

MATERIALS CHEMISTRY

Interlacing molecular threads

Materials with a fabric-like microstructure are highly elastic

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The synthesis of organic materials has typically involved linking one or more types of discrete molecular building blocks to produce structures that are extended in three dimensions. For example, repeated addition of monomers results in the formation of organic polymers that have randomly packed structures and therefore form amorphous solid materials. If the building blocks repeat in an ordered sequence, crystalline solids are formed. The properties of the resulting solids are intimately related to both their network structure and their chemical components. On page 365 of this issue, Liu *et al.* report a material that has a fabric-like woven microstructure, giving it exceptional flexibility (1).

through strong covalent bonds (4). COFs are promising materials for storing gases such as hydrogen or methane and for use as catalysts and in optoelectronic applications.

However, these materials are all built through rigid, directional bonds between their components, restricting the range of their mechanical and elastic characteristics. Liu *et al.* now report the synthesis of COF materials from molecular threads (1). These threads are woven without chemical bonds between them, creating a structure in which molecular chains can slide past each other easily. The formation of materials from interlaced threads has long been sought because such solids are expected to have mechanical and other properties different from those of traditional materials (5). However, although there are many examples of materials that

will be woven. The threads are extended by linking the thread-starting molecules with complementary linear molecules via imine bonds (a methodology extensively used in COF chemistry), resulting in a crystalline, open, extended structure denoted COF-505.

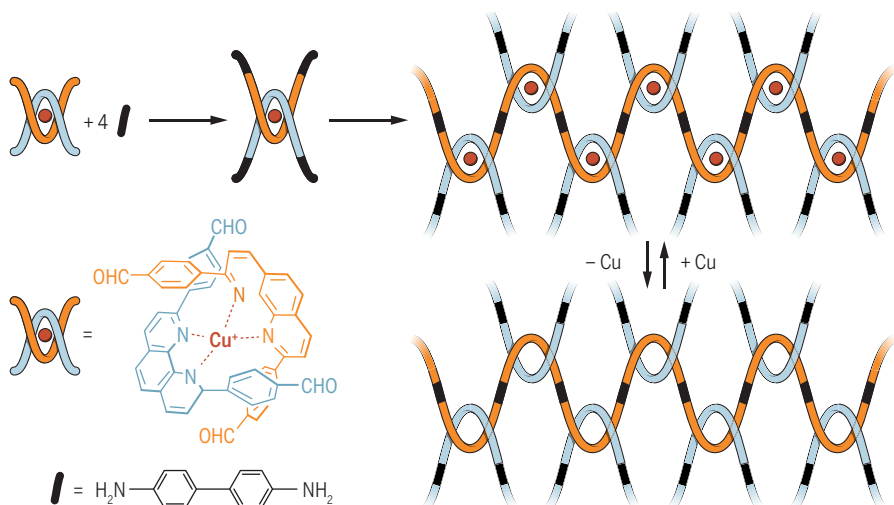
The copper cations can be easily removed, releasing the organic threads and providing them with a large degree of freedom (resulting in a loss of crystallinity). Upon elimination of the metal cations, the material undergoes a 10-fold increase in elasticity. The demetalation process is reversible, causing the solid to return to its previous crystalline state (see the figure). It is thus possible to modify the material's elastic properties through a simple process of metal complexation/decomplexation.

This synthetic approach based on the use of (removable) metal centers is comparable to the template synthesis of molecular rotaxanes, catenanes, and other materials based on interlocked rings (6, 7). Nonetheless, COF-505 is very different from other materials with interpenetrated structures: Once the metal centers are removed, there are no interlocked rings in the structure. The material is exclusively made of interlaced molecular organic threads, similar to a woven fabric (see the figure), conferring it with unique flexibility as well as dynamic and elastic properties. These properties may, for example, be useful for designing materials that can transmit mechanical stimuli in a highly controllable chemical environment or in high-pressure applications that require materials capable of absorbing impacts or of deforming reversibly while preserving their chemical and structural integrity.

It should be possible to control the elasticity of COF-505 and of future related solids and to combine it with other properties already displayed by porous COFs. In addition, it may be possible to remetalate with cations other than copper, including catalytically active cations. This would extend the scope of these materials to many more chemical applications, for example, in catalysis, providing flexible reactive microenvironments. The materials may also find application as responsive molecular sponges—for example, for the sequestration of metal cations in liquid wastes. ■

REFERENCES

1. Y. Liu *et al.*, *Science* **351**, 365 (2016).
2. H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **341**, 1230444 (2013).
3. P. J. Waller, F. Gándara, O. M. Yaghi, *Acc. Chem. Res.* **10.1021/acs.accounts.5b00369** (2015).
4. H. M. El-Kaderi *et al.*, *Science* **316**, 268 (2007).
5. R. C. Ball, M. Doi, F. F. Edwards, M. Warner, *Polymer* **22**, 1010 (1981).
6. A. I. Prikhod'ko, F. Durolo, J.-P. Sauvage, *J. Am. Chem. Soc.* **130**, 448 (2008).
7. E. V. Alexandrov, V. A. Blatov, D. M. Proserpio, *Acta Cryst. A* **68**, 484 (2012).



Molecular weaving. In a traditional COF material, organic building units are linked through covalent bonds to create rigid crystalline materials. Liu *et al.* report a COF material made from molecular threads that are connected through copper complexes. Removal of the copper ions results in a highly flexible and elastic material. This process is reversible.

A range of crystalline materials can be made by modifying or controlling the building units, resulting in materials with desired properties, such as high porosity, conductivity, and catalytic activity. Metal-organic frameworks (MOFs) (2) and covalent organic frameworks (COFs) (3) are two highly versatile classes of such materials. MOFs are constructed by joining inorganic clusters via organic linkers through coordination bonds; COFs consist of organic building units linked

contain molecular chains, synthetic chemists had not previously found a way to interlace chains in a controlled manner.

To create such interlaced materials, Liu *et al.* rely on the synthesis of COFs to form crystalline materials with covalently bound organic molecules. The novel aspect is the selection of a Cu(I) complex as one building unit. This complex contains two identical molecules that are the starting point of independent threads in the COF. The metal cations act as templates that hold each thread-starting molecule in the correct position. Thus, the position of the metal centers precisely defines the points where the threads

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