Chemistry

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Fluorous Nanodroplets Encapsulated in Well-confined $M_{12}L_{24}$ Spherical Complexes

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Introduction

The distinct properties of fluorous phases are practically useful for separation, purification, and reaction control in organic synthesis. Here, we report the formation of a liquid-like fluorous droplet, comprised of 24 perfluoroalkyl chains, confined in the interior of a 5 nanometer-sized, roughly spherical shell that spontaneously assembles in solution from 12 palladium ions and 24 bridging ligands (Figure 1). [1]

Results

When a mixture of ligand **1a** and $Pd(NO_3)_2$ in dimethyl sulfoxide (DMSO)-d_6 was heated at 70 °C for 3 h, the endo-fluorous $M_{12}L_{24}$ complex **2a** was quantitatively obtained as indicated by NMR and CSI-MS. Complexes **2b**-**d** were quantitatively prepared by the same method. We expected that the fluorous core of **2a** could accommodate (or dissolve) fluorinated compounds through fluorophilic host-guest interaction. Thus, perfluorooctane (**3**), which is hardly soluble in DMSO, was mixed with a DMSO-d_6 solution of **2a**, and the solution was analyzed by ^{19}F NMR. We observed four signals from **3** in addition to the six signals from **2a**. On average, 5.8 molecules of the guest **3** were accommodated by the capsule **2a**. The encapsulation was controllable by the lengths of fluorinated sidechains.

Crystallographic analysis confirmed the rigid shell framework and amorphous interior (Figure 2). We obtained a single crystal of a **2a**•(**3**)$_n$ complex and analyzed the crystal by X-ray crystallography. Though the rigid shell framework of **2a** was refined, the fluorous sidechains and guest molecules were completely disordered and could not be located. This indicated that the interior sidechains are enough flexible that we can consider the core as a liquid-like nanospace.

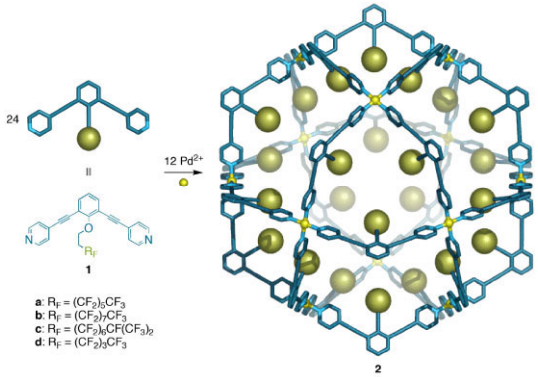

Figure 1. Self-assembly of endo-functionalized $M_{12}L_{24}$ spheres.

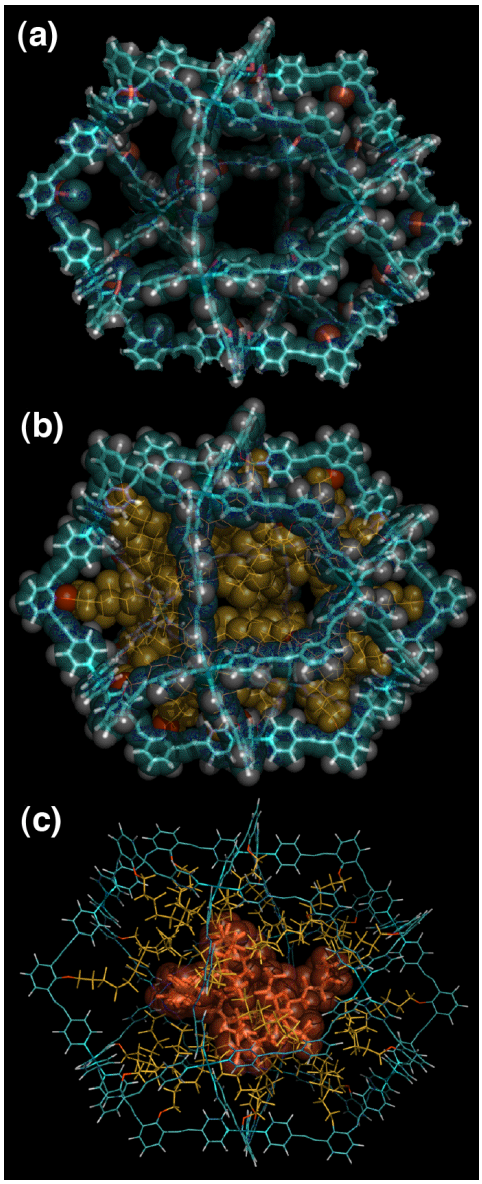

Figure 2. (a) The X-ray crystal structure of the shell framework of **2a**. (b) The $C_6F_{13}(CH_2)_2$- side chains are modeled and optimized by force-field calculations. (c) Six molecules of perfluorooctane were placed at the central void of **2a** and annealed by MD simulations.

References

[1] S. Sato *et al.*, *Science,* 313, 1273 (2006).

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