Sturdy nanoribbons are a cross between a soap bubble and a bulletproof vest

A new strategy for molecular design takes self-assembled materials where they've never gone before.

Oil and water famously don't mix. Water molecules are polar—the shapes of their electron wavefunctions give them an uneven distribution of electric charge—and they energetically favor associating with other polar molecules to compensate. Nonpolar oil molecules don't qualify.

The immiscibility can be overcome with the help of an amphiphilic substance, whose molecules have polar, hydrophilic heads and nonpolar, hydrophobic hydrocarbon tails. With their tails pointing in and heads pointing out, amphiphilic molecules—such as emulsifiers, detergents, and other surfactants—surround droplets of oil and disperse them into the water. Even with no oil around, amphiphilic molecules can arrange themselves in water into intricate, orderly structures to protect their own tails from the surrounding polar medium.

Biology makes use of that self-assembly capability all the time. Every cell in your body is enveloped by a membrane made of two layers of amphiphilic molecules. Mimicking biology's powers of self-assembly is a goal of materials researchers who strive to make new engineered biointerfacing materials. (See, for example, the article by Simone Aleandri and Raffaele Mezzenga, PHYSICS TODAY, July 2020, page 38.)

But structures assembled through hydrophobic interactions almost always require the presence of water for their continued existence. The amphiphilic molecules in a self-assembled bilayer are held to one another only through weak van der Waals interactions. When the water dries up, the structure falls apart.

Now MIT's Julia Ortony, her graduate student Ty Christoff-Tempesta, and their colleagues have developed a new self-assembled nanomaterial inspired by Kevlar, the stuff of bulletproof vests. The nanoassemblies hold together even in a water-free environment, and they can be made into a dry, solid material.[1]

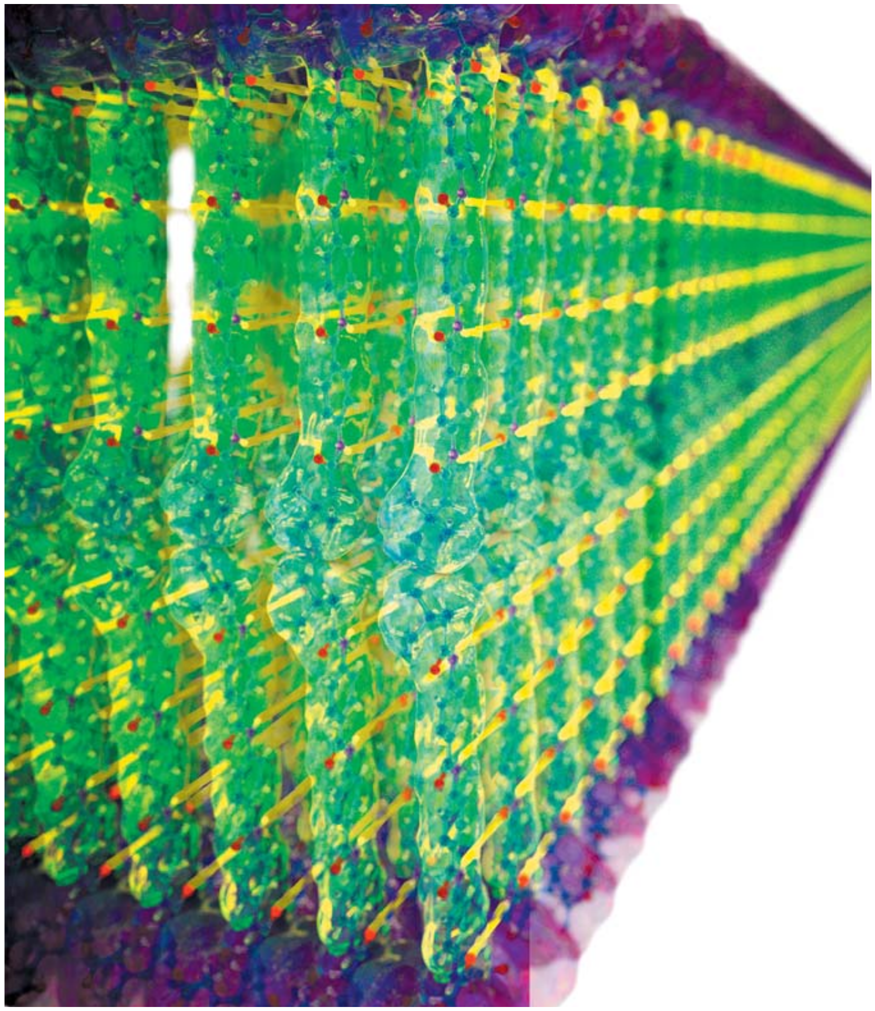

FIGURE 1. SMALL MOLECULES in water self-assemble into the bilayer nanoribbon structure shown in this computer rendering. The assembly is guided by the molecules' hydrophilic heads (purple) and short hydrophobic tails (bluish green). Between head and tail, three units of a monomer inspired by Kevlar (bright green and yellow) hold the molecules in tight formation, so the nanoribbon retains its structure even when the water dries up. (Image by Peter Allen and Ryan Allen.)

Amphiphiles assemble

Kevlar, an ultrastrong polymeric material, was developed in the 1960s and is used today in body armor, protective clothing, and many other applications. It derives its extraordinary strength from the interactions between adjacent parallel polymer chains. In one direction, the chains connect via intermolecular hydrogen bonds; in the perpendicular direction, they cling together through the stacking interactions between rigid benzene rings. Relative to most polymeric molecules, which are squiggly and floppy, Kevlar polymers are poker straight. Their inflexibility helps them line up and form interactions with their neighbors.

As a postdoc at Northwestern University in the mid 2010s, Ortony was interested in the effects of conformational dynamics on self-assembled nanomaterials.[2] Even a small change in molecular structure, she found, could make a big difference in material properties, if it affected how fluidly the molecules could move around. When she joined MIT as a new faculty member in 2016, she decided to

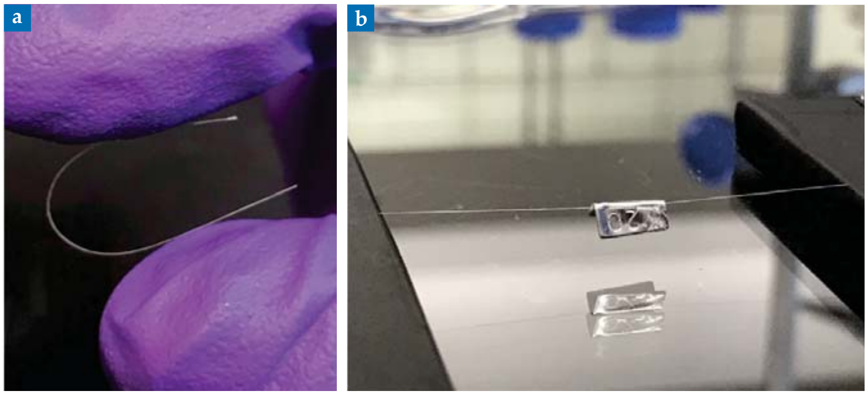

FIGURE 2. MACROSCOPIC THREADS made of aligned nanoribbons can **(a)** be bent and handled easily and **(b)** support up to 200 times their own weight: The metal fragment is a 20 mg mass, and the 5 cm thread it hangs on weighs just 0.1 mg. (Adapted from ref. 1.)

look at incorporating Kevlar's chemistry—and its conformational rigidity—into a hydrophobically assembled structure. Her goal: to create a hierarchically organized nanofiber that's stable without water.

To do that, however, she would need to venture beyond the existing understanding of what amphiphilic molecules are and how they behave. The dynamics of self-assembly are complicated; amphiphilic molecules can assemble not just into bilayers but into several other structures, depending on their size, shape, and interaction energetics. The foundational predictive theory, presented in a 44-page paper published in 1976, assumes that amphiphilic molecules' only components are their hydrophilic heads and hydrophobic tails.[3]

A snippet of Kevlar incorporated into such a molecule would be neither head nor tail but a distinct third domain. "We had no fundamental understanding of how that addition would affect the self-assembly," says Ortony. Too hydrophilic a molecule would dissolve in the water, and too hydrophobic a molecule would just precipitate out of solution. The ideal balance for creating complex structures had been identified for two-component molecules; finding it again for three-component ones would require trial, error, and iterative design.

Ortony and colleagues eventually hit upon a molecular recipe that yielded self-assembled nanoribbons: like bilayer membranes, but up to 4000 times as long as their 5 nm width. Surprisingly, the hydrophobic tails—the small bluish-green bulbs in the middle of the structure in figure 1—are short: just six carbon atoms as opposed to the 16 or so in a typical amphiphile. Between the head and tail are three units of a Kevlar-like monomer. "We tried two and we tried four," says Ortony. "Three is definitely the right number."

Tiny and tough

The nanoribbons are so much longer than they are wide because the intermolecular interactions are anisotropic: In the ribbon's long direction, the molecules are held together by hydrogen bonds between the chemical groups shown in yellow; in the short direction, by the less powerful stacking interactions between the benzene rings shown in bright green. To maintain that anisotropy, the hundreds of thousands of amphiphilic molecules in each nanoribbon must all be oriented the same way. That degree of order is unusual among hydrophobically self-assembled materials, which usually see their molecules drift and wiggle around one another and even diffuse in or out of a bilayer on time scales of hours.

To see if the ribbons' spatial order translated into temporal stability, the researchers mixed two batches of nanoribbons, one made of molecules tagged with a fluorophore and the other made of molecules tagged with a quencher. The quencher disrupts the fluorophores' fluorescence only when the molecules are in close contact—or part of the same nanoribbon. But even after two months, the mixture showed almost no change in fluorescence. Almost no molecules were moving from one nanoribbon to another.

The nanoribbons maintained their rigidity and integrity while just drifting in water, but what about under harsher conditions? Although it's not easy to rigorously measure the tensile strength of such small objects, one way to do it is to blast the material in a sonicator and analyze their fragmentation patterns. When Ortony and colleagues tried that, they found that their ribbons were stronger than steel, but Ortony cautions not to infer too much from that comparison. Most solid materials are stronger at the nanoscale than they are in bulk (see PHYSICS TODAY, November 2013, page 14). "What's most striking is that we could make this measurement at all," she says. "Other self-assembled structures would just have immediately fallen apart."

What happens when the nanoribbons are removed from water? To find out, the researchers filled a pipette with a nanoribbon suspension, drew out thin filaments, and allowed them to dry. Instead of collapsing like a soap bubble, the nanoribbons bundled together into resilient solid threads that could be handled and flexed, as seen in figure 2a, and support significant loads, as shown in figure 2b. Although not as strong as Kevlar, the threads constitute a truly solid-state self-assembled material.

The appeal of amphiphilic bilayers is that they always expose the same part of the molecule—the hydrophilic head—to the surrounding environment. Because the exact chemical identity of the head groups isn't critical for holding the structure together, they could be designed to perform tasks like pulling trace impurities out of the surrounding medium, releasing a cargo molecule, or catalyzing a surface reaction.

Furthermore, although the threads are tens of microns—or thousands of nanoribbon widths—thick, the spacing between ribbons is large enough to let atoms and small molecules in and out, so even the ribbons in a thread's interior can contribute to its chemical functionality. And because the nanoribbons are so thin, they pack a lot of active surface area into a small volume: The ribbons that make up a 0.1 mg thread, like the one shown in figure 2b, have a total surface area of some 200 cm^2. Ortony and colleagues are now exploring ways of putting their threads to work in places water can't go.

Johanna Miller

References

1. T. Christoff-Tempesta et al., *Nat. Nanotechnol.* (2021), doi:10.1038/s41565-020-00840-w.
2. J. H. Ortony et al., *Nat. Mater.* **13**, 812 (2014).
3. J. N. Israelachvili, D. J. Mitchell, B. W. Ninham, *J. Chem. Soc., Faraday Trans. 2* **72**, 1525 (1976).

Topological phases emerge in an ecological model

An exotic phenomenon in condensed-matter systems illuminates the behavior of a one-dimensional model akin to the game rock-paper-scissors.

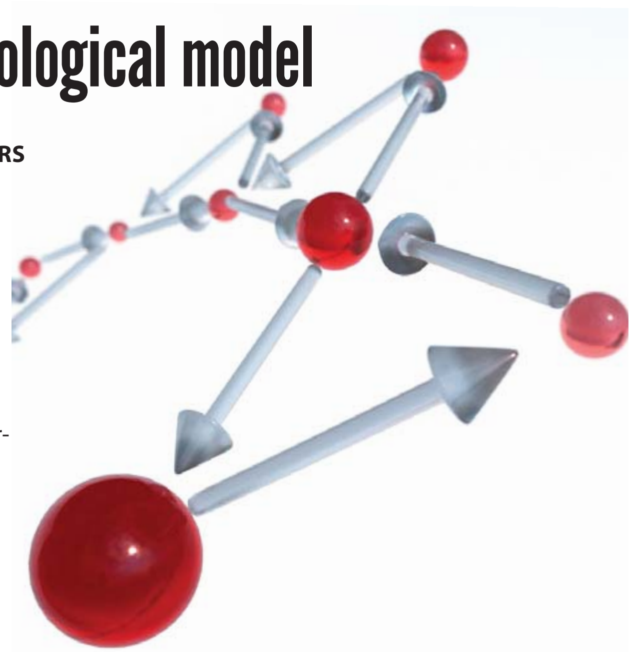

FIGURE 1. ROCK-PAPER-SCISSORS model for population dynamics. Population dynamics models incorporate interactions (arrows) between different species (red spheres). Similar to other nonlinear models, they typically show extreme sensitivity to small changes in their parameters, such as the initial population size of each species. But in the rock-paper-scissors model depicted here, Erwin Frey and his students found predictable behavior regardless of parameter tweaks. That behavior derives from the topological nature of the system's states. (Image by Cris Hohmann.)

Topology manifests itself in some of the major discoveries in condensed-matter physics of the past 50 years, including the quantum Hall effect (see the article by Joseph Avron, Daniel Osadchy, and Ruedi Seiler, PHYSICS TODAY, August 2003, page 38), topological insulators (see PHYSICS TODAY, April 2009, page 12), and the research honored by the 2016 Nobel Prize in Physics (see PHYSICS TODAY, December 2016, page 14). In topological phases of matter, the material's behavior derives from the connectedness of the band structure rather than the material's symmetries, which explain most states of matter.

When a wave—for example, an electron wavefunction—travels around a topologically nontrivial path, it gains a phase after completing a closed loop rather than returning to its initial state. Although the results of the band structure's topology are complicated to understand in detail, an essential feature is the emergence of dynamic excitations localized at the system's boundary that are stable even in the presence of defects, a property known as robustness.

Researchers have recently started to study topological effects in systems outside hard condensed matter—for example, in liquids composed of self-propelled particles[1] and some atmospheric and ocean waves.[2] Now Erwin Frey and his group members at Ludwig-Maximilians University Munich in Germany have identified topological phases in an ecological model,[3] illustrated in figure 1. The work points to the potential application of topology to other dynamic biological systems.

Rock-paper-scissors

Johannes Knebel, one of Frey's graduate students, started the project in 2015 after he attended the Boulder School for Condensed Matter and Materials Physics in Colorado. While there, he was inspired by talks on topological phases in mechanical metamaterials by the University of Pennsylvania's Tom Lubensky and the University of Chicago's Vincenzo Vitelli and William Irvine.

One mechanical metamaterial is a lattice of gyroscopes coupled by springs (see "Topological insulators: from graphene to gyroscopes," PHYSICS TODAY online, 27 November 2018). Such a system supports a mechanical compression wave that propagates only along the edge and only in one direction, similar to the currents around the edges of topological insulators.