Determination of highly-complex structures of zeolitic imidazolate frameworks through a combination of powder diffraction structure solution and periodic DFT calculations.

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Zeolitic imidazolate frameworks (ZIFs) are a class of metal-organic frameworks (MOFs), structurally and topologically related to zeolites. ZIFs are constructed from tetrahedral metal nodes connected to imidazolate linkers via metal-nitrogen coordination bonds.[1,2] Within the ZIF family, zinc imidazolate (Zn(**Im**)$_2$) has the highest number of polymorphs.

This presentation will report the crystal structure determination of two new crystal forms of zinc imidazolate (Zn(**Im**)$_2$) via a combination of direct methods and simulated annealing structure determination from powder X-ray diffraction data, guided by periodic density-functional theory (DFT) calculations and topological analysis of the structural models.

The two new forms of Zn(**Im**)$_2$ were discovered during a mechanochemical crystal form screening based on liquid-assisted grinding (LAG) methodology.[3] The new forms originated from LAG syntheses with toluene and acetophenone liquid additives, herein designated as T-ZIF and A-ZIF, respectively. Given the polycrystalline nature of mechanochemically-synthesized materials, the structures of T-ZIF and A-ZIF could not be determined from single-crystal X-ray diffraction, yet they proved to be highly complex for PXRD structure solution. The asymmetric unit of T-ZIF was expected to contain one zinc atom, one full and two half-imidazolate fragments. The A-ZIF structure proved to be even more complex, with four symmetry-independent zinc atoms and eight imidazolate linkers. In addition to that, both structures contained solvent guest molecules, which were likely disordered.

Such highly complex structures could not be solved via simulated annealing methods. Instead a multi-step structure solution procedure was developed, starting from determination of metal atom positions via direct methods procedure, implemented in EXPO2014.[4] The imidazolate linkers were then inserted between the adjacent zinc metal nodes, based on geometric considerations, and the resulting model was adjusted via Rietveld refinement.[5] Finally, guest molecules were added to the models, their positions and occupancies, optimized during the simulated annealing procedure.

Even after all these steps, some uncertainty regarding the correctness of the structural model remained: with the large number of symmetry-independent imidazolate linkers, 180° rotation of one linker with respect to the Zn···Zn axis would result in a very small change in R_{wp}, making it very difficult to assign orientations of individual linkers. A series of periodic DFT calculations, were used to determine the energy preferences for each linker orientation, with the lowest energy configuration use for Rietveld refinement.

The multi-step structure determination process was further validated by NMR and thermogravimetric analysis (TGA) measurements The NMR and TGA-derived quantities of toluene and acetophenone guests were in good agreement with the guest composition obtained form the powder diffraction data, further validating the correctness of the chosen approach for structure determination.

Finally, it was found that both T-ZIF and A-ZIF forms possess **crb** network topology. In addition to three previously-reported **crb** forms of Zn(**Im**)$_2$, this means that **crb**-Zn(**Im**)$_2$ exists in at least five distinct crystal packing arrangements, a very unusual result for ZIF chemistry.

[1] 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.* **2006**, *103*, 10186–10191.

[2] X. C. Huang, Y. Y. Lin, J. P. Zhang, X. M. Chen, *Angew. Chem. Int. Ed.* **2006**, *45*, 1557–1559.

[3] I. Brekalo, K. Lisac, J. R. Ramirez, P. Pongrac, A. Puškarić, S. Valić, Y. Xu, M. Ferguson, J. M. Marrett, M. Arhangelskis, T. Friščić, K. T. Holman, *J. Am. Chem. Soc.* **2025**, *147*, 27413–27430.

[4] A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero, A. Falcicchio, *J. Appl. Crystallogr.* **2013**, *46*, 1231–1235.

[5] H. M. Rietveld, *Acta Crystallogr.* **1967**, *22*, 151–152.