STM Manipulation of Single Molecules Provides a Route to Molecular Switching

For the past few years, research teams have investigated the electronic properties and the interaction of molecules with metallic surfaces using a scanning tunneling microscope (STM) and the synthesis of molecules for nanoscale experiments. The molecules manipulated by the STM tip must exhibit electronic effects such as switching in order to be useful in the creation of nanoscale devices. An international team of researchers affiliated with the Institut für Experimentalphysik; Freie University, Berlin; Paul Drude Institut für Festkörperelektronik, Hausvogteiplatz, Germany; and CEMES-CNRS, France, has reported results on experimental and theoretical work regarding the STM manipulation of individual porphyrin-based molecules and the related phenomena.

As reported in the January 22 issue of *Physical Review Letters*, the researchers used Cu-TBPP (Cu-tetra-3,5 di-*ter*-butyl-phenyl porphyrin) molecules evaporated on a Cu(211) surface (prepared in several steps with nanofacets and terraces by Ne sputtering and annealing to 700 K). Performing calculations by the elastic scattering quantum chemistry technique for 770 molecular orbitals, they found that the electrical resistance R of the Cu-TBPP molecules varies drastically by a 90° rotation of one leg of the molecule. Hence, by using STM, it was shown that the internal conformation of the molecule can be modified reversibly, as well as the electric properties of the molecules. Two distinct situations were emphasized, corresponding to two different phases of the molecule: The tunneling resistance through a leg decreases for the flat case, compared with the rotated case, by one order of magnitude. The two situations were called "OFF-state" and "ON-state," respectively. The researchers also observed that the switching occurs for lateral and vertical manipulation conditions as well. Experimentally, the orientation of the leg can be switched using the STM tip, causing a current variation dependent on the distance between the tip and that molecule that is in very good agreement with theoretical predictions. The conductance differs by two orders of magnitude between the ON and OFF states of the molecule, and the switching process is fully reversible.

With this work, the researchers have shown that by means of vertical and lateral manipulation, it is possible to rotate single legs around their σ-bond, in and out of the porphyrin plane, and that the controlled rotation of the legs induced by the STM tip realizes the principle of a conformational molecular switch.

CLAUDIU MUNTELE

Pseudopotential Calculations Explain the Structure and Electrical Conductance of Single-Walled Carbon Nanotubes

Carbon nanotubes have drawn the interest of many researchers because of their extremely strong mechanical properties and adjustable electrical properties. Recently, researchers at the University of California—Berkeley and Seoul National University, South Korea, have carried out first-principles calculations to investigate the structural deformation and intertube conductance of crossed carbon nanotube junctions. Each of these junctions consists of two (5,5) single-walled nanotubes (SWNT) crossing each other.

As reported in the January 22 issue of *Physical Review Letters*, the researchers employed an *ab initio* pseudopotential density functional approach in linear combination of atomic orbitals (LCAO) basis. They considered a resistive junction region and four perfect regions (metallic leads) composed of semi-infinite perfect carbon nanotubes, where the junction is modeled to consist of two (5,5) SWNTs crossing at a 90° angle. The resulting inhomogeneous linear equations for scattering states were solved to obtain the transmission coefficients, which were then used to compute the conductance within the Landauer-Büttiker formalism.

The junction's geometrical structure was determined using a constrained total-energy minimization, in which the position of the atoms near the junction was fully relaxed while fixing the center-to-center intertube distance.

"The effect of nanotube–substrate interaction," according to Steven G. Louie, a professor from UC—Berkeley, "is modeled by a resulting contact force at the junction." Calculation shows that the contact distance—the shortest distance between atoms at different tubes—is a steep function of contact force between the two crossed SWNTs only in the range of 1–10 nN. The distance saturates near 2.5 Å, and a further increase of the force would deform the tube shape.

The linear-response conductance of the crossed-tube junction was computed after the structure was known. The intratube and intertube conductance were computed as a function of the incident electron's energy for a 4-terminal device in a 4-terminal 4-probe measurement setup.

The researchers found that junction deformation plays an important role in the intratube and intertube transmissions, and thus in the intertube conductance. For moderate contact forces, a smaller contact distance corresponds to a larger intertube conductance. Their calculation results also explain the recent experimental data on this system and suggest that this system can be employed for molecular-scale electromechanical devices.

WIRAWAN PURWANTO

Six-Sided Flat Carbon Molecules Theorized

Paul von Ragué Schleyer, a computational chemist at the University of Georgia, has discovered that hexacoordinate, or six-sided flat carbon molecules, are theoretically possible. While carbon

Review Articles

The November 24, 2000, issue of *Science* contains the following review articles on Issues in Nanotechnology: H.G. Craighead, "Nanoelectromechanical Systems"; S.R. Quake and A. Scherer, "From Micro- to Nanofabrication with Soft Materials"; and E.W.H. Jager, E. Smela, and O. Inganäs, "Microfabricating Conjugated Polymer Actuators."

The January 2001 issue of *Reviews of Scientific Instruments* contains a review article by I. Walmsley, L. Waxer, and C. Dorrer on "The Role of Dispersion in Ultrafast Optics."

The January 2001 issue of the *Journal of Vacuum Science & Technology A* contains a review article by A. Keller, M. Fierz, K. Siegmann, H.C. Siegmann, and A. Filippov on "Surface Science with Nano-sized Particles in a Carrier Gas."

The January 2001 issue of *Reviews of Modern Physics* contains the following review articles: P.B. Weichman, A.W. Harter, and D.L. Goodstein, "Criticality and Superfluidity in Liquid ^{4}He under Nonequilibrium Conditions"; A. Rousse, C. Rischel, and J.-C. Gauthier, "Femtosecond X-Ray Crystallography"; and W.M.C. Foulkes, L. Mitas, R.J. Needs, and G. Rajagopal, "Quantum Monte Carlo Simulations of Solids."

The January 2001 issue of *Semiconductors* contains a review article by I.M. Vikulin, L.F. Vikulina, and V.I. Stafeev on "Magnetotransistors."

The December 2000 issue of *Physics of Atomic Nuclei* contains a review article by V.T. Voronchev and V.I. Kukulin on "Nuclear-Physics Aspects of Controlled Thermonuclear Fusion: Analysis of Promising Fuels and Gamma-Ray Diagnostics of Hot Plasma."

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normally binds with four other atoms or groups tetrahedrally to produce three-dimensional structures that have low energy requirements, making them stable, chemists used computational methods to predict that four groups around carbon molecules sometimes can lie in a plane. Several examples created in the laboratory confirmed this theory.

Von Ragué Schleyer and his research team in the Center for Computational Quantum Chemistry used computational techniques to investigate the possibility of hexacoordinate molecules with a carbon in the center of six-atom rings. As reported in the December 7 issue of *Science*, the researchers designed the boron and carbon compounds by fitting the atoms together in optimal ways, ensuring that all bond lengths were in the right ranges. They then checked their predicted planar hexacoordinate structures to verify their stability.

Open-Framework Material Consists of Cerium Oxyfluoride with CeO_6F_2 Dodecahedron

A research team from the Institute of Inorganic Synthesis at Yamanashi University, Japan, has synthesized an open framework material based on actinide oxyfluoride. As reported in the December 2000 issue of *Chemistry of Materials*, the researchers obtained cerium oxyfluoride by hydrothermal methods. The result is a compound with six dodecahedra of CeO_6F_2 linked in a basic structure forming an octahedral cage of $Ce_6O_{24}F_{12}$ interconnected by an O bridge, resulting in a channel structure with eight pore openings. The name given to the new cerium oxyfluoride is YU-1 (Yamanashi University) with the formula $H_{25.5}(NH_4)_{10.5}Ce_9O_{27}F_{18}$. As a precursor, a mixture was used of 1.0 $Ce(SO_4)_2$/0.5 H_3PO_4/1.5 $H_2N(CH_2)_2NH_2$/4.0 NH_4F/150 H_2O, which was heat treated at 160–180°C for several days. The crystalline product was washed and filtered with ethanol and deionized water and further dried.

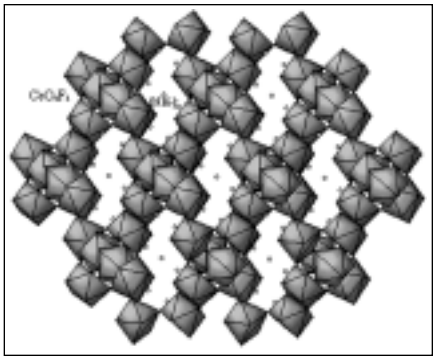

Figure: Framework of the cerium oxyfluoride YU-1 showing the hexagonal arrangement of the octahedral cages and locations of NH_4^+ cations.

Analysis on one of the crystals obtained shows that YU-1 belongs to the space group $R\bar{3}$,with the pore sizes and cages dictated by the distances between the centers of the corresponding oxygen and fluoride atoms. The octahedral cages formed by the six corner-sharing, cerium-centered CeO_6F_2 dodecahedra have a body diagonal of 5.8 Å and give rise to a framework structure with one three-dimensional channel systems. The channel systems connect opposite faces of the supercage and have elliptical eight-ring windows with O - - - O distance between 6.3 Å and 9.7 Å and F - - - F distance between 3.7 Å and 4.4 Å.

IULIA MUNTELE

Prism Coupling with Glass Spherical Microresonators Shows Optical Bistability

Optical whispering-gallery modes (WGMs) observed in microspheres are optical resonance modes that find useful applications as microspherical lasers. WGMs are widely applied in compact functional photonic devices. Some researchers are paying special attention to the fabrication method of these microspheres since it should produce a sphere with an optically smooth surface. A group of researchers from the Nagoya Institute of Technology has fabricated a prism-coupled glass microsphere containing Sm^{3+} ions and observed optical bistability of Sm^{3+} emission lines in WGMs. This pioneering experience introduces the possibility of the fabrication of all-photonic devices for optical computing using a spherical microresonator.

The investigators fabricated their microspheres starting from bulk glass of $70SiO_2$-$15B_2O_3$-$15Na_2O$, as they explain in the January 15 issue of *Optics Letters*. They mixed the glass with Sm_2O_3 in a proportion of 2 mol%. From theoretical calculations, they found that this is the optimal concentration that gives the highest probability of spontaneous emission. The glass thus produced was crushed and reheated in a vertical electric furnace at 1200°C. During the free fall of the crushed glass, it remelted and acquired a spherical shape. Scanning electron microscopy observations confirmed that the microspheres formed had smooth surfaces.

Raman spectrophotometry was used to detect the emission bands in these microspheres, after excitation with a 488-nm Ar laser beam. The bulk material revealed emission bands from 550 nm to 670 nm of the $^4G_{5/2}$–^6H_J (J = 5/2, 7/2, 9/2) transition of Sm^{3+} ions. A spherical sample with a diameter of 23 mm exhibited several sharp resonance lines with a spacing of 3.90 nm. This value is consistent with results of 3.84 nm from calculations performed using Mie's theory.

Measurements from a microsphere previously immersed in distilled water revealed resonance lines with larger half width at half maximum (HWHM). This was caused by an increase in the roughness of the surface in the chemically unstable glass after water immersion.

Glass microspheres doped with Sm^{3+} ions exhibited optical bistability due to the prism coupling between the WGM and the pump beam. Prism coupling with these spherical microresonators decreases the threshold power for laser action in the resonance peak on the $^4G_{5/2}$–$^6H_{7/2}$ transition, and increases the capacity of the microspheres to store photon energy. This effect may be explained by a double resonance condition in an inverted V configuration of the three atomic levels, $^4G_{5/2}$, $^6H_{7/2}$, and $^6H_{5/2}$. These investigators plan to complete more detailed experiments to perform numerical analyses of their data.

SIARI S. SOSA

Pd Nanostructures Obtained inside Mesoporous Materials

A research team from the Department of Chemistry and School of Molecular Science—BK21 of the Korea Advanced Institute of Science and Technology (KAIST) has reported in the December 2000 issue of *Chemistry of Materials* the realization of arrays of palladium nanostructures inside cubic MCM-48 (a type of pure silica) and hexagonal mesoporous silica (SBA-15) by chemical vapor infiltration. The researchers obtained free-standing palladium nanostructures with precisely controlled shapes and sizes, opening the possibility to use the same approach for other metals and mesoporous materials that may be useful for catalytic, optoelectronic, and energy-storage applications. In this particular case, the Pd was used for its catalytic properties in H detection.

To obtain the ball-shaped Pd nanostructures, the researchers used granular MCM-48 and SBA-15 particles with pore diameters of approximately 3 nm and 9 nm, respectively, dried for 8 h at 400°C under dynamic vacuum and a Pd metalorganic precursor. The precursor was sublimated into the empty pores of the mesoporous materials (MCM-48 and SBA-15) under vacuum at 55°C, resulting in the formation of $Pd(hfac)_2$@MCM-48 and $Pd(hfac)_2$@SBA-15 composites (hfac) = 1,1,1,5,5,5-hexafluoroacetylacetonate). The resulting composites were pyrolyzed at 150°C

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