

Striking 2D materials: exfoliation of molecular crystals

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Ultrathin nanosheets, which are often prepared from bulk crystals by exfoliating, represent an intriguing type of two-dimensional (2D) materials with mechanical, electronic, optical, and thermal properties that are distinct from their pristine bulk crystals. They are promising in various applications, including (opto)electronics, chemical sensing, catalysis, and separation, because of their unique properties and high surface area. Previously, the operationally simple exfoliation method is only applicable to bulk crystals with weak interactions between the layers, but the units of the single layers must be linked by strong covalent bonds. For example, graphene can be peeled from flake graphite. However, despite their abundance and variety, molecular crystals with layers of units linked by weak non-covalent bonding have not been investigated as sources of free-standing 2D materials. This is because the layer is believed to be too fragile to sustain its morphology after stripping from bulk crystals.

Recently, Cui's group [1] reported the successful preparation of monolayer nanosheets by liquid-phase exfoliation of molecular crystals, which is unprecedented and targeted for large-scale production. Using supramolecular coordination complexes (SCCs) as representative systems, they were able to obtain free-standing chiral 2D nanosheets with the thickness of 2.3 nm and aspect ratios (ratios of length to thickness) of up to ca. 2500:1. SCCs are discrete molecular species assembled from the coordination of metal ions and organic ligands. Specifically, metallosalen ZnL (L=L1 and L2, Figure 1a) with one pyridyl group to coordinate

another Zn atom, resulting in a hexameric metallacyclic complex that packs into three-dimensional porous frameworks directed by supramolecular interactions. Three types of SCCs crystals (Figure 1b), namely **1** ($Zn_6(L1)_6$), **2** ($Zn_6(L1)_3(L2)_3$) and **3** ($Zn_6(L2)_6$), were prepared by altering the ratio of L1 and L2. As previously confirmed, they can serve as good platforms to adsorb and enantioselectively discriminate polar molecules in solution [2]. Subsequently, these crystals were subjected to a liquid-phase exfoliation process (Figure 1c) in which solvent molecules can enter the interlayer void and split the bulk materials into layers under sonication (40 kHz, 100 W). The solvent polarity was claimed to play an important role in the procedure, and acetonitrile was chosen as the candidate after screening a large number of organic solvents. The morphology, structure, composition and property of monolayered nanosheets peeled from crystals **1–3** were verified by substantial sophisticated measurements. Amazingly, the crystalline nature of molecule-thick 2D nanosheets with highly ordered hexagonal arrays of metalacyclic molecules could be seen at the atomic level (Figure 1d–f) as assisted by the high-resolution transmission electron microscopy (HR-TEM). Surprisingly, every “vertex” of each individual molecule was clearly visible (Figure 1g, h) after correcting the effect relative to the contrast transfer function (CTF) of the objective lens, which was in good accordance with the simulation result (Figure 1i).

It is worth noting that the exfoliation of chiral SCCs may increase the difficulty of this strategy, which on the other hand, proves its universality in molecular crystals. More importantly, the introduction of chirality in SCCs adds an additional structural feature compared with achiral counter-

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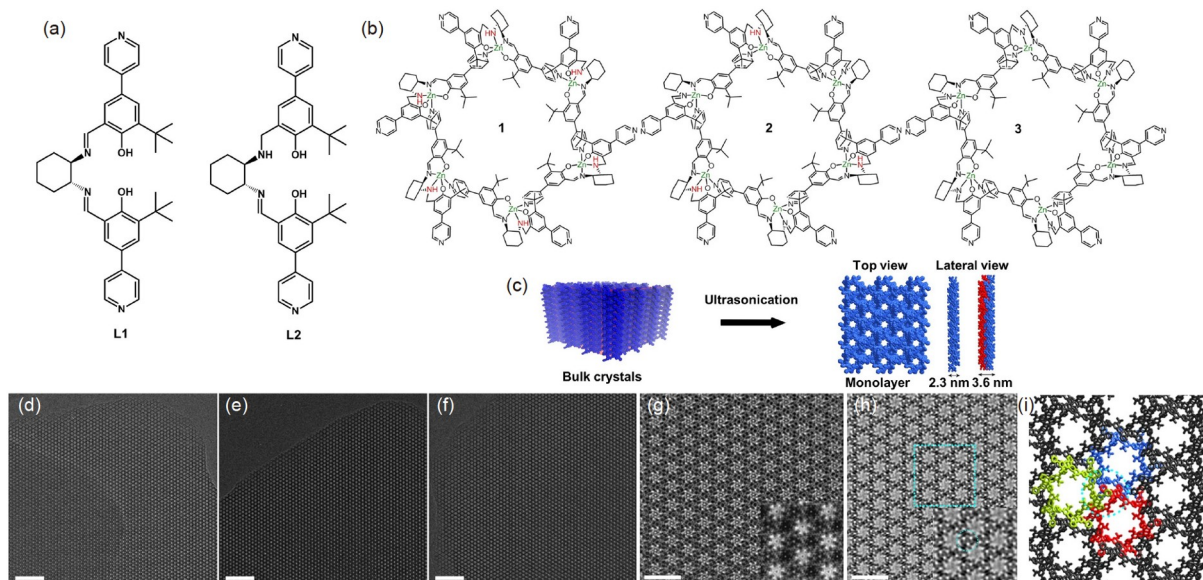


Figure 1 (a) Chiral ligand of **L1** and **L2**; (b) as synthesized SCCs **1–3**; (c) a schematic illustration of the liquid exfoliation of **1** monolayer nanosheets along the *ab* plane; (d–f) HR-TEM images of 2D nanosheets of **1**, **2**, **3**, respectively. Scale bars: 20 nm. (g) Raw HR-TEM image of a 2D monolayer nanosheet of **1**. Inset is the simulated HR-TEM image using the determined defocus value and the 2D structural model. Scale bars: 5 nm. (h) CTF-corrected image of (g). Inset is an enlarged area in (h). Scale bars: 5 nm. (i) Simulated projected potential map according to the X-ray crystal structure model of the *ab* plane [1] (color online).

parts, enabling the function of SCCs in highly demanding chirality-related areas and deciphering the underlying mechanism of chirality transfer. As a proof of concept, the obtained 2D monolayer nanosheets were employed to interact with a wide range of carbohydrates and diols, displaying notable enhancement in both the binding amount and enantiodiscrimination factor over their parent bulk crystals. In addition, Cui *et al.*'s work [3,4] also represents one of the rare studies that have achieved the synthesis of 2D nanosheets from chiral porous frameworks [5]. All these exciting results should arouse enthusiasm to deepen research on finding the limitation of in- and between-layer interactions that ensure the fabrication of free-standing layers by exfoliation. Simultaneously, how cofactors such as solvent will aid in the liquid-phase exfoliation process has not been fully understood. Furthermore, the large-scale production and application of ultrathin nanosheets will continue to in-

trigue further studies in the field.

The liquid-phase exfoliation of molecular crystals is a breakthrough with both fundamental and applied significance. Remarkably, it expands the sources of ultrathin nanosheets and provides insights into novel properties arising from structural differences between 2D materials and their parent bulk crystals.

Conflict of interest The authors declare no conflict of interest.

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