

To understand the mechanisms at play, the researchers used density functional theory in conjunction with transmission electron microscopy to study the structure and electrostatics of the domain walls. Calculating the layer-by-layer polarization, they found a discontinuity in the electrostatic potential across conducting walls and theorized that extra carriers may accumulate to compensate this step. Analysis of the electronic struc-

ture also revealed changes in the band-gap near conducting domain walls. Both effects are absent at non-conducting walls, therefore the researchers proposed that the combination of band structure changes and increased carrier concentration enable the observed conductivity.

The researchers also demonstrated a proof-of-concept for using these conduction channels in a device. They grew mono-domain BFO between in-plane

electrodes (see Figure 1) and drew domain walls between them using PFM, showing that the conductivity across the BFO scales linearly with the number of channels drawn. They showed that the process is reversible by erasing a channel and recovering the previous conductivity, suggesting the possibility of a dynamic logic or memory element that could be reconfigured with tremendous precision.

ALISON HATT

Self-Assembled Chiral Capsules Exhibit Highly Polar Interiors

The catalytic function of enzymes relies on the protein structure sequestering polar active sites from the bulk solution, creating a specific environment. Capsule molecules synthesized to mimic this environment can also serve as molecular containers or nanoreactors but their interiors are typically achiral and nonpolar, which limits their selectivity and activity. In previously reported cases where the capsule interiors were both polar and chiral, encapsulation of guest molecules was mainly hydrophobic because polar groups were too exposed to interactions with solvent. Recently, however, B. Kuberski and A. Szumna at the Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, synthesized with a one- or two-step process self-complementary homochiral and heterochiral resorcinarene capsules with buried polar groups that can encapsulate highly polar guests.

As reported earlier this year in *Chemical Communications* (DOI: 10.1039/b820990a), Kuberski and Szumna performed a Mannich reaction with resorcin[4]arene and L-phenylalanine under mild conditions that allowed the isolation of secondary amine L-1 (see Figure 1) in high yield. The researchers said that the high solubility displayed by L-1 in CDCl₃ (>70 mg/ml) and its sharp concentration-independent ¹H and ¹³C nuclear magnetic resonance (NMR) spectra can only be explained by burial of the polar functionalities in the interior of the molecule, together with a highly symmetrical con-

formation. The complementary amine and acid functionalities led the researchers to consider a dimeric capsular structure, (L-1)₂, with D₄ symmetry, which they confirmed with x-ray analysis. Sealing the capsular structure are two seams of salt bridges formed between amine and carboxyl groups, as well as numerous hydrogen bonds. All interior polar func-

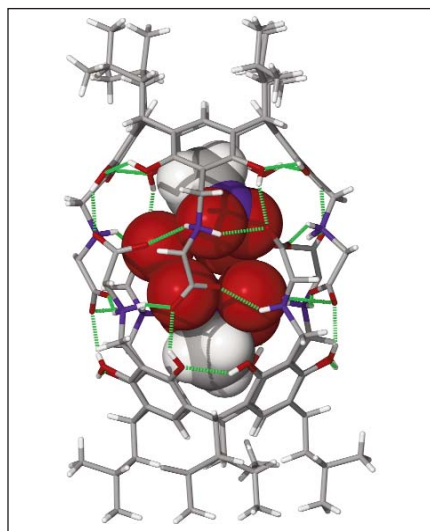


Figure 1. The x-ray structure of (L-1)₂ shows the capsule skeleton (side chains are omitted for clarity) with encapsulated (MeNO₂)₂(H₂O)₄. The red spheres are oxygen; dark gray, carbon; and light gray, hydrogen. Reprinted by permission from *Chemical Communications* (2009) (DOI: 10.1039/b820990a); ©2009 Royal Chemical Society.

tionalties are isolated from the bulk solvent by hydrophobic phenylalanine side chains. Filling the capsule, whose volume was calculated to be 310 Å³, are two nitromethane molecules, which H-bond to the host amino groups, and four water molecules, which the researchers suggest H-bond to host acid moieties.

The researchers expected increased stability from a heterocyclic capsule with S₈ symmetry (symmetry associated with rotation by 360°/8 = 45° followed by reflection through a plane perpendicular to the S₈ axis) so they mixed (L-1)₂ with its mirror image isomer, (D-1)₂. NMR spectroscopy showed quantitative formation of the heterochiral dimer, (D-1)(L-1), but only after several dissolve–evaporate cycles or treatment with 10% MeOH (>8 h) followed by redissolution in CDCl₃, showing that the heterochiral dimer is thermodynamically much more stable than the homochiral dimer. The researchers further demonstrated the existence of dimeric species in solution with diffusion NMR spectroscopy. While the researchers found indirect evidence for water encapsulation in each dimer, they detected ethanol encapsulation with NMR. Kuberski and Szumna said, “Our preliminary complexation studies indicate that (L-1)₂ is able to extract from the aqueous phase and encapsulate biologically relevant polar molecules (e.g., one or two molecules of hydroxyacids) and differentiate between enantiomers. Detailed studies on recognition and possible catalytic functions are currently under way.”

STEVEN TROHALAKI

Modeling of Hierarchical Nanostructures in Proteins Reveals Structure–Property Relationship

Modeling the multiscale behavior of protein assemblies with the goal of elucidating the relationship between structure and materials properties represents a challenge at the interface of materials science

and biology. Markus Buehler of the Massachusetts Institute of Technology (MIT) and Theodor Ackbarow of MIT and the Max Planck Institute of Colloids and Interfaces, who study the structure of protein-based materials with the aim of learning the key to their lightweight and robust strength, have discovered that the particu-

lar arrangement of proteins that produces the sturdiest product is not the arrangement with the most built-in redundancy or the most complicated pattern. Instead, the optimal arrangement of proteins in the ropelike structures they studied is a repeated pattern of two stacks of four bundled alpha-helical proteins.

This composition of two repeated hierarchies (stacks and bundles) provides great strength—the ability to withstand mechanical pressure without giving way—and at the same time great robustness—the ability to perform mechanically,

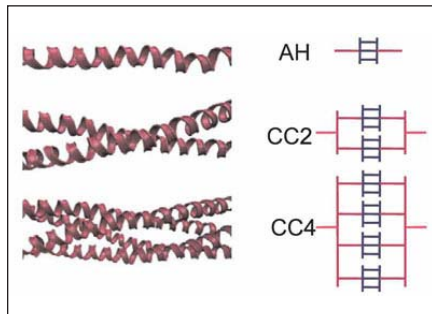


Figure 1. Illustration of different arrangements of alpha-helical protein filaments and their schematic representation in their model. (Image: Prof. Markus Buehler, MIT)

even if faults are present, the researchers said. Alpha-helices are a common protein building block of cellular filaments, hair and hoof, stabilized through weak intramolecular hydrogen bonds.

As reported in the February 18 issue of *Nanotechnology* (DOI: 10.1088/0957-4484/20/7/075103), the researchers used modeling based on molecular dynamics simulations to test the strength and robustness of four different combinations of eight alpha-helical proteins: a single stack of eight proteins, two stacks of four bundled proteins, four stacks of two bundled proteins, and double stacks of two-bundled proteins. Their molecular models replicate realistic molecular behavior, including hydrogen bond formation in the coiled springlike alpha-helical proteins (see Figure 1).

In a follow-up study that will appear in the inaugural issue of the *International Journal of Applied Mechanics*, Buehler and his graduate students Zhao Qin and Steve Cranford ran similar tests using more than 16,000 elements instead of

eight. The most successful of those again utilized the bundles of four alpha-helical proteins. That analysis shows that random arrangements of elements typically led to inferior performance, and may explain why many engineered materials are not yet capable of combining disparate properties such as robustness and strength. Only a few specific nanostructured arrangements provide the basis for optimal materials performance, and this must be incorporated in the materials design process, the research team said.

“The traditional way of designing materials is to consider properties at the macro level, but a more efficient way of materials’ design is to play with the structural makeup at the nanoscale,” said Buehler, the Esther and Harold E. Assistant Professor in the Department of Civil and Environmental Engineering. “This provides a new paradigm in engineering that enables us to design a new class of materials.”

DENISE BREHM
(Sr. Communications Officer, MIT)

Nuclear Fusion-Fission Hybrid Designed to Destroy Nuclear Waste

Researchers at The University of Texas at Austin have designed a fusion-fission hybrid system that, when fully developed, would use fusion to burn most of the transuranic waste produced by nuclear power plants. Furthermore, the system would produce energy during the process. The invention would reduce nuclear waste, making nuclear energy more broadly acceptable and thus could be used to help combat global warming.

“We have created a way to use fusion to relatively inexpensively destroy the waste from nuclear fission,” said Mike Kotschenreuther with the Institute for Fusion Studies (IFS) and Department of Physics. “Our waste destruction system, we believe, will allow nuclear power—a low carbon source of energy—to take its place in helping us combat global warming.”

As reported in the January issue of *Fusion Engineering and Design* (DOI: 10.1016/j.fusengdes.2008.11.019; p. 83), Kotschenreuther, Swadesh Mahajan, and Prashant Valanju of the IFS, and E.A. Schneider of the Department of Mechanical Engineering at the University of Texas at Austin propose destroying the waste using a fusion-fission hybrid reactor, the centerpiece of which is a high-power compact fusion neutron source (CFNS) made possible by their invention of the Super-X

Divertor—a redesign of the magnetic geometry at the plasma edge that enables safe handling of the enormous heat and neutron fluxes in CFNS—(see Figure 1).

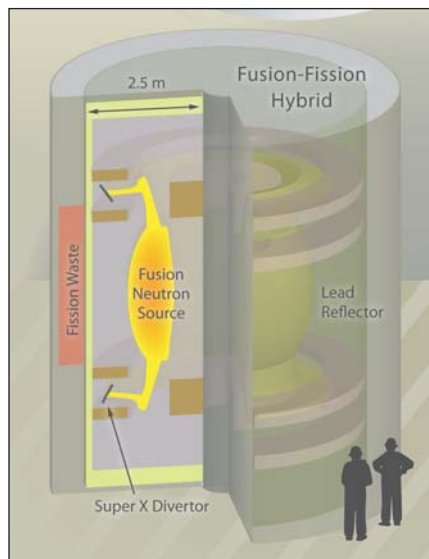


Figure 1. The compact fusion neutron source (CFNS) drives the fusion-fission hybrid. The hybrid burns long-lived waste using abundant neutrons from the CFNS. The Super-X Divertor makes it possible to handle the enormous heat produced by the CFNS. (Credit: Angela P. Wong, The University of Texas at Austin)

“The intense heat generated in a nuclear fusion device can literally destroy the walls of the machine,” said Valanju, “and that is the thing that has been holding back a highly compact source of nuclear fusion.”

The CFNS would provide abundant neutrons through fusion to a surrounding fission blanket that uses transuranic waste as nuclear fuel. The fusion-produced neutrons augment the fission reaction, imparting efficiency and stability to the waste incineration process.

The researchers’ waste destruction system would work in two major steps.

First, 75% of the original reactor waste is destroyed in standard, relatively inexpensive light water reactors (LWRs). This step produces energy, but it does not destroy highly radiotoxic, transuranic, long-lived waste, what the researchers call “sludge.”

In the second step, the sludge would be destroyed in a CFNS-based fusion-fission hybrid. The hybrid’s potential lies in its ability to burn this hazardous sludge, which cannot be stably burnt in conventional systems.

One hybrid would be needed to destroy the waste produced by 10 to 15 LWRs. The process would ultimately reduce the transuranic waste from the original fission reactors by up to 99%. Burning that waste also produces energy. Much fewer of the devices would be needed compared to