

Distance Dependent Resonance Energy Transfer Between Molecular Machine and Plasmonic Nanostructure

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Photoswitchable molecules (molecular machines) have attracted a great deal of attention over the past few years for the design of molecular sensors. Among photoswitchable molecules, azobenzene is widely studied due to its *trans-cis* photoisomerization, which produces a simple structure and optical and Raman spectra, and is photo and electrochemically active, and can be utilized for optical storage and other applications. Localized surface plasmon resonance (LSPR) properties of the metal nanostructures in conjunction with the photoswitching properties of the azobenzene molecules allow the nanoscale environment to be more controlled and to ultimately improve the sensing abilities of the metallic nanostructure. Herein, we develop an ultrasensitive molecular sensor by functionalizing the gold nanoprisms with a self-assembled monolayer of alkanethiols containing azobenzenes. This is the first study where light-induced reversible switching of azobenzenes to *cis* and *trans* conformations was detected by monitoring the λ_{LSPR} of gold nanoprisms-based sensing platforms. It was found that the λ_{LSPR} red shift was observed as the light exposure was switched from UV to blue light due to the *cis* to *trans* isomerization of the azobenzene. This shift is consistent with the increase in thickness of the local dielectric environment (0.6 nm) surrounding the nanoprisms with perhaps a contribution from electronic interaction between the nanoprisms and azobenzene. We hypothesize that this electronic interaction is the near-field resonance energy transfer (NF-RET). Changing the alkanethiol chain length altered the distance between the nanoprisms' surface to the azobenzene. The λ_{LSPR} red shift decreases as the distance between azobenzenes and nanoprisms increases due to the decrease in NF-RET. The λ_{LSPR} shift was found to be reversible as the light source was switched back and forth several times from UV to blue light. The effects of the azobenzene conformational change and its photoreversibility were also probed through surface enhanced Raman spectroscopy (SERS) demonstrating that the NF-RET between the nanoprisms and bound azobenzenes in their *cis* conformation significantly enhances the intensity of the Raman bands of the azobenzenes and is highly dependent on the distance of azobenzene from the surface of the nanoprisms. The SERS data suggested that the isomerization was controlled by first-order kinetics with a rate constant of $1.0 \times 10^{-4} \text{ s}^{-1}$. Our demonstration of light-induced photoreversibility of this type of molecular machine is the first step toward eliminating current limitations on detection of molecular motion in solid-state devices using LSPR spectroscopy with nanoprisms. Modulating the λ_{LSPR} position and controlling energy transfer across the nanostructure organic molecule interface are very important for the fabrication of plasmonic-based nanoscale devices.