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Title

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Permalink

<https://escholarship.org/uc/item/46x7c7mw>

Journal

Nature Chemistry, 9(11)

ISSN

1755-4330

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Publication Date

2017-11-01

DOI

10.1038/nchem.2883

Peer reviewed

SELF-ASSEMBLY

Supramolecular basketry

Both the topology and the mechanical strength of woven materials have inspired great synthetic efforts to replicate their structures at the nanoscale. Now, a triaxial weave has been prepared by self-assembly of a judiciously designed organic molecule through π - π and CH- π interactions.

Yi Liu

Weaving is one of humanity's oldest technologies. Directional threads called warps and wefts are guided over and under each other to form interlaced patterns, giving rise to a fabric that is stronger and more resilient than the original materials. Inspired by both the topology of the resulting fabric and the emergent mechanical properties of the entangled chains, chemists have pursued methods to weave molecules into patterns comparable to those of macroscopic fabrics. Weaving at the molecular scale, however, remains a challenge primarily due to the lack of tools to direct nanoscopic threads.

To build complex topological nanostructures, chemists generally rely on the self-assembly of predesigned molecular constituents. When it comes to weaving or braiding molecular threads, both DNA strands hybridization and metal-ligand coordination are readily available tools for chemists to devise the necessary directionality and crossover geometries for the formation of interwoven threads. Yet, despite the extensive examples of complex topological structures that have been assembled in the realms of DNA nanotechnology and coordination

polymers, only a handful of woven patterns are known^{1,2}, and a purely organic woven structure has so far remained largely unexplored.

Now, writing in *Nature Chemistry*³, Helma Wennemers and co-workers describe the supramolecular synthesis of the nanoscale replica of a Kagome weave — a traditional pattern of Japanese basketry dating back nearly 7,000 years⁴ (Fig. 1a) — using solely organic molecular components. The Kagome weave is a triaxial pattern with trihexagonal tiling, composed of equilateral triangles sharing each side with a regular hexagon and vice versa. Aesthetically, it may be considered as the planar tiling of the six-pointed star shape known as the Star of David.

The formation of the triaxial supramolecular weave takes advantage of synergistic non-covalent interactions amongst the building blocks, which consist of an oligoproline segment bearing two aromatic perylene-monoimide (PMI) side groups (**1**) (Fig. 1b). The oligoproline serves as a molecular scaffold owing to its rigid helical shape in which every third proline residue is stacked on top of another at a set distance of 9 Å. Judicious positioning of two PMI moieties — six proline residues apart —

thus sets them at 18 Å from, and parallel to, each other. Strong π - π interactions between PMIs from adjacent molecules lead to the preorganization of oligoprolines into non-covalent linear threads with alternating up- and-down facing voids at defined intervals. Such molecular arrangement allows for the formation of crossing points, the foundation for weaving. Two π -stacked PMI pairs of two neighbouring threads further engage in CH- π interactions, holding them at an angle of 60° from each other, in turn giving rise to triangular connection points that lock the threads in the triaxial architecture (Fig. 1c).

Single domains of hexagonal micrometre-sized self-assembled crystallites are revealed by transmission electron microscopic studies, from which mesh-like superstructures with 3.0 nm-wide hexagonal holes can be clearly identified. The cell parameter of 5.5 nm is twice the length of the oligoproline unit, consistent with a minimal repeating unit formed by two molecules of **1** in a head-to-tail arrangement through π - π stacking of PMI units. Grazing-incidence wide-angle X-ray scattering patterns show *d*-spacings from specific intermolecular interactions such as π - π stacking and CH- π interactions, all

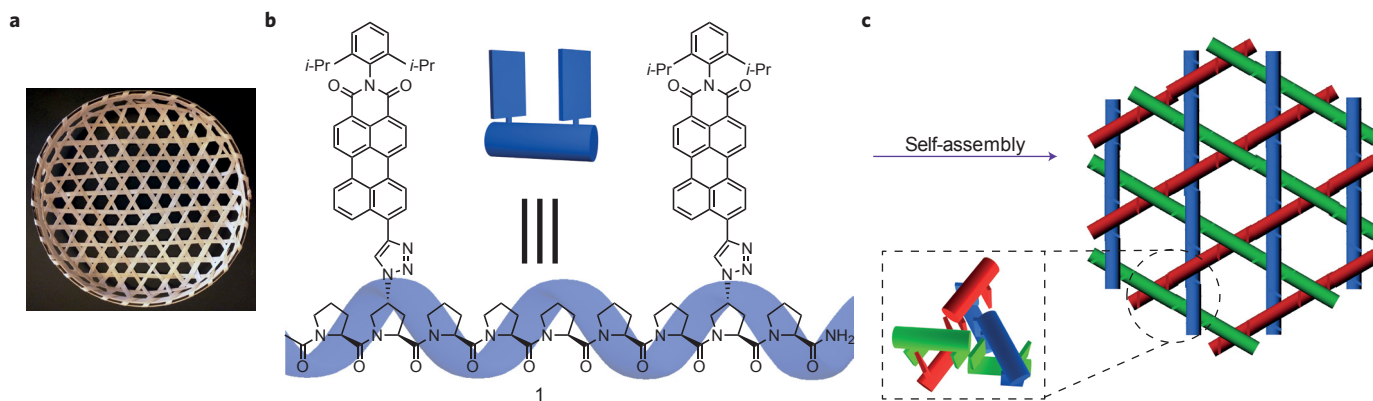


Figure 1 | Illustration and schematic representation of the triaxial weave. **a**, A picture of a basket woven in the triaxial Kagome pattern. **b**, Molecular structure of the oligoproline **1** with a helical backbone and its schematic representation. **c**, The top-down view of the woven topology from the assembly of molecule **1**. The triangular connection is highlighted in the inset. Red, green and blue colours are used to differentiate supramolecular threads that are formed from identical molecules.

commensurate with the triangular structure of the connection points in the network.

Further proof that the structure of the building unit **1** is essential for the weaving to occur is that no such triaxial woven structure is observed for molecular analogues featuring PMI units that are spaced differently, or a shorter oligoproline. A few years ago, previous work from these researchers had also revealed that subtle structural modifications of similar oligoproline-PMI conjugates resulted in different self-assembled nanostructures⁵. Thus, the successful formation of the triaxial woven network is contingent upon fulfilling several molecular geometry requirements all at once: the rigidity of the oligoproline scaffold, the exact void opening defined by the separation of the π -stacking units, and the right diameter of the oligoproline helix. The woven materials demonstrated an approximately sixfold enhancement in mechanical strength compared to non-woven threads and entities, as revealed by PeakForce quantitative nanomechanical mapping. In addition, the weave can host the growth of iridium nanoparticles into a regular hexagonal geometry, through confinement of the organometallic precursor in its holes. This prevents spontaneous aggregation that is a common problem in nanoparticle synthesis, and demonstrates the robustness of the triaxial weave and its promises for engineering hybrid materials.

Although this is not the first woven organic nanostructure, only two precedents

exist. Both are biaxial weaves whose construction relies on metal–ligand coordination to assist in the preorganization of molecular precursors. In 2016, Yaghi and co-workers built an extended woven covalent organic framework using dynamic imine chemistry in combination with copper(I)-ion templating⁶. The copper-ion templates can be reversibly removed or restored after weaving, leaving the biaxially woven structure intact while allowing its mechanical properties to switch between two elastic states. Earlier this year, Mayor and co-workers built an all-organic woven structure by crosslinking quadrirropic linkers mounted on a sacrificial metal–organic framework.⁷ Removal of the metal ions by acid treatment left woven textile sheets that could be transferred and imaged as freestanding films on different supports.

The discovery of the elusive triaxial weave represents great progress towards building advanced multi-axial weaves, which underscores a higher level of complexity and structural precision in woven structures with precisely controllable pore size and uniformity. On the other hand, despite the improved robustness that is attributable to the entangled molecular arrangement, mechanical strength remains intrinsically limited by the non-covalent nature of the forces holding the molecules together in the threads. Approaches to reinforce the covalent characteristics of the threads may provide a clear path to further improve the macroscopic properties.

Following the successful preparation of the molecular Star of David⁸, it is conceivable that the 3D triaxial extended weave — essentially an infinite tiling of these hexagrams — may also be built using methodologies analogous to Yaghi's weaving⁶. Investigations into these fascinating structures will continue to extend the limits of complexity available in interlaced topologies. More intricate types of entanglement at the nanoscale will provide insights into the fundamental structure–property relationships that may transition structural curiosities into application-focused materials. Additional structural features such as nanometre-sized pores arisen from these woven structures will also offer opportunities for engineering hierarchical and composite materials. \square

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