Visualizing atomic structure of novel three-dimensional covalent organic frameworks by 3DED and high-resolution (S)TEM

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Covalent organic frameworks (COFs) are a family of porous materials constructed through organic blocks connected by covalent bonds. Its versatility of functionality, its well-defined pores, and its high surface area / high porosity have cultivated many applications in gas storage, catalysis, and separation areas.

Determining the structure of three-dimensional COFs is important for understanding their structure-function relationships and enables the rational design of materials with better performance. The most trivial way to gather the structure information is through the single-crystal X-ray diffraction (SCXRD) method. However, the small crystal sizes of the COFs hindered the common routine of ab initio structure solution. Additionally, the poor crystallinity and polymorphism of COFs also make them difficult to analyze using powder XRD data.

Electron microscopy is widely used for structure characterization in material science and gained great success on the elucidation of many complex structures. It can investigate bulk structures of small crystals by three-dimensional electron diffraction (3DED) technique and local structures by imaging. Acquiring atomic-resolution images on 3D COFs remains challenging, especially due to the electron beam damage. In recent years, the development of electron detectors and image-acquisition methods have enabled high-resolution (S)TEM with ultralow electron doses, largely overcoming this challenge. The poor crystallinity, disorders, guest molecules, and flexible characteristics of COFs still undermine the determination of the COFs' structure.

We use the 3DED technique under cryogenic conditions to get the averaging atomic structure of novel 3D COFs. The accumulated electron dose is 6~15 e-/Å2. The structure is validated with corresponding low-dose high-resolution electron microscopy (HREM) images with relatively low position offsets. We hope this investigation will cultivate the further development of structure-solving on COFs and other organic materials.

Keywords:

3DED, Low-dose HREM, 3D COFs

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