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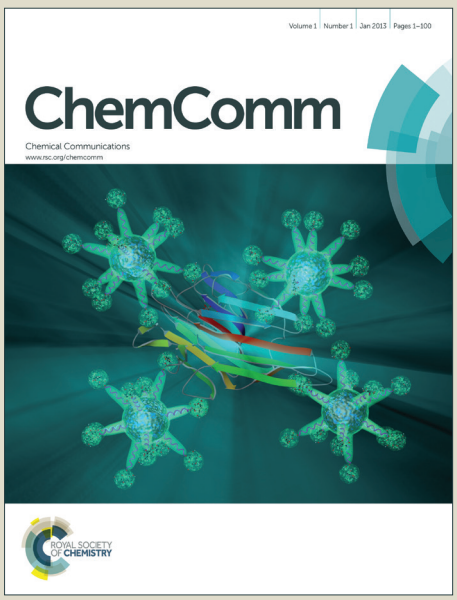

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ARTICLE TYPE

$Zn_{10}(Im)_{20}$•4DBF: An unprecedented 10-nodal zeolitic topology with 10-MR channel and 10 crystallographically independent Zn atoms

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By using a large-size amide, dibutylformamide (DBF), as a structure directing agent, a new zeolitic imidazolate framework (ZIF) was synthesized. The ZIF $Zn_{10}(Im)_{20}$•4DBF has a previously unprecedented zeolitic topology and features 10 crystallographically independent Zn atoms, 10-membered ring (MR) channel and unusual 4-connected 10-nodal net.

Zeotypes are technologically important nanoporous inorganic materials, with more than 200 framework topologies known to date.[1] During the last decade, intensive efforts have been made to develop a new class of zeolitic structures based upon hybrid metal–organic frameworks (MOFs).[2] Such work is driven by the prospect of expanding pore sizes, enhancing their functionality, and finding new properties.[2] Among them, the synthesis of zeolitic imidazolate frameworks (ZIFs) has recently gained considerable attention. ZIFs are a novel class of MOFs, formed by tetrahedral metal ions (e.g., Zn, Co) and imidazolate (Im) and/or its derivatives, resembling 4-connected net zeolites, with M-Im-M angle similar to the Si-O-Si angle (145°).[3-7]

However, currently just over 100 distinct ZIF structures adopting more than 30 zeolitic topologies have been reported so far, compared to over 200 known zeolite topologies.[2a] Thus, the main goal in ZIFs synthesis is to introduce and establish a variety of synthetic concepts, methodologies and strategies.[8,9] Obviously, different methods and strategies can lead to new compounds and topologies. An approach to a wider variety of ZIFs was achieved using simple modification of the imidazolates used with different substituents at the 2,4,5-position for the synthesis of ZIFs.[4,5] The position and type of substituents on the imidazole ring appear to play an important role in determining the framework topology, resulting in the formation of a finite number of topologies. Thus, the number of isomers, i.e. of a framework based on exactly the same imidazolate ligand, still remains relatively small.[2a, 10]

For the composition $Zn(Im)_2$ (Im=unsubstituted imdazolate) as many as nine topologically different isomers have been experimentally reported (framework types: zni, coi, cag, crb, mer, dft, gis, nog and zec). [3,5] In addition, even more are predicted to be synthetically accessible.[10] These $Zn(Im)_2$ isomers have been synthesized using an amide solvent, such as dimethylformamide (DMF), dimethylacetamide (DMA), diethylformamide (DEF) and N-methylpyrrolidone (NMP).[3,5] In fact, as a new class of MOFs with zeolitic structures, the synthetic methods and strategies from zeolite chemistry could be introduced and established in ZIFs synthesis. The structural diversity of zeolites is in a large part due to the effect of various structural directing agents (SDAs) and all of the new zeolites topology have been the product of innovations in template design, which involves novel, large and peculiar SDAs.[11] Thus, like in the synthesis of zeolites, our synthetic strategy to create new $Zn(Im)_2$ topology was based on the reasoning that structure directing interactions are caused by novel and large amide solvents.

Whereas small amides such as DMF have traditionally been used in the synthesis of $Zn(Im)_2$, in this article, by using a novel, large-size and commercially available amide, dibutylformamide (DBF) as solvent, a new compound was synthesized. The as-synthesized compound was characterized and formulated by elemental microanalysis and single-crystal X-ray diffraction studies as $Zn_{10}(Im)_{20}$•4DBF. The solvent DBF has been rarely used for ZIF synthesis and possesses long/flexible twin carbon chains in contrast with previously used amides such as DMF, DMA, NMP, DEF (Scheme S1). As observed in the crystalline structure, the DBF apparently serves a structure-directing role. The $Zn_{10}(Im)_{20}$•4DBF has a previously unprecedented zeolitic (4-connected) topology and features 10 crystallographically independent Zn atoms, 10-membered ring (MR) channel and unusual 4-connected 10-nodal net. Prior to this work, the presence of 4-connected 10-nodal net and 10 crystallographically independent Zn atoms are unprecedented in all 4-connected ZIFs frameworks, which represent the highest value. And only one example containing a 10-MR channel (zec topology) was reported in $Zn(Im)_2$ isomers.[3b]

$Zn_{10}(Im)_{20}$•4DBF was synthesized using a solvothermal reaction of $Zn(OAc)_2$•$2H_2O$ with an excess of imdazole in DBF at 50 °C. The purity of the as-synthesized compound was confirmed by similarities between the simulated and experimental powder X-ray diffraction (PXRD) patterns (Fig. S1).

The crystal structure analysis reveals that $Zn_{10}(Im)_{20}$•4DBF crystallizes in an orthorhombic with non-centrosymmetric space group *P2(1)2(1)2(1)*. There are 10 crystallographically unique zinc atoms, 20 different Im molecules and 4 DBF guest molecules in the asymmetric unit of $Zn_{10}(Im)_{20}$•4DBF (Fig. 1a). An unusual feature of $Zn_{10}(Im)_{20}$•4DBF is the existence of 10 crystallographically unique zinc atoms, which may help to produce a complex structure. So far, the upper limits of the crystallographically unique zinc atoms were delimited to six (zec topology) in $Zn(Im)_2$ isomers (Table S2)[3b] as well as in all the 4-connected ZIFs reported (moz-ZIF-100, 10 crystallographically unique zinc atoms, but one Zn atom is tri-coordinated[5c]).

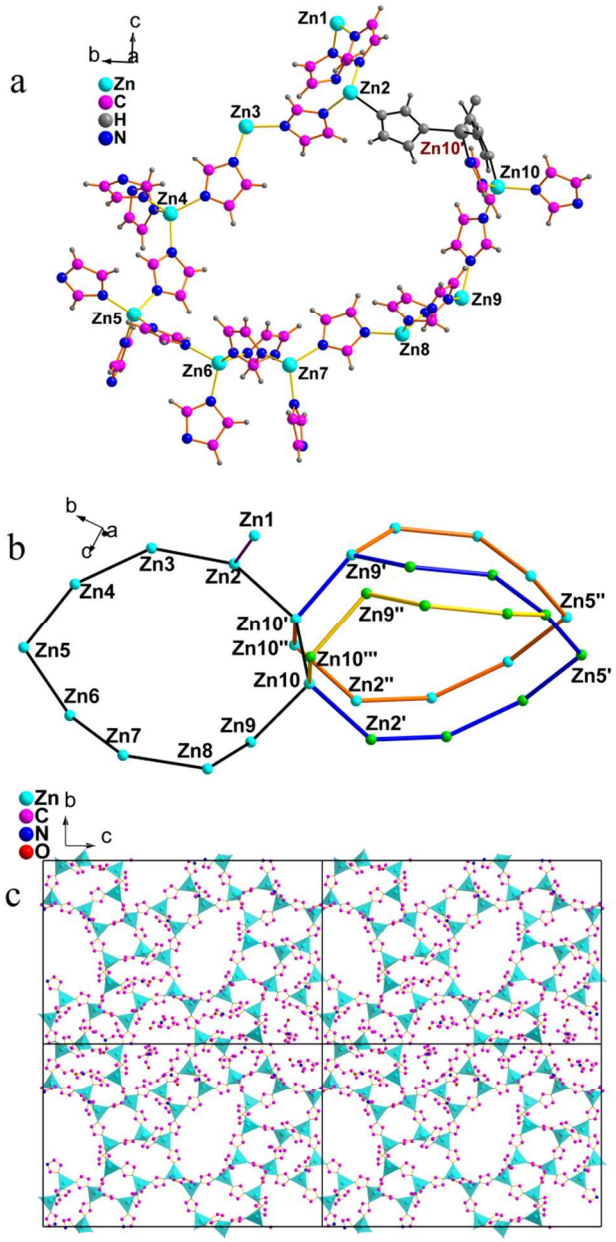

Fig. 1 (a) A ball-and-stick representation of the asymmetric unit of $Zn_{10}(Im)_{20}$•4DBF (guests were omitted for clarity and the gray Zn10′ atom and Im molecules were added); **(b)** The ball-and-stick diagram shows that the Zn10 atom plays a key role in the interconnection of the 10-MR. (Im molecules and guests were omitted); **(c)** Polyhedron representation of the supercell (2×2×2) framework (guest DBF were not removed from the middle pores).

One of the most unique features of this framework is the formation of a 10-MR along the *a* axis that consists of Zn2–Zn9 and two Zn10 atoms (Fig. 1a and b). The presence of 10-MR is also confirmed by the vertex symbols of the Zn-atoms ($5.6_2.5.6_2.6.10_3$ for Zn2 and $4.5.4.5.8_3.10_3$ for Zn3, Table S3). As shown in Fig. S2, 10-ring is surrounded by five 4-rings, two 5-rings, three 6-rings and one 10-ring, respectively. Fig. 1b shows that the Zn10 atom plays a key role in the interconnection of the 10-MR, consequently, leading to a one dimensional (1D) 10-MR channel framework with a pore size of ca. 9.8635(2) × 12.1150(2) Å (Fig. 1c and Fig. S2). So far, 10-MR are quite rare and is the largest channel-opening found in $Zn(Im)_2$ frameworks (Table S2). Prior to this work, only one example of $Zn(Im)_2$ containing a 10-membered ring (zec topology) has been reported.[3b]

All the Zn atoms are coordinated via four N atoms from four different Im ligands and each of the Im ligands links two Zn atoms in forming a three dimensional (3D) porous network (Fig. 1c). Two DBF molecules that each occupies half crystallographic sites reside in the near center of a 10-MR channel and one more DBF molecule (occupying one crystallographic site) locates across the shared edge of the 10-MR channel and 4-MR channel (Fig. 1c). In addition, the other two DBF molecules (each occupying one crystallographic site) are trapped in the 6-MR channel and 4-MR channel, respectively. Therefore, it is reasonable to regard DBF as an SDA.

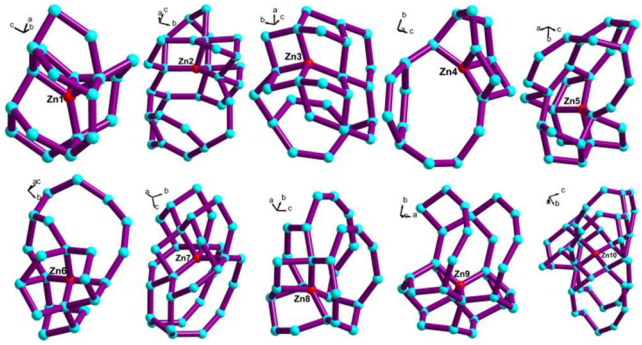

Fig. 2 Route expression of the shortest ring on each angle of Zn atoms in $Zn_{10}(Im)_{20}$•4DBF. (10-nodal net, 10 independent Zn atoms are shown in coordination sequences of Zn1, Zn2, Zn3, Zn4, Zn5, Zn6, Zn7, Zn8, Zn9 and Zn10, which have 10 topologically distinct kinds of vertex, Table S2)

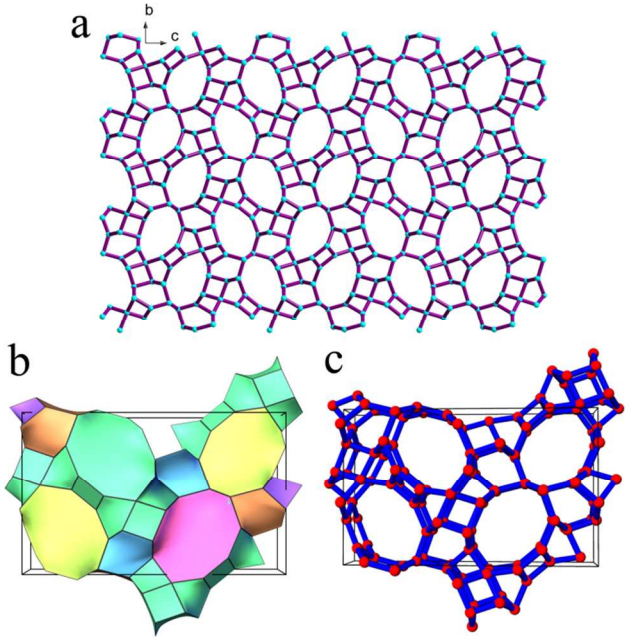

Fig. 3 (a) The topology structure of $Zn_{10}(Im)_{20}$•4DBF; **(b)** The simple tiling of the 3-periodic net in $Zn_{10}(Im)_{20}$•4DBF shows only a primitive proper tiling (PPT1); **(c)** The 3D net of PPT1 when all tiles were removed showing various 1D channels formed with various rings (all viewed along the *a* axis).

A simplified standard method was adopted for the topological analysis of the framework (coordination sequences and vertex symbols, Fig. 2 and Table S3). The most striking feature here is the $Zn_{10}(Im)_{20}$•4DBF that contains 10 kinds of vertex ($4.6.5.6_2.5.6_2$ for Zn1; $5.6_2.5.6_2.6.10_3$ for Zn2; $4.5.4.5.8_3.10_3$ for Zn3; $4.5.4.5.10_3$.* for Zn4; $4.5_2.4.8_3.8_3.8_4$ for Zn5; $4.6_2.6.6_3.6_2.8_2$ for Zn6; $4.6_2.6.6_2.6.6_2$ for Zn7; $4.6.4.6_2.6.6$ for Zn8; $4.6.6.6_2.6.6_2$ for Zn9 and $6.6.6.6.6_2.6_2$ for Zn10), which indicates that the framework is a (4,4,4,4,4,4,4,4,4,4-connected) 10-nodal network. And $Zn_{10}(Im)_{20}$•4DBF has 10 independent zinc atoms, which represent 10 different nodes with the point symbol $(4.5^2.6^3)(4.6^4.8)(4.6^5)_2(4^2.5.6.7.8)(4^2.5^2.6.7)_2(4^2.6^4)(5^2.6^3.8)(6^6)$, which represents an unprecedented topology (Fig. 3a).

It is noticeable that most topologies found in all ZIFs are uninodal[2a], and there is only one example (moz-ZIF-100) with up to 10 kinds of vertices, but one vertex is 3-coordinated[5c]. The upper limits of were delimited to 5 (nog topology) in $Zn(Im)_2$ isomers (Table S2).[3b] Thus, $Zn_{10}(Im)_{20}$•4DBF has 10 kinds of vertices, representing the highest value among the 4-connected ZIFs. Indeed, the most complex zeolite has 24 kinds of vertices.[1] The fact that the number of possible topologies increases exponentially with the number of vertices suggests that there is vast potential for ZIFs synthesis using large amides as SDAs.

Because this structure is a complex nanoporous 3D framework with a new topologic type, it is of interest to study the tiling of the net. TOPOS analysis shows that there exists only one primitive proper tiling (PPT1, Fig. 3b) in the unitcell. In Table S2 we list the numbers of vertices, faces, edges and tiles of $Zn(Im)_2$ isomers. There are six kinds of tiles in PPT1 (Fig. 3b and Fig. S3) corresponding to $[4.6^2]$, $[6^3]$, $[6.10^2]$, $[6.10^2]$, $[6^5]$ and $[4^5.5^4.6^4.10^2]$ (represented in six different colours). TOPOS analysis also revealed the presence of 16 essential rings (faces) in this 3D net, which is more than we saw along the *a* axis. These 16 rings contain three 4-membered rings, two 5-membered rings, eight 6-membered rings and three 10-membered rings. If all the tiles are removed, a 3D net, which is built from the 10 different Zn atom nodes can be seen (Fig. 3c), indicating clearly an amazing 1D nanoporous framework along the *a* axis.

The thermal analysis (TG-DSC) of the $Zn_{10}(Im)_{20}$•4DBF was investigated. Fig. S4 shows a ca. 25.1 wt.% weight loss from RT to 350 °C, which was assigned to the loss of four DBF molecules and is in good agreement with the calculated values (calculated for $Zn_{10}(Im)_{20}$•4DBF, 24.0 wt.%). The solid residue (30.5 wt.%) obtained after TG-DSC was ZnO (calculated: 31.0 wt.%). Furthermore, the strong ν (C=O)-stretching vibration of DBF at 1669 cm^{-1} was the dominating feature of the IR spectra of $Zn_{10}(Im)_{20}$•4DBF (Fig. S6). These results suggest that the DBF solvent molecules are present in the cavities. The N_2 sorption properties of $Zn_{10}(Im)_{20}$•4DBF were also investigated. The as-synthesized sample was immersed in dried CH_2Cl_2-MeOH mixture for 24 h and was subsequently activated/degassed on a surface area and pore size analyzer at 30 °C for 10 h. The activated sample was characterized by PXRD to confirm that it has the same structure with as-synthesized sample (Figure S7). It was found to exhibit Type I isotherm, indicating its microporous nature (Figure S8). The Langmuir surface area was measured as 463 $m^2\ g^{-1}$ (BET: 319 $m^2\ g^{-1}$) with micropore volume of 0.14 $cm^3\ g^{-1}$(total pore volume: 0.16 $cm^3\ g^{-1}$). The micropore volume value is in good agreement with the calculated pore volume of $Zn_{10}(Im)_{20}$•3DBF (0.16 $cm^3\ g^{-1}$) when the two DBF molecules in the near center of a 10-MR channel (each occupying half crystallographic site) are released from the unobstructed channel (see supporting information).

Conclusions

In conclusion, we have successfully synthesized a novel zeolitic imidazolate framework with unprecedented zeolitic topology, $Zn_{10}(Im)_{20}$•4DBF, using a large-size amide, dibutylformamide as a solvent and structure directing agent. The framework of $Zn_{10}(Im)_{20}$•4DBF has a 10-MR channel, 10 crystallographically independent Zn atoms and an unusual 4-connected 10-nodal net. Thus, $Zn_{10}(Im)_{20}$•4DBF has 10 kinds of vertices (10-nodal net), representing the highest value among the 4-connected ZIFs discovered to date, which underlines the rich synthetic and structural chemistry of ZIFs that have yet to be explored. Work is in progress to expand the strategy towards the construction of new ZIFs, which involves innovations in SDA design wherein different and available amides, and varying/increasing the size, shape and flexiblity of the amide will be explored.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [The detailed synthesis procedures, experimental characterization including PXRD, TG-DSC, N_2 sorption, and FT-IR and crystallographic/topology data are described in detail in the Supporting Information]. See DOI: 10.1039/b000000x/

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