

planets⁸, constraining their composition and climate, respectively. Liquid water could exist, or have existed, on any of the TRAPPIST-1 planets⁹, but predictions are difficult to make. For instance, although the estimated densities of the planets are consistent with their being similar in composition to Earth, they could instead be volatile-rich — containing a large fraction of water and ices — like the Galilean moons.

We also know from Jupiter's moons that a crucial factor for predicting the climate of a planetary body is the heating of its interior owing to friction caused by tides. This effect is responsible for widespread volcanism on Io and is the reason why Europa is thought

to have a subsurface ocean. Tidal heating is expected for the TRAPPIST-1 planets because they exist in near-resonant orbits.

Could any of the planets harbour life? We simply do not know. But one thing is certain: in a few billion years, when the Sun has run out of fuel and the Solar System has ceased to exist, TRAPPIST-1 will still be only an infant star. It burns hydrogen so slowly that it will live for another 10 trillion years (ref. 10) — more than 700 times longer than the Universe has existed so far, which is arguably enough time for life to evolve. ■ SEE FUTURES P.512

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MATERIALS SCIENCE

Organic analogues of graphene

Chemists have long aspired to synthesize two-dimensional polymers that are fully conjugated — an attribute that imparts potentially useful properties. Just such a material has been prepared using a solid-state polymerization reaction.

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One of the greatest breakthroughs in materials science was the isolation of graphene¹ — a two-dimensional carbon crystal, obtained by stripping off (exfoliating) a single layer of atoms from graphite using adhesive tape. This discovery prompted the emergence of 2D materials as a new paradigm in science and technology. Nevertheless, graphene's potential use as a semiconductor in electronic devices has been limited because its bandgap (a property that controls the conductivity of materials) is zero, which enforces metal-like conduction. This problem has stimulated growing interest in synthesizing organic analogues of graphene that might exhibit useful properties, including a tunable bandgap^{2,3}. Writing in *Nature Chemistry*, Liu *et al.*⁴ report a breakthrough in this field: the synthesis of an organic graphene analogue known as a 2D-conjugated aromatic polymer (2D-CAP).

Graphene is the largest 2D system in nature to be conjugated — that is, some of its electrons (its π -electrons, in scientific jargon) are delocalized within a planar framework of alternating single and double bonds. This conjugation is responsible for the material's remarkable mechanical, electronic and optoelectronic properties⁵. Synthesizing extended (micrometre-scale), fully conjugated and ordered 2D structures has been a long-standing goal for polymer scientists. Until now, the main approaches

pursued to address this challenge have fallen into three categories⁶: the formation of 2D covalent organic frameworks (COFs; porous crystalline solids constructed from organic building units connected by strong covalent bonds); surface-mediated polymerization; and solid-state topochemical polymerization.

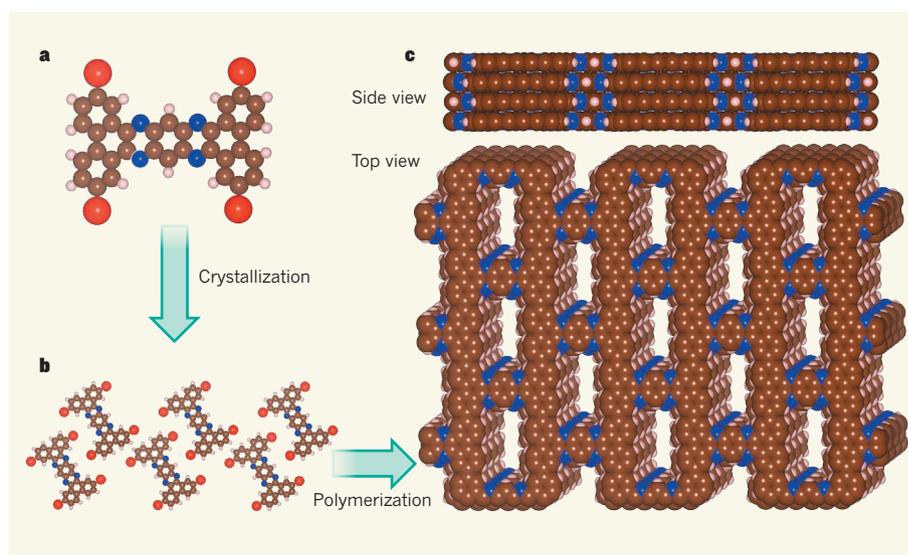


Figure 1 | Synthesis of a two-dimensional conjugated aromatic polymer. a, b, Liu *et al.*⁴ prepared an aromatic monomer (a) that crystallizes in a packing arrangement (b) that pre-organizes the molecules for a polymerization reaction. c, When the crystals were heated, polymerization occurred to form a material composed of flat, stacked layers; side and top views are shown. Individual layers of the polymer can be peeled off the stacked system. Carbon atoms, brown; nitrogen, blue; bromine, red; hydrogen, pink. Structures were prepared using VESTA 3 software¹¹.

In each approach, the type and strength of the bonds formed between reacting molecules determine the robustness of the final product⁷.

COFs are typically made using dynamic and reversible covalent-bond-forming reactions, which enables self-correction of any structural defects that form during the synthesis⁶. Unfortunately, most COFs have limited chemical stability, and tend to decompose under ambient conditions. However, 2D-conjugated COFs made using irreversible covalent double bonds were recently reported⁸, which form as crystalline flakes up to 100 μm long. In parallel, surface-confined reactions have been used to make flat, conjugated polymers in which the largest ordered domains are of the order of just a few square nanometres^{9,10}. The third approach — solid-state topochemical polymerization — takes place when monomers form a crystal in which the molecules have the proximity and orientation needed

to react with each other. Several groups have reported the crystal-to-crystal transformation of monomers into layered polymers using this strategy⁶. However, these polymers were not fully conjugated 2D polymers, and could be exfoliated only by applying heat or certain solvents, or both.

Enter Liu and colleagues. The basic building block of their 2D-CAP is a planar molecule that contains several aromatic rings — rings of atoms whose stability is enhanced by complete delocalization of their π -electrons. The authors judiciously designed this aromatic monomer so that it can form an ordered arrangement that, when heated, undergoes a crystal-to-crystal solid-state polymerization (Fig. 1).

Liu *et al.* first attempted the polymerization of their monomer on the surfaces of single crystals of gold, using a process in which the monomer lost its bromine atoms on heating and then formed covalent carbon-carbon bonds with its neighbours at the positions where their bromine atoms were detached. This yielded an undesirable mixture of 1D and 2D polymers. But when the authors pre-ordered the monomer by crystallizing it, the reaction yielded a monocrystalline polymer that was fully conjugated and formed of planar layers. The layers are stacked with a distinct lamellar structure that can be readily exfoliated into micrometre-sized sheets just 1 nm thick. The fact that individual layers could be exfoliated using adhesive tape suggests that 2D-CAP is a close analogue of graphene.

The building block's shape and the stacking of the polymers result in the formation of uniform 1D channels (approximately 0.6 nm in diameter) through the 2D-CAP. Liu *et al.* demonstrated that these aligned channels can be used to store sodium ions in an energy-storage device that can be quickly charged and discharged at room temperature. In other words, the polymer can be used as an organic anode in a sodium-ion battery.

Less than a decade ago, extended, planar, fully conjugated polymers were considered to be just a dream². The exciting properties of Liu and colleagues' 2D-CAP open up new horizons in the field of 2D materials and will inspire future efforts in this arena. A potential drawback of the authors' approach, if applied to other monomers, is that, when heated, some monomers might decompose before polymerization occurs. A variety of monomers must therefore be designed that polymerize at temperatures low enough to prevent decomposition. Flexible synthetic routes are also needed that allow different monomers and polymers to be made easily, because this in turn will allow the properties of 2D polymers to be tuned. Another promising direction of research could be to choose two different monomers that can co-crystallize before reacting to form a single polymer.

The 2D-CAP reported by Liu *et al.* might have promising properties in addition to

those described. For example, its electronic and optoelectronic properties are yet to be measured. Such measurements will require exfoliated polymer sheets to be overlaid onto different substrates, so that they can be used as the active layer in devices such as field-effect transistors.

Liu and colleagues' approach paves the way for a general, controlled synthesis of extended crystalline 2D-conjugated materials, and might form the basis of a new branch of crystal engineering. Such organic analogues of graphene would constitute a class of material that might be useful in various technologies, thanks to the enhancement of electronic properties that arises from π -conjugation in two dimensions. Applications might include organic transistors faster than those available today, and highly efficient solar cells and sensors. ■

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CANCER

A targeted treatment with off-target risks

It emerges that blood-cancer-targeting drugs that block a tumour-survival pathway also activate a mutation-causing enzyme in mice and in human cells. This might have implications for the clinical use of these drugs. SEE LETTER P.489

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Chemotherapy drugs cause DNA damage that triggers the death of rapidly dividing cancer cells¹, and are the standard treatment for many cancers. However, because these drugs also affect healthy dividing cells, chemotherapy can cause undesirable damage that results in short-term side effects such as nausea and hair loss. DNA damage from chemotherapy also risks increasing the number of mutations that might, in the longer term, result in other cancers or enable the original tumour to develop resistance to treatment. By contrast, targeted therapies are designed to block specific molecular pathways in cancer cells and induce tumour-cell death without causing DNA damage. On page 489, Compagno *et al.*² report studies of mouse models and human cells showing that two targeted drugs that are commonly used instead of chemotherapy in the treatment of certain blood cancers unexpectedly increase DNA damage in both healthy cells and tumour cells.

The targeted drugs in question are ibrutinib

(Imbruvica) and idelalisib (Zydelig). These two compounds are the first examples of an emerging class of targeted-therapy agent that has revolutionized the treatment of certain tumours arising from immune cells known as B cells^{3,4}, and both compounds have been approved for use in treatment by the US Food and Drug Administration (FDA). The drugs, often described as B-cell-receptor inhibitors, block the action of enzymes that transmit signals from receptor proteins on B cells (Fig. 1). These receptors sustain survival and maintain the tumour cells in anatomical sites that provide a nurturing environment. This B-cell-specific mechanism helps to explain both the drugs' efficacy and their relatively innocuous side-effect profile⁵.

Clinical trials of both ibrutinib and idelalisib revealed unprecedented rates of leukaemia tumour regression, specifically in the most common adult leukaemia, chronic lymphocytic leukaemia (CLL), including in high-risk groups of people with CLL who tend not to respond to other classes of therapy^{6,7}. Ibrutinib is also approved for the treatment of other cancers, such as relapsed mantle-cell