

Solvent dependence in Platonic structures of resorcinarene-based capsule

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Resorcinarene-based amphiphiles including C-Methylresorcinarene and C-undecylresorcinarene (Figure 1a) self-assemble into spherical hexameric structures in apolar solvents such as chloroform and benzene.[1] The pioneer work for the characterization of the hexameric structure based on single-crystal X-ray diffraction was demonstrated by MacGillivray and Atwood in 1997.[1] The X-ray analysis was conducted for the single-crystal prepared from nitrobenzene, which elucidated the formation of a capsule-like structure consisting of 6 resorcinarene units and 8 water molecules with incorporating 60 hydrogen bonding. This resorcinarene-based hexameric capsule possesses high applied potential for catalysis carriers and still gets attention as interesting supramolecular aggregates.[2] The structural configuration of C-undecylresorcinarene capsule is associated with core-shell structures where undecyl-tails are placed on the surface on the core composed of hydrogen bonding network and solvent molecules, which might be categorized into reverse micelle structures.

As mentioned above, the structure of resorcinarene-based hexameric capsule has been clarified by single-crystal X-ray structural analysis. Though the way is extremely useful in elucidating the real structure in molecular level, the greatest problem is that the effects of environmental conditions such as various temperature and solvent composition on the aggregate structure are ignored when preparing single crystals. As an alternative method for visualizing the aggregate structure in solutions as it is, small angle neutron scattering (SANS) is very useful and can be conducted at the required experimental conditions (e.g. various temperature levels and solvent compositions). Atwood,

Kumari, and coworkers have revealed that C-alkylpyrogallolarene, whose structure is almost identical with that of C-alkylresorcinarene, forms hexameric capsules with a core-shell geometry in chloroform by using SANS measurements.[3] The SANS study also has illuminated the structure of metal-organic pyrogallolarene-based capsules whose morphologies can be controlled by metal ion species. In this experiment, we investigate the solvent effect on the Platonic structure of C-undecylresorcinarene capsules using SANS measurements.

Figure 1b shows SANS profiles of C-undecylresorcinarene capsules in deuterated apolar solvent including toluene-d₈ and chloroform-d. The scattering intensity approached to $q=0$ at low- q region in the both systems, indicating the formation of spherical scatterers. The oscillation behaviors of the both profiles are similar to each other, but the q value at minimum position in toluene-d₈ is larger than that in chloroform-d, indicating a difference in their structures. Since the inside of the C-undecylresorcinarene capsule contains the apolar solvent, and the large difference in the values of SLD between the deuterated solvents and the C-undecylresorcinarene molecule, we employed spherical hollow model as the fitting model where solvent molecules are located in the core. The fitting model could reproduce the experimental data, indicating the presence of solvent molecule in the capsule core. The size of the solvent pool in the capsule core in chloroform-d is almost consistent with reported value. However, it is relatively large compared to that in toluene-d₈, which indicates the difference in the network structure through the hydrogen bonding among the hydroxyl groups in resorcinarene moiety and water molecules in each apolar

solvent. In toluene-*d*8, the full-stretched length of resorcinarene molecule (~1.6 nm) almost agree with that of shell thickness while the shell thickness in chloroform-*d* is smaller than the actual molecular size. This presumably suggests that the alkyl chains are flexibly mobile in the hexameric structure and efficiently cover the capsule core to minimize the interfacial free energy between the capsule core and the outer solvent.

[1] Leonard R. MacGillivray et al. *Nature*, 1997, 389, 469-472

[2] Qi Zhang et al. *Acc. Chem. Res.* 2018, 51, 2107 - 2114

[3] Harshita Kumari et al. *J. Am. Chem. Soc.*, 2011, 133, 18102-18105

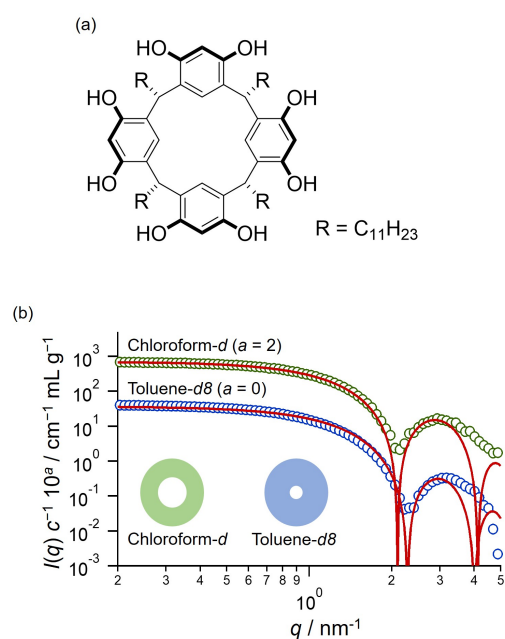


Fig. 1. Figure 1. (a) Chemical structure of C-undecylresorcinarene. (b) SANS profiles of C-undecylresorcinarene capsule. The red curves were calculated using spherical hollow model whose cross-sectional images are inserted.