



## Science Concentrates

April 10, 2006

Volume 84, Number 15

p. 54

- [Photosynthesis mystery cracked](#)
- [Final synthetic hurdle cleared for sarain A](#)
- [Semiconductors from sea sponges](#)
- [Si analogs of crown ethers](#)
- [Using viruses to make nanowires](#)

---

## Photosynthesis mystery cracked

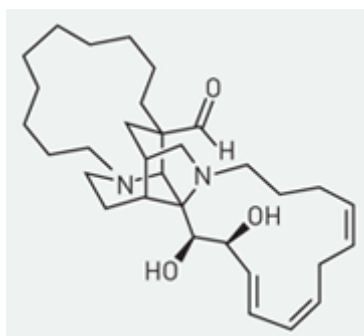


Courtesy  
of Jessica Chuang

During photosynthesis, energy harvested from the sun is used to move electrons through a protein-cofactor complex known as the photosynthetic reaction center (PRC). When the structure of the PRC was first revealed a decade ago, scientists were surprised to find two potential electron-transfer paths, even though electrons use only one, says [Steven G. Boxer](#) of Stanford University. He along with [Dewey Holten](#) and Christine Kirmaier of Washington University St. Louis, and coworkers have now shown why electrons take one path (passing through cofactors shown in green) and not the other (red) ([Biochemistry](#) **2006**, *45*, 3845). Previously, scientists

speculated that differences in the cofactors' electronic coupling or their energies might account for the electrons' preference for only one of the two roughly equidistant paths. Kirmaier's team demonstrates that energetics is paramount: The researchers first cut off electron transfer down the green branch by removing a cofactor. They then show that they can coax electrons into taking the red branch instead by adjusting the energies of its cofactors with a series of carefully chosen mutations.

## Final synthetic hurdle cleared for sarain A

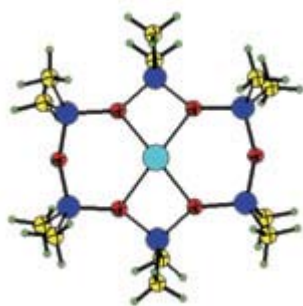


Reniera sarai, a Mediterranean sea sponge, is a rich source of structurally complex alkaloids called sarains that have antibacterial, insecticidal, and antitumor activities. The compounds feature a diazatricyclic core and two macrocyclic side rings that several competing research groups have tried to synthesize for more than a decade. For sarain A (shown), intermediates containing the core structure and the saturated macrocyclic ring have been made, but attempts to further construct the more intricate macrocyclic ring containing the diol and triene functionalities have been thwarted. Neil K. Garg, Sheldon Hiebert, and [Larry E. Overman](#) of the University of California, Irvine, now report the key final steps needed to generate the second ring (*Angew. Chem. Int. Ed.*, published online March 27, [dx.doi.org/10.1002/anie.200600417](https://doi.org/10.1002/anie.200600417)). The team used a palladium-catalyzed Stille coupling between tin and iodine to close the triene ring and a subsequent oxidation-deprotection sequence to generate the aldehyde and diol functional groups.

## Semiconductors from sea sponges

Because it resembles a giant cheese puff, the marine organism *Tethya aurantium*—also known as the orange puffball sponge—might seem like a tasty snack. But *T. aurantium* is actually loaded with tiny glass spicules. The sponge makes these spicules with the help of silicatein enzymes, which feature a nucleophilic hydroxyl group and a hydrogen-bonding imidazole group in their catalytic center. These moieties catalyze the hydrolysis and structurally direct the polycondensation of silicon alkoxide precursors into silica and poly(silsesquioxanes). Now materials scientists have developed a synthetic mimic of these biological catalysts for creating semiconductor materials (*Proc. Natl. Acad. Sci. USA* **2006**, *103*, 5652). [Daniel E. Morse](#) of the University of California, Santa Barbara, and coworkers created a micropatterned surface containing hydroxyl and imidazole groups in the proper juxtaposition to be hydrolytically active. They then used the assembly to catalyze the hydrolysis of a gallium oxide precursor and then to template the gallium oxide and GaOOH products.

## Si analogs of crown ethers



Courtesy  
of Jack Passmore

Over the years, chemists have reported that when they carried out reactions involving alkali-metal cations in the presence of silicone grease, they isolated unexpected salts containing cyclic dimethylsiloxane cations such as  $\text{Li}[(\text{CH}_3)_2\text{SiO}]_6^+$ . This happened in [Jack Passmore](#)'s lab at the University of New Brunswick. So he and his coworkers decided to see if they could produce such salts directly from an alkali-metal cation and a cyclic dimethylsiloxane, a reaction that apparently had not been reported. They succeeded in preparing high yields of  $\text{Li}[(\text{CH}_3)_2\text{SiO}]_n^+$  salts, where  $n = 5$  or  $6$  and

the anion is a weakly coordinating polyfluoroalkoxyaluminate (*Angew. Chem. Int. Ed.*, published online March 20, [dx.doi.org/10.1002/anie.200504262](https://doi.org/10.1002/anie.200504262)). Their synthetic work and calculations "imply the existence of a new class of host-guest complexes for the cyclic siloxanes that is similar to, but less extensive than, that for the crown ethers," they write. The structures of these complexes (such as the one shown, where Li is light blue; Si, dark blue; and O, red) imply that the cyclic dimethylsiloxanes act as "pseudo crown ethers and provide rare examples of silicon ethers behaving as Lewis bases," they note.

## Using viruses to make nanowires

To [Angela M. Belcher](#) of MIT, viruses and their DNA provide a versatile means for making nanoscale materials and gadgets. "What you have is these DNA sequences that code for the growth and assembly of a functional device," Belcher says. In her latest foray into "virus-enabled synthesis," Belcher and seven colleagues tweaked the genome of the rod-shaped virus M13 so that each of its roughly 2,700 major coat proteins would sport a string of four glutamate molecules. In water, the negative charges of these appendages proved irresistible to cobalt ions, which once in place on the viral surface could then be readily oxidized. The result: cobalt oxide wires the size and shape of M13 viruses (*Science*, published online April 6, [dx.doi.org/10.1126/science.1122716](https://doi.org/10.1126/science.1122716)). One goal is to make electrodes for tiny batteries. That's why Belcher's group used another genetic technique to weave a 12-amino-acid motif that binds gold atoms into some of the coat proteins. The hybrid gold-cobalt oxide nanowires produced have energy capacities almost one-third higher than that of cobalt oxide-only nanowires.

**Chemical & Engineering News**

**ISSN 0009-2347**

**Copyright © 2006 American Chemical Society**