Metal–Organic Frameworks

DOI: 10.1002/anie.200802680

Template-Directed Assembly of Zeolite-like Metal–Organic Frameworks (ZMOFs): A usf-ZMOF with an Unprecedented Zeolite Topology**

*Yunling Liu, Victor Ch. Kravtsov, and Mohamed Eddaoudi**

Dedicated to Professor Gérard Férey

Metal–organic frameworks (MOFs) have been recognized for their great potential to act as crystalline functional solid-state materials formed by deliberate assembly of judiciously selected molecular building blocks (MBBs).[1] The ongoing efforts and advancements to rationally design and construct made-to-order MOFs, and to gain better understanding of the relationship between structure and properties, have afforded access to unique structural properties and to potential applications in desired areas, such as hydrogen storage, carbon dioxide sequestration, renewable catalysts, and drug delivery.[2] Porous zeolite-like metal–organic frameworks (ZMOFs) are a unique subset of MOFs, which are topologically related to inorganic zeolites.[3] These anionic ZMOFs are constructed utilizing the single-metal-ion-based MBB approach[4] that permits the generation of rigid and directional tetrahedral building units (TBUs) based on heterochelation of 6–8-coordinate single-metal ions by angular ditopic organic linkers. The linkers serve to replace the O^{2-} bridges in traditional zeolites, while maintaining the placement of tetrahedra at similar angles (average $\sphericalangle$M-L-M $\approx 145°$), decorating and expanding the native zeolite-net topology.[3,5] The ZMOFs' chemical stability in aqueous solutions, forbidden interpenetration, extra-large cavities, and anionic character offer great potential for their tunability and use as functional platforms to target suitable applications.[3]

The increase, in the last century, of synthesized inorganic zeolite topologies, as well as the discovery of mesoporous silicate materials, is, in part, attributed to the introduction of structure-directing agents (SDAs) that exploit the anionic character of the frameworks.[6,7] The broad scope of reported tetrahedron-based zeolite structures, over 179 known structures, and the great number of hypothetical topologies[8] suggest that novel ZMOFs, based on the assembly of rigid and directional TBUs, either correlated to known zeolites or having unrevealed topologies, can be accessed using SDAs.

Herein, we report the potential use of structure-directing agents, templates to construct new zeolite-like metal–organic frameworks, based on the assembly of predefined TBUs, $MN_4(CO_2)_4$, with N_4 being the judiciously selected bis-bidentate bridging ligand, 4,5-imidazoledicarboxylate (Himdc). Indeed, reactions between 4,5-imidazoledicarboxylic acid (H_3imdc) and $In(NO_3)_3{\cdot}2H_2O$ in a *N,N*-dimethylformamide/acetonitrile/water ($DMF/CH_3CN/H_2O$) solution, with 1,2-diaminocyclohexane (1,2-dach) as the SDA, have yielded a novel ZMOF with an unprecedented zeolite topology, usf-ZMOF (usf refers to the University of South Florida). The as-synthesized compound was characterized and formulated by elemental microanalysis and single-crystal X-ray diffraction studies as $In_5(C_5N_2O_4H_2)_{10}(C_6N_2H_{16})_{2.5}$-$(C_5N_2O_4H_2)_{10}(C_6N_2H_{16})_{2.5}(C_3H_7NO)_4(C_2H_3N)_2(H_2O)_{10}$, (usf-ZMOF, $In_5(Himdc)_{10}(1,2\text{-}H_2dach)_{2.5}(DMF)_3(CH_3CN)_2$-$(H_2O)_{10}$).[9] The usf-ZMOF compound was insoluble in water and common organic solvents. The purity of the as-synthesized compound was confirmed by similarities between simulated and experimental X-ray powder diffraction (XRPD) patterns (see the Supporting Information).

In the crystal structure of usf-ZMOF (Figure 1), there are three crystallographically independent In^{III} ions and seven symmetry-none-quivalent Himdc ligands; each indium metal ion is coordinated to four nitrogen atoms and four oxygen atoms of four separate Himdc ligands, respectively, to form an eight-coordinate MBB, $InN_4(CO_2)_4$ (Figure 1b), which can be regarded as a tetrahedral 4-connected building unit (Figure 1c). Each independent Himdc is coordinated to two In^{III} ions by forming two rigid five-membered rings by N-, O-heterochelation, where the In–N bonds direct the topology. The assembly of the 4-connected nodes results in the generation of two distinct polyhedra, namely the gmelinite (gme) cage consisting of 24 tetrahedrally coordinated atoms (T-atoms) and a new cage, that we term the "usf cage", containing 32 T-atoms, which link together through their faces to form a MOF with a zeolite-like topology (Figure 1d). The

---

[*] Dr. Y. Liu, Dr. V. C. Kravtsov, Prof. Dr. M. Eddaoudi
Department of Chemistry, University of South Florida
4202 East Fowler Avenue (CHE 205), Tampa, FL 33620 (USA)
Fax: (+1) 813-974-3203
E-mail: eddaoudi@cas.usf.edu
Dr. Y. Liu
State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry
Jilin University, Changchun 130012 (P.R. China)
Dr. V. C. Kravtsov
Institute of Applied Physics of Academy of Sciences of Moldova, Academiei 5
MD2028 Chisinau (Moldova)

[**] We gratefully acknowledge the financial support of the National Science Foundation (DMR 0548117) and the Department of Energy DOE-BES (DE0FG02-07ER4670).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802680.

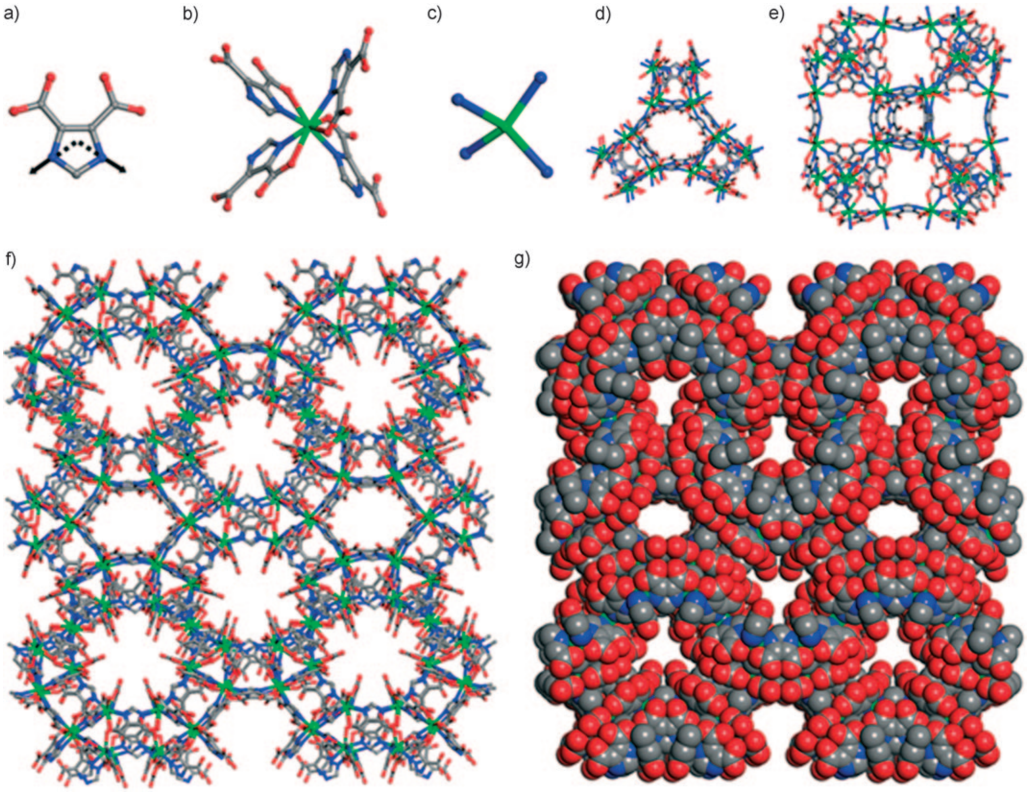

Figure 1. Molecular structure of usf-ZMOF determined by single-crystal X-ray diffraction: a) bridging angle of the Himdc ligand, b) eight-coordinate MBBs that can be viewed as c) four-connected TBUs, d) ball-and-stick representation of a gme cage in usf-ZMOF, e) ball-and-stick representation of the new usf cage in usf-ZMOF, f) ball-and-stick representation of the framework of usf-ZMOF viewed along the *a* direction, g) space-filling representation of the framework of usf-ZMOF viewed along the *a* direction. C gray, In green, N blue, O red. Guest molecules and hydrogen atoms are omitted for clarity.

usf-ZMOF represents the first synthesized extended structure to have this singular topology referred to in the RCSR database as **med** topology.[10]

The 4-connected net of the usf-ZMOF, made by linking indium centers, has a unique topology (that is, **med** topology) and is based on the assembly of two distinct cages (Figure 2a–b), both comprising three types of faces. The smaller cage is known as a gme cage, originally encountered in the gmelinite zeolite[7] and is also present in two other zeolites (EAB and offretite), which has the face symbol $[4^9 6^2 8^3]$, and consists of 24 vertices, delimiting nine 4-membered-ring (MR) faces, two 6MR faces, and three 8MR faces. The new cage, usf-ZMOF consists of 32 vertices, delimiting ten 4MR, four 6MR, and four 8MR faces, and has the face symbol $[4^{10} 6^4 8^4]$. As such, this cage is distinct from other cages in zeolites with the same number of vertices, specifically the paulingite cage $[4^{12} 8^6]$ and the AWW cage $[4^8 6^8 8^2]$ (see the Supporting Information). Each gme tile (Figure 2c) has 14 faces that are shared by seven adjacent gme tiles and seven usf tiles (Figure 2d). Each usf tile has eighteen faces that are shared by four other usf tiles and fourteen gme tiles.

To confirm the novelty of the usf-ZMOF network topology, the coordination sequences for each of the three independent vertices, represented by In^{III} ions, were calculated, and then compared with known zeolite topologies.[11] Accordingly, the trinodal net does not correspond to any known zeolite; however, shortly after the synthesis and characterization of our usf-ZMOF, the aforementioned topology appeared in the database of hypothetical zeolite structures, confirming its potential as a suitable target topology for the synthesis of inorganic based zeolites and/or zeolite-analogues.[8]

The hypothetical zeolite structure has the same space group, vertex symbols, and coordination sequences as usf-ZMOF.[8] Nevertheless, the number of tetrahedral vertices in usf-ZMOF per unit volume is nine-times less than the yet-to-be-constructed inorganic analogue. The unit cell volume of usf-ZMOF (45 245 Å^3) is 9.55-times higher than its hypothetical analogous zeolite (4735.68 Å^3), which can be translated into a commonly used notation, framework density (FD, number of tetrahedral vertices per 1000 Å^3), in zeolites to assess the openness of a given framework. The FD of usf-ZMOF is 1.77, while the hypothetical zeolite has an FD of 16.89, indicating the relative openness of usf-ZMOF.[7]

The as-synthesized usf-ZMOF unit cell contains 80 indium(III) metal ions and 160 doubly deprotonated Himdc ligands to give an overall framework formula of $([In_{80}(Himdc)_{160}]^{80-})_n$, wherein the negatively charged framework is neutralized by 40 doubly protonated 1,2-dach molecules and the remaining free volume is occupied by neutral guest molecules (i.e. DMF, CH_3CN, and H_2O). The space occupied by neutral and cationic guest molecules alone represents 50 % of the cell volume or 22 838 Å^3 per unit cell.

The anionic character, extra-large cavities, large openings (ca. 1.1 nm), and chemical stability in aqueous solutions of usf-ZMOF have allowed the full exchange of 1,2-H_2dach cations with various organic and inorganic cations. Accordingly, cationic probes, such as acridine orange molecules, have been encapsulated in usf-ZMOF using a similar exchange method and characterization (see the Supporting Information), as in the case of rho-ZMOF.[3] Several inorganic cations (Na^+, Li^+, Mg^{2+}) have been introduced into the usf-ZMOF by ion exchange of the as-synthesized extra-framework cations.

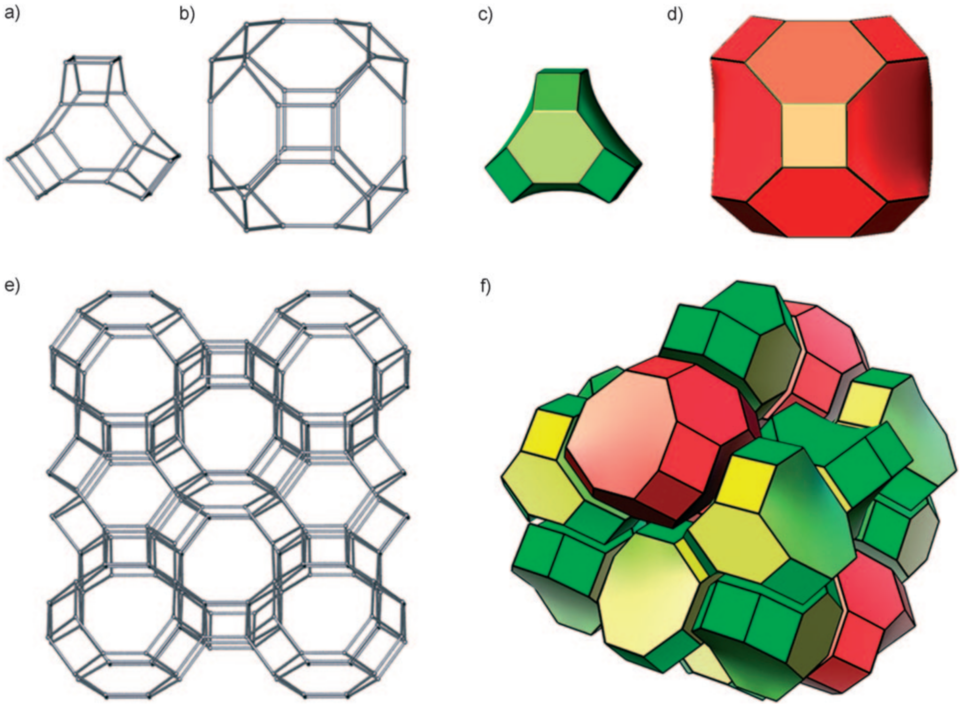

Figure 2. The framework topology and natural tiling of usf-ZMOF: a) ball-and-stick view of a gme cage in usf-ZMOF, b) ball-and-stick view of the new usf cage in usf-ZMOF with the simplified tetrahedron knot, composed of 32 indium atoms: ten 4MR, four 6MR, four 8MR, c) the gme cage, d) the usf cage, e) topology of the framework of usf-ZMOF viewed along *a* direction, f) natural tiling of usf-ZMOF (gme cages are shown in green, usf cages in red).

Ion exchange was monitored by atomic absorption, and the structural integrity of the framework was confirmed by the preservation of crystallinity, as demonstrated by XRPD studies (see the Supporting Information).

In order to explore the gas sorption properties of usf-ZMOF, the extra-framework cations present in the as-synthesized compound were fully exchanged with dimethylammonium (DMA)cations. Gas sorption experiments were performed on the DMA-exchanged usf-ZMOF, and the fully evacuated framework exhibits permanent microporosity, as evidenced by the reversible type I nitrogen and argon sorption isotherms (Figure 3). The apparent Langmuir surface area for usf-ZMOF was estimated to be 520 $m^2 g^{-1}$. The pore volume was calculated using the Dubinin-Radushkevich equation[12] to be 0.20 $cm^3 g^{-1}$, which corresponds to the expected 30% available free volume (the remaining 20% free volume is occupied by DMA cations).

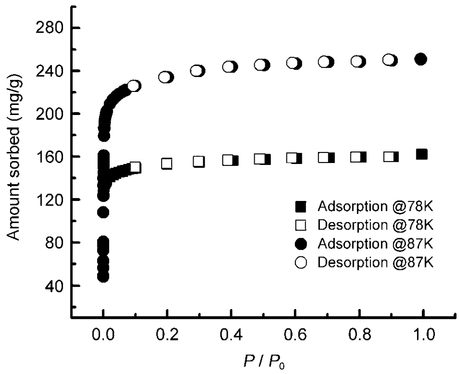

Figure 3. Nitrogen and argon sorption isotherm on usf-ZMOF at 78 K and 87 K.

Owing to the importance of localized high charge density on the hydrogen-sorption energetics of porous materials and the anionic character of usf-ZMOF, preliminary hydrogen-sorption studies were performed on usf-ZMOF and indicate a relatively enhanced isosteric heat of sorption at lower loadings that can be correlated to the charged nature of the cavities. Further studies are underway to explore the extra-large cavities and anionic character of the usf-ZMOF as a platform for gas storage, sensing, catalysis, and separations.

Herein, we have demonstrated the potential impact of structure directing agents (SDAs) on our single-metal-ion-based molecular building block approach to synthesize novel zeolite-like metal–organic frameworks (ZMOFs) as evidenced by the construction of the usf-ZMOF, having an unprecedented topology. Work is in progress to expand this strategy to the construction of other ZMOFs, wherein different SDAs, suitable single-metal-ion-based TBUs, and potential bis-chelating bridging ligands will be explored.

Experimental Section

Usf-ZMOF: In a sealed 20 mL vial, 4,5-Imidazoledicarboxylic acid (0.014 g, 0.087 mmol), $In(NO_3)_3 \cdot 2H_2O$ (0.015 g, 0.0435 mmol), DMF (1 mL), CH_3CN (1 mL), H_2O (0.5 mL), 1,2-diaminocyclohexane (0.1 mL, 1.75 M in DMF), and HNO_3 (0.5 mL, 3.5 M in DMF) were heated to 85 °C and that temperature maintained for 12 h. The colorless polyhedral crystals were collected and air-dried, yielding the product (0.023 g, 56% based on $In(NO_3)_3 \cdot 2H_2O$). Elemental analysis (%) calcd for usf-ZMOF, $In_5(Himdc)_{10}(1,2\text{-}H_2dach)_{2.5}(DMF)_3(CH_3CN)_2(H_2O)_{10}$: C 32.87, H 3.88, N 14.67; found C 33.12, H 3.95, N 14.82. FT–IR (4000–600 cm^{-1}): $\tilde{\nu} = 1655$(s), 1579(m), 1465(s), 1439(w), 1388(s), 1329(w), 1311(w), 1252(m), 1107(s), 1060(w), 1024(w), 848(m), 783(s), 656(vs).

Received: June 7, 2008
Revised: July 17, 2008

Keywords: indium · metal–organic frameworks · porous materials · template synthesis · zeolite analogues

[1] a) A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466–3492; *Angew. Chem. Int. Ed.* **1999**, *38*, 3268–3292; b) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714; c) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658; d) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388–2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; e) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, *Acc. Chem. Res.* **2005**, *38*, 273–282; f) O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511–512; g) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, *Acc. Chem. Res.* **2005**, *38*, 217–225; h) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040–2042; i) Q. R. Fang, G. S. Zhu, M. Xue, J. Sun, Y. Wei, S. L. Qiu, R. R. Xu, *Angew. Chem.* **2005**, *117*, 3913–3916; *Angew. Chem. Int. Ed.* **2005**, *44*, 3845–3848.

[2] a) G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191–214; b) B. Wang, A. P. Cote, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Nature* **2008**, *453*, 207–211; c) X. Lin, J. Jia, P. Hubberstey, M. Schröder, N. R. Champness, *CrystEngComm* **2007**, *9*, 438–448; d) S. H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp, T. E. Albrecht-Schmitt, *Chem. Commun.* **2006**, 2563–2565; e) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986; f) R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, K. Kindo, Y. Mita, A. Matsuo, M. Kobayashi, H. C. Chang, T. C. Ozawa, M. Suzuki, M. Sakata, M. Takata, *Science* **2002**, *298*, 2358–2361; g) J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, *128*, 1304–1315.

[3] a) Y. L. Liu, V. Ch. Kravtsov, R. Larsen, M. Eddaoudi, *Chem. Commun.* **2006**, 1488–1490; b) M. Eddaoudi, J. F. Eubank, Y. L. Liu, V. Ch. Kravtsov, R. Larsen, J. A. Brant, *Stud. Surf. Sci. Catal.* **2007**, *170*, 2021–2029; c) D. F. Sava, V. Ch. Kravtsov, F. Nouar, L. Wojtas, J. F. Eubank, M. Eddaoudi, *J. Am. Chem. Soc.* **2008**, *130*, 3768–3770.

[4] a) Y. Liu, V. Ch. Kravtsov, D. A. Beauchamp, J. F. Eubank, M. Eddaoudi, *J. Am. Chem. Soc.* **2005**, *127*, 7266–7267; b) Y. Liu, V. Ch. Kravtsov, R. D. Walsh, P. Poddar, H. Srikanth, M. Eddaoudi, *Chem. Commun.* **2004**, 2806–2807; c) J. A. Brant, Y. Liu, D. F. Sava, D. Beauchamp, M. Eddaoudi, *J. Mol. Struct.* **2006**, *796*, 160–164.

[5] a) X. C. Huang, J. P. Zhang, X. M. Chen, *Chin. Sci. Bull.* **2003**, *48*, 1531–1534; b) X. C. Huang, Y. Y. Lin, J. P. Zhang, X. M. Chen, *Angew. Chem.* **2006**, *118*, 1587–1589; *Angew. Chem. Int. Ed.* **2006**, *45*, 1557–1559; c) K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 10186–10191; d) H. Hayashi, A. P. Cote, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Nat. Mater.* **2007**, *6*, 501–506; e) L. C. Tabares, J. A. R. Navarro, J. M. Salas, *J. Am. Chem. Soc.* **2001**, *123*, 383–387; f) E. Barea, J. A. R. Navarro, J. M. Salas, N. Masciocchi, S. Galli, A. Sironi, *J. Am. Chem. Soc.* **2004**, *126*, 3014–3015; g) J. Y. Zhang, A. L. Cheng, Q. Yue, W. W. Sun, E. Q. Gao, *Chem. Commun.* **2008**, 847–849.

[6] a) C. S. Cundy, P. A. Cox, *Chem. Rev.* **2003**, *103*, 663–701; b) A. Corma, M. J. Díaz-Cabañas, J. Martínez-Triguero, F. Rey, J. Rius, *Nature* **2002**, *418*, 514–517; c) M. E. Davis, *Nature* **2002**, *417*, 813–821; d) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710–712.

[7] C. Baerlocher, L. B. McCusker, Database of Zeolite Structures, http://www.iza-structure.org/databases/.

[8] M. D. Foster, M. M. J. Treacy, Database of Hypothetical Zeolites, http://www.hypotheticalzeolites.net/.

[9] Crystallographic data of usf-ZMOF: $C_{50}H_{20}In_5N_{20}O_{40}$, $M_r = 2114.96$, tetragonal, $I4_1/amd$, $a = 29.572(2)$ Å, $c = 51.739(8)$ Å, $V = 45245(8)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.242\ \mathrm{g\,cm^{-3}}$, $2\theta_{max} = 48.1°$ ($0 \leq h \leq 3$, $0 \leq k \leq 33$, $0 \leq l \leq 59$), $T = 100$ K, 18354 measured reflections, $R_1 = 0.1049$, $wR_2 = 0.2651$ for 5282 reflections ($I > 2\sigma(I)$), and $R_1 = 0.1729$, $wR_2 = 0.3051$ for 9320 independent reflections (all data) and 702 parameters, GOF = 1.004. Data were collected on a Bruker SMART-APEX CCD diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), operating in the ω and ϕ scan mode and corrected for Lorentz and polarization effects. The SADABS program was used for absorption correction. The structure was solved by direct methods and the structure solution and refinement were based on $|F^2|$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All crystallographic calculations were conducted with the SHELXTL software suite. CCDC 690432 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] The **med** topology refers to **M**ohamed **Ed**daoudi (**med**), and its addition to the RCSR database is attributed to usf-ZMOF, of which we informed Prof. Michael O'Keeffe upon its discovery; M. O'Keeffe, Reticular Chemistry Structure Resource, http://rcsr.anu.edu.au/.

[11] Vertex symbols for usf-ZMOF: In1 (4, 4, 4, 6, 8, 8), In2 (4, 4, 4, 6, 8, 8), In3 (4, 4, 6, 6, 8, 8); coordination sequences for usf-ZMOF: In1 (CS_1 to $CS_{10} = 4$, 9, 18, 32, 48, 67, 93, 123, 154, 190, $CUM_{10} = 739$), In2 (CS_1 to $CS_{10} = 4$, 9, 18, 31, 47, 69, 96, 125, 156, 192, $CUM_{10} = 748$), In3 (CS_1 to $CS_{10} = 4$, 10, 18, 30, 50, 72, 92, 120, 158, 198, $CUM_{10} = 753$).

[12] S. J. Gregg, K. S. W. Sing, *Adsorption, Surface Area and Porosity*, 2nd ed., Academic Press, London, **1982**.