

Researchers develop solution-processible single-crystal porous organic polymer

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Synthetic organic polymers are typically insoluble polycrystalline or amorphous products rather than single crystals. The direct synthesis of single-crystal porous polymers remains a challenge in polymer science and crystal engineering.



However, many biomacromolecules found in nature can achieve singlecrystal form assisted with multiple supramolecular interactions, implying that reversible supramolecular interactions can be used to modulate the crystallinity of porous polymer materials.

In a study published in *Nature Synthesis*, the research groups led by Prof. Liu Tianfu and Prof. Cao Rong from Fujian Institute of Research on the Structure of Matter of the Chinese Academy of Sciences proposed a strategy to achieve <u>single crystals</u> of a porous polymer.

In the hierarchical structures of natural protein crystals and some <u>nucleic</u> <u>acids</u>, 1D covalent chains generate highly crystalline or even singlecrystal products through a synergistic combination of non-covalent supramolecular interactions, and further fold into specific spatial conformations as secondary, tertiary and quaternary structures. Inspired by this, the researchers envisioned that the judicious choice of 1D chains with tunable dynamic covalent bonds and supramolecular interactions might yield direct synthesis of a single-crystal porous polymer with desired cavities, ion channels and functionalities.

They designed and synthesized a single-crystal porous polymer-based hydrogen-bonded organic framework (PHOF-1) through a one-pot route and confirmed its structure by single-crystal X-ray diffraction studies.

The researchers found that 1,4-phenylenebisboronic acid monomers polymerize into a tetramer to afford a nine-membered $B_4O_5^{2-}$ cluster (primary structure), which further extends into 1D covalent chains (secondary structure) that are non–covalently cross-linked by <u>hydrogen</u> <u>bonds</u> and <u>electrostatic interactions</u> (tertiary structure), ultimately evolving to afford a hydrogen-bonded organic framework (quaternary structure).

Compared with insoluble 2D or 3D crosslinked porous polymers, the 1D



polymer chains show excellent solubility and solution processability. The dissolved PHOF-1 maintains the consecutive 1D chain structure with a very narrow molecular weight distribution and can regenerate reversibly in single-crystal or amorphous states depending on the solvent evaporation rate.

Taking advantage of the solution processibility, the researchers continuously coated PHOF-1 onto a non-woven fabric to afford a functional composite textile capable of capturing NH₃.

This design strategy may open a new avenue for the exploration of singlecrystal porous <u>polymer</u> materials with precise structural information, confined pore spaces, and straightforward solution processibility.

More information: Bai-Tong Liu et al, A solution processible singlecrystal porous organic polymer, *Nature Synthesis* (2023). <u>DOI:</u> <u>10.1038/s44160-023-00316-4</u>

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