Supramolecular Dynamics of Host-Guest Complexes Involving Cucurbit[7]uril

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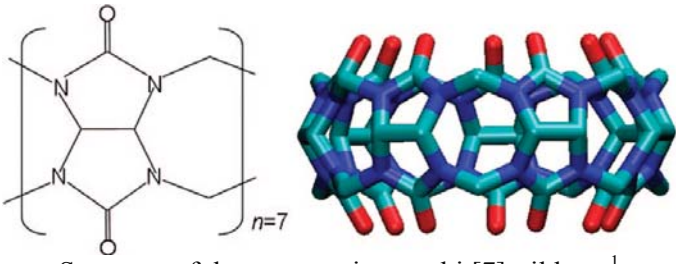

Structure of the seven unit cucurbit[7]uril host [1]

Cucurbit[7]uril (CB[7]) is a symmetric macrocyclic host composed of seven glycoluril units and twelve methylene bridges, as seen in the above figure. CB[7] has numerous potential applications as it binds a wide variety of positively charged and aromatic compounds with high equilibrium constants due to the negative electron density of the carbonyl groups around its portals and its hydrophobic interior[2].

The formation of host-guest complexes with CB[7] can be followed by a change in fluorescence intensity of the guest. Protonated 2-napthyl-1-ethylamine (NpAm) as a model fluorescent guest gives up to a 40% increase in fluorescence intensity when bound to CB[7] and has an equilibrium constant for CB[7] complex formation (K) of $5x10^6$ M^{-1}, as determined previously in our group using steady-state fluorescence and stopped-flow kinetic techniques. NpAm was used to probe the binding kinetics of guests that do not fluoresce. This was done with guests such as protonated trans-1,4-diaminocyclohexane (DAC), a guest with a similar equilibrium constant ($K\sim10^7$)[3] of CB[7] complex formation, and with protonated 1-adamantylamine (ADA), a guest with a higher binding constant ($K\sim10^{12}$)[3]. Competitive binding in the presence of sodium cations was also explored. It is known that Na^+ and H_3O^+ bind to the CB[7]'s portals, and previously, the binding constants have been obtained in combination with NpAm. The presence of Na^+ and H^+ lower the apparent binding constants of guests. These studies provide an essential step for the development of a competitive assay for the binding dynamics of a variety of guests to cucurbiturils.

NpAm as a fluorescent probe does have minor drawbacks. It was previously found to cause a red-shifted emission when exposed to low intensity 280nm excitation light for extended periods of time. The cause of this new emission was explored by a series of experiments used to probe the stability and identity of the emission. It was found to be a stable product whose formation is likely caused by a photochemical reaction from the UV irradiation and only forms in the presence of CB[7]. In light of this minor difficulty with NpAm, investigation of alternate fluorescent probes, acridine orange and 4',6-diamino-2-phenylindole (DAPI), which can potentially be used for kinetic studies with CB[7], were explored.

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