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Foldamer Made Photoswitchable

Foldamers are molecules that reversibly switch between folded and unfolded conformations in response to changes in temperature or solvent composition. The dynamic nature of this reversible conformational change makes foldamers suitable for responsive materials in biological and nanoscience applications. Foldamers that respond to light are desirable because the stimulus is noninvasive and its location, intensity, and timing can be controlled. Toward this end, researchers from Max-Planck Institut für Kohlenforschung in Germany have developed the first example of a photoswitchable foldamer (see Figure 1).

As reported in the March 13 issue of *Angewandte Chemie International Edition* (DOI: 10.1002/anie.200503849; p. 1878), MPI researchers A. Kahn, C. Kaiser, and S. Hecht incorporated a photoisomerizable core connecting two strands of a foldamer—

amphiphilic oligo(metaphenylene ethynylene) previously developed and reported in the literature. The trans-azobenzene core mimics a dimer repeat unit of the foldamers. Îrradiation at 365 nm converts the azobenzene core conformation from trans to cis. The researchers deliberately chose foldamer chain lengths that are not long enough to individually fold into helices or with the core in a cis conformation but that will form a helix when connected, that is, by the core in a trans conformation (see Scheme I). The researchers also introduced enantiomerically pure (S)-α-methyl(ethylene glycol) side chains to bias the sense of the helix and thereby allow them to monitor the conformational transition with circular dichroism spectroscopy. While the photochemical helix-coil unfolding transition occurs in seconds, thermal reversion at room temperature takes place over several

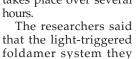
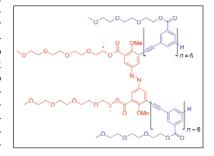




Figure 1. Irradiation of the photoisomerizable core (red) in the center of a helically folded backbone (blue) induces a reversible helix-coil transition. (Courtesy of S. Hecht and R.S. Stoll.)



Scheme I. Molecular structure of the photoswitchable foldamer includes the azobenzene core (red) and the two foldamer strands, amphiphilic oligo(meta-phenylene ethynylene) (blue).

developed not only "can provide fundamental insight into the folding and unfolding mechanisms by enabling time-resolved measurements but promises applications in smart delivery devices based on photoresponsive dynamic receptors."

STEVEN TROHALAKI

Layer-by-Layer Assembly Technique Used to Study Fluorescence Quenching by Gold Nanoparticles

Functionalized metal nanoparticles are of great interest for fluorescence-based sensing and biomedical diagnosis and treat-

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ment. In the case of metal-polymer core-shell structures, the fluorescence of the organic dye may be quenched because of complex interactions with the metal core. To study the effect of separation distance on fluorescence quenching, G. Schneider and G. Decher of Institut Charles Sadron and Université Louis Pasteur, along with N. Nerambourg, R. Praho, M. Werts, and M. Blanchard-Desce of Université de Rennes, have described an approach in which up to 20 polyelectrolyte layers (the last layer being fluorescently labeled) were coated on gold nanoparticles. The core-shell distance was altered by tailoring the thickness of adsorbed, nonfluorescent polymers, which were used as spacer layers in the core-shell structure.

As reported in the March 8 issue of *Nano Letters* (10.1021/ nl052441s; p. 530), gold particles (diameter, 13 nm) were synthesized by the reduction of tetrachloroauric acid with trisodium citrate. Spacer layers of polyallylamine hydrochloride (PAH) and polystyrene sulfonate (PSS) were adsorbed consecutively using electrostatic layer-by-layer assembly to obtain gold nanoparticles coated with 2, 10, and 20 layers of Au(PAH/PSS)_n. Fluorescein

isothiocyanate (FITC) and lissamine rhodamine B sulfonyl chloride (LISS) were covalently attached to PAH to obtain PAH-FITC and PAH-LISS, which were then adsorbed onto the Au(PAH/PSS)_n core–shell particles, followed by the adsorption of a final PSS layer. After each coating step, the particles were washed thoroughly by successive centrifugation/re-suspension cycles. Transmission electron microscopy and *in situ* UV-visible absorption spectra were used to characterize the structural and photophysical properties of the nanoparticle dispersions.

The researchers said that the addition of dye-functionalized polyelectrolytes does not perturb layer growth or the aggregation state of the solution. For n > 5 layers, the surface plasmon resonance from the gold particles reaches a fixed position and intensity, 534 nm in the case of PAH-FITC and 533 nm for PAH-LISS, and obscures the dye-related absorption bands. The surface-plasmon band was removed by slow dissolution of the gold core by adding cyanide ions to the solution. Dissolution of the gold core is accompanied by a strong increase in fluorescence, and reveals the weak dye-related absorption band.

Fluorescence quenching is distance-dependent and remained significant 8 nm from the metal core. The fluorescence quenching seems to be caused by a decrease in radiative transition probabilities induced by the gold core. The researchers said that despite quenching, dye fluorescence remains sufficiently bright for diagnostic and sensing applications.

JEREMIAH T. ABIADE

Highly Porous Inorganic Thin Films Formed Using Polymer Microsphere Templates

The use of colloidal templates as self-assembled building blocks for fabricating ordered submicrometer structures of various materials has been explored in recent years. These templates have been used to fabricate photonic crystals and synthesize catalysts and sensors. However, synthesis of compounds with complex compositions using this method has been difficult due to the wet chemical techniques used and the ability of the chemicals to infiltrate the voids between the colloids with the precursors. A study done at the Massachusetts Institute of Technology has now demonstrated the successful application of



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