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COMMENTARY

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Precision weaving at the molecular scale: Polymer networks with remarkable mechanical robustness

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Two-dimensional (2D) materials have emerged as a focal point of scientific research due to their exceptional properties derived from ultra-thin sheet morphologies and extremely high surface areas. These characteristics confer unique physical and chemical properties, making them highly attractive for applications in condensed matter physics, materials science, and chemistry. The ability to engineer materials at the molecular level to achieve customized functionalities is an essential pursuit in modern materials science.

Inspired by the complex topology of weaving—a technique that interlaces threads to create fabrics—scientists have explored the concept of weaving molecular wires into 2D patterns. This molecular weaving offers a promising strategy for constructing materials with tailored properties, potentially leading to innovations in electronics, catalysis, and energy storage.

Significant strides have been made in molecular weaving, particularly in the synthesis of 2D and three-dimensional (3D) woven materials. In 2000, Busch

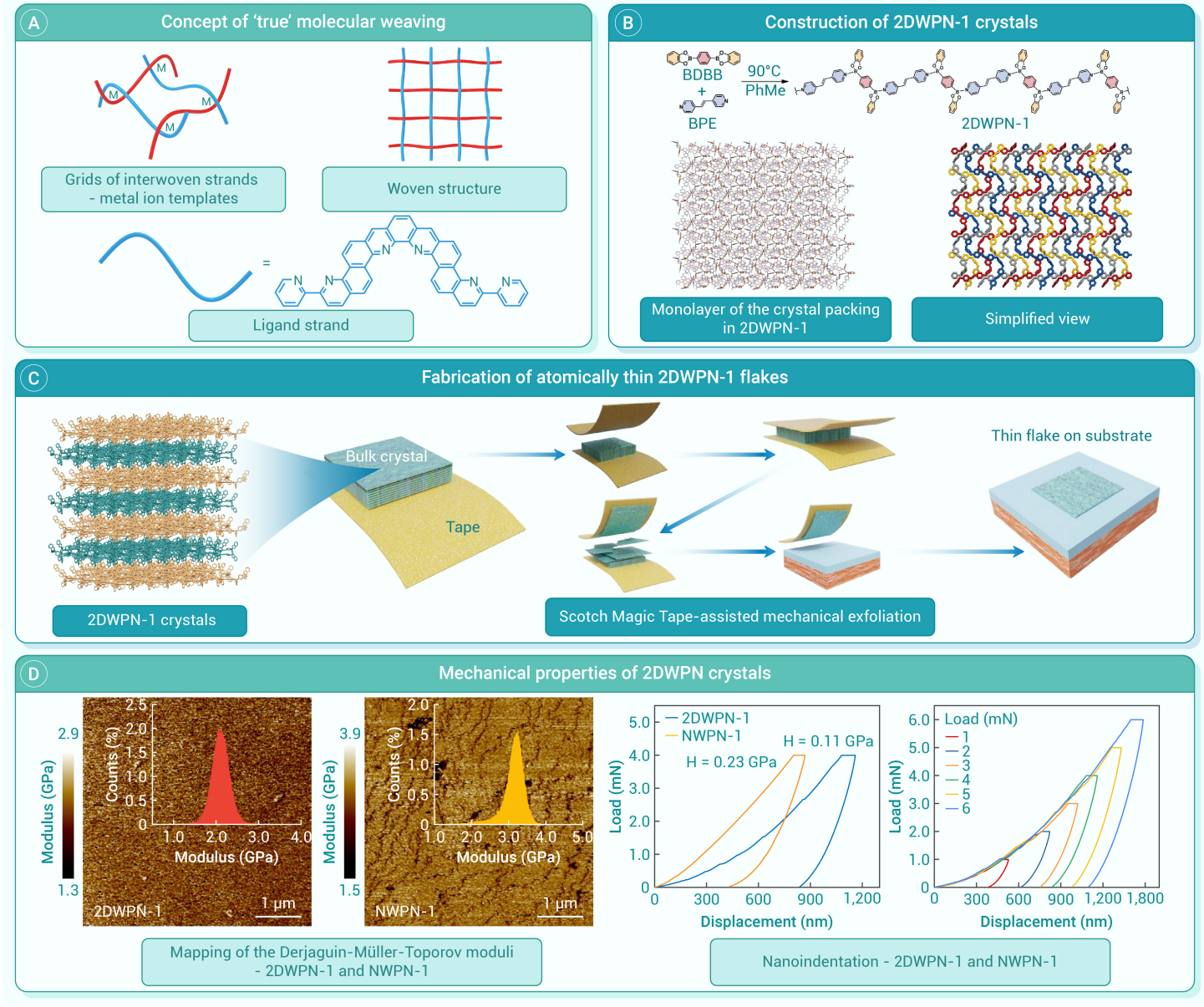

Figure 1. Fabrication, characterization, and mechanical properties of atomically thin 2DWPN-1 flakes (A) Grids of interwoven strands, assembled using metal ion templates, envisioned by Busch and Hubin to be used to construct materials made of woven polymer strands. Reproduced with permission.[1] Copyright 2000, Elsevier. (B) Synthesis of 2DWPN-1. (C) Schematic illustration of the exfoliation of 2DWPN-1 nanosheets. (D) Study of the mechanical properties of 2DWPN-1 and NWPN-1. Reproduced with permission.[5] Copyright 2024, Springer Nature.

proposed a vision of interlaced molecular design,[1] which includes the concept of "real" molecular weaving—weaving molecular chains into macroscopic threads (Figure 1A). More than a decade later, Liu et al. demonstrated a molecular fabric analog using metal-organic frameworks, creating helical organic threads with a woven texture.[2] Phenanthroline ligands on a copper metal complex directed the addition of organic linkers via imine bonds to create helical organic threads with woven texture. Removing the copper allowed the strands to slide against each other and increased the elasticity of the material 10-fold. Robin *et al.* further advanced the field by describing a triaxial-patterned supramolecular woven network formed through $\pi-\pi$ stacking interactions.[3] In 2020, Young et al. synthesized layered 2D molecular woven fabrics by tessellating metal-coordinated woven grids into polymer networks using disulfide bonds.[4] These studies collectively showcased the feasibility of constructing woven molecular architectures.

Despite these advancements, achieving perfect two-dimensional biaxial braided patterns using purely organic molecular wires remains a significant challenge. Previous efforts often relied on metal coordination or resulted in materials with imperfections and limited structural control. The synthesis of defect-free, free-standing 2D woven polymer networks composed solely of organic molecules has not been fully realized. The lack of such materials has hindered detailed structural studies of the formation mechanism and structure of two-dimensional woven materials. Moreover, examples of free-standing 2D monolayer woven sheets exfoliated from layered materials remain scarce, limiting the exploration of their surface properties and structural features—aspects crucial for potential applications in nanotechnology and materials science.

In a recent study published in Nature Chemistry (Figure 1B), Huang et al. reported a significant breakthrough in the field by developing a two-dimensional free-standing structure through a molecular weaving technique, employing dative boron-nitrogen (B–N) bonds to create a stable polymer network (2DWPN-1).[5] This approach leverages the intrinsic conformational flexibility of these linkages, facilitating the formation of the desired woven structure.

The synthesis of 2DWPN-1 begins with a dehydration reaction between 1,4-phenylenediboronic acid and catechol to create 1,4-bis (benzodioxaborole) benzene (BDBB). Subsequently, BDBB was combined with 1,2-bis (4-pyridyl) ethylene (BPE) in methylbenzene (PhMe) at 90°C to induce polymerization. During the slow cooling of the mixture, the woven polymerization process occurs, driven by the formation of dative B–N bonds. These bonds play a pivotal role in facilitating conformational flexibility, which is essential for the weaving of polymer threads into a stable two-dimensional structure. The resulting structure features a distinct two-over, two-under pattern that resembles traditional woven textiles. Importantly, the adjustable angles of the dative B–N bonds provide the necessary flexibility to achieve this desired topology.

The synthesis method resulted in the formation of centimeter-scale, yellow, single crystals of 2DWPN-1, which were further analyzed to understand the material's properties. Field-emission scanning electron microscopy revealed that the synthesized material formed a layered crystal structure, with molecule-thick nanosheets stacked in an organized manner. Atomic force microscopy analysis showed that each layer had a thickness of approximately 1.3 nm, and the loose arrangement between layers enabled the mechanical exfoliation of monolayers from the bulk crystal (Figure 1C). Single-crystal X-ray diffraction provided detailed information regarding the molecular structure, showing that the crystals belong to the orthorhombic P_{bca} space group, with the network exhibiting a helical pattern of B–N-linked polymer chains. Low-dose cryogenic transmission electron microscopy allowed for high-resolution imaging of the woven polymer network, providing direct evidence of the interwoven topology and a comprehensive view of the intricate structure formed by the BPE and BDBB components.

The study also demonstrated the influence of the solvent on the formation of the woven topology. In the synthesis of a non-woven polymer network (NWPN-1), the use of m-xylene instead of PhMe resulted in a different structure without the woven configuration. This comparison highlighted the critical role of solvent choice in determining the polymer's topology and provided insights into the mechanism of topology formation. The steric properties of the solvent molecules were found to be essential in guiding the weaving process.

The mechanical properties of the woven polymer network 2DWPN-1 were analyzed and compared with the non-woven NWPN-1 to assess the impact of the woven topology (Figure 1D). The woven polymer network demonstrated exceptional flexibility, setting it apart from non-woven polymer structures in mechanical performance. This difference in modulus values indicates that the woven topology imparts greater flexibility to the material, as it allows for more conformational freedom of the polymer chains. The helical polymer chains, woven in a two-over, two-under pattern, enabled the dispersal of external forces throughout the material's structure, preventing the concentration of stress that might lead to structural failure. Nanoindentation experiments also confirmed that 2DWPN-1 exhibited greater displacement under applied load, further indicating enhanced flexibility. The stress-dispersing capabilities of the woven network were attributed to the ability of molecular strands to slide relative to each other through interwoven nodes without compromising the integrity of the entire structure. These interwoven nodes, created by B–N-linked BPE and BDBB components, provided a robust framework that effectively dispersed the mechanical load, resulting in improved material flexibility. The unique mechanical properties make 2DWPN-1 suitable for applications where a combination of flexibility and mechanical resilience is required.

The development of a flawless, purely organic, free-standing two-dimensional woven polymer network driven by dative B–N bonds marks a pivotal advancement in the field of two-dimensional materials. By overcoming significant challenges in molecular weaving, this study opens new avenues for the design and application of materials with tailored properties. The detailed investigation of the network's structure and the successful exfoliation of monolayer nanosheets provide valuable insights that will inspire future research and technological innovations. Future research should focus on expanding the diversity of woven materials, exploring their functional applications, and scaling up their production. With continued innovation, molecular weaving could redefine the landscape of 2D materials, offering unprecedented opportunities for material design and application.

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AUTHOR CONTRIBUTIONS

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DECLARATION OF INTERESTS

The authors declare no competing interests.