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New ‘chain mail’ material of interlocking molecules is tough, flexible and easy to make

By **Robert Sanders**, Media relations | JANUARY 18, 2023

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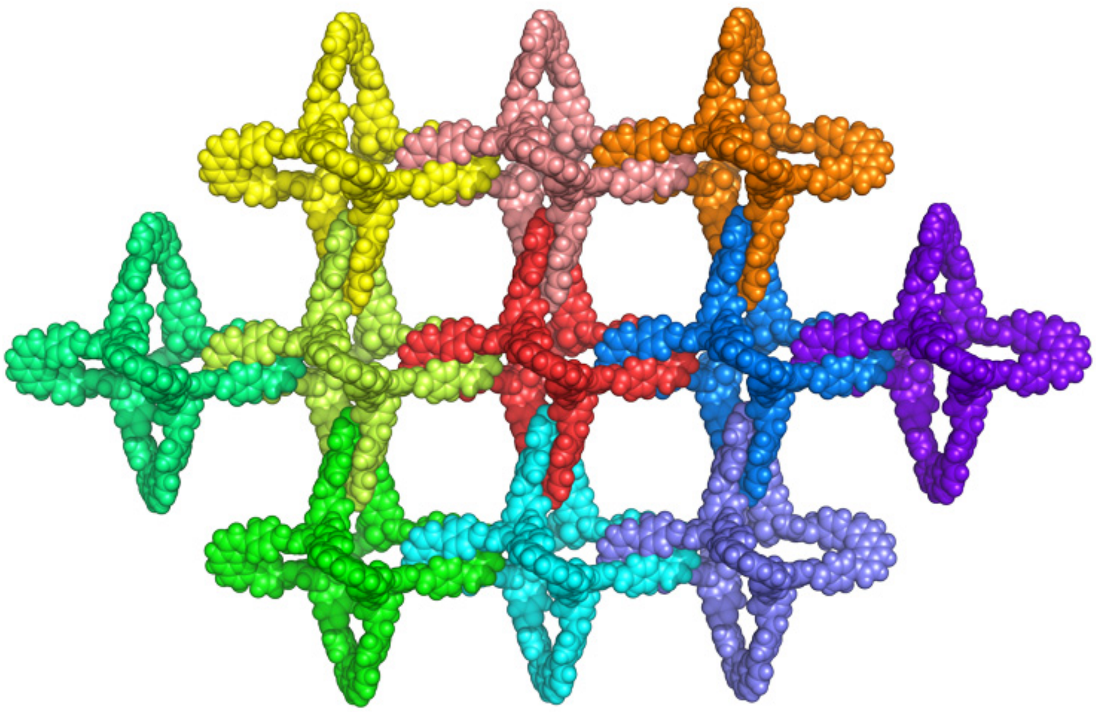


The individual building blocks of a catenane are polyhedral molecules — a type of adamantane — that link arms to form a 2D mesh or 3D network that is sturdy but flexible. (Image credit: Tianqiong Ma, UC Berkeley)

University of California, Berkeley, chemists have created a new type of material from millions of identical, interlocking molecules that for the first time allows the synthesis of extensive 2D or 3D structures that are flexible, strong and resilient, like the chain mail that protected medieval knights.

The material, called an infinite catenane, can be synthesized in a single chemical step.

French chemist Jean-Pierre Sauvage shared the 2016 Nobel Prize in Chemistry for synthesizing the first catenane — two linked rings. These structures served as the foundation for making molecular structures capable of moving, which are often referred to as molecular machines.

But the chemical synthesis of catenanes has remained laborious. Adding each additional ring to a catenane requires another round of chemical synthesis. In the 24 years since Sauvage created a two-ring catenane, chemists have achieved, at most, a mere 130 interwoven rings in quantities too small to see without an electron microscope.

The new type of catenane, produced in the laboratory of **Omar Yaghi**, UC Berkeley professor of chemistry, can be produced with an unlimited number of linked units in three dimensions. Because the individual units interlock mechanically and are not connected by chemical bonds, the structures can be flexed without breaking.

“We think that this has really important implications, not just in terms of making tough materials that don’t fracture, but also materials that would go into robotics and aerospace and armored suits and things like this,” said Yaghi, the James and Neeltje Tretter Chair Professor of Chemistry, co-director of the **Kavli Energy NanoSciences Institute** and the **California Research Alliance by BASF**, and chief scientist at UC Berkeley’s Bakar Institute of Digital Materials for the Planet.

Yaghi and his colleagues, including first author Tianqiong Ma, a UC Berkeley postdoctoral fellow, reported **details of the chemical process** this week in the journal *Nature Synthesis*.

Reticular chemistry

The leap forward in catenane production is possible using a type of chemistry that Yaghi invented more than 30 years ago: reticular chemistry. He describes it as “stitching molecular building blocks into crystalline, extended structures by strong bonds.”

Molecular 3D chainmail COFs

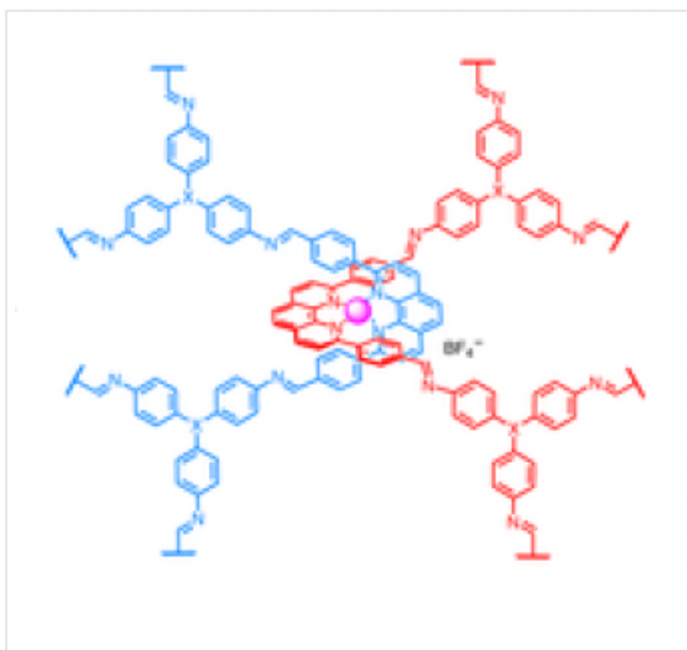
separating gases such as carbon dioxide, hydrogen and water vapor. More than 100,000 varieties of MOFs have been made to date.

To make MOFs, it’s necessary only to synthesize the right hybrid molecules — metal clusters connected to an organic ligand — and mix them in a solution so that they link up to form a rigid and highly porous 3D network. The chemical groups inside the framework are chosen to bind and release — depending on temperature — specific molecules and reject others.

One MOF that Yaghi created can pull water from even the driest air and then release it when heated, allowing water capture in deserts.

To make catenanes, Yaghi and Ma synthesized a molecule with a crossing between two identical halves, covalently linked by a copper atom. The structure, what they call a catena-COF, is reminiscent of two linked boomerangs with a copper atom where they cross. When mixed, these molecules link up to form a porous 3D network of interlocking building blocks. The building blocks, a type of polyhedral molecule called adamantane, essentially lock their six arms to form an extended framework.

“What’s new here is that the building units have these crossings, and because of the crossings, you get interlocking systems that have interesting, flexible and resilient properties,” Yaghi said. “They’re programed to come together in one step. That’s the power of reticular chemistry. Instead of building them up one unit at a time to make the larger structure, you actually have them programmed such that they come together and grow on their own.”



The molecule with a crossing can be chemically altered so that the final catenane interacts with specific compounds. Yaghi calls these materials (∞) catenanes, using the symbol for infinity.

The building block of an infinite catenane, or catena-COF, consists of two crossed molecules with a copper atom at the center. When mixed, they link up to create an extended, 3D material of interlocking molecules.

"I think that is a first step towards making materials that can flex and potentially can stiffen in response to stimuli, like a particular motion," he said. "So, in certain orientations, it could be very flexible, and in certain other orientations, it could become stiff, just because of the way the structure is built."

He noted that while these catenanes extend in three directions on a microscopic level, they can be made thin enough for two dimensional uses, as in clothing. Recently, some scientists have reported that they have created MOFs and COFs by 3D printing, so it may be possible to 3D print catenanes, as well, much like weaving a cloth.

"Traditionally, this interlocking has been done through a multistep, arduous process to make only molecules that have one or two or three interlocking rings, or polyhedra. But to make materials that have amazing properties, like toughness and resiliency, you need millions and millions of these interlockings to be made," he said. "The traditional way of making them just doesn't cut it. And reticular chemistry comes in with the building block approach and finds a way of doing it in one step. That's really the power of this report."

The work was partly supported by King Abdulaziz City for Science and Technology and the Defense Advanced Research Projects Agency (DARPA, HR001-119-S-0048). The researchers used resources of the Advanced Light Source at Lawrence Berkeley National Laboratory (DOE DE-AC02-05CH11231).

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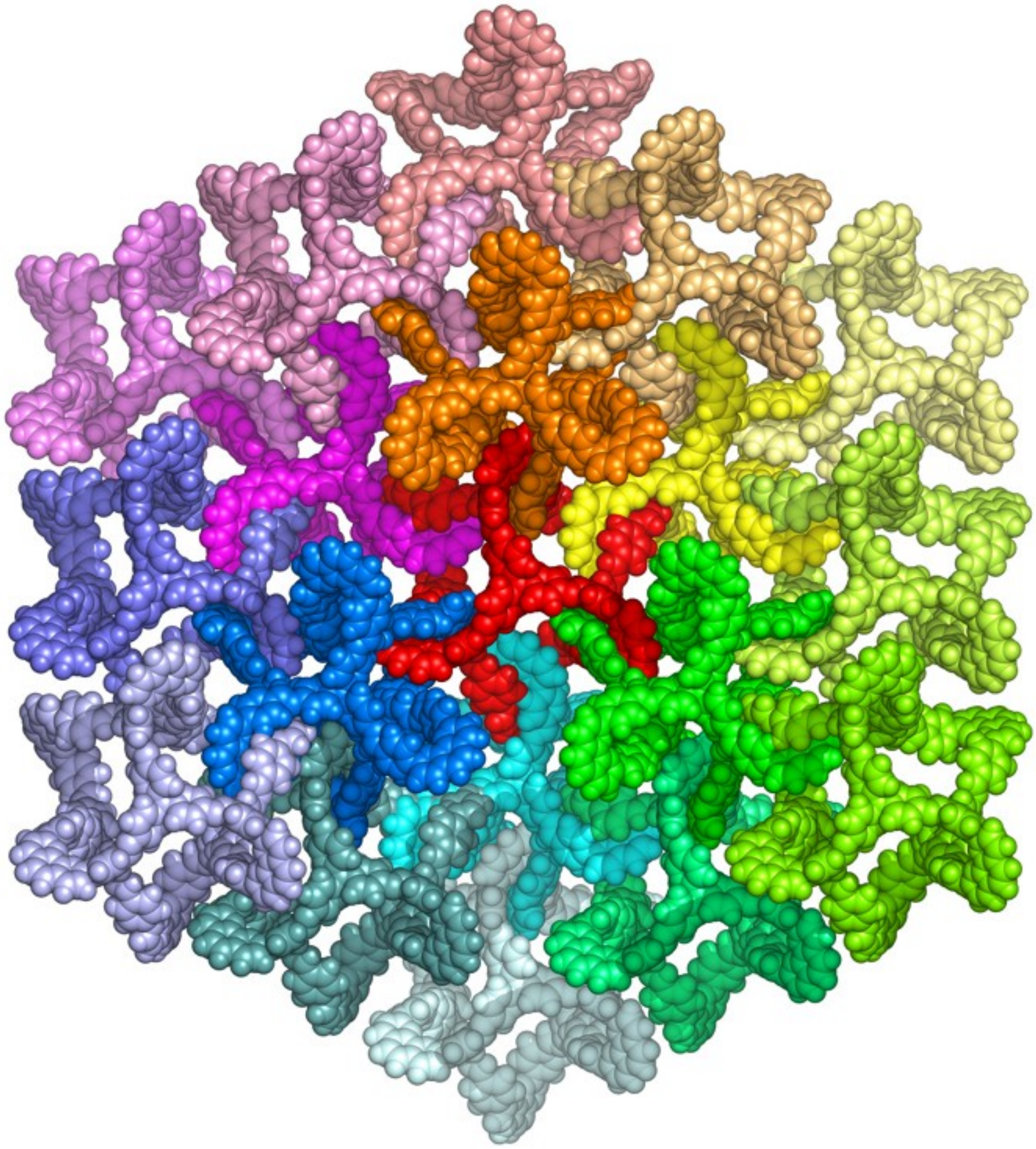
METAL-ORGANIC FRAMEWORKS

Chain-link molecules form flexible networks

Catenated covalent organic frameworks could find use as additives or membranes

by ***Mark Peplow, special to C&EN***

January 17, 2023



Credit: ***Nat. Synth.***

The new covalent organic framework's building blocks form an interlinked network that is soft and flexible. Different colors identify individual blocks.

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Covalent organic frameworks (COFs) are **porous lattices** that are finding uses in gas storage, **water filtration**, and catalysis. Now, researchers led by Omar Yaghi at the University of California, Berkeley, have built a new breed of COFs from interlocking molecules called catenanes, which hang together like chain links in a 3D network (*Nat. Synth.* 2023, DOI: **10.1038/s44160-022-00224-z**). “This physical interlocking allows materials to absorb the energy from stress,” Yaghi says, adding that this feature might make such COFs useful as materials additives.

The researchers built their catenane COFs by condensing Y-shaped triamines with aldehyde-bearing molecules coordinated around a copper(I) ion. The geometry of these precursors ensures that they form organic polyhedra with three fused rings, a shape similar to the structure of the compound adamantane. Each polyhedron is more than 3 nm wide and interlocks with six of its neighbors to form an extensive network containing millions of polyhedra.

Using aqueous potassium cyanide to wash out the copper template ions frees the polyhedra to **move around** without actually separating from one another. That makes the COFs soft and flexible, potentially attractive properties in applications as diverse as filtration membranes and soft robotics. The motion of the interlocking parts also means that the COF’s pores can stretch to accommodate incoming guest molecules “almost like an enzyme adapting its active site to a substrate,” Yaghi says.

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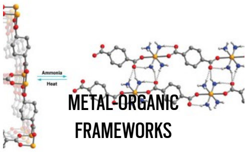

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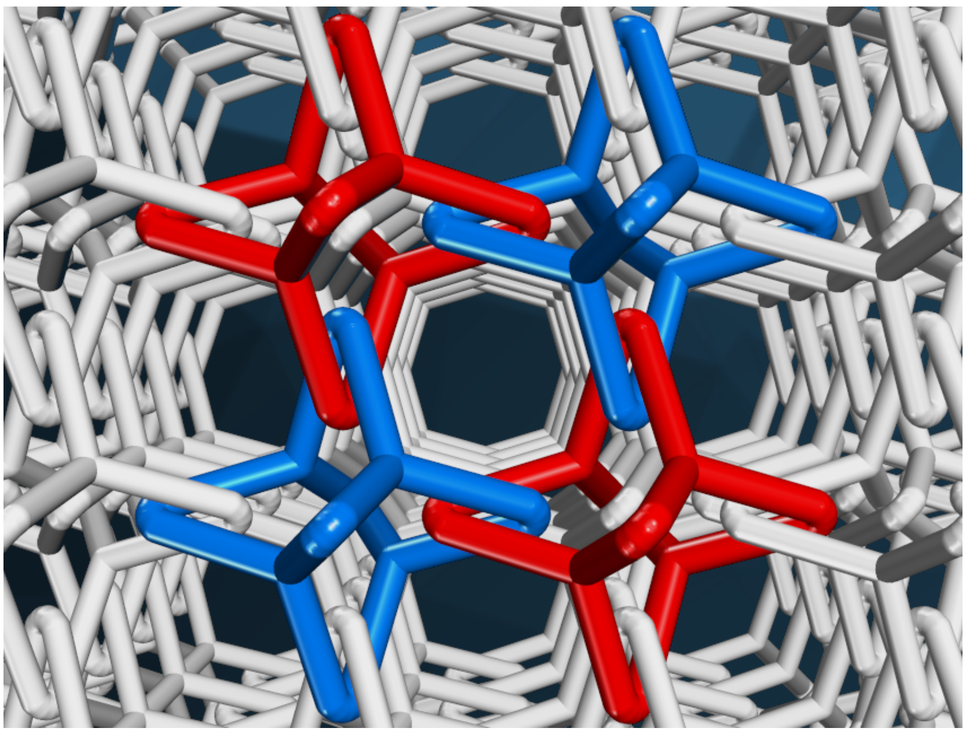

Author: ChemistryViews
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NEWS

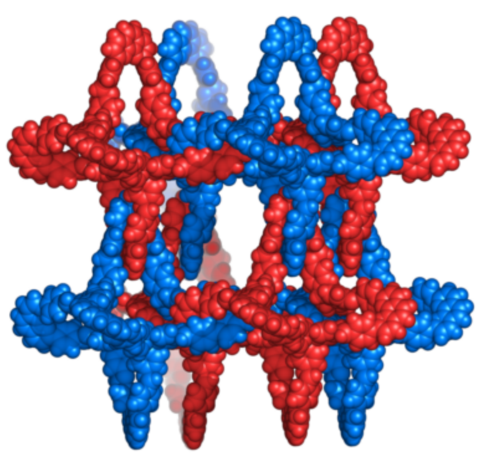
Molecular Chainmail

Catenanes are mechanically-interlocked structures with two or more interlocking rings that have potential, e.g, as molecular machines. However, building molecular structures with very large numbers of interlocking rings, as for example in a chainmail-like structure, is a challenge. To achieve this, many rings must interlock in a precise, concerted fashion, and in an ordered arrangement. A potentially useful approach to tackling this challenge is reticular chemistry. In reticular chemistry, instead of building chemical structures one molecule at a time, extended structures such as metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) are generated in a one-step reaction using molecular building blocks.

Omar M. Yaghi, University of California, Berkeley, and Kavli Energy NanoScience Institute, Berkeley, CA, USA, and colleagues have used reticular chemistry to create 3D chainmail structures composed of millions of interlocking polyhedra (simplified structure pictured above). They call these catenated covalent organic frameworks "infinite" catenanes ([∞]catenanes). In the product, each polyhedron is interlocked with six others, creating an extended 3D chainmail.

Catena-COFs

The team first conceptually dissected the target chainmail structure into its most fundamental units. Molecular building blocks with the desired shapes were then linked together using established imine reactions. The team linked Cu(I)-bis[4,4′-(1,10-phenanthroline-2,9-diyl)dibenzaldehyde]tetrafluoroborate ($[Cu(PDB)_2]BF_4$) with tris-(4-aminophenyl)amine (TAPA), tris-(4-aminophenyl)methane (TAPM), or tris-(4-aminophenyl)methanol (TAPMol). The copper ions were used to coordinate two PDB units each, with the four aldehyde groups pre-organized in a roughly tetrahedral arrangement. The condensation reactions with the employed amine linkers then gave the desired interlocked, adamantane-like polyhedra (example of a partial structure pictured below, colors used to make the discrete polyhedra easier to see).



The team achieved postsynthetic removal of the copper(I) ions (up to 90 %) by adding aqueous KCN to obtain the corresponding COF. The researchers anticipate that such interlocking structures could be useful in flexible materials that retain their robustness and resilience. This could have applications, e.g., in soft robotics, bullet-proof structures, or materials that require stiffening on demand.

- Catenated covalent organic frameworks constructed from polyhedra,
  Tianqiong Ma, Yi Zhou, Christian S. Diercks, Junpyo Kwon, Felipe Gándara, Hao Lyu, Nikita Hanikel, Pilar Pena-Sánchez, Yuzhong Liu, Nicolas J. Diercks, Robert O. Ritchie, Davide M. Proserpio, Osamu Terasaki, Omar M. Yaghi,
  Nat. Synth. **2023**.
  https://doi.org/10.1038/s44160-022-00224-z

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Chemical chainmail constructed from interlocked coordination polymers

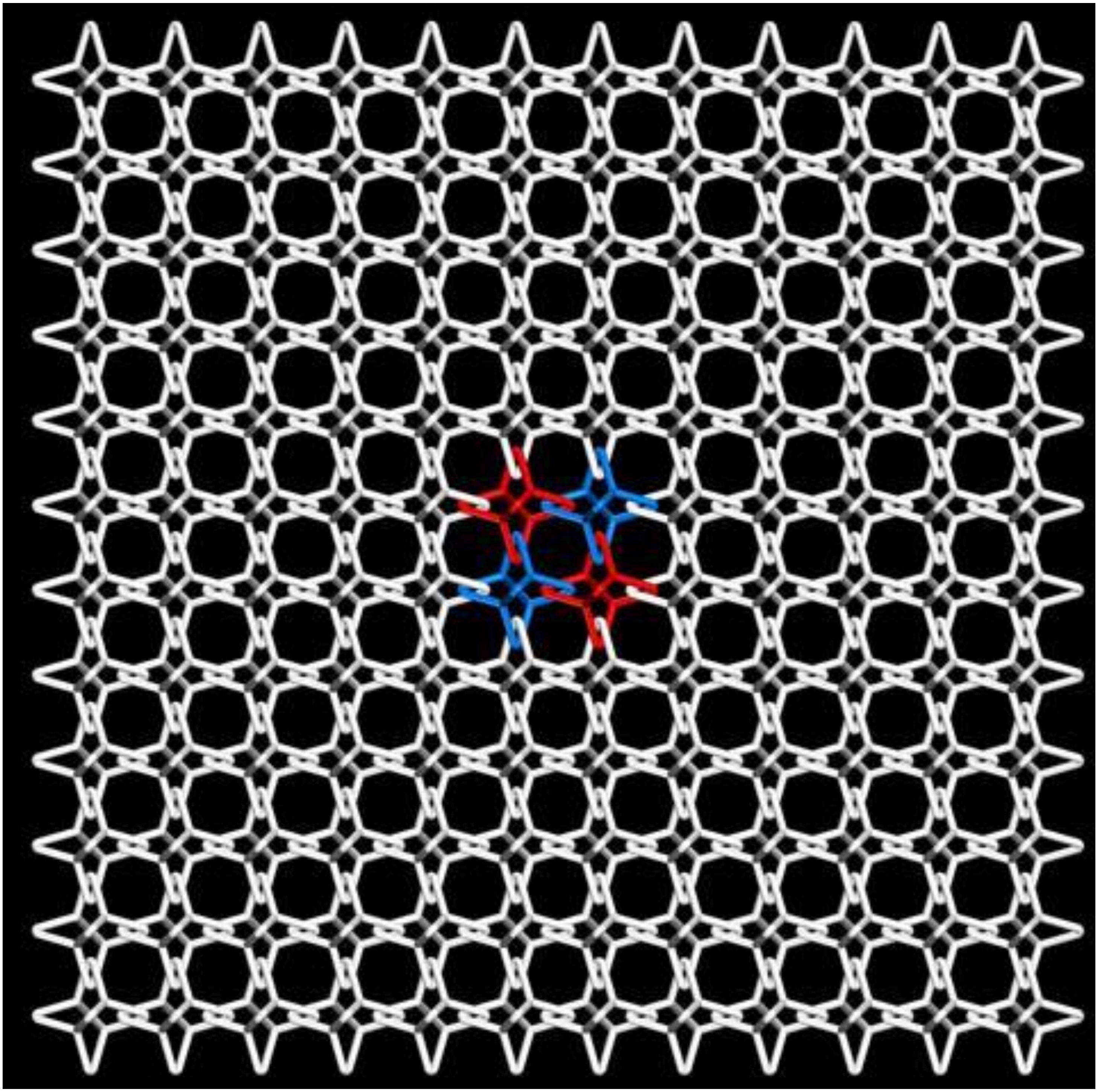
BY FERNANDO GOMOLLÓN-BEL | 27 JANUARY 2023

Interlocked molecules have entered a new dimension. Researchers have synthesised an 'infinite three-dimensional catenane' by constructing concatenated covalent–organic frameworks (COFs). This chemical chainmail is extraordinarily flexible and resilient, which could lead to applications in materials science and synthetic biology.

'Chemists have always thrived on controlling atoms and molecules to create larger structures with new properties,' says lead author Omar Yaghi, from the University of California Berkeley. 'This is the first example of a three-dimensional interlocked COF structure,' he says. The perfect crystalline structure of the material means the interlocking is homogeneous and uninterrupted throughout the network. 'On a molecular level, molecular interlocking allows many degrees of freedom, a mechanism to dissipate energy such as external stress,' continues Yaghi. Therefore, the COF chemical chainmail exhibits extreme flexibility, yet it's almost unbreakable.

The COF is prepared following a building blocks approach, originally developed in the field of reticular chemistry. 'This strategy offers designability and a simple methodology to yield complex structures,' says Yaghi. After identifying the right molecular geometries for the chemical chainmail, researchers functionalised them with moieties that easily react with one another – in this particular case aldehydes and amides, which condense into imine bonds.

Leslie Hamachi, an expert in COFs based at California Polytechnical State University, who wasn't involved in the study, explains this is 'the first interlocked chainmail with repeating linked rings'. Although previous papers reported other interpenetrated structures, such as chains and woven threads, 'a three-dimensional extended crystallite' had never before been achieved. 'New topologies – ways to intertwine the material – lead to different mechanical properties,' she adds.



Source: © Omar Yaghi et al

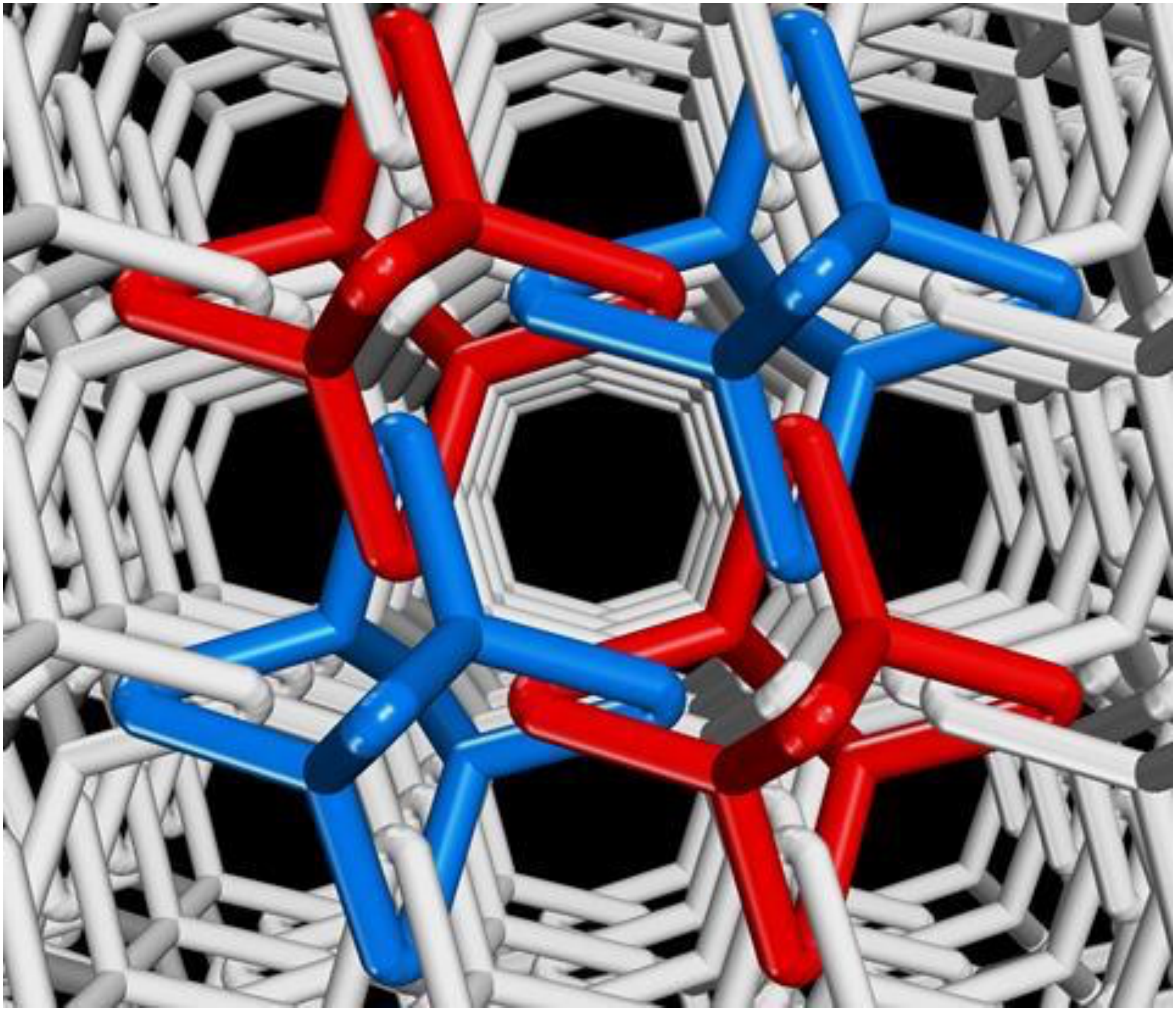
The chemical chainmail's interlinked structure makes it exceptionally strong

Moreover, the synthesis is really straightforward, despite the complexity of the catenated COF. 'Two molecules come together, after mixing them with a catalyst in a liquid solvent and applying heat,' says

Source: Omar Yaghi et al

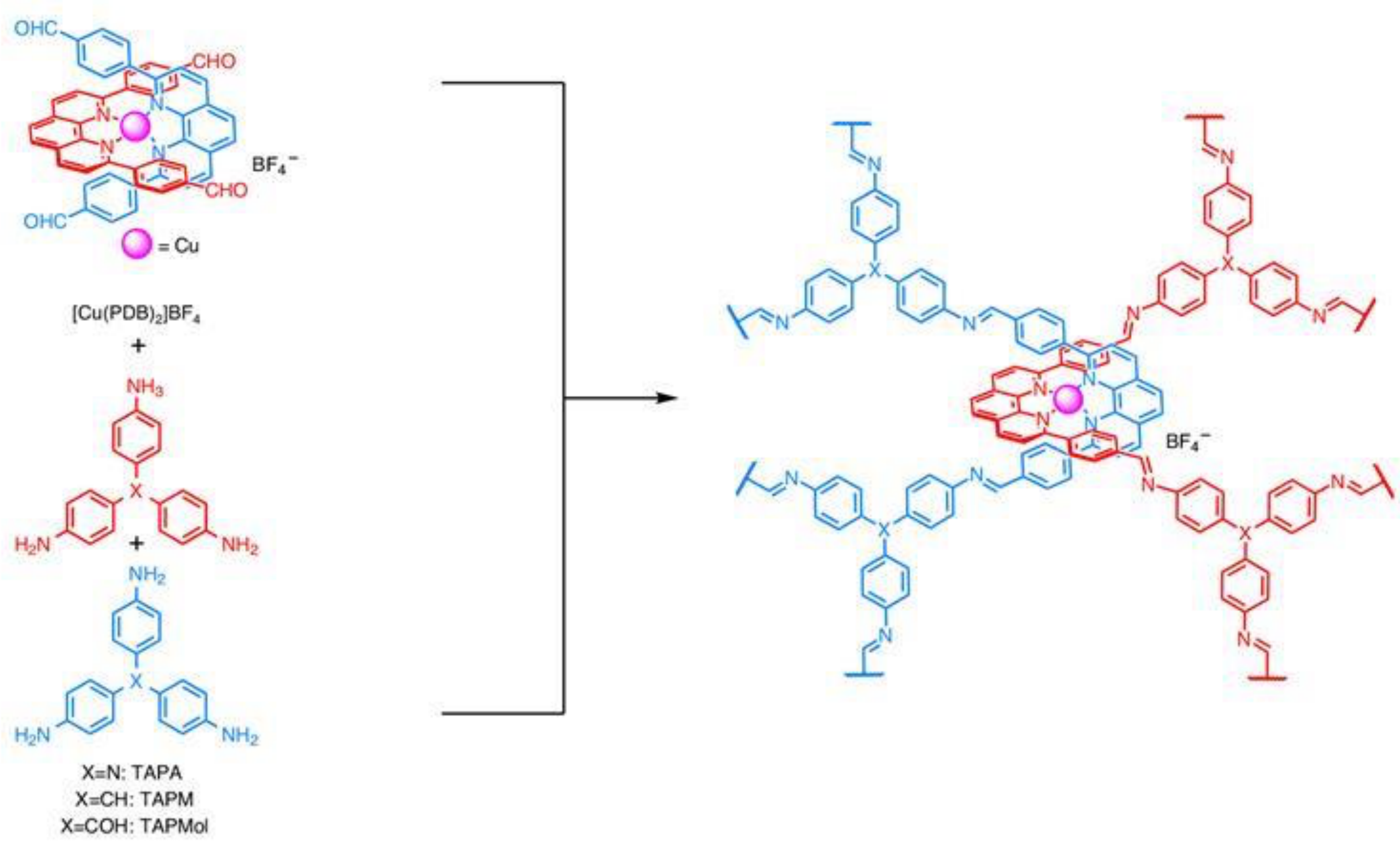
Hamachi. 'After some days, the material forms as a solid at the bottom of the container.' One of the precursors was prepared specifically for this reaction, however 'the others are commercially available', she explains. This will facilitate further research into this type of interlocked structures.

The biggest challenge, according to Yaghi, was finding the right conditions. 'We've been addressing this since the discovery and development of the first COFs in our lab, back in 2005,' he says. Furthermore, the team needed building blocks with the exact 'embracing' parts and pieces, otherwise the resulting structure wouldn't lock together in an infinite pattern of chain links. 'Now, we create high complexity constructions, containing millions and millions of interlocking polyhedra in only one step,' adds Yaghi.



Source: © Omar Yaghi et al

The linking of the COF units takes place above and below the plane of the structure to create a truly 3D connected material



Source: © Tianqiong Ma et al/Springer Nature Limited 2023

Synthetic strategy used to build the 3D interlinked COF

Beyond the applications in materials science, researchers dream of applications in synthetic biology. Viruses, for example, have capsids with interlocking rings that adapt to different cargo sizes, expanding and shrinking accordingly. Chainmail COFs could provide an alternative for molecular vessels and drug delivery. Other applications could emerge in the field of biomaterials. 'The resilient flexibility of the COF chainmails could find uses in artificial muscles, skin and cartilage,' explains Yaghi.

References

T Ma *et al*, *Nat. Synth.*, 2023, DOI: 10.1038/s44160-022-00224-z