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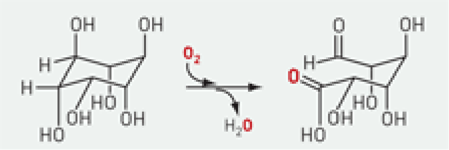
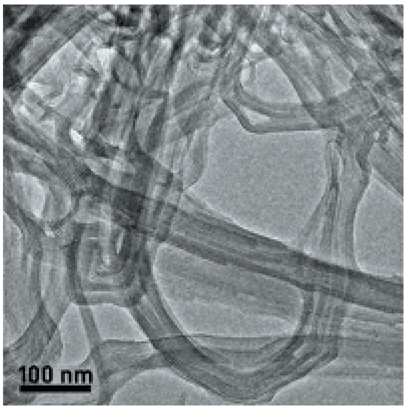
Diiron oxygenase cleaves C-H bond in an unexpected way



An iron-containing oxygenase has been found to use an unconventional strategy for cleaving C−H bonds. J. Martin Bollinger Jr., Carsten Krebs, and coworkers at Pennsylvania State University report that the enzyme *myo*-inositol oxygenase (MIOX) operates by a mechanism different from that of related diiron enzymes. The pair of iron atoms in MIOX uses O_2 to cleave a single C−H bond in the cellular messenger molecule *myo*-inositol to produce d-glucuronate (shown). The researchers find that MIOX starts its catalytic cycle with one iron as Fe(II) and the other as Fe(III), unlike all of its diiron oxygenase brethren, which start with both irons in the +2 oxidation state (*Biochemistry* **2006,** *45*, 5393 and 5402). This suggests that MIOX's Fe(II)/Fe(III) cofactor is unlikely to go on to generate the high-valent Fe(IV)=O species its relatives use to oxidize their substrates, Bollinger says. The researchers proved their hunch by using deuterium-labeled substrate and electron paramagnetic resonance spectroscopy, showing that the oxygenating species in MIOX is in fact an Fe(III)/Fe(III) superoxide species (*Proc. Natl. Acad. Sci. USA* **2006,** *103*, 6130).

Nanoribbon glow



Courtesy of Taeghwan Hyeon

A low-temperature solutionphase synthesis method can be used to prepare ultrathin semiconductor nanoribbons that exhibit unique electronic properties. Jin Joo, Taeghwan Hyeon, and their coworkers at Seoul National University, South Korea, have developed a novel Lewis acid-base preparation method in which cadmium cations and selenocarbamate anions react in the presence of octylamine at 70 °C to yield multigram quantities of 1.4-nm-thick, 10- to 20-nm-wide CdSe ribbons (shown, *J. Am. Chem. Soc.* **2006,** *128*, 5632). In contrast, the team notes, conventional colloidal synthesis methods typically involve decomposition of precursors at about 300 °C. On the basis of spectroscopy measurements, the group reports that the nanoribbons exhibit a sharp photoluminescence band with a line width comparable with the value associated with a single room-temperature quantum dot. That property is a result of the uniform thinness of the structures, the researchers say.

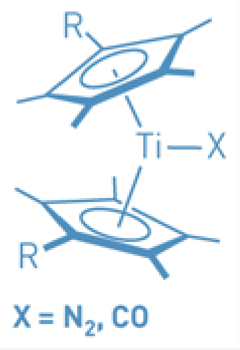
New vaccine candidate for leishmaniasis

A new type of carbohydrate vaccine candidate has been developed for leishmaniasis, a protozoan tropical disease that causes serious disfigurement and an estimated 60,000 deaths per year. There are currently no effective vaccines, but Peter H. Seeberger's group at the Swiss Federal Institute of Technology, Zurich, and colleagues at the Swiss Tropical Institute, Basel, and Pevion Biotech, Bern, have now developed a promising candidate (*ACS Chem. Biol.* **2006,** *1,* 161). They prepared synthetic carbohydrates resembling a leishmania antigen, made them immunologically active by linking them to both a phospholipid and a flu-virus coat protein, and then incorporated the conjugate into immunostimulating reconstituted influenza virosomes (IRIVs, liposomes with virus-derived lipid membranes). The formulations elicited a potentially long-lived (T-cell-dependent) antibody response in mice, and the antibodies recognize and react with native leishmania antigens. The results represent the first evidence that IRIVs have "great potential for the design of safe and effective synthetic carbohydrate vaccines," the researchers write. Such vaccines "should find application for diseases, including bacterial, viral, and parasitic infections and cancer," they add.

Solar-cell-based logic gates

Sophisticated electronic devices featuring molecule-based circuitry may one day be available, thanks in part to a Brazilian study. Chemists at the University of São Paulo have designed an electrochemical cell that functions as a logic gate (basic circuitry used in computation) that produces electrical output signals in response to light input signals. Basing their design on a dye-sensitized Grätzel-type cell normally used for photovoltaic conversion of sunlight into electricity, Luis F. O. Furtado, Koiti Araki, Henrique E. Toma, and coworkers constructed so-called XOR and INH logic gates that are triggered by light with 350-nm and 420-nm wavelengths (*Angew. Chem. Int. Ed.* **2006,** *45*, 3143). According to the team, the key to the design is a novel dye, a ruthenium pyrazine carboxylate material, that accepts rather than injects electrons into an adjacent semiconductor layer when the device is irradiated. That configuration enables the direction of the photocurrent output to be controlled by the wavelength of the light, they explain.

Elusive N_2, CO complexes made



Bis(cyclopentadienyl) titanium sandwich compounds (titanocenes) have intrigued chemists because their reactivity makes them potentially useful for dinitrogen activation. But the compounds also have perplexed chemists because the reactivity, which can lead to titanium dimer formation, has hindered the study of the monomeric complexes. Introducing bulky and electron-withdrawing silyl substituents onto the cyclopentadienyl rings has helped. This strategy has now led Tamara E. Hanna, Emil Lobkovsky, and Paul J. Chirik of Cornell University to prepare the first isolable monomeric titanocenes with one N_2 or CO ligand (one shown, R = $Si[CH_3]_2C_6H_5$), as well as disubstituted titanocenes containing N_2, CO, or both ligands (*J. Am. Chem. Soc.* **2006,** *128,* 6018). Chirik's group previously prepared disubstituted N_2 titanocenes in which the cyclopentadienyl R substituent was $Si(CH_3)_3$ or branched alkyl groups. It turns out that the slightly bulkier $Si(CH_3)_2C_6H_5$ groups are a perfect match to stabilize the monosubstituted complexes. The results provide new insight into how N_2 coordination to transition metals can be controlled by careful manipulation of cyclopentadienyl substituents, the team notes.

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