Reversible molecular switching in confined environments

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Reversible photoswitching of compounds such as azobenzenes,[1] spiropyrans,[2] and diarylethenes[3] has been investigated extensively for several decades. However, most of these studies have been carried out on molecules moving around freely in solution. If we are to fully realize the potential of these molecular switches in the context of real-world applications, it is necessary to interface them with larger entities,[4–7] such as planar surfaces, polymer chains, or inorganic nanoparticles. In this talk, I will discuss how placing azobenzene – arguably the simplest and most robust molecular photoswitch – under confinement can affect its switching properties. First, I will describe the behavior of azobenzene on the surfaces of metallic nanoparticles. In particular, I will report on our recent finding that on-nanoparticle intermolecular interactions between azobenzene and hydroxy-terminated ligands can increase the rate of thermal back-isomerization by more than three orders of magnitude.[8] In the second part of the talk, I will focus on azobenzenes confined within the cavity of a water-soluble, flexible coordination cage. We have recently demonstrated that owing to its flexibility, the cage can efficiently encapsulate – and solubilize in water – a variety of structurally diverse azobenzenes.[9] Depending on the structure of azobenzene, inclusion complexes of 1:1 or 2:1 stoichiometry were observed. Likewise, photoisomerization properties depended on the azobenzene structure, whereby subtle differences in the substitution pattern on the azobenzene core translated into vastly different switching behaviors. We found, for example, that whereas the parent azobenzene could be switched to form a 1:1:1 *trans*-azo/*cis*-azo/cage ternary complex, irradiating a 2:1 trans-tetrafluoroazobenzene/cage was accompanied by the expulsion of one equivalent of the guest and its precipitation from the solution. We took advantage of this finding to fabricate[7] a novel reversible information storage medium, whereby images could be created and erased using green and blue light, respectively.

References

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