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XPS (Fig. 3). The additional proton then reacts with the adsorbed OH to form H_2O ("E" in Fig. 5). In the 2 + 2–electron pathway, H_2O_2 is formed by reaction of the adsorbed OOH species with another proton ("F" in Fig. 5), followed by readsorption of H_2O_2 and its reduction by two protons to generate H_2O. The OH species detected in the post-ORR XPS measurement may arise from the four-electron mechanism, but it is also possible that the OH species next to the pyridinic N may arise from the reaction with H_2O_2 in the 2 + 2–electron mechanism. In either pathway, the carbon atoms next to pyridinic N with Lewis basicity play an important role as the active sites at which oxygen molecules are adsorbed as the initial step of the ORR.

In summary, we have demonstrated that pyridinic N in nitrogen-doped graphitic carbons creates the active sites for ORR under acidic conditions, based on studies of HOPG model catalysts and N-GNS powder catalysts. Carbon atoms next to pyridinic N are suggested to be the active sites with Lewis basicity at which O_2 molecules are adsorbed as the initial step of the ORR.

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SUPPLEMENTARY MATERIALS

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MOLECULAR FRAMEWORKS

Weaving of organic threads into a crystalline covalent organic framework

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A three-dimensional covalent organic framework (COF-505) constructed from helical organic threads, designed to be mutually weaving at regular intervals, has been synthesized by imine condensation reactions of aldehyde functionalized copper(I)-bisphenanthroline tetrafluoroborate, $Cu(PDB)_2(BF_4)$, and benzidine (BZ). The copper centers are topologically independent of the weaving within the COF structure and serve as templates for bringing the threads into a woven pattern rather than the more commonly observed parallel arrangement. The copper(I) ions can be reversibly removed and added without loss of the COF structure, for which a tenfold increase in elasticity accompanies its demetalation. The threads in COF-505 have many degrees of freedom for enormous deviations to take place between them, throughout the material, without undoing the weaving of the overall structure.

Weaving, the mutual interlacing of long threads, is one of the oldest and most enduring methods of making fabric, but this important design concept has yet to be emulated in extended chemical structures. Learning how to link molecular building units by strong bonds through reticular synthesis (*1*) into weaving forms would be a boon to making materials with exceptional mechanical properties and dynamics. To successfully design weaving of chains into two- and three-dimensional (2D and 3D) chemical structures (Fig. 1, A and B), long threads of covalently linked molecules (i.e., 1D units) must be able to cross at regular intervals. It would also be desirable if such crossings serve as points of registry, so that the threads can have many degrees of freedom to move away from and back to such points without collapsing the overall structure. Structures have been made by weaving metal-organic chains (*2*), but designing well-defined materials and assembling their structures by weaving is challenging, and weaving in crystalline inorganic or covalent organic extended structures is undeveloped.

We report on a general strategy and its implementation for the designed synthesis of a woven material [covalent organic framework-505 (COF-505)]. This COF has helical organic threads interlacing to make a weaving crystal structure with the basic topology of Fig. 1B, and we show that this material has an unusual behavior in elasticity. Although terms such as interweaving (*3*), polycatenated (*2*), and interpenetrating (*4*–*6*) have been used to describe interlocking of 2D and 3D extended objects (Fig. 1, C and D), most commonly found in MOFs, we reserve the term "weaving" to describe exclusively the interlacing of 1D units to make 2D and 3D structures (Fig. 1, A and B). Weaving differs from the commonly observed interpenetrating and polycatenated frameworks because the latter are topologically interlocking

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(i.e., interlocking rings) (Fig. 1, C and D, insets), whereas the weaving constructs that we envision have many more degrees of freedom for enormous spatial deviations, by each of the threads, to take place independently and still preserve the underlying topology. Such freedom may enable reversible control over the mechanical properties of materials.

Our synthetic strategy is shown in Fig. 2, where we start with the aldehyde functionalized derivative of the well-known complex salt Cu(I)-bis[4,4'-(1,10-phenanthroline-2,9-diyl)dibenzaldehyde] tetrafluoroborate, Cu(PDB)$_2$(BF$_4$) (Fig. 2A). The position of the aldehyde groups approximates a tetrahedral geometry and can be used in reticular synthesis as a building block to be linked with benzidine (BZ) and make an imine-bonded PDB-BZ threads weaving arrangement, with the tetrafluoroborate anions occupying the pores (Fig. 2B). The orientation of the PDB units in a mutually interlacing fashion ensures that the threads produced from linking the building units are entirely independent, with the Cu(I) ions serving as templates (points of registry) to bring those threads together in a precise manner at well-defined intervals. Because the PDB-BZ threads are topologically independent of the Cu(I) ions, the resulting woven structure is formally a COF (termed COF-505). The overall tetrahedral geometry of the aldehyde units ensures the assembly of the threads into a 3D framework (Fig. 2B). The topology of this framework is that of diamond, as expected from the principles of reticular chemistry (*1*). We show that when we remove the Cu(I) ions, the structure and its topology remain intact regardless of how the threads deviate from their points of registry, and upon remetalating, the overall structure is reversibly restored. We find a tenfold increase in elasticity when going from the metalated to the demetalated forms of the material.

The copper(I)-bisphenanthroline core of the Cu(PDB)$_2$ (without the aldehyde functionality) has been studied extensively as a discrete molecule for the formation of supramolecular complexes (*7*–*9*); however, as yet it has not been used to make extended structures, especially of the type discussed here. The tolerance for robust reaction conditions (*7*, *10*) makes this complex suitable for imine COF synthesis, especially in weak acidic conditions. Thus, the tetrahedral building unit, Cu(PDB)$_2$, was designed bearing aldehyde groups in the para positions of the two phenyl substituents (Fig. 2A). The synthesis of Cu(PDB)$_2$(BF$_4$) molecular complex was carried out by air-free Cu(I) complexation of 4,4'-(1,10-phenanthroline-2,9-diyl)dibenzaldehyde, according to a previously reported procedure (*11*). The single-crystal structure of this complex revealed a distorted tetrahedral geometry around the Cu(I) center, with a dihedral angle of 57° between the two phenanthroline planes. This distortion likely arises from the π-π interaction between the phenanthroline and neighboring phenyl planes (*12*, *13*).

We synthesized COF-505 via imine condensation reactions by combining a mixture of Cu(PDB)$_2$(BF$_4$) (15 mg, 0.016 mmol) and BZ (6.0 mg, 0.032 mmol) in tetrahydrofuran (THF, 1 mL) and aqueous acetic acid (6 mol/L, 100 μL). The reaction mixture was sealed in a Pyrex tube and heated at 120°C for 3 days. The resulting precipitate was collected by centrifugation, washed with anhydrous THF, and then evacuated at 120°C for 12 hours to yield 18.7 mg [94.4%, based on Cu(PDB)$_2$(BF$_4$)] of a dark brown crystalline solid (COF-505), which was insoluble in common polar and nonpolar organic solvents.

Fourier-transform infrared spectroscopy (FT-IR) and solid-state nuclear magnetic resonance (NMR) spectroscopy studies were performed on COF-505 to confirm the formation of imine linkages. A molecular analog of COF-505 fragment, Cu(I)-bis[(1,10-phenanthroline-2,9-diyl)bis(phenylene)bis(biphenyl)methanimine)] tetrafluoroborate, Cu(PBM)$_2$(BF$_4$), was used as a model compound and synthesized by condensation of Cu(PDB)$_2$(BF$_4$) and 4-aminobiphenyl (*12*). The FT-IR spectrum of COF-505 shows peaks at 1621 and 1196 cm^{-1} [1622 and 1197 cm^{-1} for Cu(PBM)$_2$(BF$_4$)], which are characteristic C=N stretching modes for imine bonds (*14*, *15*). Furthermore, the ^{13}C cross-polarization with magic-angle spinning (CPMAS) solid-state NMR spectrum acquired for COF-505 displays a series of peaks from 140 to 160 part per million, similar in shape and occurring at chemical shifts characteristic of those expected for C=N double bonds. To differentiate imine bonds from C=N double bonds of the phenanthroline unit, a cross-polarization and polarization inversion (CPPI) technique was applied, which leaves the signal for quaternary ^{13}C groups unchanged, whereas the residual tertiary ^{13}CH signal should approach zero (*16*). The decreased intensity of the ^{13}CH signal under these conditions confirmed the existence of imine CH=N double bond. Overall, these observations served as initial confirmation of having covalently linked imine extended threads in COF-505.

Before determining the single-crystal structure of COF-505, we studied the morphology and purity of the as-synthesized material. We found, using scanning electron microscopy (SEM), crystallites of ~200 nm are aggregated into spheres of 2 μm in diameter (Fig. 3A), which possibly arises from weak interactions of the synthesized material with the solvent, THF. No other phase was observed from SEM images taken throughout the material (*12*).

A single submicrometer-sized crystal (Fig. 3B) from this sample was studied by 3D electron diffraction tomography (3D-EDT) (*17*–*19*). One EDT data set was collected from the COF-505 (Fig. 3C) by combining specimen tilt and electron-beam tilt in the range of –41.3° to +69.1° with a beam-tilt step of 0.2°. From the acquired data set, 3D reciprocal lattice of COF-505 was constructed that was identified as a *C*-centered orthorhombic Bravais lattice. The unit-cell parameters were a = 18.9 Å, b = 21.3 Å, c = 30.8 Å, and V = 12399 Å^3, which were used to index reflections observed in both powder x-ray diffraction (PXRD) pattern and Fourier diffractograms of high-resolution transmission electron microscopy (HRTEM) images (Fig. 3D to F). The unit-cell parameters were further refined to be a = 18.6 Å, b = 21.4 Å, c = 30.2 Å, and V = 12021 Å^3 by Pawley refinement of PXRD pattern (Fig. 3G). The observed reflection conditions were summarized as hkl: $h+k = 2n$; $hk0$: $h,k = 2n$; $h0l$: $h = 2n$; and $0kl$: $k = 2n$, which suggests five possible space groups—*Cm2a* (no. 39), *Cmma* (no. 67), *Cmca* (no. 64), *Cc2a* (no. 41), and *Ccca* (no. 68). Three of them—*Cm2a*, *Cmma*, and *Ccca*—were excluded because their projected plane group symmetries along [1-10] did not coincide with that of the HRTEM image, *pgg* (Fig. 3E). Furthermore, by performing Fourier analysis of the HRTEM images and imposing symmetry to the reflections, Cu(I) positions were

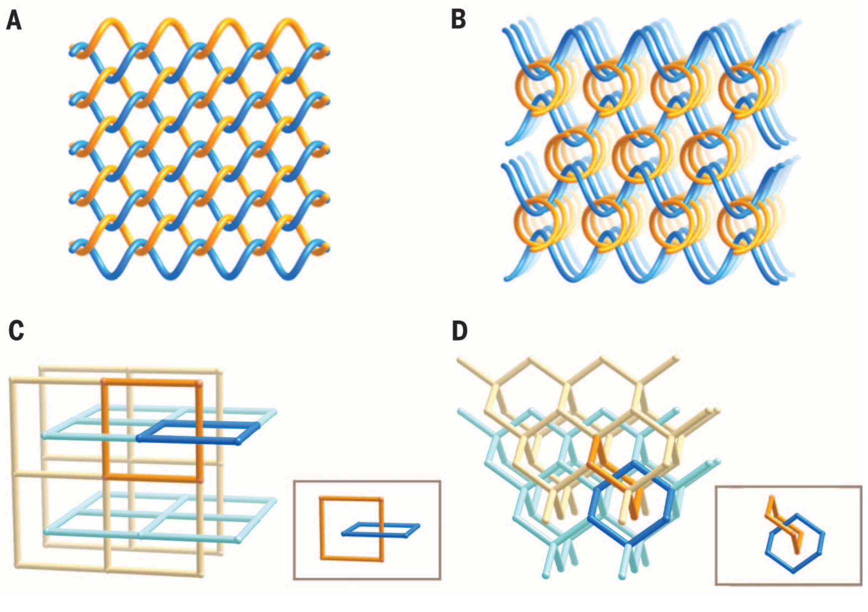

Fig. 1. Weaving and entanglement. Illustrations of weaving of threads in two (**A**) and three (**B**) dimensions, compared with entanglements of sheets (**C**), 3D arrangements (**D**), and their interlocking of rings (insets).

determined from the reconstructed 3D potential map (Fig. 3F). The structure of COF-505 was built in Materials Studio by putting Cu(PDB)$_2$ units at copper positions and connecting them through biphenyl (reacted BZ) molecules. The chemical compositions were determined by elemental analysis; therefore, once the number of copper atoms in one unit cell was obtained, the numbers of other elements in one unit cell were also determined, which indicates that the unit-cell framework is constructed by 8 Cu(PDB)$_2$ and 16 biphenyl units. However, symmetry operations of the space group *Cmca* require two PDB units connected to one copper onto a mirror plane perpendicular to *a* axis, which is not energetically favorable geometry. The final space group determined, *Cc*2*a*, was used to build and optimize a structure model. The PXRD pattern calculated from this model is consistent with the experimental pattern of activated COF-505 (*12*).

According to the refined model, COF-505 crystallizes in a diamond (**dia**) network with the distorted tetrahedral building units Cu(PBD)$_2$ and biphenyl linkers BZ linked through trans imine bonds. As a result, covalently linked adamantane-like cages 19 by 21 by 64 Å are obtained and elongated along the *c* axis (dimensions are calculated based on Cu-to-Cu distances). This size allows two diamond networks of identical frameworks to form the crystal. These frameworks are mutually interpenetrating (when the Cu centers are considered) in COF-505 crystals along the *c* direction, where the frameworks are related by a C$_2$ rotation along the *b* axis, leaving sufficient space for BF_4^- counterions (*20*). We note that when the structure is demetalated, as demonstrated below, the COF is mutually woven (Fig. 2B).

Fundamentally, each of the threads making up the framework is a helix (Fig. 4A). For clarity, only a fragment of one weaving framework is shown. The helices are entirely made of covalently linked organic threads. As expected, they are weaving and being held by Cu(I) ions at their points of registry (Fig. 4B). These threads are propagating in two different directions along [110] and [–110]. Although the helices are chemically identical, they have opposite chirality, giving rise to an overall racemic weaving framework (Fig. 4, C and D) of the same topology as in Fig. 1B. We note that in the context of reticular chemistry, the points of registry play an important role in crystallizing otherwise difficult-to-crystallize threads and to do so into 2D or 3D frameworks. This arrangement is in stark contrast to the parallel manner in which such 1D objects commonly pack in the solid state.

The COF-505 structure is a woven fabric of helices, so we sought to remove the Cu centers and examine the properties of the material before and after demetalation. Heating COF-505 in a KCN methanol-water solution (*8*) yielded a demetalated material. Using inductively coupled plasma (ICP) analysis, we found that 92 to 97% of the Cu(I) copper ions had been removed (*12*). The dark brown color of COF-505 [from the copper-phenanthroline metal-to-ligand charge transfer (MLCT) (*21*)] changed to pale yellow as

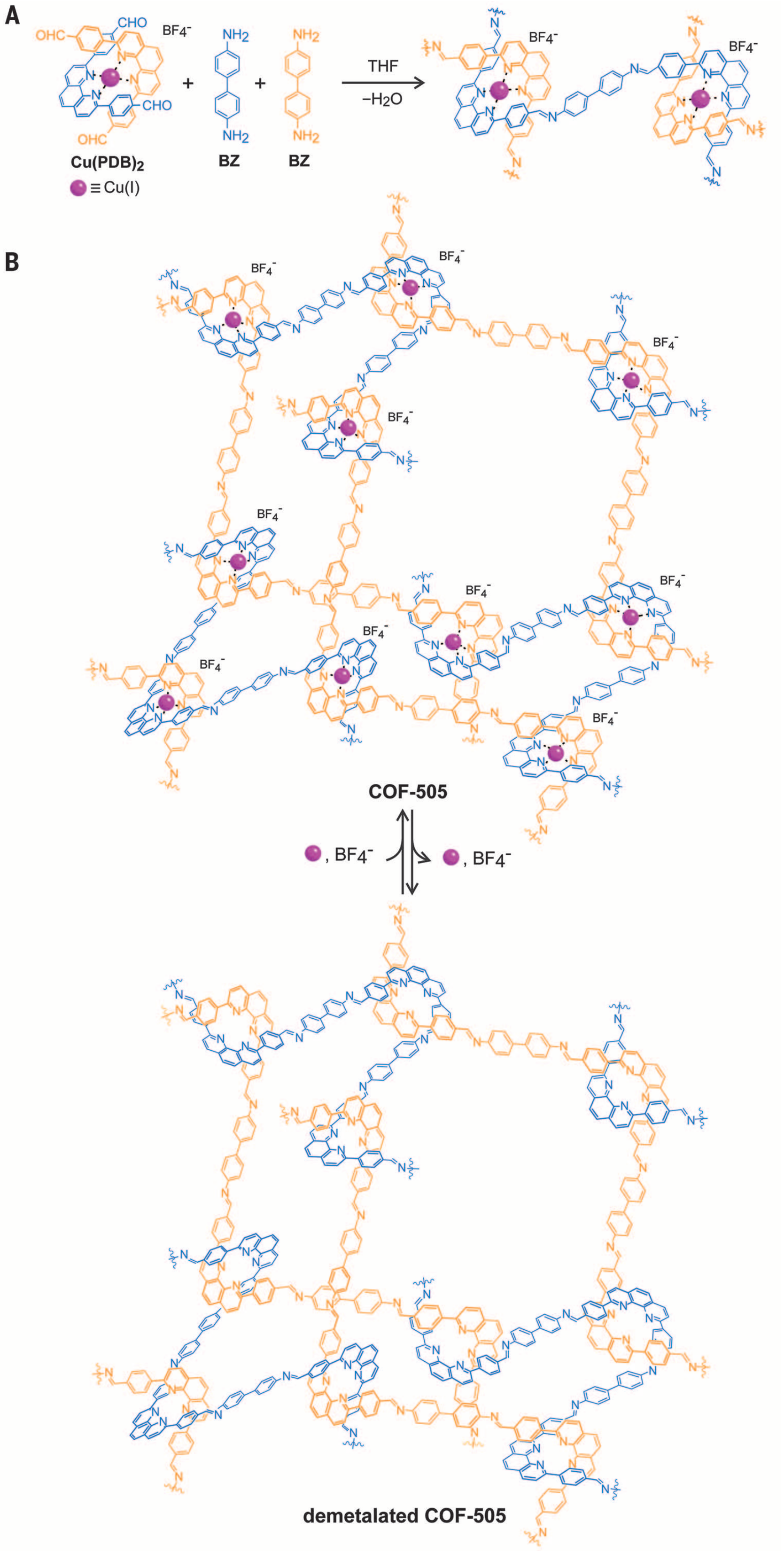

Fig. 2. A general strategy for the design and synthesis of weaving structures. COF-505 was constructed from organic threads using copper(I) as a template (**A**) to make an extended weaving structure (**B**), which can be subsequently demetalated and remetalated.

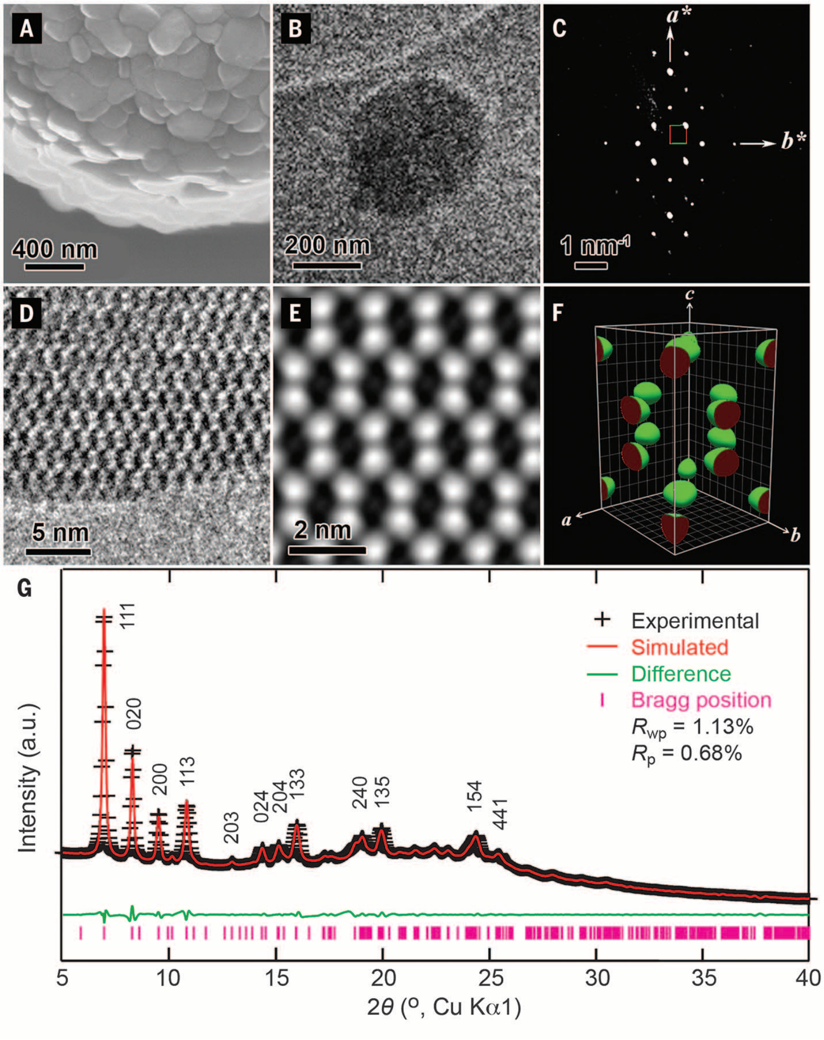

Fig. 3. Morphology and electron microscopy studies of COF-505. (**A**) Crystallites aggregated on a crystalline sphere observed by SEM. (**B**) TEM image of a single sub-µm crystal used for 3D-EDT. (**C**) 2D projection of the reconstructed reciprocal lattice of COF-505 obtained at 298 K from a set of 3D-EDT data. (**D**) HRTEM image of COF-505 taken with the [1-10] incidence. (**E**) 2D projected potential map obtained by imposing *pgg* plane group symmetry on Fig. 1D. (**F**) Reconstructed 3D electrostatic potential map (threshold, 0.8). (**G**) Indexed PXRD pattern of the activated sample of COF-505 (black) and the Pawley fitting (red) from the modeled structure.

demetalation proceeded (*12*). Although the crystallinity of demetalated material decreased compared with COF-505, SEM images show similar morphology before and after demetalation (*12*). Additionally, the imine linkages were also maintained; the FT-IR peaks at 1621 and 1195 cm^{-1} (*12*) are consistent with those of COF-505 (1621 and 1196 cm^{-1}, respectively). Furthermore, the material could be remetalated with Cu(I) ions by stirring in a $CH_3CN/CHCl_3$ solution of $Cu(CH_3CN)_4(BF_4)$ to give back crystalline COF-505. This remetalated COF-505 has identical crystallinity to the original as-synthesized COF-505, as evidenced by the full retention of the intensity and positions of the peaks in the PXRD (*12*). In the FT-IR spectrum, the peak representing imine C=N stretch was retained (*12*), indicating that the framework is chemically stable and robust under such reaction conditions.

Given the facility with which demetalation can be carried out and the full retention of the structure upon remetalation can be achieved, we examined the elastic behavior of the metalated and demetalated COF-505. A single particle of each of these two samples was indented by a conical tip of an atomic force microscope (AFM), and the load-displacement curves were recorded for both loading and unloading process (*22*). The effective Young's moduli (neglecting the anisotropy of the elasticity) of the two COF-505 materials was ~12.5 and 1.3 GPa for the metalated and demetalated particles, respectively (*12*). Notably, this tenfold ratio in elasticity upon demetalation of COF-505 is similar to the elasticity ratio for porous MOFs to polyethylene (*23*). The distinct increase of elasticity could be attributed to the loose interaction between the threads upon removal of copper. Moreover, the elasticity of the original COF-505 could be fully recovered after the process of demetalation and remetalation, being facilitated by the structure of weaving helical threads that easily "zip" and "unzip" at their points of registry. The large difference in elasticity modulus is caused by loss of Cu(I) ions, which in total only represent a minute mole percentage (0.67 mol%) of the COF-505 structure.

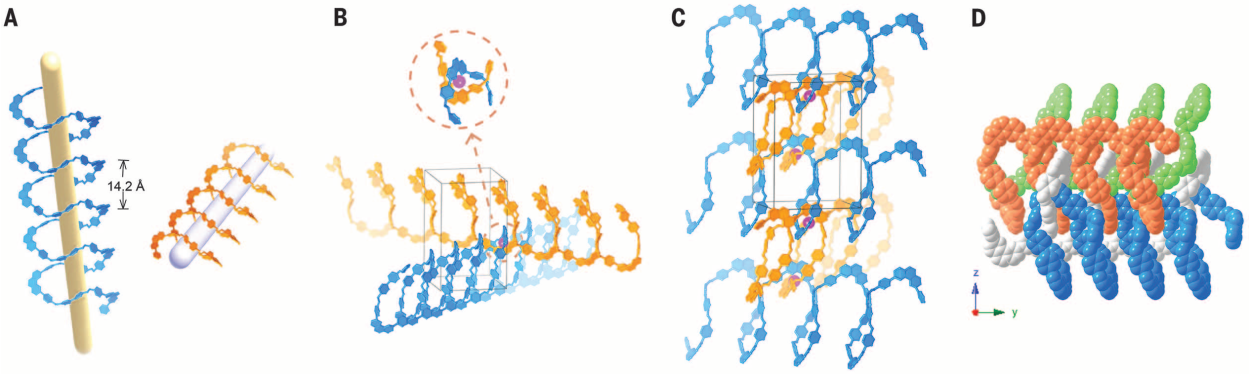

Fig. 4. Single-crystal structure of COF-505. The weaving structure of COF-505 consists of chemically identical helices (marked in blue and orange because they are of opposite chirality) with the pitch of 14.2 Å (**A**). The orange helices propagate in the [1-10] direction, whereas the blue helices propagate in the [110] direction with copper (I) ions as the points of registry (**B**). Neighboring blue helices are woven with the orange helices to form the overall framework (**C**). Blue and orange helices and their C_2 symmetry-related green and gray copies are mutually woven (**D**). Additional parallel helices in (C) and (D) are omitted for clarity.

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SUPPLEMENTARY MATERIALS

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PHOTOPHYSICS

Direct observation of triplet energy transfer from semiconductor nanocrystals

Cédric Mongin,[1] Sofia Garakyaraghi,[1] Natalia Razgoniaeva,[2] Mikhail Zamkov,[2] Felix N. Castellano[1]*

Triplet excitons are pervasive in both organic and inorganic semiconductors but generally remain confined to the material in which they originate. We demonstrated by transient absorption spectroscopy that cadmium selenide semiconductor nanoparticles, selectively excited by green light, engage in interfacial Dexter-like triplet-triplet energy transfer with surface-anchored polyaromatic carboxylic acid acceptors, extending the excited-state lifetime by six orders of magnitude. Net triplet energy transfer also occurs from surface acceptors to freely diffusing molecular solutes, further extending the lifetime while sensitizing singlet oxygen in an aerated solution. The successful translation of triplet excitons from semiconductor nanoparticles to the bulk solution implies that such materials are generally effective surrogates for molecular triplets. The nanoparticles could thereby potentially sensitize a range of chemical transformations that are relevant for fields as diverse as optoelectronics, solar energy conversion, and photobiology.

Semiconductor nanocrystals represent an important class of stable light-emitting materials that can be systematically tuned as a result of size-dependent quantum confinement, producing intense absorptions and photoluminescence ranging from the ultraviolet (UV) to the near-infrared (near-IR) (*1*, *2*). Their prominence continues to expand, owing to extensive optoelectronic, photochemical, and biomedical applications (*3*–*9*). Substantial research effort has been expended on funneling energy into these nanomaterials to produce enhanced photoluminescence via Förster transfer and on exploiting the energized semiconductor nanocrystals to deliver or accept electrons from substrates (*10*–*14*), sometimes en route to solar fuels photosynthesis (*15*–*18*). Tabachnyk *et al.* and Thompson *et al.* independently demonstrated the reverse triplet energy transfer process to that described here, wherein molecular organic semiconductors transfer their triplet energy to PbSe and PbS nanocrystals in thin films that interface both materials (*19*, *20*). However, the extraction of triplet excitons from semiconductor quantum dots and related inorganic nanomaterials remains largely unexplored. Semiconductor nanocrystals potentially offer considerable advantages over molecular photosensitizers in terms of facile preparative synthesis, photostability, size-tunable electronic and photophysical properties, high molar extinction coefficients, and trivial postsynthesis functionalization. Moreover, the inherently large (and energy-consuming) singlet-triplet energy gaps characteristic of molecular sensitizers can be circumvented by using nanomaterials with ill-defined spin quantum numbers and closely spaced (1 to 15 meV) excited-state energy levels (*21*–*24*). The broadband light-absorption properties of inorganic semiconductors are extendable into the near-IR region and can potentially be exploited for numerous triplet excited-state reactions, thus enabling stereoselective photochemical synthesis, photoredox catalysis, singlet oxygen generation, photochemical upconversion, and excited-state electron transfer. Here we provide definitive experimental evidence that triplet energy transfer proceeds rapidly and efficiently from energized semiconductor nanocrystals to surface-anchored molecular acceptors. Specifically, CdSe nanocrystals are shown to serve as effective surrogates for molecular triplet sensitizers and can readily transfer their triplet excitons to organic acceptors at the interface with near-quantitative efficiency.

The nanoparticle-to-solution triplet exciton transfer strategy that we implemented is shown schematically in Fig. 1; this diagram depicts all of the relevant photophysical processes and the associated energy levels promoting material-to-molecule triplet exciton migration. We employed oleic acid (OA)–capped CdSe nanocrystals (CdSe-OA) as the light-absorbing triplet sensitizer in conjunction with 9-anthracenecarboxylic acid (ACA) and 1-pyrenecarboxylic acid (PCA) as triplet acceptors in toluene. The carboxylic acid functionality enables adsorption of these chromophores on the CdSe surface through displacement of the OA capping ligands; subsequent washing steps isolate the desired CdSe/ACA or CdSe/PCA donor/acceptor systems. Selective green light excitation of CdSe/ACA or CdSe/PCA sensitizes triplet exciton migration from the semiconductor to the surface-bound molecular acceptor. We directly visualized this interfacial Dexter-like

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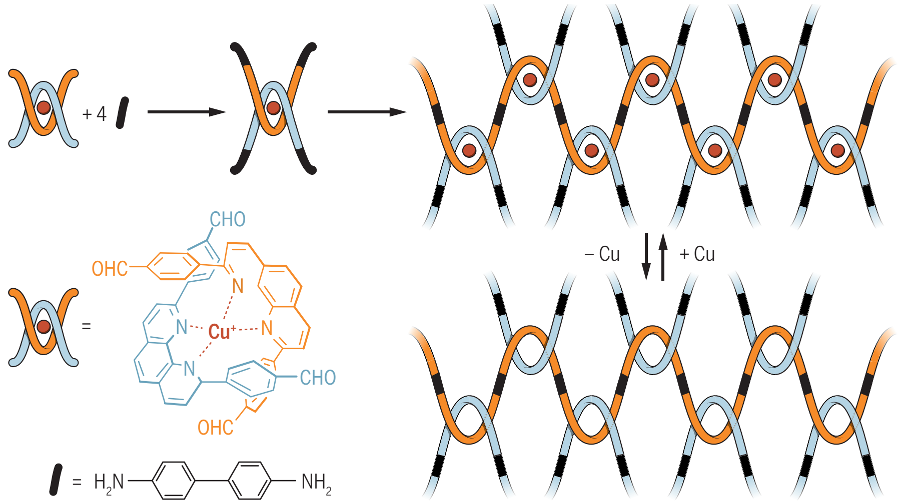
MATERIALS CHEMISTRY

Interlacing molecular threads

Materials with a fabric-like microstructure are highly elastic

By **Enrique Gutierrez-Puebla**

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*).



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 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 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 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. ■

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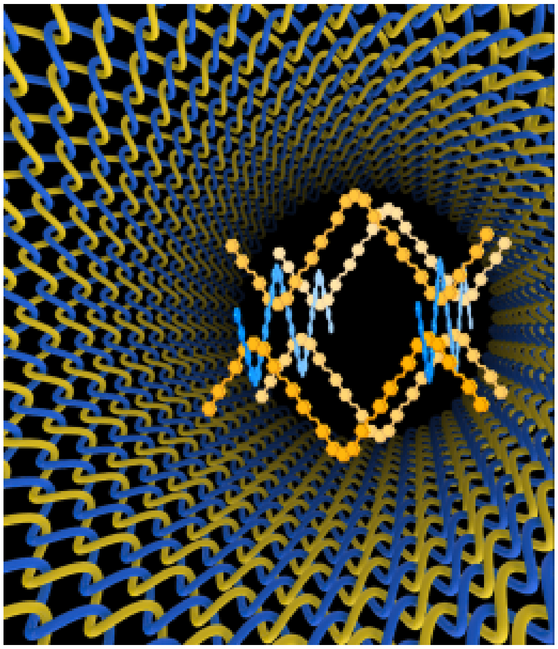
10.1126/science.aad9671

ILLUSTRATION: P. HUEY/SCIENCE

Weaving a New Story for COFS and MOFs

First Materials to be Woven at the Atomic and Molecular Levels Created at Berkeley

News Release Lynn Yarris • **JANUARY 21, 2016**



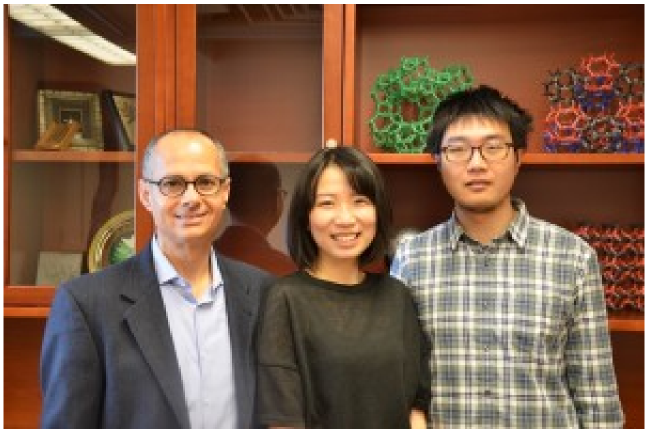
COF-505 is the first 3D covalent organic framework to be made by weaving together helical organic threads, a fabrication technique that yields significant advantages in structural flexibility, resiliency and reversibility over previous COFs.

There are many different ways to make nanomaterials but weaving, the oldest and most enduring method of making fabrics, has not been one of them – until now. An international collaboration led by scientists at the U.S. Department of Energy (DOE)'s Lawrence Berkeley National Laboratory (Berkeley Lab) and the University of California (UC) Berkeley, has woven the first three-dimensional covalent organic frameworks (COFs) from helical organic threads. The woven COFs display significant advantages in structural flexibility, resiliency and reversibility over previous COFs – materials that are highly prized for their potential to capture and store carbon dioxide then convert it into valuable chemical products.

"We have taken the art of weaving into the atomic and molecular level, giving us a powerful new way of manipulating matter with incredible precision in order to achieve unique and valuable mechanical properties," says Omar Yaghi, a chemist who holds joint appointments with Berkeley Lab's Materials Sciences Division and UC Berkeley's Chemistry Department, and is the co-director of the Kavli Energy NanoScience Institute (Kavli-ENSI).

"Weaving in chemistry has been long sought after and is unknown in biology," Yaghi says. "However, we have found a way of weaving organic threads that enables us to design and make complex two- and three-dimensional organic extended structures."

Yaghi is the corresponding author of a paper in Science reporting this new technique. The paper is titled “Weaving of organic threads into a crystalline covalent organic framework.” The lead authors are Yuzhong Liu, Yanhang Ma and Yingbo Zhao. Other co-authors are Xixi Sun, Felipe Gándara, Hiroyasu Furukawa, Zheng Liu, Hanyu Zhu, Chenhui Zhu, Kazutomo Suenaga, Peter Oleynikov, Ahmad Alshammari, Xiang Zhang and Osamu Terasaki.



(From left) Omar Yaghi, Yuzhong Liu and Yingbo Zhao led the discovery of how to weave materials at the atomic and molecular level to produce complex organic extended structures.

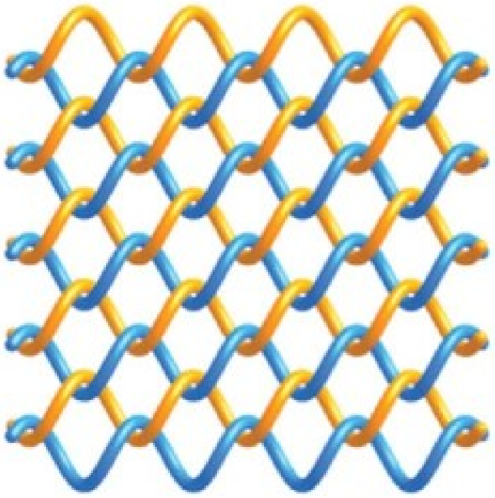
COFs and their cousin materials, metal organic frameworks (MOFs), are porous three-dimensional crystals with extraordinarily large internal surface areas that can absorb and store enormous quantities of targeted molecules. Invented by Yaghi, COFs and MOFs consist of molecules (organics for COFs and metal-organics for MOFs) that are stitched into large and extended netlike frameworks whose structures are held together by strong chemical bonds. Such frameworks show great promise for, among other applications, carbon sequestration. Through another technique developed by Yaghi, called “reticular chemistry,” these frameworks can also be embedded with catalysts to carry out desired functions: for example, reducing carbon dioxide into carbon monoxide, which serves as a primary building block for a wide range of chemical products including fuels, pharmaceuticals and plastics.

In this latest study, Yaghi and his collaborators used a copper(I) complex as a template for bringing threads of the organic compound “phenanthroline” into a woven pattern to produce an immine-based framework they dubbed COF-505. Through X-ray and electron diffraction characterizations, the researchers discovered that the copper(I) ions can be reversibly removed or restored to COF-505 without changing its woven structure. Demetalation of the COF resulted in a tenfold increase in its elasticity and remetalation restored the COF to its original stiffness.

“That our system can switch between two states of elasticity reversibly by a simple operation, the first such demonstration in an extended chemical structure, means that cycling between these states can be done repeatedly without degrading or altering the structure,” Yaghi says. “Based on these results, it is easy to imagine the creation of molecular cloths that combine unusual resiliency, strength, flexibility and chemical variability in one material.”

Yaghi says that MOFs can also be woven as can all structures based on netlike frameworks. In addition, these woven structures can also be made as nanoparticles or polymers, which means they can be fabricated into thin films and electronic devices.

"Our weaving technique allows long threads of covalently linked molecules to cross at regular intervals," Yaghi says. "These crossings serve as points of registry, so that the threads have many degrees of freedom to move away from and back to such points without collapsing the overall structure, a boon to making materials with exceptional mechanical properties and dynamics."



Weaving, the mutual interlacing of long threads, is an ancient method of making fabric, but only now has it been emulated in extended chemical structures.

This research was primarily supported by BASF (Germany) and King Abdulaziz City for Science and Technology (KACST).

Additional Information

For more about the research of Omar Yaghi go here

# # #

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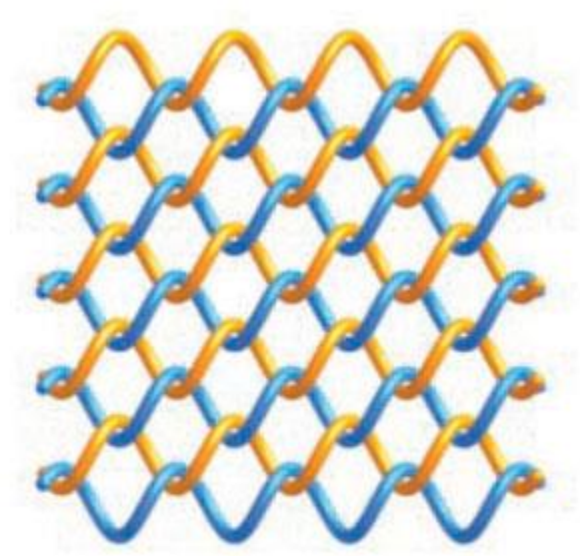
Updated: January 21, 2016

TAGS: carbon capture and storage, carbon dioxide emissions, chemistry, energy, materials sciences, Materials Sciences Division, nanoscience, nanotechnology, science

Molecular threads woven into flexible fabric

21 January 2016**Tim Wogan**

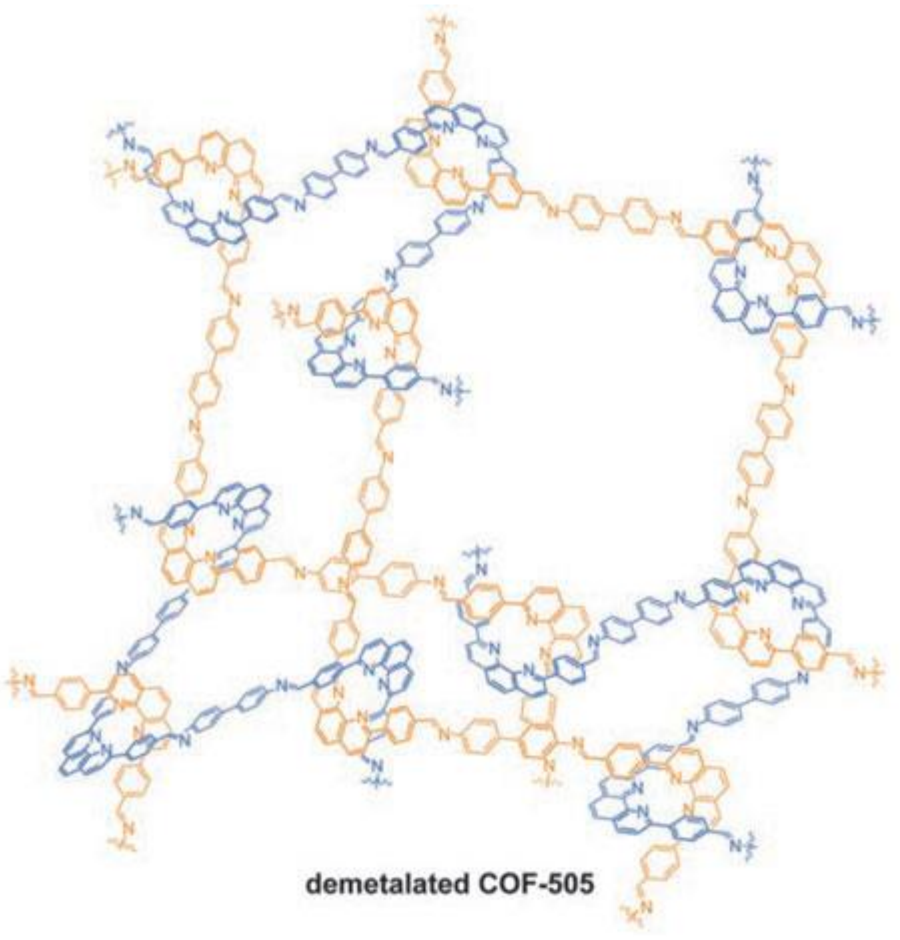


The polymer chains are mechanically interlocked, creating a molecular woven fabric © Science/AAAS

Researchers have found a way to **weave long-chain organic molecules into an interlacing pattern without irreversibly bonding them together**. The resulting molecular 'fabric', which has unusual properties, could potentially lead to a variety of other materials with applications from porous crystals and polymer chemistry to information storage.

Fabrics made of woven fibres have found uses from clothing to ropes and carpets, because they are both strong and flexible. Chemists would like to be able to weave together molecular chains, but have 'not really learned how to do this', according to**Omar Yaghi** of the University of California, Berkeley, in the US, who led the team behind the research. In thermoplastic polymers, he explains, the chains lie approximately parallel, sliding past one another when the material deforms. Conversely, in molecular frameworks, the molecules are bonded at the crossing points, producing rigid, inflexible structures.

Yaghi and colleagues built an interwoven covalent organic framework using the aldehyde-functionalised derivative of the complex salt Cu(I)-bis[4,4'-(1,10-phenanthroline-2,9-diyl)dibenzaldehyde]tetrafluoroborate – $Cu(PDB)_2(BF_4)$ – in which the Cu^+ ion forms four coordination bonds to the N atoms on each of the PDB chains, locking the aldehyde groups into an approximately tetrahedral arrangement. By adding benzidine (BZ), the researchers joined multiple salt molecules in a condensation reaction to produce long, imine-bonded PDB-BZ chains repeatedly interlaced around the Cu^+ ions. The chains were held in position by the coordination bonds to the metal ions, making the structure relatively rigid. However, the metal ions could then be removed by heating the material with potassium cyanide in a solution of methanol and water, allowing the chains to slide past each other while remaining interlaced and making the material 10 times as elastic. The original properties could be recovered by simply stirring in a solution of $Cu(CH_3CN)_4(BF_4)$.



Removing the copper ions creates a flexible network of individual polymer strands © Science/AAAS

'I view this weaving strategy as an additional level of sophistication in the precise design and making of new materials,' says Yaghi. He now intends to explore the potential of weaving together other types of long-chain molecule, perhaps with multiple types of molecule woven within a single structure. Further into the future, he suggests more complex patterns could encode information, but he says there are immediate applications: 'Taking all kinds of polymers that we see in everyday life and incorporating this weaving in their structure to add more robustness, dynamics and resilience.'

Jean-Pierre Sauvage of the University of Strasbourg in France, whose group developed the idea of templating around a metal ion, describes the work as 'a great paper'. 'The strategy is much related to what was done by my group in the past,' he says, 'but the fact that a material was obtained instead of a simple molecule adds a new and important dimension to the field.' **Tomislav Friscic** of McGill University in Canada agrees: 'The whole material design is just beautiful,' he says, 'I see absolutely no reason why this can't be modifiable into different topologies, different dimensionalities and completely different chemistries.'

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Nano-weaving: Synthesis of threaded polymers begins

Date: January 21, 2016

Source: Stockholm University

Summary: For the first time, scientists have been able to weave a material at molecular level.

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FULL STORY

For the first time, scientists have been able to weave a material at molecular level. The research is led by University of California Berkeley, in cooperation with Stockholm University. The new material is presented in the scientific journal *Science.*

Weaving is a well-known way of making fabric, but has until now never been used at the molecular level. Scientists have now been able to weave organic threads into a three-dimensional material, using copper as a template. The new material is a COF, covalent organic framework, and is named COF-505. The copper ions can be removed and added without changing the underlying structure, and at the same time the elasticity can be reversibly changed.

"It almost looks like a molecular version of the Vikings chain-armour. The material is very flexible," says Peter Oleynikov, researcher at the Department of Materials and Environmental Chemistry at Stockholm University.

COF's are like MOF's porous three-dimensional crystals with a very large internal surface that can adsorb and store enormous quantities of molecules. A potential application is capture and storage of carbon dioxide, or using COF's as a catalyst to make useful molecules from carbon dioxide.

The research is led by Professor Omar Yaghi at University of California Berkeley. At Stockholm University Professor Osamu Terasaki, PhD Student Yanhang Ma and Researcher Peter Oleynikov have contributed to determine the structure of COF-505 at atomic level from a nano-crystal, using electron crystallography methods.

"It is a difficult, complicated structure and it was very demanding to resolve. We've spent lot of time and efforts on the structure solution. Now we know exactly where the copper is and we can also replace the metal. This opens up many possibilities to make other materials," says Yanhang Ma, PhD Student at the Department of Materials and Environmental Chemistry at Stockholm University.

"Weaving of organic threads into a crystalline covalent organic framework" is published in Science 22 januari 2016.

Story Source:

The above post is reprinted from materials provided by **Stockholm University**. *Note: Materials may be edited for content and length.*

Journal Reference:

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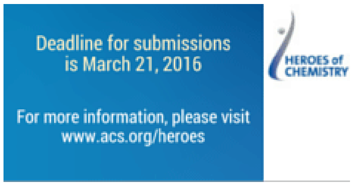

Volume 94 Issue 4 | **p. 26** | **Concentrates**
Issue Date: January 25, 2016

Tapestry Woven From Organic Threads

Materials Chemistry: Interlaced covalent organic framework with reversible elasticity could lead to thin films, electronic devices

By **Stu Borman**

0 0
Email Print

Department: **Science & Technology**
News Channels: **Materials SCENE**, **Nano SCENE**
Keywords: **molecular threads**, **covalent organic framework**

In an extension of chemical domesticity, researchers have shown that organic chemistry is good not only for cooking but for weaving as well. Several types of supramolecular structures—catenanes, rotaxanes, molecular knots, and molecular Borromean rings—have interwoven two- and three-dimensional parts. Now, **Osamu Terasaki** of Stockholm University; **Omar M. Yaghi** of the University of California, Berkeley; and coworkers have designed and constructed the first structures in which 1-D molecular "threads" are interwoven, forming a crystalline covalent organic framework (*Science* 2016, DOI: **10.1126/science.aad4011**). The researchers first synthesized a copper(I) bisphenanthroline complex in which the two organic groups adopt an interlaced inverted-U orientation. They then added benzidines to the ends of the organic groups and linked the benzidines by forming imine bonds, creating a woven material they call COF-505. The copper ions can be removed and reinserted reversibly. The demetalation increases the material's elasticity 10-fold because the threads can move around more easily without copper present. The material could be used for preparing controllably flexible thin films and electronic devices. "Interweaving organic threads in the solid state is totally new and will lead to unexplored materials with unexpected properties," comments **Jean-Pierre Sauvage** of the University of Strasbourg.

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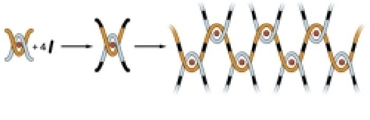

Benzidines (black) are added to the ends of copper bisphenanthrolines. A condensation reaction then links the bisphenanthrolines to form a woven material (right).

Credit: Science/Courtesy of Enrique Gutierrez-Puebla

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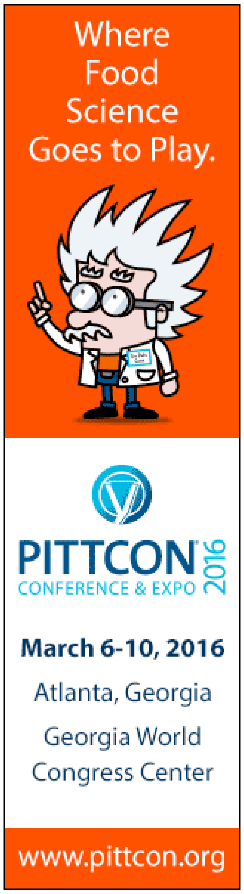
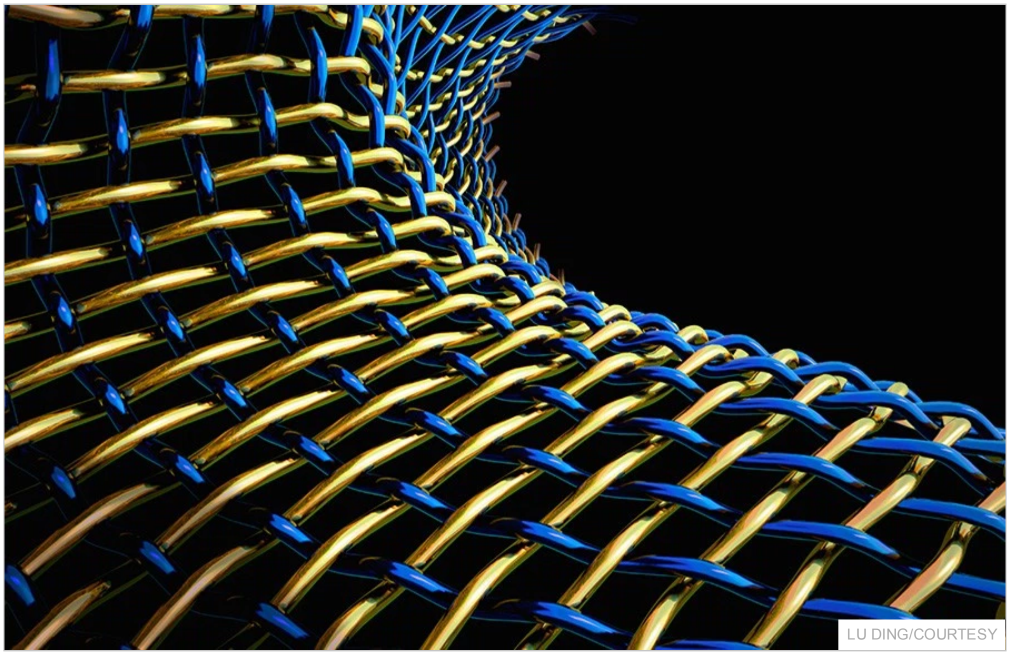


THE DAILY CALIFORNIAN
Monday, January 25, 2016

NEWS

RESEARCH & IDEAS MONDAY, JANUARY 25, 2016

Researchers weave organic threads into molecular framework



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BY KIMBERLY NIELSEN | STAFF

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Easily taken for granted as a simplistic art form, weaving remains one of the most elegant means of producing durable materials — and scientists are only beginning to realize its potential in areas ranging from clean energy applications to electronics manufacturing.

An international team of scientists affiliated with the Lawrence Berkeley National Laboratory and UC Berkeley recently discovered how to produce structurally dynamic materials by weaving microscopic threads into molecular structures called covalent organic frameworks, or COFs. The technique has never been implemented on such a miniscule level before, said Omar Yaghi, co-director of the Kavli Energy NanoSciences Institute, campus chemistry professor and an author of the study.

“What this study really demonstrates is that it’s a new way of making materials,” Yaghi said. “It’s no surprise that weaving is the oldest method of making robust yet elastic, dynamic materials.”

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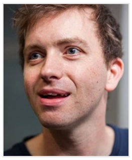


CULTURE SHOT

Research contributors published a report detailing the research in Science, an academic journal, last Friday.

COFs are porous three-dimensional crystals ideal for storing large amounts of molecules. Invented by Yaghi in 2005, COFs were originally composed of "organic building blocks" stitched together by strong covalent bonds, forming a net. But the newly-designed COF-505 model utilizes a copper ion framework, which can be removed without affecting the basic structure of the COF.

"You can imagine this material as a kind of fabric that is so soft that you can wear it, but at the same time robust enough that you won't break it," said Yuzhong Liu, a doctoral candidate in the campus chemistry department.

The researchers also redefined material synthesis methods by uniting molecules via mechanical, rather than chemical, bonds. Weaving organic threads in an "up and down" fashion gives traditionally rigid materials versatility and allows scientists to fuse unrelated compounds together.

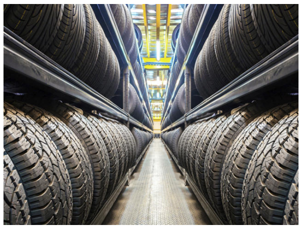
According to scientists involved with the project, the effects could be far-reaching. Christian Diercks, a UC Berkeley professor in the department of chemistry, notes that because the COFs are made from "molecular building blocks," they can be structurally altered by scientists more easily than other crystalline structures. Hiroyasu Furukawa, an assistant researcher on the project, said in an email that scientists can now rework COF structures to suit different purposes, providing new opportunities for researchers in chemistry, physics and engineering.

Liu predicted that future COF designs could be created to allow it to transition between different elasticity states with light triggers, rather than by manually removing the copper ion framework.

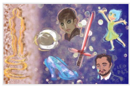
Yaghi believes the new COF design highlights the potential for scientific discovery to improve pre-existing systems and open doors to new ideas.

"If you can think it and imagine it, it should be possible to make," said Yaghi. "That's why this report is exciting: It shows that with a slight twist in thinking, you can make something people thought could not be made."

Kimberly Nielsen covers research and ideas. Contact her at knielsen@dailycal.org.



Oscar nomination analysis and predictions from Daily Cal Arts

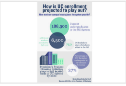


ALBUM REVIEWS

Hoodie Allen drops free EP filled with silly pop-rap goodness

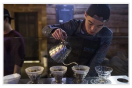
UC

Campus considers housing options for additional students entering next year



CITY

Gourmet coffee shop opens on Durant Ave, seeks to impart life advice



CONCERTS

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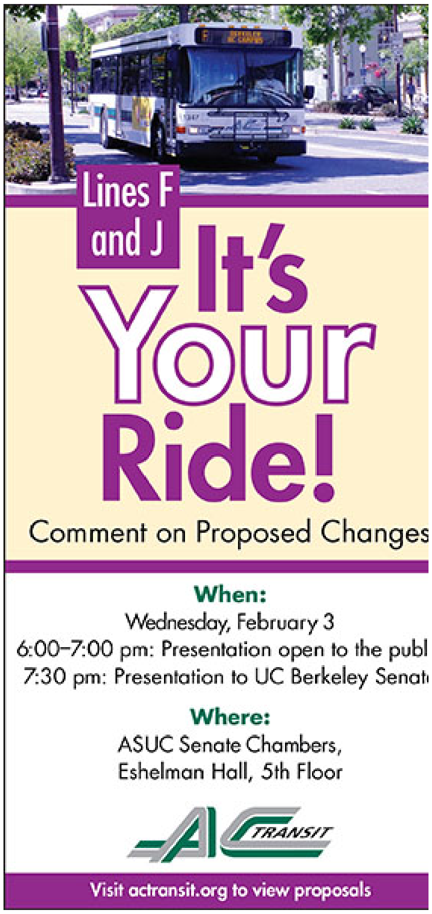


expansion of the ocean, whereas the central and eastern Pacific saw decreases.
Proc. Natl Acad. Sci. USA **http://dx.doi.org/10.1073/pnas.1519132113 (2016)**

METABOLISM

Beige fat boosts metabolism

Human 'beige' fat cells implanted in mice can improve the animals' glucose metabolism and liver-fat profiles.

The presence of beige fat — brown fat cells within white fat-storing tissue — is correlated with better metabolic health, but it was not known whether beige fat causes this. To see whether there is a causal link, Silvia Corvera of the University of Massachusetts Medical School in Worcester and her colleagues grew human beige fat cells in the lab, placed them in mice, and found that they formed well-defined adipose tissue. Animals with the implants had lower blood-glucose levels, absorbed the glucose more quickly than did untreated controls, and had less fat in their livers.

The results suggest that beige fat could have therapeutic use, the authors say.
Nature Med. **http://dx.doi.org/10.1038/nm.4031 (2016)**

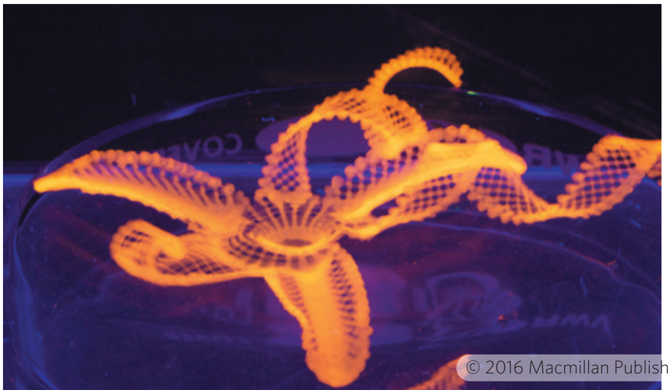
MATERIALS

Add water for 3D-printed flowers

Researchers have 3D-printed hydrogel composites that swell and morph into flower shapes when immersed in water.

Lakshminarayanan Mahadevan and Jennifer Lewis at Harvard University in Cambridge, Massachusetts, and their colleagues used an ink made of cellulose fibrils embedded in a hydrogel matrix, which mimics plant-cell walls and swells in water. By controlling the alignment of the fibrils in the ink during printing, the team produced flat materials that bend and twist when placed in water, producing structures that mimic flowers (**pictured**).

The approach could be used to create designer, shape-changing structures for biomedical applications or smart textiles, the authors say.
Nature Mater. **http://dx.doi.org/10.1038/nmat4544 (2016)**



NATURE MATER.

CHEMISTRY

Polymers woven into stretchy web

Organic polymers woven into a 3D framework offer a new way of making flexible materials with tunable properties.

Covalent organic frameworks are highly porous structures with many promising applications, but they are typically rigid. Omar Yaghi of the University of California, Berkeley, Osamu Terasaki of Stockholm University and their colleagues created such a framework, dubbed COF-505. It is made of individual building blocks of copper ions that carry fragments of a polymer. Joining these units together with linear molecules formed crystals with the same tetrahedral geometry as diamond.

The researchers then removed the copper ions to leave interwoven, helical polymer threads that were collectively ten times more elastic than the precursor. The copper ions could also be replaced, raising the possibility of loading the polymer weave with metal catalysts, or of using it to absorb metal ions from liquid waste.
Science **351, 365–369 (2016)**

SOCIAL SELECTION *Popular topics on social media*

House bugs crawl over social media

Many commenters on Twitter this week felt their skin crawl after reading that some US households are home to more than 200 different species of insects and other creatures, according to one study. Entomologists collected more than 10,000 specimens of arthropods (insects and other animals with exoskeletons and segmented bodies) from 50 homes in Raleigh, North Carolina, and found surprising diversity. Their results, published in *PeerJ*, suggest that the average home contained 93 different species, from spiders and flies to cockroaches and beetles. Out of the 304 arthropod families identified, 149 were rare. And only 5 out of the 554 rooms examined — 4 bathrooms and 1 bedroom — contained no bugs at all. Joachim Maes, an ecologist at the European Commission's Institute for Environment and Sustainability in Ispra, Italy, tweeted: "We are literally surrounded by biodiversity." The study analysed only the types of species present, and the authors recommend a more-in-depth study of confined spaces in homes — such as under the stairs — to get more-accurate data on the number and diversity of household bugs.
PeerJ **4, e1582 (2016)**

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ANIMAL BEHAVIOUR

Voles console stressed friends

ZACK JOHNSON

Prairie voles seem to console their distraught cage-mates — a behaviour previously seen only in humans and in other animals with advanced cognition, such as great apes and elephants.

James Burkett, Larry Young and their colleagues at Emory University in Atlanta, Georgia, separated pairs of prairie voles (*Microtus ochrogaster*; **pictured**) in the lab and measured how long the rodents groomed each other when they were reunited. Voles spent significantly more time grooming partners that had been subjected to noise and mild electric shocks during the separation period, even though they had not observed the stressful event.

The unstressed voles showed the same levels of stress hormones as their stressed cage-mates. This response disappeared when the researchers chemically blocked the brain receptor for oxytocin, a hormone involved in empathy in humans.

Further research on this consolation behaviour in rodents could yield insight into certain psychiatric disorders that involve a lack of empathy, the authors say.
Science **351, 375–378 (2016)**

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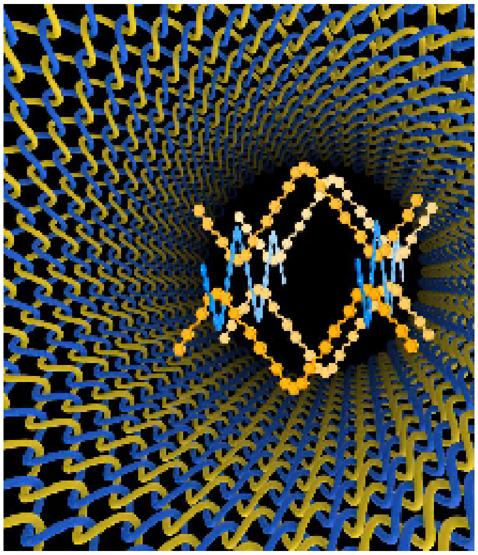
Weaving molecular threads gives highly elastic fabric-like material

By Prachi Patel

Materials Research Society | Published: 12 February 2016



An artist's illustration of a three-dimensional covalent organic framework (COF) made by weaving together helical organic threads, a fabrication technique that yields significant advantages in structural flexibility, resiliency, and reversibility over previous COFs. Credit: Omar Yaghi, Berkeley Lab and UC Berkeley

Researchers have found a way to interlace long organic molecules like threads without chemically linking them. The resulting fabric-like material is exceptionally flexible and elastic. The technique could lead to new kinds of resilient materials for storing hydrogen and carbon dioxide, removing metal ions from liquid wastes, and for use as catalysts.

"You can bend and stretch fabric, and it doesn't break because its threads slide against each other without unraveling the whole structure," says Omar Yaghi, a chemistry professor at the University of California, Berkeley. "We have reproduced this fabric weaving idea on a molecular level so the molecular chains can slide against each other. This changes the way we think about making materials."

The new material, reported recently in *Science* , is a twist on covalent organic frameworks (COFs). Traditional COFs, first developed by Yaghi and his co-workers, are crystalline materials with high porosity, surface areas, conductivity and catalytic activity. They consist of organic building blocks linked through strong covalent bonds. But these rigid bonds restrict the material's elasticity. When the material is flexed, the bonds can break and the entire material can collapse.

To synthesize a woven COF, Yaghi and his colleagues used conventional COF chemistry with a key additional building unit: a Cu(I) complex, Cu(I)-bis[4,4'-(1,10-phenanthroline-2,9-diyl)dibenzaldehyde] tetrafluoroborate, $Cu(PDB)_2(BF_4)$. They combined the Cu(I) complex and benzidine in tetrahydrofuran and acetic acid, sealed and heated the reaction mixture at 120°C for three days, and then separated the resulting brown crystalline precipitate, which is the COF.

Two identical aldehyde groups in the Cu(I) complex act as the starting point of independent helical imine-bonded PDB-benzidine threads in the COF. The Cu(I) ionsact as templates, holding each aldehyde group in the right position approximating a tetrahedral geometry, which ensures that the threads assemble into a three-dimensional (3D) framework. The ions' positions are the points where the threads are woven. "The copper ion seeks out parts of

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Materials News

Weaving molecular threads gives highly elastic fabric-like material
Materials Research Society

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'Chameleon' camouflages itself with plasmonic skin chemistry world this thread that are equally spaced from each other and brings them together in an up and down pattern like a weave," Yaghi explains.

The researchers removed the copper ions in the material by heating it in a methanol-water solution. This demetalation resulted in a loss of the material's crystallinity, accompanied by a 10-fold increase in elasticity. Furthermore, the researchers showed that the Cu(I) ions could be reintroduced by stirring the COF in a copper salt solution, and the resulting metal-containing solid reverted to its original stiffness.

Yaghi says that the new COFs should be more robust for gas storage use since their structure would not collapse with repeated use. By using metal ions other than copper, the materials could also find new catalysis applications.

"Making a true woven fabric containing organic molecules had never been done nor even envisioned in the past," says Jean-Pierre Sauvage, a professor of chemistry at Louis Pasteur University Strasbourg. The extremely efficient strategy that the researchers used, the resulting material properties, and the reversibility of the metalation process make the advance "revolutionary" and "ground-breaking," he says.

"This is a very clever experiment which has produced a highly novel material by design," says Mercouri Kanatzidis, a chemistry professor at Northwestern University. "The interwoven structure is stunning. This will open new horizons in supramolecular materials."

See the abstract in *Science*.

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