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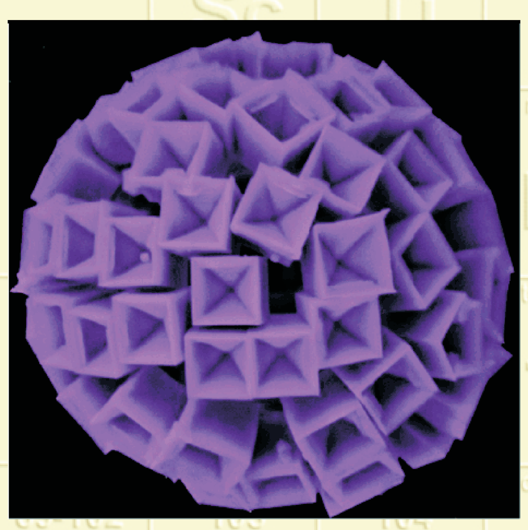
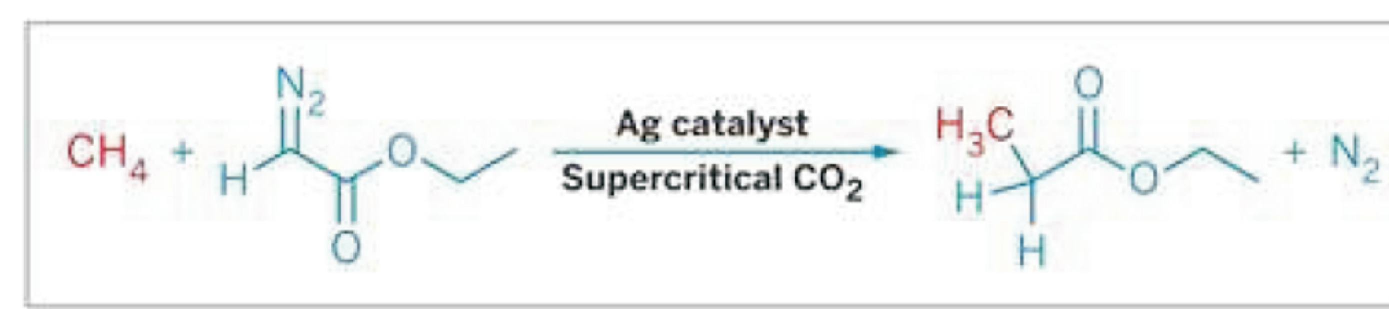
Sorpresa salada

The spectacular spherulite seen in this colorized scanning electron micrograph is none other than table salt, or sodium chloride. The structure is something of a departure for NaCl, which almost always forms cubic crystals. This new ability to grow salts in unusual shapes could help researchers figure out how to improve control of the crystallization of water-soluble compounds. Researchers led by Zhongping Zhang and Suhua Wang, of the Chinese Academy of Sciences' Institute of Intelligent Machines discovered they could coax NaCl and its chemical cousin KCl into the surprising structures when they grew the crystals at the interface of metastable water microdroplets and an organic solution of cyclohexane and acetone (*Angew. Chem. Int. Ed.*, **2011**, *50*, 6044). Each hollow sphere is composed of dozens of single crystals shaped like hoppers, or square funnels. The spherulite pictured here is made up of crystals 10 µm across. Cyclohexane appears to play a critical role in the crystallization because only cubic crystals form when it is absent from the solution. Zhang, Wang, and colleagues think that cyclohexane stabilizes the water microdroplets by reducing diffusion of acetone into the water. Once the acetone does diffuse into the water, the salt solution becomes supersaturated and crystallization begins. But cyclohexane outside the droplets curtails crystal growth. As a result, the hopper-shaped crystals form,arranged in a hollow microsphere.



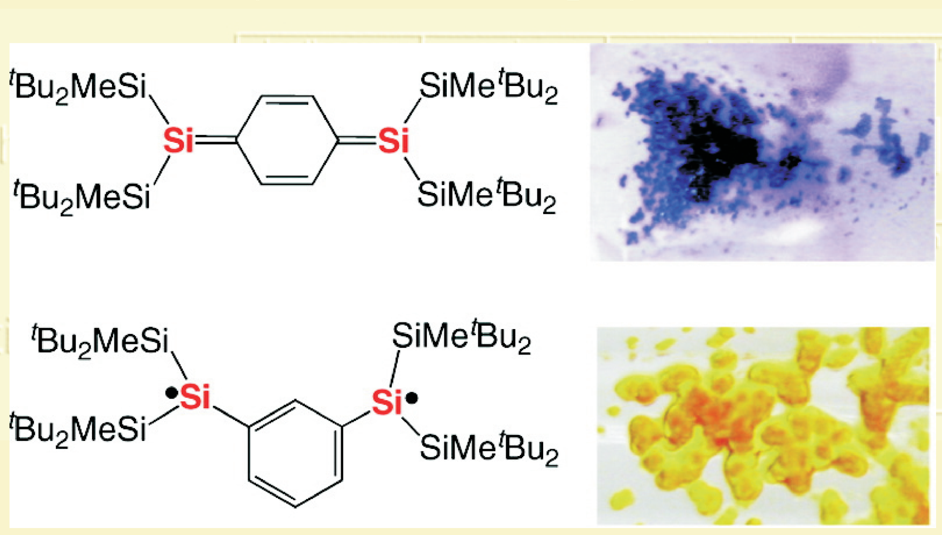
Activació supercrítica

Methane is a molecule that rarely bows to chemists' will, but researchers in Spain and France have coaxed it to do their bidding by using a silver catalyst and supercritical carbon dioxide solvent (*Science*, **2011**, *332*, 835). Few successful functionalizations of methane have been reported, so Gregorio Asensio of Spain's University of Valencia, Michel Etienne of France's University of Toulouse, Pedro J. Pérez of Spain's University of Huelva, and colleagues decided to apply theirelectron-poor silver catalysts to the problem. Designed with heavily halogenatedversions of so-called scorpionate ligands, which grip silver like a scorpion's pincers, the catalysts were known to insert carbenes into relatively inert alkane C–H bonds. At first, however, the chemistry was problematic for methane because of side reactions and solubility issues. The researchers solved the problems by switching their solvent to supercritical CO_2, which doesn't react with intermediates and is miscible with methane. They show that a carbene generated from ethyl diazoacetate inserts into a methane C–H bond to make a new C–C bond, forming ethyl propionate, a chemical commonly used in the food and flavor industry.



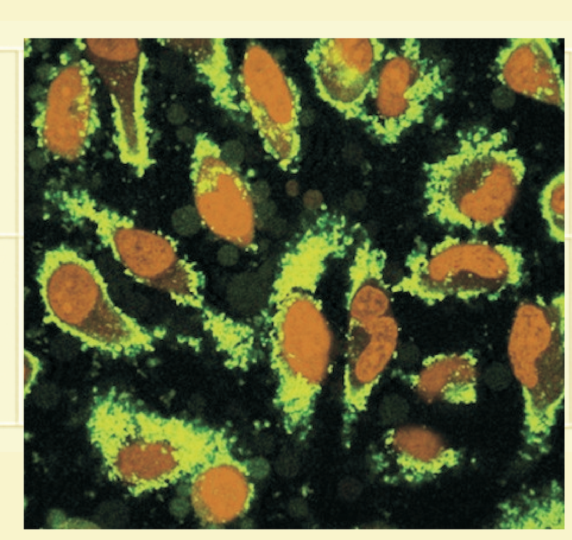
Silici molt radical

Using carbon analogs as a guide, Takeshi Nozawa and coworkers of Japan's University of Tsukuba have synthesized isomeric *p*- and *m*-disilaquinodimethanes, the latter of which represents the first stable silicon-based diradical species (*J. Am. Chem. Soc.*, **2011**, *133*, 5773). Organic free radicals featuring an unpaired electron on a carbon atom are used in a variety of chemical reactions, but versions with two or more radical centers, of interest for making organic magnetic materials, are more challenging to make and stabilize. Isolable silicon, germanium, tin, and lead single radicals have also been reported, but oligoradicals containing these elements have remained elusive until now. Sekiguchi's group used *p*- and *m*-quinodimethane derivatives as model compounds: The para isomer takes on a quinonoid form and has a nonradical singlet ground state, whereas the meta isomer has a biradical triplet ground state. When the researchers made the silicon analogs, the *p*- and *m*-disilaquinodimethanes, they observed the same behavior. In the para isomer, conjugated Si=C bonds form, but in the meta isomer, the silicon 3p and carbon 2p orbitals can't overlap, preventing π bonding. The two compounds have different spectra—the para isomer is purple and the meta isomer is yellow—and display different reactivities.



Nanodiamants contra el càncer

Faceted nanoparticles shaped somewhat like cut diamonds not only can deliver drugs to tumor cells but also can ensure that the small molecules stick around long enough to do some good (*Sci. Trans. Med.*, **2011**, *3*, 73a2171). Chemotherapy often fails because cells protect themselves by pumping out foreign substances via transmembrane transporter proteins. As a result, physicians have to administer cancer therapeutics at high, and sometimes harmful, concentrations for them to be efficacious. Nanoparticles —materials that can't as easily be kicked out of cells and can hold high concentrations of bound molecules—show promise as drug delivery vehicles. The 2- to 8-nm-diameter carbon-based nanodiamonds, in particular, "have unique electrostatic properties that promote potent binding of drugs" and are ideal for chemotherapy, says Dean Ho, Northwestern University. By binding the cancer agent doxorubicin to nanodiamonds, Ho and his team demonstrated particle-mediated delivery of the drug to both liver and mammary gland tumor cells in mice. In both cases, seven days after injection, the drug-loaded nanodiamonds killed about three times as many tumor cells as doxorubicin alone. What is new and striking about this work, is that the nanodiamond-doxorubicin formulation blocks tumor growth in the mice with drug-resistant mammary gland tumors cells.



As shown by fluorescence microscopy, nanodiamonds (green) loaded with doxorubicin can be taken up by HeLa cells (nuclei are orange), which are typically 20–30 µm in size.

Any Internacional de la Química 2011

Breus

• Joaquim Sales, del Departament de Química Inorgànica, ha publicat el llibre «La Química a la Universitat de Barcelona» en què es descriu la presència de la química i la biografia dels seus professors a la UB, des del retorn de Cervera, el 1837,fins la creació de la Facultat de Química el 1975.

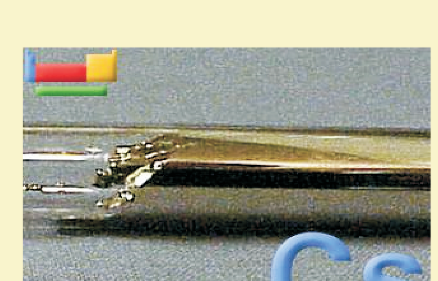
• A www.periodicvideos.com/feature_elements_song.htm hi ha un vídeo penjat sobre la famosa cançó de Tom Lehrer «The Elements»

• Per tal de commemorar l'any de la Química, diversos països han fet emissions especials de segells amb motius químics, a pubs.acs.org /cen/newscripts/ 89/8911newscripts.htm, se'n recullen uns quants.

• L'ONU fa una crida a millorar el reciclatge dels metalls, atès que a hores d'ara, dels 60 metalls amb importància econòmica, en prou feines d'una tercera part se'n recicla el 50%. (unep.org/resourcepanel/publications/ recyclingratesofmetals/tabid/56073/default.aspx).

• El carbur de bor, B_4C, és un material pirotècnic de color verd més intens i més verd ambientalment, que les sals de bari tradicionals. (*Angew. Chem. Int. Ed.*, **2011**, *50*, 4624)

L'element



L'element número 55, **cesi**, fou el primer element descobert amb l'espectroscopi, per Robert W. Bunsen i Gustav R. Kirchhoff el 1860 en identificar dues línies blaves intenses, en unes aigües minerals de Durkkeim (Alemanya). El nom prové del llatí "caesius" que vol dir blau cel. És un element no gaire abundant (3 ppm a la terra) i es troba en silicats complexos com la pol·lucita, $Cs_4H_4Al_4Si_9O_{27}$. Entre les seves aplicacions destaca com a component dels rellotges atòmics, ja que el 1967 s'establí la definició de segon com 9 192 631 770 períodes de la radiació corresponent a la transició entre dos nivells hiperfins de l'estat fonamental de l'àtom de Cs-133. Tradicionalment s'ha emprat en cèl·lules fotoelèctriques i làmpades d'IR. L'isòtop radioactiu, Cs-137, té una vida mitjana de 30 anys, i és un dels principals responsables de la radioactivitat ambiental deguda a accidents nuclears.