

Supramolecular Architectures Comprising Conformationally Flexible Cavity

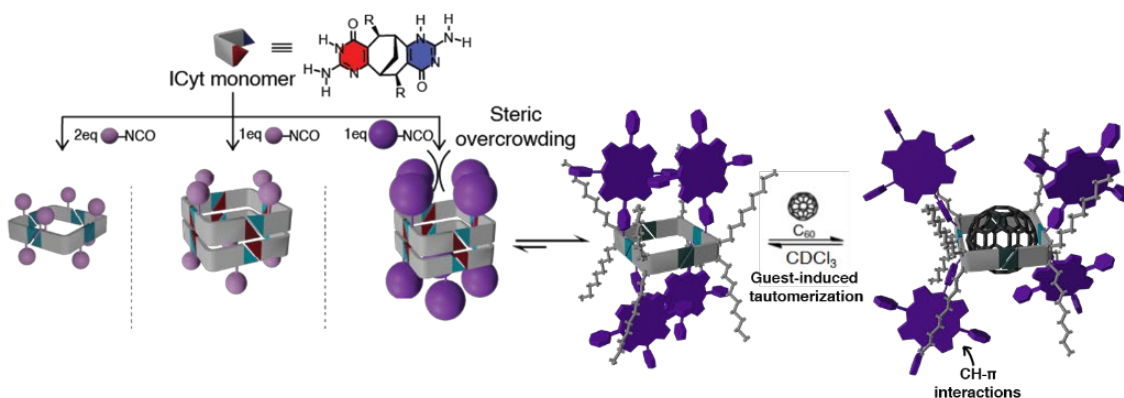
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Supramolecular chemistry has grown tremendously by implementing insights acquired from biological processes into state-of-art architectures at the molecular level. The next stage is to introduce function into the supramolecular architectures, however, synthetic self-assembling systems are still underdeveloped, and there are several challenges that must be overcome before fully functional molecular devices can be achieved. The individual components utilized in the bottom-up construction must be equipped with appropriate shape and symmetry to be able to aggregate in well-defined, controlled manner and to overcome the entropic penalty arising from the loss of disorder. The current discoveries in the field emphasize on more dynamic models of molecular recognition, such as induced-fit and conformational selection in pursuit of synthetic receptors, catalysts or cross-membrane transporters. These advances stress the necessity to go beyond conventional rigid supramolecular architectures, challenging us to develop reversible biomimetic supramolecular systems encompassing conformationally flexible frameworks.

To contribute to these efforts, we became interested in development of hollow supramolecular architectures with adaptable cavity utilizing enantiopure bicyclo[3.3.1]nonane monomers. The cavity size of the supramolecular capsules was tuned by introducing different types of hydrogen-bonding modes into the system. Asymmetrical bicyclo[3.3.1]nonane monomers embedded with isocytosine and ureidopyrimidinone units on opposite sides tends to assemble into octameric tubes as a result of social self-sorting. We anticipated that introduction of bulky tetraphenylporphyrin urea substituents could be used as a straightforward approach to access different binding properties, without the necessity to redesign the whole hydrogen-bonding motif. Additionally, the dynamic nature of concave capsule was demonstrated by entrapping fullerene C₆₀ as a guest. Remarkably, guest molecule induced the conformational changes of the host needed for efficient accommodation of the guest by shifting the equilibrium from closed to open-ended form [1].



References

- [1] A. Jozeliūnaitė, A. Neniškis, A. Bertran, A. Bowen, M. di Valentin, S. Raišys, P. Baronas, K. Kazlauskas, L. Vilčiauskas, E. Orentas, *J. Am. Chem. Soc.*, **2023**, *145*, 455–464.