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DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

1. Li, G., Su, Z., Canil, L., Hughes, D., Aldamasy, M.H., Dagar, J., Trofimov, S., Wang, L., Zuo, W., Jerónimo-Rendon, J.J., et al. (2023). Highly efficient p-i-n perovskite solar cells that endure temperature variations. Science *379*, 399–403.
2. deQuilettes, D.W., Vorpahl, S.M., Stranks, S.D., Nagaoka, H., Eperon, G.E., Ziffer, M.E., Snaith, H.J., and Ginger, D.S. (2015). Solar cells. Impact of microstructure on local carrier lifetime in perovskite solar cells. Science *348*, 683–686.
3. Jiao, H., Ni, Z., Shi, Z., Fei, C., Liu, Y., Dai, X., and Huang, J. (2022). Perovskite grain wrapping by converting interfaces and grain boundaries into robust and water-insoluble low-dimensional perovskites. Sci. Adv. *8*, eabq4524.
4. Noguera-Gómez, J., Fernández-Guillen, I., Betancur, P.F., Chirvony, V.S., Boix, P.P., and Abargues, R. (2022). Low-demanding in situ crystallization method for tunable and stable perovskite nanoparticle thin films. Matter *5*, 3541–3552.
5. Aydin, E., Bastiani, M., and Wolf, S. (2019). Defect and Contact passivation for perovskite solar cells. Adv. Mater. *31*, 1900428.
6. You, S., Zeng, H., Liu, Y., Han, B., Li, M., Li, L., Zheng, X., Guo, R., Luo, L., Li, Z., et al. (2023). Radical polymeric p-doping and grain modulation for stable, efficient perovskite solar modules. Science *379*, 288–294.
7. Jiang, Q., Tong, J., Xian, Y., Kerner, R.A., Dunfield, S.P., Xiao, C., Scheidt, R.A., Kuciauskas, D., Wang, X., Hautzinger, M.P., et al. (2022). Surface reaction for efficient and stable inverted perovskite solar cells. Nature *611*, 278–283.
8. Bai, S., Da, P., Li, C., Wang, Z., Yuan, Z., Fu, F., Kawecki, M., Liu, X., Sakai, N., Wang, J.T.W., et al. (2019). Planar perovskite solar cells with long-term stability using ionic liquid additives. Nature *571*, 245–250.
9. Tada, A., Geng, Y., Wei, Q., Hashimoto, K., and Tajima, K. (2011). Tailoring organic heterojunction interfaces in bilayer polymer photovoltaic devices. Nat. Mater. *10*, 450–455.

Poly[*n*]catenane from reticular chemistry

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Poly[*n*]catenanes exhibit intriguing properties, while their synthesis is the primary challenge to explore their widespread applications. In a recent issue of *Nat. Synth.*, Yaghi and co-workers report the synthesis of a series of three-dimensional [∞]catenane frameworks from reticular chemistry.

Polycatenanes are a class of polymers containing mechanically interlocked components (rings or polyhedra).[1] The mechanical bonds present in the catenated moieties allow the components to rotate, elongate, and twist relative to their interlocked partner, thus giving the materials unique dynamics and intriguing physical and material properties. With the rapid development of high-yield synthetic methodologies for catenanes,[2] several different types of their polymeric counterparts have been realized through the control of catenation and polymerization processes.[3] Among these polycatenane structures, the poly[*n*]catenane (*n* denotes the number of mechanically linked units) in which the entire architecture is composed of only interlocked components is the most challenging and attractive target because the optimized density of mechanical bonds within the structure displays maximum effects on the material properties. Despite the fact that a few synthetic approaches have been explored to synthesize the poly[*n*]catenane with up to 130 units by improving the selectivity and yield of the catenation step,[4] the formation of an infinite three-dimensional analog remains elusive. Reticular chemistry has enabled the synthesis of diverse periodically extended structures toward specific applications by varying the structure of building blocks, nets (or graphs), and isoreticular chemistry.[5] Introduction of suitable building blocks containing pre-organized crossings into reticular assembly provides an alternative to form the poly[*n*]catenanes that are not readily accessible through the conventional route.

In a recent issue of *Nat. Synth.*, Yaghi and co-workers[6] have presented a creative route towards catenated covalent organic frameworks (COFs) using reticular chemistry. More importantly, the developed reticulation approach along with the structural resolution process demonstrates powerful generality in the synthesis of other 2D/3D [∞]catenanes and woven COFs. This elegant work paves the way for the design and preparation of framework materials with unique dynamics and exceptional mechanical properties arising from orderly mechanical bonds and

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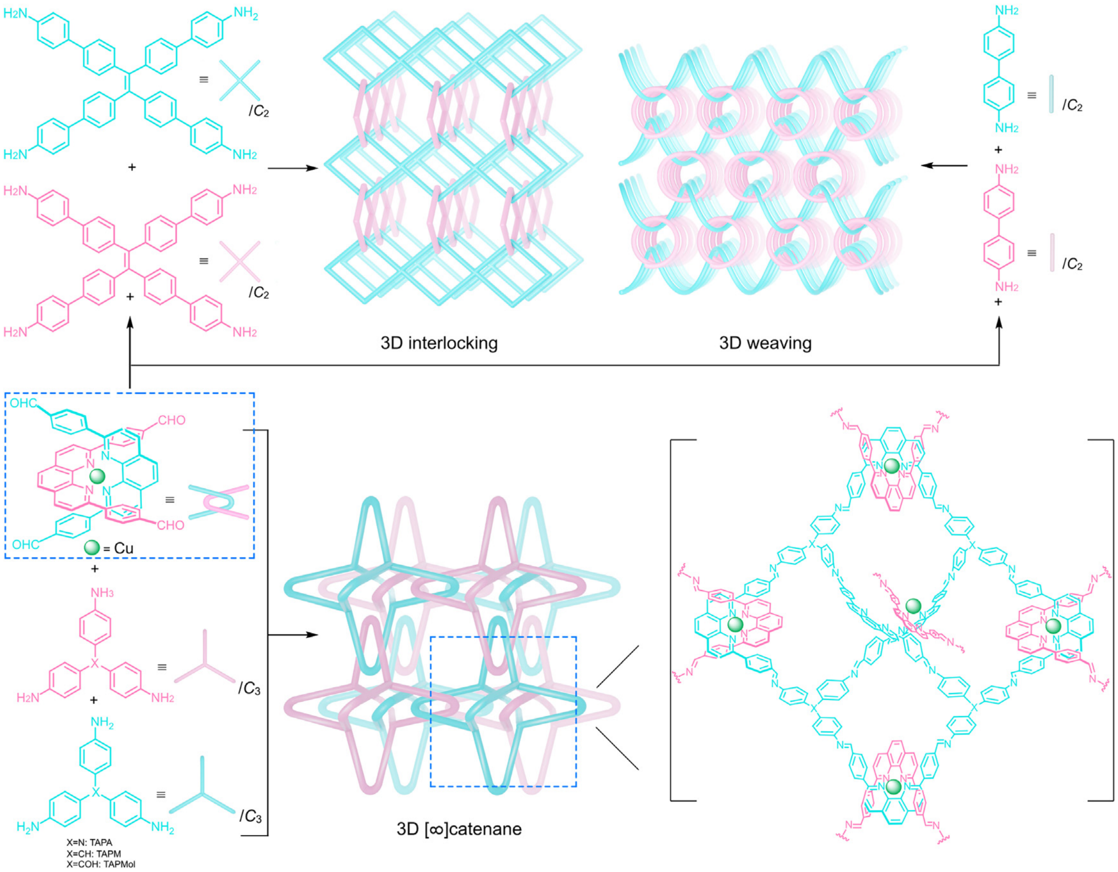

Figure 1. Synthesis of different 3D interlocking frameworks through a reticular chemistry approach

The tetrahedral copper(I)-phenanthroline complex featuring single crossing is employed as the 4-connected building block to generate the architectures with required mechanical bonds. Reticulation of the copper(I) complex with tritopic linkers results in the formation of 3D [∞]catenane framework containing adamantane-like polyhedra. Instead, the use of rectangular tetratopic and linear ditopic units can lead to the construction of 3D interlocking frameworks and woven materials, respectively. The above-mentioned examples demonstrate the combination of molecular nanotopology with reticular chemistry and provide a powerful route towards the synthesis of interlocking frameworks, which may not be accessible by employing other reported tactics.

entanglements. Moreover, it also offers the opportunity to establish a more complete understanding of the structure-property relations of these materials in an experimental manner.

The research process is divided into four key parts, namely (1) topology identification; (2) framework preparation; (3) structure characterization; and (4) property investigation. The first step offers fundamental support for the selection of building blocks and structural determination of the resulting catenane framework. Through the analysis of the reticular chemistry structure resource (RCSR) database, the authors envisage that the **bor** topology, featuring triangular and tetrahedra building blocks linked alternatively to generate a 3D arrangement, is a suitable candidate for the desired target. Replacement of the tetrahedra units with precursors containing pre-organized crossing points produces the designed 3D [∞]catenane consisting of interlocked adamantane-like polyhedra. Several other potential topologies, such as **sod** and **bcu** nets, can also be transformed into 3D interlocking frameworks via a similar process, proving the power of reticular chemistry.

The 2,9-diphenyl-1,10-phenanthroline copper(I) complex ($[Cu(dpp)_2]^+$) with two intertwined ligands, reported by Sauvage et al.[7] in the first practical synthesis of a [2]catenane, is chosen as the 4-connected vertices as it features approximately tetrahedral geometry. Installation of aldehyde groups at 4 and 4′ positions of the phenyl rings, forming $[Cu(pdb)_2]^+$ complex, allows it to meet the angel requirement of adamantane-like polyhedron and build up frameworks through imine condensation. This building block was previously used in the synthesis of weaving[8] and interlocking frameworks[9] by connecting it with linear and rectangular linkers, respectively (Figure 1). Three tritopic amine linkers, tris-(4-aminophenyl)amine (TAPA), tris-(4-aminophenyl)methane (TAPM), and tris-(4-aminophenyl)methanol (TAPMol), are selected as the 3-connected vertices, which are differentiated on the central atoms (–N, –CH, –COH). The backbone flexibility embedded in the central atoms of amines, along with the rotation of imine bonds, fixes the structural derivations between a standard polyhedron and experimental one.

With the addition of an acidic catalyst and monofunctional amine modulator, three [∞]catenane COFs, namely COF-805 (from TAPA), COF-806 (from TAPM), and COF-807 (from TAPMol), are successfully prepared. The absence of characteristic signals for both aldehyde and amine units in Fourier transform infrared (FT-IR) spectra and ^{13}C cross-polarization magic-angle spinning NMR (^{13}C CP/MAS NMR) spectra, combined with high thermal stability of resulting solids measured by thermogravimetric analysis, implies the conversion of starting materials to imine COFs. Direct evidence for the imine bond formation comes from a new ^{1}H-^{13}C correlation signal observed in ^{1}H-^{13}C heteronuclear correlation spectroscopy. The results are further supported by powder X-ray diffraction (PXRD) patterns, indicating the new highly crystalline phases have been formed. Similar PXRD patterns of three COFs suggest that the three frameworks have similar 3D arrangements with minor differences.

The most challenging part of this work is to precisely identify the crystal structures of these catenane COFs. 3D electron diffraction combined with selected area electron diffraction was first applied to determine the unit cell parameters and symmetry. After eliminating the interference from multiple scattering, the authors confirmed that COF-805 crystallized in an *F* cubic lattice whereas COF-806 and COF-807 are in *P* lattices, and the lattice parameter *a* of COF-805 is twice that of COF-806 and COF-807. Despite these differences, three COFs display the same C_6+C_4 symmetry, confirming they are isoreticular structures with **bor-y** topology. Both structural similarities and differences are further supported by high-resolution transmission electron microscopy (HRTEM) images. Through the integration of the obtained datasets, the space group for each COF is deduced. Molecular models of interlocked polyhedra with **bor-y** topology are built and fitted into the [∞]catenane frameworks with distinct space groups and unit cells. The initial projections, however, didn't match with the HRTEM images. By analyzing the HRTEM images in more detail, a doubly interpenetrated **bor-y** topology (**bor-y-c***), in which two subnets of **bor-y** are related by inversion, is constructed. Additionally, the calculated reticular formula of the three COF models is in line with both the empirical formula and elemental analysis results, which again confirms the **bor-y-c*** topology.

The above-mentioned analysis clearly demonstrates that the three COFs feature the same topology, and it is apparent that the minor variations obtained in the experiments are mainly attributed to the structural differences in the amine linkers. Specifically, the geometries of the central atoms (trigonal planar N (TAPA) versus tetrahedral C (TAPM and TAPMol)) and the direction of C–H (TAPM) or C–OH (TAPMol) bonds relative to the cavity of polyhedron directly determine both the size and conformation of a single polyhedron. The changes further remotely influence the orientations of polyhedra when they are interlocked with each other in the framework, resulting in variations in symmetry and unit cell size among three COFs. The conclusion is in good agreement with the different alignments of bright spots observed in HRTEM images. Overall, Yaghi and coworkers have established a textbook example to elucidate the structural details of such topologically complex frameworks through a comprehensive experimental analysis combined with simulations.

Compared with structural information obtained from three COFs, the SEM images show the polyhedron-shaped morphologies that match well with both internal symmetries and simulation results. Therefore, the degree of catenation can be calculated. The results indicate that a 500-nm-sized COF-805 crystal contains over five million interlocked polyhedra, which is four orders of magnitude higher than that of the reported longest organic poly[*n*]catenane (n = 130). COF-806 and COF-807 with larger crystals process even higher degrees of catenation.

The nature of mechanical bonds endows the COFs with dynamic properties, while the metal templates restrict the motion of polyhedra within the framework. Wholly organic [∞]catenane COFs are obtained by demetallation with KCN without affecting the backbones. Approximately 90% of copper(I) ions are removed, which leads to the increase in structural freedom and loss of crystallinity. Although more copper(I) ions are captured by the materials during the remetallation step, the crystallinity cannot be restored. Nevertheless, the crystallinity of a 60% demetallated COF-806 sample can be recovered through a remetallation followed by an acid-catalyzed recrystallization process, indicating the regeneration of the ordered catenate-COFs requires a high activation energy to correct the "mismatched" coordination between free chelate residues and copper ions and reorganize the distorted polyhedra to the original arrangement. The better mechanical flexibility makes the catenate-COFs uptake more guest molecules through backbone expansion and feature higher creep depth than that of the catenand-COFs. In contrast, both elastic modulus and hardness drop by more than 60% after removal of the metal ions. All of the results are as expected for woven materials.[10]

By introducing Sauvage's seminal work on the copper(I)-templated synthesis of [2]catenanes with the principles of reticular chemistry, the team's investigation has delivered a simple yet efficient and robust synthetic approach in the construction of a series of 3D COFs containing mechanically interlocked components. These interpenetrated units offer the frameworks significant dynamics with emerging properties. The combination of molecular nanotopology with reticular assembly will undoubtedly open the door to a brand-new era of smart new materials and molecular devices.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

1. Bruns, C.J., and Stoddart, J.F. (2016). The Nature of the Mechanical Bond: From Molecules to Machines (John Wiley & Sons, Inc).
2. Gil-Ramírez, G., Leigh, D.A., and Stephens, A.J. (2015). Catenanes: fifty years of molecular links. Angew. Chem. Int. Ed. Engl. *54*, 6110–6150.
3. Liu, G., Rauscher, P.M., Rawe, B.W., Tranquilli, M.M., and Rowan, S.J. (2022). Polycatenanes: synthesis, characterization, and physical understanding. Chem. Soc. Rev. *51*, 4928–4948.
4. Wu, Q., Rauscher, P.M., Lang, X., Wojtecki, R.J., de Pablo, J.J., Hore, M.J.A., and Rowan, S.J. (2017). Poly[*n*]catenanes: synthesis of molecular interlocked chains. Science *358*, 1434–1439.
5. Yaghi, O.M. (2020). The reticular chemist. Nano Lett. *20*, 8432–8434.
6. Ma, T., Zhou, Y., Diercks, C.S., Kwon, J., Gándara, F., Lyu, H., Hanikel, N., PenaSánchez, P., Liu, Y., Diercks, N.J., et al. (2023). Catenated covalent organic frameworks constructed from polyhedra. Nat. Synth. https://doi.org/10.1038/s44160-022-00224-z.
7. Sauvage, J.-P. (2017). From chemical topology to molecular machines (Nobel lecture). Angew. Chem. Int. Ed. Engl. *56*, 11080–11093.
8. Liu, Y., Ma, Y., Zhao, Y., Sun, X., Gándara, F., Furukawa, H., Liu, Z., Zhu, H., Zhu, C., Suenaga, K., et al. (2016). Weaving of organic threads into a crystalline covalent organic framework. Science *351*, 365–369.
9. Liu, Y., Diercks, C.S., Ma, Y., Lyu, H., Zhu, C., Alshmimri, S.A., Alshihri, S., and Yaghi, O.M. (2019). 3D covalent organic frameworks of interlocking 1D Square Ribbons. J. Am. Chem. Soc. *141*, 677–683.
10. Zhang, Z.-H., Andreassen, B.J., August, D.P., Leigh, D.A., and Zhang, L. (2022). Molecular weaving. Nat. Mater. *21*, 275–283.

High-entropy argyrodite lithium superionic conductors

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In a recent study published in *ACS Materials Letters*, Lin and colleagues reported a compositionally complex superionic conductor, $Li_{6.5}[P_{0.25}Si_{0.25}Ge_{0.25}Sb_{0.25}]S_5I$, for solid-state battery applications. This (multi-cation substituted) argyrodite-based electrolyte material has a configurational entropy greater than 1.5 R and was found to exhibit high ionic conductivity at room temperature (~13 mS/cm) and a low activation energy for lithium transport (~0.2 eV).

Developing next-generation solid electrolytes is paramount to the advancement of bulk-type solid-state batteries to compete with or outperform conventional Li-ion batteries.[1] Because the diffusion pathways of superionic conductors are strongly dependent on the cation and/or anion configuration, ion mobility can be modulated by altering the host structure via doping or substitution.[2] Apart from the ionic conductivity (ideally, $\sigma_{\mathrm{ion,rt}} \geq 10$ mS/cm), (electro)chemical stability, stiffness, and yield stress are factors that need to be taken into account in the design of high-performance solid electrolytes. A new strategy for modifying crystal structure, thereby potentially leading to improved or even unprecedented properties, is the high-entropy materials (HEMs) concept.

HEMs refer to materials having five or more elements occupying a single crystallographic site (typically with equimolar compositions) that are characterized by configurational entropies $\Delta S_{\mathrm{conf}} \geq 1.5\ R$, with R representing the ideal gas constant. In addition to manifold interactions, so-called "cocktail effects," the introduction of various elements causes lattice distortions. Originally, this was shown for high-entropy alloys; only recently, the HEMs concept has been applied to ceramics with different crystal structures such as oxides, sulfides, or carbides.[3]

In the field of solid electrolytes, only a few examples have been

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