

# Hirshfeld Atom Refinement for Polymeric Structures: A Study on MOFs and COFs

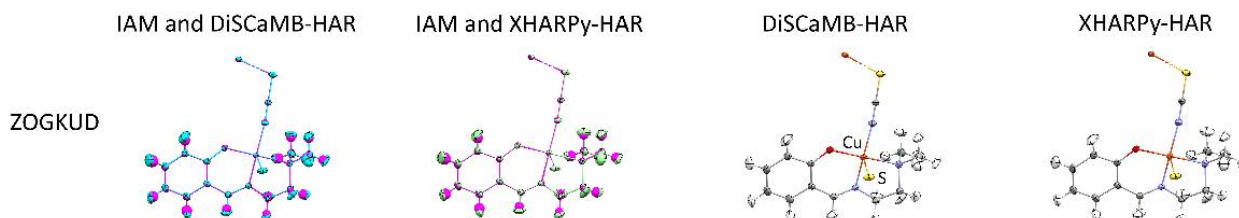
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Metal organic frameworks (MOFs) and covalent organic frameworks (COFs) are polymers which due to their porosity are suitable for various applications, such as gas separation and storage, water harvesting and purification, catalysis, sensing and energy storage. Many of these materials can form crystals amenable to single crystal X-ray diffraction analysis. This enables using methods from the realm of quantum crystallography, such as Hirshfeld atom refinement (HAR). However, the application of HAR to refine crystal structures of network compounds has been limited thus far with only a few reported cases [1, 2], including one MOF [3]. This group of compounds is challenging not only due to the presence of transition metal atoms but also because quantum crystallography methods are mostly tailored to molecular crystals.

This work presents a study on the applicability of HAR to MOFs, COFs, and other coordination polymers. In total, successful HARs have been performed for 20 X-ray structures using classical HAR (DiSCaMB-HAR), which involves calculating wave function for a single molecular fragment surrounded by a cluster of atomic monopoles and dipoles. Additionally, for 4 crystal structures, HAR employing wave function derived from calculations with periodic boundary conditions (PBC) [4] was carried out (XHARPy-HAR). For 8 structures classical HAR was achieved without constraints imposed on hydrogen positions or thermal parameters, while for one structure, all hydrogen ADPs were refined. Among the structures refined with classical HAR, there was also one structure measured at the pressure of 1 GPa. In the case of HAR with PBC, one structure could be refined anisotropically (Figure 1), whereas for the other three, only isotropic refinement was feasible. The experimentally determined positions of hydrogen atoms were compared to the results of geometry optimization. IAM underestimated the bond lengths formed by H atoms by on average 0.125 Å (mean absolute difference (MAD) with the theoretical bond lengths of 0.154 Å), classical HAR underestimated them by only 0.025 Å (MAD = 0.082 Å). In the case of HAR with PBC, the underestimation of X-H bond lengths was only 0.007 Å (MAD = 0.031 Å). The differences were even slightly lower if mean neutron bond lengths were used as a benchmark. The 20 structures were ranked by data and refinement quality statistics, which showed that the advantage of HAR over IAM was strongly pronounced for one third of all the structures characterized by the highest quality and that HAR with PBC was attainable only for the highest-quality structures. These preliminary findings suggest that for polymeric structures, such as MOFs and COFs, atomic scattering factors provided by classical HAR may be sufficient to obtain structural parameters comparable to those resulting from HAR with PBC.



**Figure 1.** Crystal structures of the compound obtained which could be anisotropically refined with DiSCaMB-HAR and XHARPy-HAR (on the right). On the left, DiSCaMB-HAR (cyan) and XHARPy-HAR (light green) structures are overlaid with the IAM structures (magenta).

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