METAL-ORGANIC FRAMEWORKS

Three-dimensional COF crystals keep growing

Strategy yields crystals big enough to reveal previously elusive structural details

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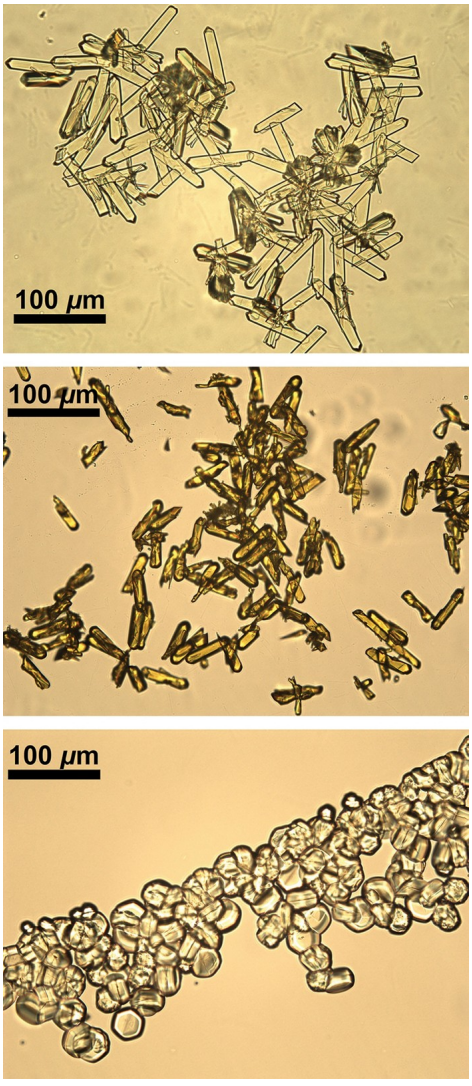
Exceptionally high porosity and surface area coupled with chemical tunability make covalent organic frameworks (COFs) attractive materials for various applications, such as storing and separating gases. But the inability to prepare these metal-free covalently-bonded materials as large single crystals has hampered their development. That's quickly changing.

Last month, researchers reported a route to making **large 2-D COF single crystals** (C&EN, June 25, page 10). Now, another team of scientists reports a strategy for growing large 3-D imine-based COF crystals—large enough to deduce previously unknown structural details via single-crystal X-ray diffraction (*Science* 2018 **DOI: 10.1126/science.aat7679**).

The new study was carried out by a large group led by Wei Wang of Lanzhou University, Junliang Sun of Peking University, and **Omar M. Yaghi** of the University of California, Berkeley. The improved crystallization hinges on using a large excess of aniline during imine COF synthesis. Doing so leads to formation of terminal benzene-imine moieties on the surface of the growing COF crystal. That feature provides an error-correction mechanism that prevents immediate precipitation of tiny crystals, often measuring less than 0.5 μm, allowing them instead to grow up to 100 μm in length.

Thanks to the quality and size of these crystals, the team was able to measure for the first time structural distortions, the arrangement of water guest molecules, the extent of lattice interpenetration, and other COF properties with atomic precision.



Credit: ***Science***

The imine-based COF crystals shown here (LZU-79, top; hydrated COF-300, middle; LZU-111, bottom) are the largest COF single crystals ever grown and analyzed.

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