Orthogonal Stimuli Responsive Tri-stable Rotaxanes

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Early prototypes of molecular machines, molecular shuttles, were based on bi-stable rotaxanes: structures where the presence of two recognition sites, one responsive to an external stimulus, allowed the reversible and controlled movement of a macrocycle along the thread.[1] An evolution of such systems are tri-stable rotaxanes potentially including multiple rings. We report the synthesis and characterization of rotaxanes comprising a DB24C8 macrocyclic component and a thread containing three recognition sites: ammonium (AmH^+), bipyridinium (BPY^{2+}) and triazolium (Trz^+) (Figure 1). AmH^+ and BPY^{2+} are responsive to fully orthogonal stimuli, pH and electrochemical, which allowed to precisely direct the macrocycle translation along the thread and eventually reset the system. Moreover, characterization of the thermodynamic properties allowed to determine the factors affecting the pK_a of the AmH^+ station. Orthogonal stimuli responsive tri-stable rotaxanes represent the starting point for the creation of processive linear motors and the development of molecular logic gates, where different binary logic outputs could be determined according to the relative position of the macrocycle and the order of the inputs.

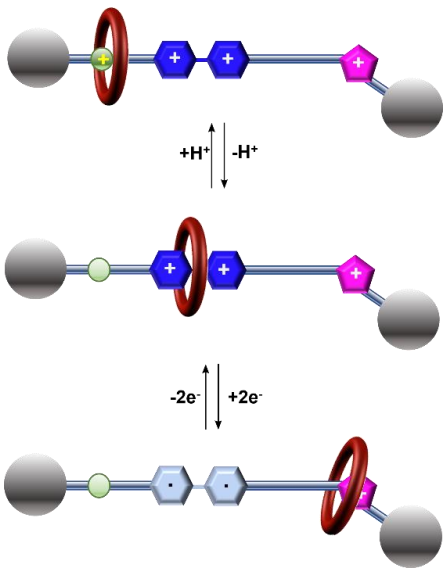

Figure 1: Schematic representation of the stimuli induced motion of the macrocycle along the axle.

[1] Bruns, C. J. ; Stoddart, J. F. "The Nature of the Mechanical Bond: from Molecules to Machines", 2017 by John Wiley & Sons, Inc. Hoboken, New Jersey.