

## Nanoscale Molecular Valves Actuated by Light KC 02-3-01

### **Motivation**

Molecular nanocomposites offer unique properties that derive from the motion of molecular components within rigid inorganic scaffolds. In one aspect of our work, we seek to make and understand new types of functional nanocomposite materials that control fluid flow by way of “molecular valves.”

### **Accomplishment**

Recently, significant progress towards this goal has been made by our efforts to combine photoresponsive azobenzene ligands with robust nanoporous silica, such that absorption of light energy into the material both opens and closes molecular valves anchored to the pore surfaces. In these materials, azobenzene ligands are anchored to the pore surfaces of a uniform silica mesostructure that has bare pore volume of  $\sim 127 \text{ \AA}^3$ . This allows the rigid inorganic framework to precisely position azobenzene ligands in 3D configurations so that the well known photo-induced *trans*  $\leftrightarrow$  *cis* isomerization results in a well-defined change in effective pore size (molecular length of the *cis* conformation is  $3.4 \text{ \AA}$  shorter than that of the *trans* conformation). UV (360 nm) light induces the *trans* to *cis* isomerization, which can be reversed by visible light (435 nm) absorption. XRD patterns, TEM images, and 2D grazing incidence small angle X-ray scattering data showed a highly ordered *body-centered cubic* (*bcc*) mesostructure. Azobenzene ligands integrated in the nanocomposite films did not photoisomerize before the Brij surfactant was removed, indicating a minimum pore size for photoisomerization. These results also locate the photosensitive azobenzene ligands within the uniform nanopores of the self-assembled films and emphasize the need to accommodate the steric demands of the photoisomerization process by engineering the pore size.

The mesoporous films exhibited reversible photo and thermal isomerization as detected using UV/vis spectroscopy. To demonstrate pore size change in response to light, we performed a “chronoamperometry” experiment using an azobenzene-functionalized nanocomposite thin film modified electrode as the working electrode in an electrochemical cell. The chronoamperometry experiment used ferrocene dimethanol (FDM) as a molecular probe and provided a measure of mass transport through the nanocomposite film by monitoring the steady-state oxidative current at constant potential for the reaction ( $\text{FDM} \rightarrow \text{FDM}^+ + e^-$ ) taking place on the working electrode surface (indium-doped tin oxide). Thus, changes in the transport due to photoisomerization are reflected as changes in current. The current-time curve clearly showed a reversible response to alternating UV and visible light exposure. The UV/vis data acquired under the same experimental conditions correlated the conformational changes of azobenzene moieties in the nanocomposite film with the oxidative current changes measured in the chronoamperometry experiment. (Note: The slow response time of the material is due to the very low intensity of the light sources.)

### **Significance**

The 3D organization of photoresponsive azobenzene ligands allows transduction of photon energy into a useful mechanical response with potential applications in externally controlled membranes or microfluidic channel systems. The 3D composite architecture should also enhance mechanical and thermal stabilities of the switchable ligands, which is important for their integration into nanostructures. This is an excellent example of work to be performed at the DOE Center for Integrated Nanotechnology (CINT).

### **Performers**

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