Kinetic pathways for the formation of a pseudorotaxane nanosphere

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Complex chemical (super)structures are key to living systems in the natural world. In order to understand the formation and function of these nano-assemblies in living systems, supramolecular chemistry has developed to a primary research area. Concepts such as cooperativity, multivalency, pre-organization and self-assembly are well studied in supramolecular synthesis. However, how structures are formed under kinetic control by self-assembly is not well-understood, despite its crucial role in Nature as these are self-assembled structures in non-equilibrium states.[1] Mastering this can open a new course in making supramolecular structures under kinetic control rather than thermodynamic control to realize new structures that are otherwise inaccessible. In order to study such phenomena, we propose a multicomponent supramolecular system in which the final thermodynamic product can be obtained via two different routes that include different kinetic pathways and different metastable intermediate structures. The assembly under study is a $M_{12}L_{24}$ cage decorated with pseudorotaxanes. More specific, the spherical complex also known as the $M_{12}L_{24}$ Fujita cage[2] is exohedrally functionalized with docking sites for Stoddart's famous "blue box" macrocycle (Figure 1).[3] The pseudorotaxane decorated assembly can be obtained either via first cage formation, then addition of ring, or via the second pathway in which the ring is already present during cage formation. We indeed observed that both routes yield the same product, however, the kinetic pathways differ from each other. We will discuss the difference in the kinetic pathways that are followed with this particular system to gain fundamental insight in the formation of products under kinetic control rather than thermodynamic control.

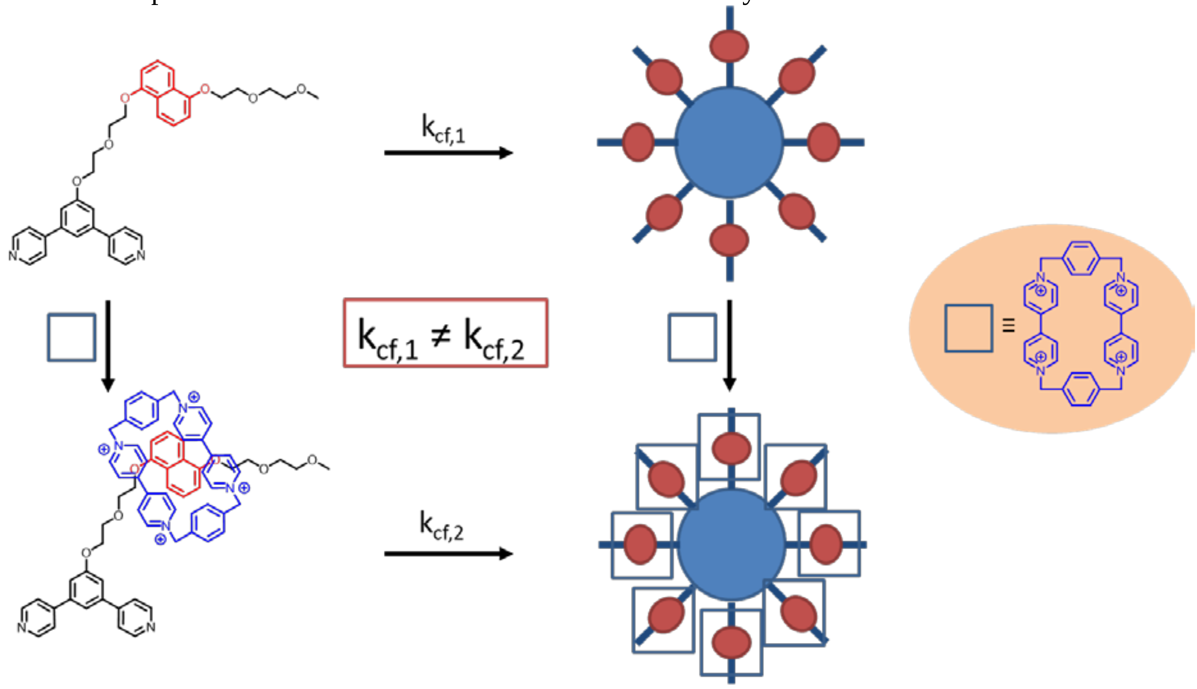

Figure 1: the different routes towards the cage pseudorotaxane with the first rate constant for cage formation $k_{cf,1}$ and the second rate constant for cage formation $k_{cf,2}$.

1) Bohne, C. *Langmuir* **2006**, *22*, 9100–9111.
2) Harris,K.; Fujita, D.; Fujita, M. *Chem. Commun*, **2013**, *49*, 6703–
3) 6712 Ashton, P.; Ballardini, R.; Balzani, R.; Boyd, S.; Credi, A.; Gandolfi, T.; Gómez-López, M.; Iqbal, S.; Philp, D.; Preece, J.; Prodi, L.; Ricketts, H.; Stoddart, F.; Tolley, M.; Venturi, M.; White, A.; Williams, D. *Chem. Eur. J.* **1997**, *3*, 152–170.