

have different excitation maxima, but when incorporated together they form a tandem system for fluorescent resonant energy transfer (FRET) so that when excited at the optimal wavelength for FITC, the dye-impregnated silica NPs emit unique colors based on their dye ratios. The researchers synthesized the NPs by a modified Stöber synthesis route, in which the dyes were incorporated into the structure as the NPs grew. The NPs thus prepared were found to be uniform in size, colloidal stable, and strongly fluorescent.

To demonstrate the utility of the material, the researchers derivatized amine-modified NPs with biotin and attached them to avidin-derivatized microspheres. Under confocal fluorescent microscopy, these microsphere-NP complexes emitted light at the characteristic wavelength of the particular NP they contained. The researchers said that this approach can be generalized to label the NPs with other biopolymers for use in barcoding assays and multiplex bioanalysis. According to the researchers, the NPs can also be used as optical materials for display technologies.

KRISTA L. NIECE

### Highly Ordered TiO<sub>2</sub> Nanotube Array Improves Dye-Sensitized Solar Cells

Dye-sensitized solar cells (DSCs) are potentially a cheap and environmentally friendly alternative to silicon-based photovoltaics. Based on an effect analogous to photosynthesis, DSCs have achieved light-to-electricity conversion efficiencies of more than 11%. In the February 8 issue of *Nano Letters* (p. 215; DOI: 10.1021/nl052099j), G.K. Mor, C.A. Grimes, and colleagues at the Pennsylvania State University have reported the fabrication of a DSC based on an ordered array of TiO<sub>2</sub> nanotubes. Although the photocurrent efficiency of their device is only about 3%, their results suggest that nanotube-based DSCs may achieve conversion efficiencies 10 times as high, significantly exceeding silicon-based solar cells.

Standard DSCs are typically based on a 10- $\mu$ m-thick film of randomly arranged TiO<sub>2</sub> nanoparticles. The nanoparticles are coated with a molecular layer of an organic dye (often extracted from blackberries, raspberries, or pomegranates) that releases electrons when illuminated with sunlight. The large surface area of the dye-coated nanoparticles enhances the efficiency of the light collection, and the released electrons become the device's photocurrent. However, the mobility of the released electrons is limited by scattering at the disordered boundaries between nanoparticles, which reduces the overall efficiency. To address this problem, the Penn State team grew

ordered arrays of TiO<sub>2</sub> nanotubes 360 nm in length on glass substrates by anodizing a 500-nm-thick titanium film, and then immersed the arrays in a ruthenium-based dye. When exposed to full sunlight, the resulting devices generated photocurrent with a relatively low efficiency of 2.9%. However, the lifetime of liberated electrons was significantly longer than in nanoparticle devices, implying much less electron scattering by the ordered nanotube array.

The team concluded that the conversion efficiency was limited by the relatively short length of the nanotubes, and that by improving the fabrication procedure to grow micrometer-scale nanotubes, the efficiency could be boosted to close to the ideal limit of 31%. If this proves to be the case, high-efficiency, dye-sensitized solar cells could become an important competitor to standard silicon solar cells, both in terms of lower

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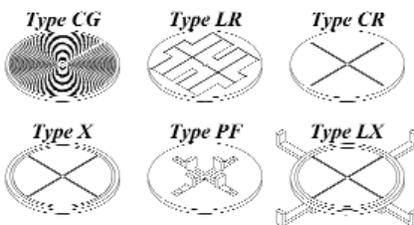
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production costs and reduced environmental pollution during fabrication.

COLIN MCCORMICK

### Researchers Examine Growth and Optical Properties of Gold Nanoparticles in Stained Glass

Stained glass is best known from its extensive use in Gothic churches, although

its production dates back to ancient civilizations of Egypt and Rome. A colored "stain" is achieved when colorless metal-doped glass is heated at high temperatures. Annealing of gold-doped glass results in the formation of colloidal gold, which gives rise to a characteristic ruby-red color through surface plasmon resonance (SPR). However, tuning the SPR

### Octahedral Nanocontainer Molecules Formed Spontaneously

Applications for nanocontainer molecules include stabilizing short-lived chemical species, accelerating chemical reactions, and directing regioselectivity and stereochemistry of reaction products. Supramolecular approaches to the self-assembly of nanocontainers, which involve hydrogen bonding or metal coordination chemistry, are efficient and quantitative. In contrast, nanocontainers constructed from cavitands (i.e., molecules whose constrained structure accommodates a cavity) typically require multiple steps. Recently, however, researchers from the Department of Chemistry and Chemical Biology at Rutgers University have used dynamic covalent chemistry to synthesize nanocontainers from 18 components in a single step and in high yield, greatly improving the simplicity and efficiency of nanocontainer synthesis.

As reported in *Angewandte Chemie International Edition* (DOI: 10.1002/anie.200504049), Rutgers University researcher R. Warmuth and co-researchers discovered a spontaneous formation of an octahedral nanocontainer (**B**), composed of six cavitands (**A**) linked together with 12 diamino bridges via 24 newly formed imine bonds (see Figure 1). Yields of up to 82% were achieved. The researchers used  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy and electrospray ionization mass spectroscopy to validate the structure of **B**. Although the researchers were unable to isolate and purify **B**, they were able to reduce all 24 imine bonds and purify the trifluoroacetate salt of the resulting polyamino nanocontainer (**C**) with reverse-phase high-pressure liquid chromatography and isolate it in an overall 63% yield. Although crystals suitable for x-ray structure determination could not be obtained, the researchers used molecular mechanics (MM) calculations to estimate the cavity volume at  $1700 \text{ \AA}^3$ , which is large enough to encapsulate multiple guest molecules. Pulse-field gradient spin-echo NMR measurements and application of the Stokes-Einstein equation yielded a solvodynamic diameter of 3.2 nm, which is consistent with the MM model. The researchers also used MM to show that the formation of **B** requires each ethylenediamine to be in an *anti* conformation.

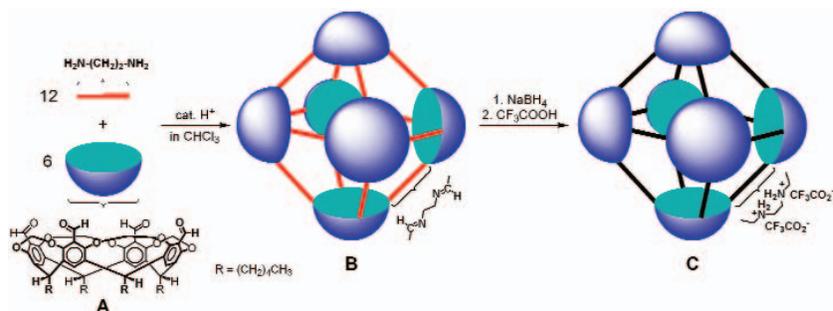


Figure 1. An octahedral nanocontainer (**B**) composed of six cavitands (**A**) linked together with 12 diamino bridges via 24 newly formed imine bonds; **B** is reduced to polyamino nanocontainer (**C**).

The researchers said, "We see potential uses for [**C**] and analogues in drug- or pesticide-delivery systems, wastewater detoxification, separation technology, and as molecular reactors for controlled oligomerizations of organic and inorganic molecules." In addition, the researchers said that "other covalent nanoassemblies with spherical or tubular shapes and different properties could be accessible through such multicomponent synthesis."

STEVEN TROHALAKI