Light-fueled transformations of a dynamic cage-based molecular machine

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Abstract

In a chemical equilibrium, the formation of high energy species – in a closed system – is inefficient due to microscopic reversibility. Here, we demonstrate how this restriction can be circumvented by coupling a dynamic imine equilibrium to a light-induced *E*/*Z* isomerization of a tris-azobenzene imine cage **1**. The self-assembled all-*E*-cage (**1-*EEE***) is highly stable and resists intermolecular nucleophile-imine exchange reactions that would "open" the constrained structure. Upon photoswitching (Step I, figure 1), a mixture (**1-PSS$_{340}$**) containing 95% of the switched isomers (**1-*ZZZ***, **1-*ZZE***, and **1-*ZEE***) is generated. The isomerization process in the constrained molecular architecture results in highly unstable species compared with **1-*EEE***. These isomers react with a nucleophile (step II, figure 1), thus allowing the "opening" the cage (**Open 1**). Subsequent (photo)isomerization (Step III, figure 1) of the azobenzenes present in the different species in the mixture results in an out-of-equilibrium state that favors the regeneration of **1-*EEE*** (step IV, figure 1). We then used this principle to perform a light-induced cage-to-cage transformation with a competing aldehyde.

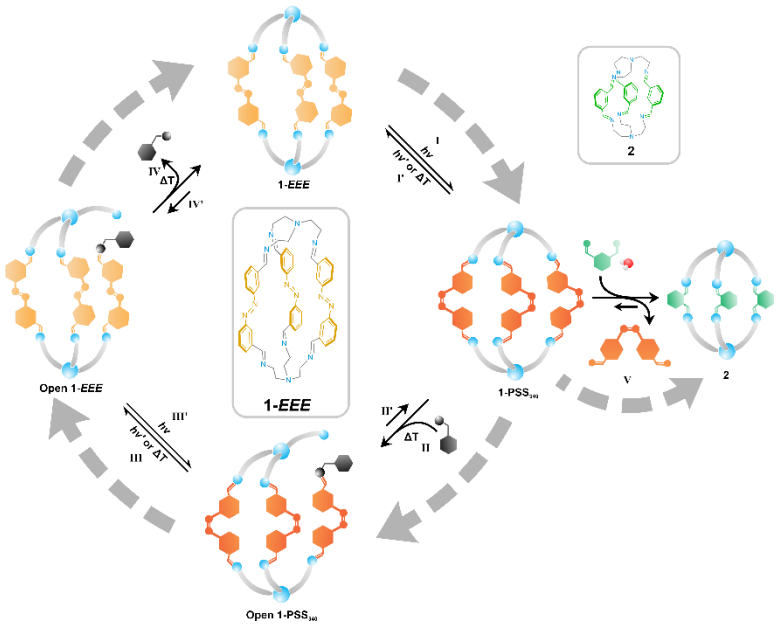

Figure 1. **Light-induced transformations of 1**. Cage opening cycle: Step I. *E*/*Z* Isomerization of **1**. Step II Intermolecular a nucleophile(black)/imine exchange ("cage opening"). Step III *Z*/*E* isomerization of **1-PSS$_{340}$**. The result Open **1-*EEE*** mixture is out-of-equilibrium. Step IV relaxation of the out-of-equilibrium state leading to **1-*EEE*** by an intramolecular amine/imine exchange. Light-induced cage-to-cage transformation. Step V the aldehyde exchange aided by water as competing nucleophile yields cage **2** from **1-PSS$_{340}$**.