Miniature size induced fit and cage effect found in crown ether host-guest complexes

Crown-ethers (CEs), abbreviated as 3*n*-Crown-*n* (3*n*C*n*), (*n*= 4–8), are macrocyclic molecules built with several oxyethylene $(-CH_2-CH_2-O-)_n$ units. In 1967, Pedersen discovered the first CE, dibenzo18C6, and was awarded Nobel Prize in 1987 because CEs have opened a new field of chemistry, called host-guest chemistry. CE can capture variety of cations and molecules, where CE is called “host” and the cation or molecules “guest”. CE has two characteristic features. First is that different size (*n*) of CE captures different size of cation. For example, in aqueous solution 12C4 captures Li^+ ion most while 18C6 captures K^+ ion most among various alkali metal cations. This is called size-recognition. Second is that CE can adjust its flexible structure to fit the shape of guest. This is called “induced-fit”. “Induced-fit” theory, proposed by Koshland in 1985, is well known as an extension of “lock-and- key” theory in specific “enzyme-substrate” or “antigen-antibody” reaction, etc. However, showing the direct experimental evidence of the induced fit and obtain the outcome of the fitting is not so easy.

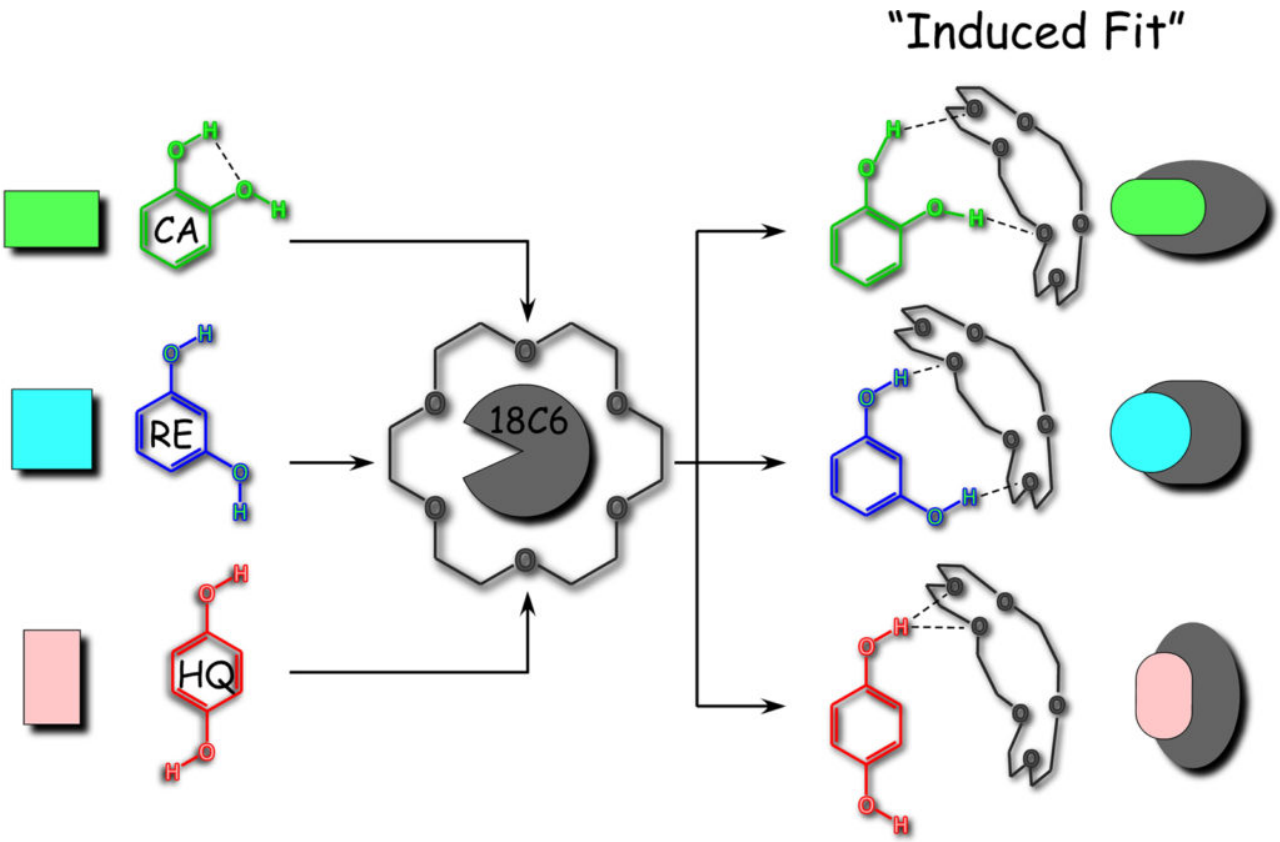

Fig. 1. Induced fit between crown-ether and benzenediols

Now, experiments at Hiroshima University reported a miniature size “induced-fitting” in 18C6•benzenediols complex and found a surprising outcome of the complex formation. Benzenediol has three structural isomers, *ortho* (catechol, CA), *meta* (resorcinol, RE)) and *para*-dihydroxybenzene (hydroquinone, HQ)) (See Fig. 1). Each benzenediol has additional isomers (conformers) due to the relative orientation of two hydroxyl (OH) groups. The Hiroshima group generated cold (~10 K) gas phase 18C6•benzenediol host-guest complexes in a vacuum chamber. They investigated the change of the OH groups before and after the complex formation by infrared (IR) absorption measurements.

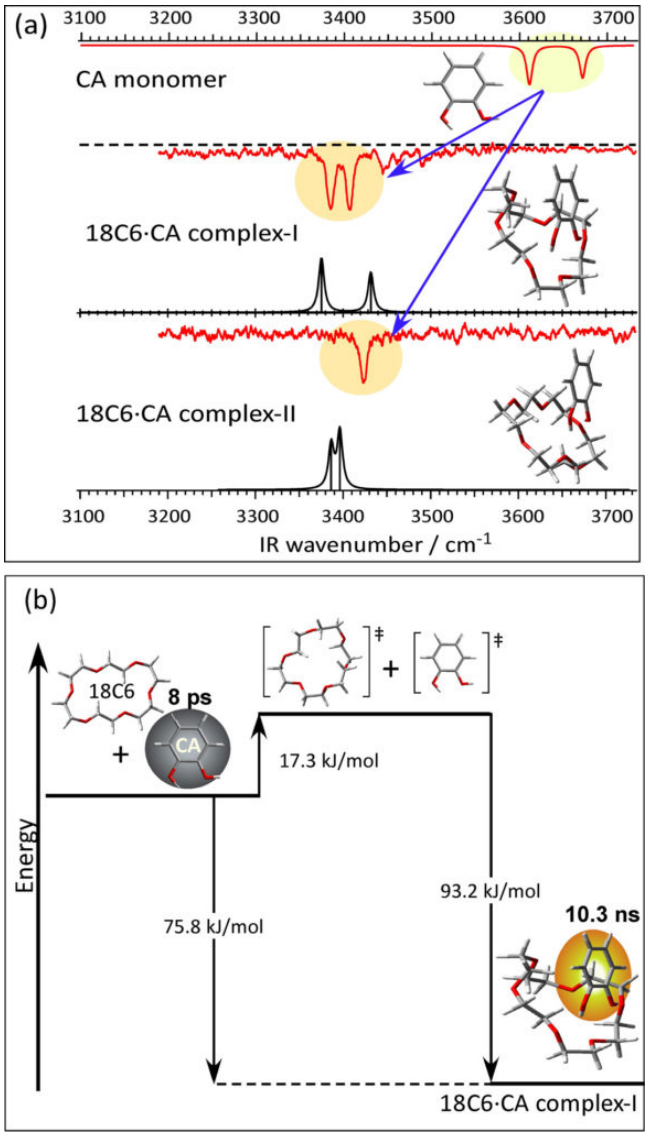

Fig. 2. (a) IR spectra of the OH stretch vibration of CA and 18C6•CA complex. Red curves are the observed spectra and black ones are the calculated ones. (b) Energy levels of 18C6 and CA monomer (left), distorted ones (middle), and 18C6•CA complex (right). Also shown are the energy difference and S1 state lifetime of CA in the monomer and complex.

Figure 2 (a) shows the IR spectrum of CA monomer and 18C6•CA host-guest complex. Also shown are the theoretically obtained structures and IR spectra, reproducing the observed ones. The structures and IR spectra indicate that two OH groups of CA are independently hydrogen-bonded to the oxygen atoms of 18C6, and 18C6 simultaneously changes to a best-matched structure to incorporate CA. This cooperative movement largely stabilizes the unified complex. Figure 2 (b) shows the energy levels of bare form 18C6 and CA (left), the distorted one (middle), and the complex (right). We can see the distortion energy (17.3 kJ/mol) is easily compensated by large binding energy (75.8 kJ/mol). Similar cooperative movement is found in 18C6•RE and 18C6•HQ complexes. Both RE and HQ change their conformation to higher energy ones (10~30 kJ/mol), but their binding energies are as large as 80 kJ/mol due to cooperative effect.

Finally, the group found a surprising change in the photophysics of guest species upon the complex formation. That is the lifetime of S_1 electronic state of bare CA (8 picosecond) is largely elongated in the18C6•CA complex (10.3 nanosecond). This means CA becomes 1,280 times brighter by forming the complex. The elongation of the lifetime is caused by that CE plays a role of preventing an H atom release from CA in S_1, that is CE works as a cage not to release the H atom. Thus, even for small size molecules, “induced-fit” is effectively working and in the present case CE controls not only the geometry but also the character (electronic structure) of guest species. This type of study is essential for the molecular level understanding of “induced-fit”.

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Publication

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