

Investigating binding dynamics of guests with cucurbit[n]uril, $n = 6,7$

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Cucurbit[n]urils are macrocyclic molecules favoured in guest-host chemistry due to their barrel-like structure — a hydrophobic inner cavity capped by polar carbonyl groups. They are characterized by the number of repeating glycouril subunits, which allow for cavity sizes capable of enveloping guest molecules ranging from simple alkanes to large, polycyclic compounds. Complexation is driven by the hydrophobic effect and ion-dipole interactions between carbonyl groups on the macrocycle and positive charges on the guest molecule.

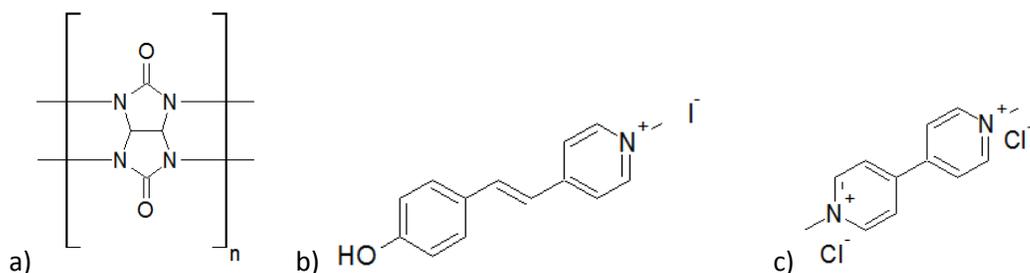


Figure 1: a) Structure for cucurbit[n]uril ($n = 6, 7$), CB[n]. b) Structure for 1-methyl-(4,4'-hydroxystyryl)pyridinium iodide, HSP⁺. c) Structure for methyl viologen dichloride, MV²⁺.

CB[6] has a height of 9.1 Å and an inner diameter of 3.9 Å, which allows for the incorporation of HSP⁺. The absorbance spectrum of HSP⁺ at neutral pH has a peak at 395 nm that decreases its signal strength upon complexation with CB[6]. Stopped-flow kinetics track the change in absorbance of HSP⁺ at 368 nm over time. By varying the concentration of CB[6] in the experiment and applying the equation $k_{obs} = k_+ * [CB[6]] + k_-$, an equilibrium constant $K = k_+ / k_-$ is obtained. A two-step function was observed in the presence of 0.1 M Na⁺, describing a pre-equilibrium process during the inherent dead time of the equipment, i.e. under 1.5 ms, and a detectable process on the order of 250 ms. These results help identify the binding mechanisms involved in the complexation of HSP⁺ and CB[6].

CB[7] boasts a slightly larger cavity with a diameter of 5.4 Å. The inclusion of MV²⁺ in CB[7] has been previously explored through ¹H-NMR measurements¹. Preliminary kinetic studies using stopped-flow measurements show a pre-equilibrium process occurring during the dead time of the stopped-flow, as well as a longer process on the order of 2 seconds. The pre-equilibrium process cannot be avoided even when the concentration of available CB[7] is limited by the presence of co-cations (e.g. Na⁺), indicating that a two-step mechanism occurs.

References

- (1) Kim, H. J. Inclusion of methylviologen in cucurbit [7] uril. *Proc. Natl. Acad. Sci. U. S. A.* **2002**, *99*, 5007.