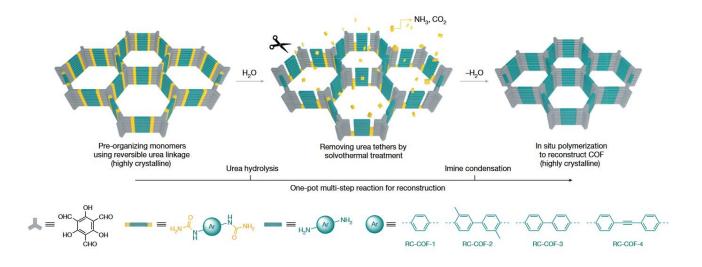
Reconstructed covalent organic frameworks

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Use of urea linkage to preorganize a COF and reconstruct it by a solvothermal treatment

Who are the corresponding authors and what are their research areas?

The corresponding authors are prof. Wei Hong Zhu (East China University of Science and Technology and prof. Andy Cooper (University of Liverpool). The first is interested in organic sensitizers for solar cells and organic photochromic materials, whereas the second is a world-leading researcher in organic materials synthesis and autonomous discovery of new materials.

What is the main claim of the article?

They show how it is possible to reconstruct a Covalent Organic Framework (COF) by a solvothermal treatment of a urea-based preorganized COF. A highly crystalline, highly stable COF is achieved, leveraging the tradeoff between stability and structural order that is normally associated with the synthesis of these materials.

Nature is a high-impact journal (impact factor of 49.9 in 2022) that covers a wide range of scientific topics. The article is suitable for this journal because it shows a new, general approach for synthesizing COFs that considerably improves their properties (as surface area or porosity) and that may have an industrial application.

How is it demonstrated?

First, they synthesized a urea COF and heat it up to 170°C, observing a change in color and a shift in the X-ray diffraction patterns. They also tried different solvent systems, finding that only water (together with temperature increase) is able to promote the change.

Then, they synthesized an analog of the final COF by direct polymerization, observing that the solvothermally treated COF and the polymerized based COF had the same resonance peaks on the CP-MAS NMR spectra. They also checked that the reconstructed COF is more crystalline using X-ray diffraction and how it is more porous by N_2 adsorption experiments. They also extended the synthetic procedure to other COFs and performed computational studies, showing how the solvothermal treatment removes the urea linking fragments, but due to non-covalent attractive forces, the crystalline network is maintained before undergoing irreversible polymerization that yields the final COF. These COFs are therefore more crystalline due to the tethering effect of the urea fragments before the polymerization.

What are the typical experimental conditions?

The solvothermal treatment typically involves a Pyrex sealed test tube containing the urea COF in water that is heated at 160 °C for 72h.

Which are the key related papers?

J. Am. Chem. Soc., 141, 5, 1807–1822 (2019): a perspective on COFs, their synthesis and applications

Chem. Soc. Rev. **49**, 8469–8500 (2020): review that highlights the dichotomy stability-crystallinity associated with MOFs synthesis.

Additional comments, including additional elements of interest

This method is interesting from the industrial point of view as it does not require an inert atmosphere to avoid monomer oxidation (in contrast to other COFs synthetic procedures). The urea COF is less reactive and avoids monomer oxidation during the reaction. Therefore, it implies saving energy and resources while synthesizing a product with better properties.