Poster

Hirshfeld atom refinement of metal-organic framework crystal structures

M. Arhangelskis[1], Y. Xu[1], M. L. Chodkiewicz[1], M. Woińska[1], D. Trzybiński[1], I. Brekalo[2] F. Topić,[3] K Woźniak[4]

[1]Faculty of Chemistry, University of Warsaw, 1 Pasteura Street, Warsaw 02-093, Poland, [2] Department of Physical Chemistry, Ruđer Bošković Institute, Bijenička Cesta 54, 10000 Zagreb, Croatia, [3]Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal H3A 0B8, Canada.

m.arhangelskis@uw.edu.pl

Metal-organic frameworks (MOFs) are microcrystalline materials, composed of transition metal nodes connected by organic linker molecules. MOFs are renowned for their applications in gas storage and separation, sequestration of atmospheric greenhouse gases, water purification and degradation of toxic agents, all of these applications stemming from the porous nature of these materials [1,2]. Detailed understanding of MOF host-guest chemistry and sorption properties relies on the knowledge of the crystal structure with precise assignment of atoms belonging both to the host framework and the guest species. Yet, owing to the difficulties of obtaining high quality MOF single crystals, as well as common occurrence of disorder, assignment of guest species poses a challenge and cases of incorrect assignment of guest molecules have been reported [3,4]. Consequently, there is a pressing need for improved accuracy of MOF structure refinement, with a key role placed on the methods of quantum crystallography.

This presentation will report the first use of Hirshfeld atom refinement (HAR) for a MOF structure,[5] namely that of the *crb* polymorph of zinc imidazolate, colloquially known as ZIF-2 [6]. The polymeric nature of the structure meant that conventional molecule-based implementation of HAR could not be used, and instead a recently-developed fragmentation method was employed. In the fragmentation approach, some of the metal-linker bonds were broken by terminating the bonding sites with hydrogen atoms, the resulting fragment then subjected to quantum-mechanical calculations similar to conventional HAR.

The structural model obtained with the fragmentation HAR approach showed major improvements compared to the previous structures of ZIF-2 refined with the independent atom model (IAM). Unconstrained refinement of hydrogen atom positions resulted in C-H bond lengths comparable to standard neutron-diffraction values. Moreover, hydrogen atom displacement parameters were refined anisotropically. Finally, previously unreported disorder of the guest NN-dimethylformamide guest molecules was identified, demonstrating how detailed structure analysis enabled by HAR method improves the description of guest species within MOF pores.

Performance of the fragmentation HAR approach was evaluated with different quantum-mechanical methods as well as basis sets, allowing to suggest methodology for the ultimate balance of accuracy and computational cost. Finally, structural model obtained with fragmentation HAR was compared with an alternative method based on the partitioning of the calculated periodic wavefunction [7].

The presented approach offers high promise for the future detailed structural analysis of newly-synthesized MOFs, including detailed analysis of guest molecules found within framework voids.

[1] Sung Cho, H., Deng, H., Miyasaka, K., Dong, Z., Cho, M., Neimark, A. V, Ku Kang, J., Yaghi, O. M. & Terasaki, O. (2015). *Nature* **527**, 503.

[2] Nugent, P., Belmabkhout, Y., Burd, S. D., Cairns, A. J., Luebke, R., Forrest, K., Pham, T., Ma, S., Space, B., Wojtas, L., Eddaoudi, M. & Zaworotko,

M. J. (2013). *Nature* **495**, 80.

[3] Poręba, T., Macchi, P. & Ernst, M. (2022). *Nat. Commun.* **13**, 5288.

[4] Wang, B., Xie, L.-H., Yuan, D. & Chen, B. (2022). *Nat. Commun.* **13**, 5287.

[5] Xu, Y., Chodkiewicz, M. L., Woińska, M., Trzybiński, D., Brekalo, I., Topić, F., Woźniak, K. & Arhangelskis, M. (2023). *Chem. Commun.* **59**, 8799.

[6] Park, K. S., Ni, Z., Cote, A. P., Choi, J. Y., Huang, R., Uribe-Romo, F. J., Chae, H. K., O'Keeffe, M. & Yaghi, O. M. (2006). *Proc. Natl. Acad. Sci.*

103, 10186.

[7] Ruth, P. N., Herbst-Irmer, R. & Stalke, D. (2022). *IUCrJ* **9**, 286.

Dr. Paul Niklas Ruth is thanked for the advice regarding the use of HAR with periodic wavefunction.