Materials chemistry

Fragile nanosheets stripped from crystals

Claudia Backes

Two-dimensional materials have been restricted to systems in which strong chemical bonds hold atoms together in sheets. Now, 2D materials consisting of molecules linked by weak non-covalent bonds have been peeled from crystals. See p.606

Much research is currently focused on the fabrication and characterization of two-dimensional nanomaterials, which are often produced by peeling ultrathin sheets of atoms from crystals. It is widely thought that this method requires the crystals to contain layers of atoms held together by strong covalent bonds, with only weak binding between the layers. On page 606, Dong *et al.*[1] show that this is not always the case. The authors demonstrate that 2D nanosheets with high aspect ratios (ratios of length to thickness) can be obtained from crystals, suspended in liquids, when the molecules in the layers are held together only by weak non-covalent bonds.

The authors chose supramolecular coordination complexes (SCCs) as model systems for their study. In these complexes, specially designed organic molecules act as electron donors (ligands) to form networks of bonds with metal cations, which are electron acceptors. Dong and colleagues' ligands are star-shaped, and form complexes in which six metal cations are placed at each point of the star (Fig. 1).

Not only do the ligands bridge and connect the metal cations, but they also contain aromatic units (groups that contain benzene rings or related ring systems) that hold the molecules together through non-covalent bonds. The resulting crystals can be viewed as stacks of sheets, similar to the layered structure of van der Waals crystals, such as graphite. But, unlike typical van der Waals crystals, the sheets are not continuous networks of covalent bonds. Instead, they are composed of discrete molecules.

In van der Waals crystals, individual layers can be peeled off mechanically (exfoliated) to produce 2D materials. These materials have intriguing electronic, optical, mechanical and thermal properties that are distinct from those of the bulk crystals. Moreover, the high surface area of 2D materials is of interest for a range of applications, such as (opto)electronics, sensing, catalysis and energy conversion and storage[2,3].

A technique known as liquid-phase exfoliation was originally developed to peel sheets of atoms from graphite, and was subsequently extended to other van der Waals crystals[4,5]. In this technique, crystals are suspended in a liquid, and energy is provided – for example, using ultrasound – to enable exfoliation. The liquid can be chosen to prevent reaggregation of the exfoliated sheets[5]. This well-established process has been applied to tens of van der Waals crystals, and has provided nanosheets in quantities large enough for potential applications to be explored in diverse areas. Unfortunately, the high energies necessary to achieve exfoliation typically also fracture the sheets[6]. Dong and colleagues' discovery that liquid-phase exfoliation can be applied to SCCs is therefore astonishing, because these complexes are much more fragile than van der Waals crystals.

> **"This demonstration could greatly expand the palette of nanomaterials."**

Dong *et al.* prepared 2D sheets from SCCs by applying ultrasound to crystals dispersed in organic solvents – the first time that liquid-suspended sheets of discrete molecules have been produced 'top-down' from bulk crystals. Microscope images reveal that the nanosheets are as thin as 2 to 3 nanometres, with lateral dimensions of up to 12 micrometres, and are remarkably crystalline with no observable defects. The authors used other characterization techniques to show that the 2D material is composed of the same molecules as the bulk crystals.

The ligands in the SCCs can be designed in such a way that stacks of chiral molecules form in the complexes[7]. In chemistry, chirality is a geometric property of molecules that distinguishes between isomers that are mirror images of each other. The SCCs can therefore act as platforms for chiral sensing of biologically active molecules or pharmaceuticals: molecules with a certain chirality bind with higher affinity to the SCCs than do their mirror-image isomers, a phenomenon known as enantioselectivity. Dong *et al.* show that their 2D materials are better at chiral sensing than are bulk SCCs. On exfoliation, the high surface area of the 2D materials exposes more, and potentially different, binding sites to the environment for chiral molecules from those available in the bulk crystals, resulting in a

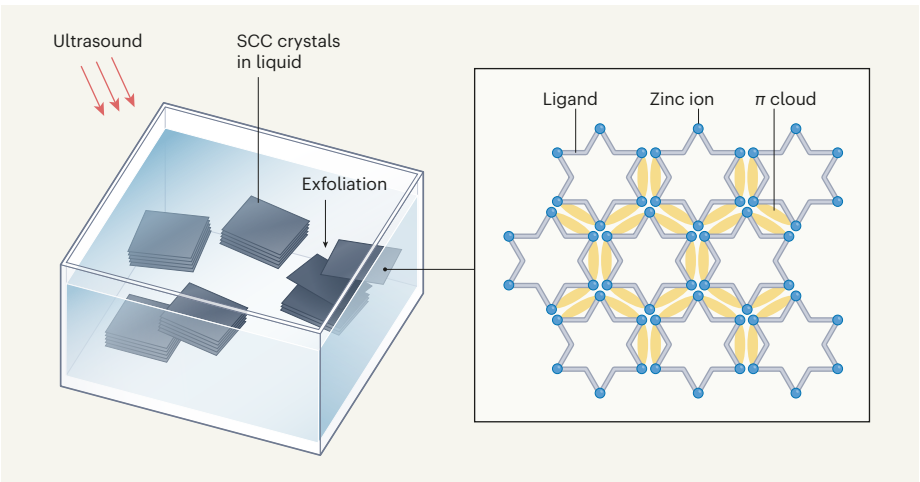

Figure 1 | Exfoliation of supramolecular coordination complexes. Dong *et al.*[1] suspended crystals of a supramolecular coordination complex (SCC) in a liquid and subjected them to ultrasound. The crystals consist of stacked sheets, each of which is assembled from star-shaped organic ligand molecules bound to zinc ions. Delocalized electrons (π clouds) in the ligands interact with each other to form non-covalent bonds between molecules, holding the sheets together. The authors observe that single and double sheets peel off (exfoliate) from the crystals in their experiments. Liquid-phase exfoliation has previously been used to peel off sheets from crystals such as graphene, in which the atoms in the layers are held together strongly by covalent bonds. By contrast, the sheets in SCCs were thought to be too fragile to survive exfoliation.

three- to fourfold enhancement of enantioselective recognition.

The demonstration that liquid-phase exfoliation can be applied to molecular crystals suggests that nanomaterials with high aspect ratios can be readily obtained from other SCCs, or indeed from the tens of thousands of crystalline organic compounds that are available, which would greatly expand the palette of nanomaterials. However, many open questions remain. First, it is not clear which types of organic crystal might be used for exfoliation. Furthermore, what governs 'exfoliability' and the morphology of the nanostructures formed?

Dong *et al*. calculated that the in-layer bonds in their SCCs, although weaker than those in van der Waals crystals, are about twice as strong as the binding between layers. This could explain why the SCCs cleave preferentially to produce sheets. Moreover, at first glance, this is in line with the current understanding that the morphology of the nanomaterials produced by liquid-phase exfoliation is determined by the ratio of the in-plane to out-of-plane binding strengths[8,9]. At second glance, however, there is a quantitative mismatch with the ratios that lead to similar outcomes for van der Waals crystals. For example, graphene sheets exfoliated from graphite have a comparable (if not lower) aspect ratio to that of the SCCs, but the ratio of in-layer to between-layer binding strength is much higher[8,9]. This might mean that other factors also have a role in controlling the outcome of liquid-phase exfoliation of SCCs, such as the penetration of solvent between layers. It is therefore crucial to work out the exfoliation mechanism for SCCs.

Furthermore, the choice of solvent will be important for the liquid-phase exfoliation of other organic crystals: on the one hand, the crystals must not dissolve in the liquid; but on the other hand, there must be sufficient interaction between the solvent and the nanosheets to prevent reaggregation. For many systems, finding a solvent that strikes the right balance could be extremely difficult. A possible way forward could be the use of surfactant solutions, such as those that were used[10] last year for the liquid-phase exfoliation of molecular crystals of the organic semiconductor rubrene, which yielded nanobelts and nanorods. Finally, for practical applications, post-processing methods will be needed – for example, to select certain sizes of nanosheet and to deposit sheets precisely onto substrates. The development of such methods remains a challenge for all nanosheets produced by liquid-phase exfoliation[11].

Nonetheless, the report of a simple method for producing liquid-suspended nanomaterials from molecular crystals is an exciting breakthrough for both fundamental and applied research. If it increases the range of 2D nanomaterials that can be made, it might help to answer the question of how the optical, electrical, thermal and mechanical properties of exfoliated molecular crystals differ from those of their bulk counterparts.

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Astronomy

Radio bursts from among the oldest stars

Vikram Ravi

Luminous bursts of radio emission are linked to highly magnetized neutron stars known as magnetars. Now, bursts have been detected from a globular star cluster, an environment thought to be devoid of magnetars. **See p.585**

If you were to look up at the sky with radio goggles, you would notice bright flashes at random locations roughly once every minute. Over the past 15 years, astronomers have detected more than 600 sources of such bursts, which have a range of luminosities, durations and rates of repetition. More than 20 sources have now been traced to specific galaxies, the diversity of which is similarly astounding. But such varied observations have not yet produced incisive insights into the burst mechanism. Now, on page 585, Kirsten *et al.*[1] report a surprising source of extragalactic radio bursts among some of the Universe's oldest stars, and, in *Nature Astronomy*, Nimmo *et al.*[2] provide a detailed analysis of these bursts. The discovery differs from previous findings of sources among young stars, and challenges ideas on the formation of magnetars – the most magnetized objects in the Universe.

A breakthrough in our understanding of fast radio bursts occurred in 2020, when three papers reported the discovery of a particular burst from an active magnetar in the Milky Way, known as SGR 1935+2154 (refs 3–5). All known magnetars in the Milky Way are thought to have formed in the terminal supernova explosions of some massive stars[6], and SGR 935+2154 is located in a supernova remnant. The most massive stars live for only a few tens of millions of years, so observations of supernovae tell us that their associated stars are probably still forming. All galaxies known to host sources of fast radio bursts are likely to be currently forming stars[7].

The source that Kirsten and colleagues investigated is located in a cluster of astronomically ancient stars on the far outskirts of Bode's Galaxy in Ursa Major. It is known as FRB 20200120E and it vigorously emits bursts as short as 60 nanoseconds (Fig. 1). The authors showed that FRB 20200120E cannot be a magnetar formed in the supernova of a massive star, because it resides in a globular star cluster. Globular clusters are compact collections of typically a few hundred thousand stars. They are found in the haloes of galaxies, and they are several billion years old. Massive stars in globular clusters will have exploded soon after the formation of the cluster, and any magnetars formed at this time will have deactivated after around 10,000 years as their magnetic fields decayed.

Thus, if FRB 20200120E represents an active magnetar, it must have formed through means that we have yet to witness. The possibilities are fantastic. For example, a white dwarf star could have accreted so much mass from a companion star – or simply swallowed a companion whole – that it exceeded the Chandrasekhar mass limit. This limit is the theoretical maximum mass above which a white dwarf ceases to be a white dwarf, and instead might collapse to form a magnetar. The detailed studies carried out by Nimmo *et al.* and a second team[8] offer a tantalizing clue to the origin of FRB 20200120E's bursts.