Mining Unexpected Binding Mode and Catalysis in Cucurbituril Chemistry by 'High-Energy' Water

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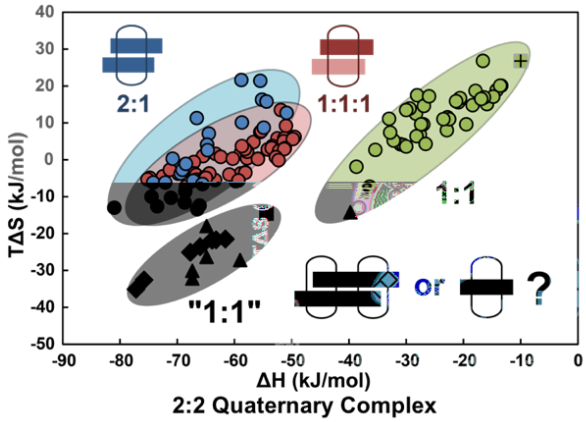
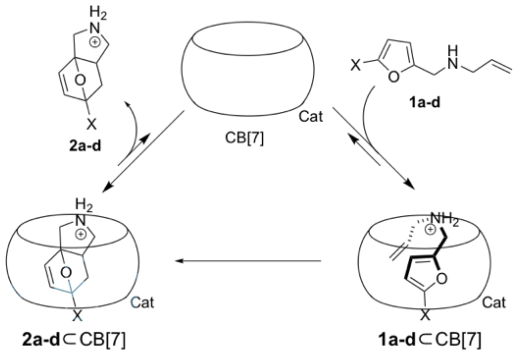
Cucurbit[n]urils (CB[n]) contained in-cavity water molecules whose conformational space and hydrogen-bond formation ability is constrained by the geometrically confined and hydrophobic cavity. The release of these 'high-energy' water into the aqueous bulk provides a strong enthalpic driving force to the host-guest association. The enthalpic change of such binding event is quantitatively determined by the number of in-cavity water being released. This becomes a key strategy of my researches that utilize enthalpy changes as a probe to sketch precise binding mode, e.g. 2:2 quaternary complex[1] and to explore possible functionality, e.g. artificial Diels-Alderase[2].



2:2 Quaternary Complex



Artificial Diels-Alderase

2:2 Quaternary Complex: Through revisiting enthalpy changes of previously reported 1:1 stoichiometry binding events, several CB[8]-mediated complexes are verified to be unexpected 2:2 quaternary complexes showing a binding motif of two overlapping diarylviologens held in place with two CB[8] molecules. The stacking of two highly-conjugated diarylviologens in one quaternary motif affords the complexes enhanced conductance when being considered as a single molecular conductor.

Artificial Diels-Alderase: *N*-allyl-2-furfurylamine derivatives (with unsaturated sidechain) exhibit larger enthalpy changes than *N*-alkyl-2-furfurylamine (with saturated sidechain) when binding with CB[7]. This inspires us to find an unexpected hair-pin induced conformation (HIC) of the former within CB[7] cavity, which rearranges them from an unreactive state into a highly reactive conformation, thereby catalyzing the Diels-Alder reactions. The half-lives of reactions in HIC were dramatically shortened by at least three orders of magnitude comparing to background reactions.

References

[1] Wu, G.; Olesińsk, M.; Scherman, O. A. et al. *J. Am. Chem. Soc.* **2017**, *139*, 3202.
[2] Palma A.; Wu, G; Scherman, O. A. et al. *Angew. Chem. Int. Ed.* **2017**, accepted.

Biography

Guanglu Wu (吴光鹭) received his B.Sc. degree in Chemistry and completed his Ph.D. degree under the supervision of Prof. Xi Zhang at Tsinghua University, China in 2013. His Ph.D. research involved investigating the self-assembly of bolaamphiphiles and its counterion effect. In December 2014, he began a postdoctoral position with Prof. Oren A. Scherman in the Melville Laboratory for Polymer Synthesis at the University of Cambridge funded by the Leverhulme Trust (project: Natural Material Innovation for Sustainable living). His current research concerns Cucurbituril mediated host-guest assembly and its application as well as modification of wood for tall timber building.