Cd1–$N1^{i}$, 2.329 (4) Å, Cd1–$N4^{ii}$, 2.367 (4) Å, Cd1–O1, 2.332 (3) Å and Cd1–$O1^{i}$, 2.332 (3) Å. These values are found to be consistent with bond distances reported in literature [7]. The axial angle of O1–Cd1–$O1^{i}$ is 170.69 (15)° while the N–Cd–N equatorial angles are in range, 81.55–102.82°. All the carboxylate groups of BTC moiety adopted monodentate mode (μ_3-BTC^{3-}) while the free oxygen of the COOH group is engaged in hydrogen bonding with the –NH moiety of the pyrazole ring (N2–H2···O2, H2···O2, 1.900 Å).

More insight into the structure revealed that Cd-BTC is arranged into a 2D neutral graphite like three connected sheets with hexagonal rings along the *c* axis (Fig. S2). Zheng et al. reported the similar kind of cationic Indium-BTC honeycomb layers, which were pillared through another BTC molecule and resulted in a 3D porous network [8]. In the case of **1**, Cd-BTC forms a 2D neutral sheet structure which is due to Cd^{2+} ion (instead of In^{3+} in [8]). The second honeycomb sheet was stacked on first with an offset and was pillared by BPz molecules which ultimately resulted in a porous 3D MOF (Fig. S3).

From topological point of view, the overall framework is made up of two types of polyhedral cages, i.e., cubo-octahedral and octahedral. The cubo-octahedral cage is constructed from twelve Cd(II) ions, twelve BPz and eight BTC molecules which consists eight triangular and six square faces (Fig. 2). It can enclose a sphere of diameter 6 Å inside its pore. The octahedral cage involves six Cd(II) ions, six BPz and two BTC molecules

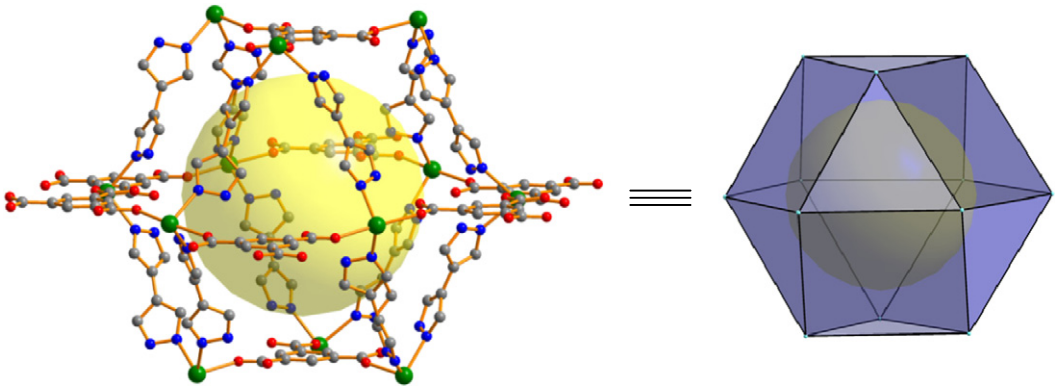

Fig. 2. The cubo-octahedral cage with its schematic diagram which is constructed from twelve Cd(II) ions, twelve BPz and eight BTC molecules and has eight triangular and six square faces.

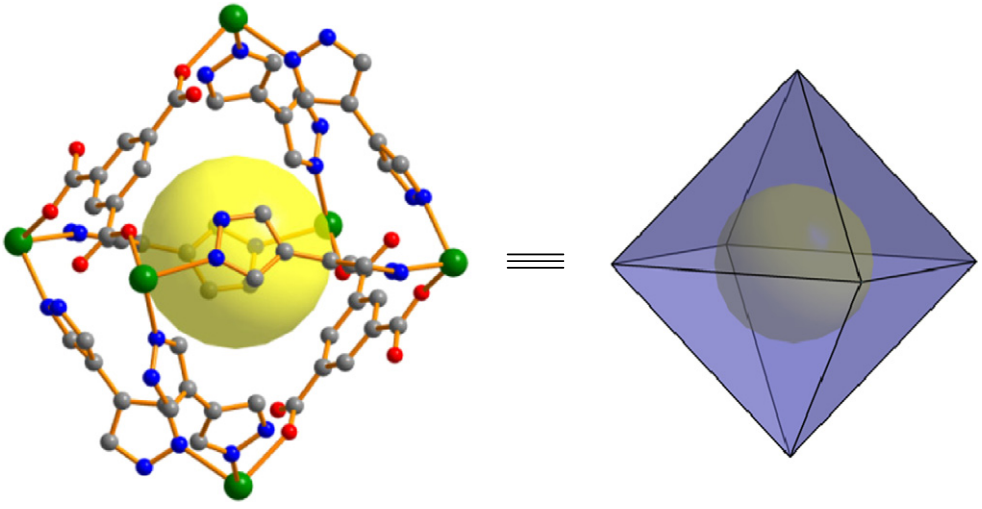

Fig. 3. The octahedral cage with its schematic diagram which is constructed from six Cd(II), six BPz and two BTC molecules.