

Press Release

For immediate release

## HKU Chemists Develop Organic Supramolecular Crystals with High Hydrogen Storage Performance Promising to Enhance the Efficiency of Fuel Cell Vehicles

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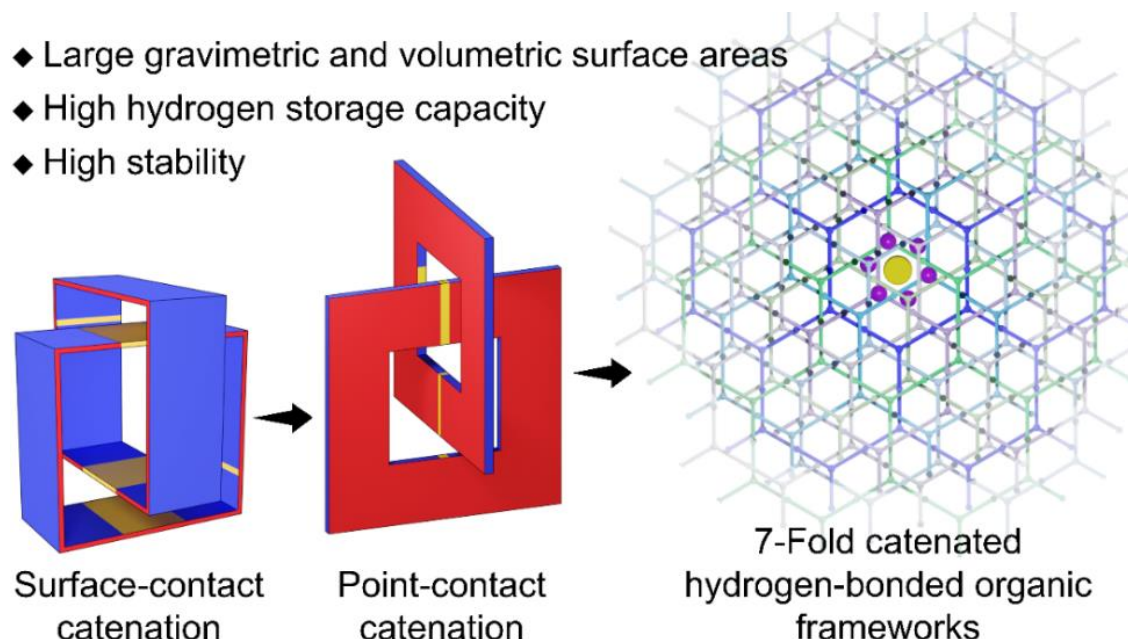


Figure 1. The control point-contact catenation strategy, guided by hydrogen bonding endows supramolecular crystals with both high volumetric and gravimetric storage capacities for hydrogen. Image adapted from Zhang et al., 2024, *Nature Chemistry*.

Hydrogen is often seen as the fuel of the future on account of its zero-emission and high gravimetric energy density, meaning it stores more energy per unit of mass compared to gasoline. Its low volumetric density, however, means it takes up a large amount of space, posing challenges for efficient storage and transport. In order to address these deficiencies, hydrogen must be compressed in tanks to 700-bar pressure, which is extremely high. This situation not only incurs high costs but also raises safety concerns.

For hydrogen-powered fuel-cell vehicles (FCVs) to become widespread, the US Department of Energy (DOE) has set specific targets for hydrogen storage systems: 6.5% of the storage material's weight should be hydrogen (gravimetric storage capacity of 6.5 wt%), and one litre of storage material should hold 50 grams of hydrogen (a volumetric storage capacity of 50 g L<sup>-1</sup>). These targets ensure that vehicles can travel reasonable distances without excessive fuel.

One promising strategy to achieve these targets is to develop porous adsorbent materials, such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and porous organic polymers (POPs). All these materials share a common feature: they possess a porous structure that allows them to effectively trap and store hydrogen gas. This approach also aims to facilitate hydrogen storage at lower pressure, such as within 100 bar.

Despite advancements in surpassing the DOE's gravimetric target, many adsorbent materials still struggle to meet volumetric capacity needs, and few can balance both volumetric and gravimetric targets. From an industrial standpoint, volumetric capacity is more crucial than gravimetric capacity, as vehicle storage tanks have limited space. A hydrogen storage system's volume directly impacts the driving range of FCVs. Therefore, developing hydrogen adsorbents that maximise volumetric capacity while maintaining excellent gravimetric capacity is essential. Achieving this goal involves balancing a high volumetric and gravimetric surface area within the same material.

Researchers are investigating various materials for hydrogen storage, with organic supramolecular crystals assembly from organic molecules through noncovalent interactions, being a promising option as a result of their recyclability. Their potential remains largely untapped, however, because designing supramolecular crystals with balanced high gravimetric and volumetric surface areas, while maintaining stability, is difficult.

A phenomenon known as catenation, which involves mechanically interlocked networks in porous materials, typically enhances stability. Catenation, however, often reduces surface area by blocking accessible surfaces, making the material less porous and generally undesirable for hydrogen storage. Efforts are usually made to minimise or avoid it.

To unlock the potential of supramolecular crystals for hydrogen storage, a collaborative research team led by Professor Fraser STODDART, along with Research Assistant Professors, Dr Chun TANG, Dr Ruihua ZHANG from the Department of Chemistry, The University of Hong Kong (HKU), and Professor Randall Snurr from the Department of Chemical and Biological Engineering, the Northwestern University, US, demonstrated a controlled 'point-contact catenation strategy'. This innovative approach uses hydrogen bonds, the cross-section of which can be seen as a 'point', rather than the traditional  $[\pi \cdots \pi]$  stacking which involves large 'surface' overlap, to guide catenation in a precise manner in supramolecular crystals. Based on this strategy, researchers create a well-organised framework that minimises surface loss caused by interpenetration and tailors the pore diameter (~1.2–1.9 nm) for optimal hydrogen storage.

As a result, the research team obtained a supramolecular crystal with record-high gravimetric ( $3526 \text{ m}^2 \text{ g}^{-1}$ ) and balanced volumetric ( $1855 \text{ m}^2 \text{ cm}^{-3}$ ) surface areas among all the reported (supra)molecular crystals, in addition to high stability, whilst (i) bringing about excellent material-level volumetric capacity ( $53.7 \text{ g L}^{-1}$ ), (ii) balancing high gravimetric capacity (9.3 wt%) for hydrogen storage under practical pressure and temperature swing conditions ( $77 \text{ K}/100 \text{ bar} \rightarrow 160 \text{ K}/5 \text{ bar}$ ), and (iii) surpassing the DOE ultimate system-level targets ( $50 \text{ g L}^{-1}$  and 6.5 wt%) both volumetrically and gravimetrically, albeit at cryogenic temperatures.

### **Innovative design**

Designing organic supramolecular crystals that balance high gravimetric and volumetric surface areas, while also maintaining high stability, is a momentous challenge, which has hindered its potential for many applications. The team, however, has proposed a point-contact catenation strategy that utilises point-contact interactions involving hydrogen bonding to minimise surface loss during catenation. This design strategy endows these supramolecular crystals with balanced high volumetric and gravimetric surface areas, high stability, and ideal pore sizes for hydrogen storage. This research unlocks the potential of organic supramolecular crystals as promising candidates for onboard hydrogen storage and highlights the potential of a directional catenation strategy in designing robust porous materials for applications.

## About the research team



Photo 2: From the left: Dr Ruihua Zhang, Professor Fraser Stoddart and Dr Chun Tang from HKU Department of Chemistry.

This research is a collaboration between Professor Fraser Stoddart and Research Assistant Professors Dr Chun Tang, Dr Ruihua Zhang from the Department of Chemistry (Faculty of Science, HKU) and Professor Randall Snurr's team from the Department of Chemical and Biological Engineering (Northwestern University, United States). Research Assistant

Professor Dr Ruihua Zhang, from Professor Stoddart's team, led the design and synthesis of the highly catenated supramolecular crystals and is the first author of the article published recently in *Nature Chemistry*. Other HKU-affiliated researchers, including Drs Han Han, Guangcheng Wu, Yong Wu and Professor Aspen X.-Y. Chen, also made contributions to this research project.

**About the research paper:** 'R. Zhang; H. Daglar; C. Tang\*; P. Li; L. Feng; H. Han; G. Wu; B. N. Limketkai; Y. Wu; S. Yang; Aspen X.-Y. Chen; C. L. Stern; C. D. Malliakas; R. Q. Snurr\*; J. F. Stoddart\*; Balancing Volumetric and Gravimetric Capacity for Hydrogen in Supramolecular Crystals. *Nature Chemistry* 2024'

The journal paper can be accessed from here: <https://www.nature.com/articles/s41557-024-01622-w>

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