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C&EN

CHEMICAL & ENGINEERING NEWS

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ELEMENT 114 CONFIRMED

Ten years after scientists in Dubna, Russia, first reported synthesizing nuclei of element 114 in a high-energy accelerator, researchers at Lawrence Berkeley National Laboratory have independently confirmed those results, according to a study published in *Physical Review Letters* (2009, 103, 132502). Reproducing experimental results is the bedrock of the scientific method. Yet the extremely low probability of making superheavy nuclei, which in the case of element 114 was done by firing ^{48}Ca ions into a plutonium target, presented formidable challenges to successfully reproducing the Dubna results. As explained by Kenneth E. Gregorich, who co-led the Berkeley team with Heino Nitsche, eight days of almost continuously bombarding the target with ^{48}Ca ions yielded just two atoms of element 114. The nuclei, $^{286}114$ and $^{287}114$, which survived for about 0.1 and 0.5 seconds, respectively, before disintegrating, were identified by tracking a series of α -particle emission and fission events that were correlated in time and position in the Berkeley team's detector. These lifetimes, which are relatively long for superheavy isotopes, are viewed by the scientists as evidence in support of the so-called island of stability—a region on the chart of nuclides where certain proton-neutron combinations may lead to long-lived superheavy isotopes.—MJ

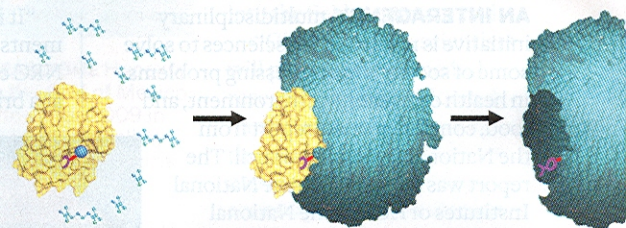
IMPROVED SELECTIVITY IN MAKING METALLIC CARBON NANOTUBES

A new way of preparing single-walled carbon nanotubes allows chemists to control the tubes' chirality, which is the property that renders their conductivity behavior either semiconducting or metallike (*Science* 2009, 326, 116). Standard nanotube synthesis methods usually produce a mixture of semiconducting and metallic tubes, which are difficult to separate. A team led by Avetik R. Harutyunyan of the Honda Research Institute USA, in Columbus, Ohio, used iron nanocatalysts deposited onto a SiO_2/Si framework and varied the environment in which the catalysts were annealed—using a helium or argon environment, different ratios of H_2 and H_2O , and different temperatures. The right combination of these variables produced nanotubes from methane that were up to 91% metallic, compared with the typical 33%. Although numerous re-

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MICROGEL ENZYME INHIBITOR

A polymer formed around an enzyme—a construction known as a molecularly imprinted polymer (MIP)—can selectively inhibit the enzyme much better than a related small-molecule inhibitor, indicating that MIPs could be useful for drug development (*J. Am. Chem. Soc.*, DOI: 10.1021/ja901600e). Scientists have had aspirations of using MIPs for analytical chemistry and biochemical applications, but the biological activity of the molded macromolecules has remained unprobed. A group led by Karsten Haupt of Compiègne University of Technology, in France, targeted the protease trypsin by linking one of the enzyme's known inhibitors, benzamidine, to methacrylic acid to make a polymerizing agent. The researchers then used the benzamidine-methacrylate combo as an anchoring point to synthesize polymer microgels around trypsin molecules. After removing the trypsin template, they tested the resulting MIPs' ability to inhibit protease activity. They found that the MIPs inhibit the enzyme nearly 1,000 times better than benzamidine alone and that the inhibition is selective for trypsin over two related enzymes. In addition to functioning as enzyme inhibitors, Haupt and colleagues suggest that MIPs could be developed for other protein interactions to control different kinds of biological activity.—JK



Using a small molecule as an anchor (red), a polymer (blue) is formed around an enzyme (yellow), which is then removed to yield a potent enzyme inhibitor.

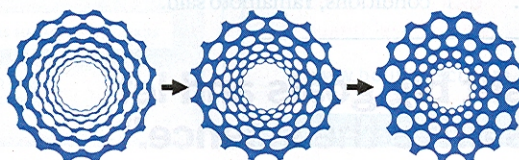
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search groups have had success in devising ways to control carbon nanotube chirality, the mechanisms have remained elusive. The new work by Harutyunyan and coworkers, however, identifies a correlation between catalyst morphology and the resulting nanotube electronic structure. "Our results indicate that, with further optimization, direct control over nanotube structure during growth may well be feasible," the researchers write.—EKW

EVAPORATING POLYMER PRODUCES WEBBY PATTERNS

Controlling the evaporation of a drop of diblock copolymer under just the right conditions leads to self-assembly of web-like macrostructures, report Suck Won

Hong, Jun Wang, and Zhiqun Lin of Iowa State University (*Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.200903552). The ordered structures could be useful in preparing multifunctional materials for optoelectronic devices or as platforms to study cell adhesion and motility. The researchers dissolved the asymmetric diblock copolymer polystyrene-*b*-poly(methylmethacrylate) in toluene and pinned a drop of the solution onto a silicon substrate with a 1-cm-diameter lens. Interactions between polystyrene and the silicon led to the formation of hundreds of ordered, concentric "coffee rings" with a serpentine or wavelike shape at the outer edges of the drop as it evaporated. Hong and colleagues then annealed the rings using acetone vapor and found that the rings became interconnected to form periodic ellipsoidal or circular wells 20 μm across and 80–100 nm deep in a macroscale web



Wavy concentric rings (left), formed by evaporating a drop of polymer solution, can be annealed into a web of ellipsoidal (center) or circular wells (right).

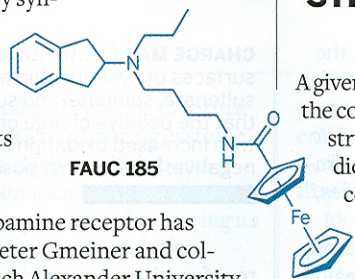
of polymer. The approach is “a simple, scalable, low-cost, lithography-free method” for creating ordered nanostructured materials, the researchers write.—JK

ENGINEERED RESPONSE TO A FAUX DOPAMINE

By engineering a dopamine receptor to respond only to an artificial ligand, researchers may have opened new avenues for studying neurotransmission. Malfunctioning dopamine signaling underlies schizophrenia and other diseases, so researchers are eager to understand the process. Dopamine receptors are G-protein-coupled receptors, and one way researchers learn more about this class of proteins is to re-tool them so they ignore their natural binding partners in favor of an artificial ligand. Such engineered proteins, called receptors activated solely by synthetic ligands

(RASSLs), are valuable complements to genetic knockouts for studying signaling. However,

a RASSL for a dopamine receptor has proven elusive. Peter Gmeiner and colleagues at Friedrich Alexander University, in Erlangen, Germany, have now identified the first RASSL for a dopamine receptor (*ACS Chem. Neurosci.*, DOI: 10.1021/cn900001b). By changing a key phenylalanine residue to a bulkier tryptophan, the team abolished the receptor's binding affinity for dopamine. With FAUC 185, a synthetic ligand they developed, the team showed they can activate the mutant dopamine receptor in vitro.—CD



SEROTONIN HARNESSSES SMALL RNAS TO STRENGTHEN SYNAPSES

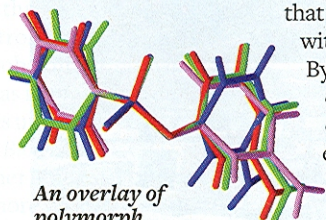
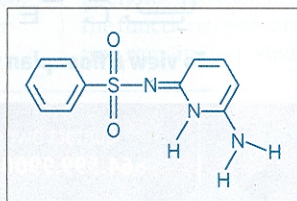
Nobel Laureate Eric R. Kandel and colleagues have discovered a new role for neurotransmitters: They can regulate microRNAs, which generally inhibit protein synthesis (*Neuron* 2009, 63, 803). The findings clarify how synapses are strengthened and could shed light on the formation of lasting memories, which depends on protein synthesis. Kandel, a Columbia University neuroscientist; Thomas

Tuschl, a molecular biologist at Rockefeller University; and coworkers made the observations in the sea snail *Aplysia californica*, which is often used as a model organism in neuroscience because of its large neurons. The researchers determined that serotonin, a neurotransmitter released during learning, reduces levels of several microRNAs found in the sea snail's brain. Depletion of miR-124, the most abundant of the microRNAs, unleashes production of the transcription factor known as CREB (cAMP response element binding protein) and the subsequent biochemical chain of events that strengthens existing synapses and creates new synapses. This pathway is responsible for the formation of long-term memory. The researchers believe that the same microRNA regulatory process will be found in mammals.—SLR

STRUCTURE PREDICTION CAUTIONARY TALE

A given chemical compound, depending on the conditions, can adopt multiple crystal structures known as polymorphs. Predicting these polymorphs in order to control the crystallization process is a long-sought goal, and it is critical in drug development. But making such predictions remains a tough job.

Adam J. Matzger and Saikat Roy of the University of Michigan have taken a close look at the accuracy of predicting polymorphs by revisiting the crystallization of 6-amino-2-phenylsulfonylimino-1,2-dihydropyridine (below), which was used as a test molecule in a crystal-structure-prediction blind test in 2001. Since then, a second polymorph has been found, and now, using a technique called polymer-induced heteronucleation, Matzger and Roy have found a third polymorph (*Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.200903285). Multiple calculation methods predict that form II is the most



An overlay of polymorph form I (pink), IIA (green), IIB (blue), and III (red) of the predicted crystal structures of a dihydropyridine compound show subtle differences.

stable of the three forms, but, in reality, experimental measurements show that it's actually the least stable. In addition, Matzger and Roy's analysis of the 2001 test results found that nobody predicted the existence of form I, which is the most stable, or form III. Their observations suggest that extra caution is required with crystal structure prediction and that computational methodologies need to be improved.—CHA

COLORFUL ORGANIC NANOCOLLOIDS

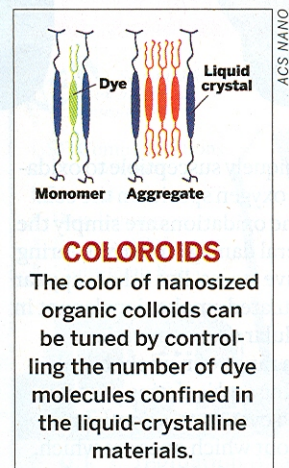
Nanosized organic colloidal particles can fluoresce in a wide range of wavelengths in a manner reminiscent of inorganic quantum

dots by controlling the aggregation of dye molecules inside the colloids, according to scientists at the Naval Research Laboratory, in Washington, D.C. (*ACS Nano*, DOI: 10.1021/nn9007498). These novel fluorescent

nanoparticles and the wealth of functionalized derivatives that potentially can be made from them may find use in a host of fluorescence imaging and biological-labeling applications. Christopher M. Spillmann, Jawad Naciri, Banahalli R. Ratna, and coworkers formed the colloidal particles by reacting a polymerizable organic compound that exhibits a liquid-crystalline phase with a diimide perylene chromophore.

By adjusting the ratio of the organic components, the research team controlled the number of dye molecules confined in the liquid crystals. In that way, the researchers caused the dye molecules to assemble into dimers, trimers, and

larger aggregations, which led to increasingly larger red shifts in the colloids' emission spectra. The colloidal particles, which have a long shelf life, can be prepared from other perylene derivatives, thereby extending the range of colors available from organic colloids, the researchers say.—MJ



COLOROIDS

The color of nanosized organic colloids can be tuned by controlling the number of dye molecules confined in the liquid-crystalline materials.