

Discrete and Well-Defined Hydrophobic Phases Confined in Self-Assembled Spherical Complexes

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Introduction

Long alkyl chains have a tendency to aggregate and form localized hydrophobic environments in polar solvent. This tendency has been exploited to prepare a variety of artificial structures, such as micelles, vesicles, core-shell structured polymers, and dendrimers, where the localized hydrophobic environments show interesting properties. These artificial long alkyl chain assemblies, as well as biomembranes, are typically structurally dispersed. The structural disparities result in a distribution of properties. Here we report discrete and well-defined assemblies of alkyl chains confined in a 5 nm spherical coordination shell (Fig. 1). The shell framework quantitatively assembles from 12 Pd²⁺ ions and 24 bent ligands and sharply defines the boundary of the interior hydrophobic phase of long alkyl chains. Furthermore, the nature of hydrophobic interior can be easily tuned by varying length of the alkyl chains.

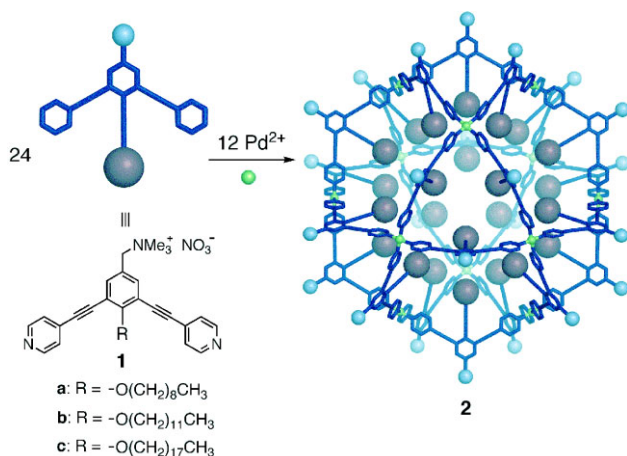


Figure 1 Self-assembly of M₁₂L₂₄ complexes **2a–c**.

Results

Amphiphilic ligands **1a–c** bearing inner alkyl chains and outer quaternary ammonium groups were designed expecting that, after self-assembly into spheres **2a–c**, the inner alkyl chains would form a localized hydrophobic phase within the sphere. When ligand **1a** (10 μmol) was treated with Pd(NO₃)₂ (6 μmol) in DMSO-*d*₆ for 1 h at 70 °C, the formation of M₁₂L₂₄ spherical complex **2a** as a single product was observed by ¹H NMR spectroscopy. Spheres **2b** and **2c** were also prepared in the same fashion. After anion exchange from nitrate ions (NO₃⁻) to triflate ions (CF₃SO₃⁻), cold-spray ionization mass spectrometry (CSI-MS) clearly confirmed the M₁₂L₂₄ composition of **2a–c** with molecular weights of 20304, 21313, and 23337 Da, respectively.

The rigid shell framework of the M₁₂L₂₄ complex was revealed by X-ray crystallographic analysis of complex **2b**. Synchrotron X-ray irradiation provided high quality data and the structure of the exterior shell with a diameter of 4.7 nm and the peripheral cationic groups (Fig. 2a) were clearly identifiable. Only the initial –OCH₂CH₂– segment could be located due to severe disorder of the remainder of the alkyl side chains. Therefore, the disordered alkyl chains were separately modeled and attached to the shell crystal structure, then simulated annealing by molecular dynamics calculation gave an optimized structure (Figure 2b).

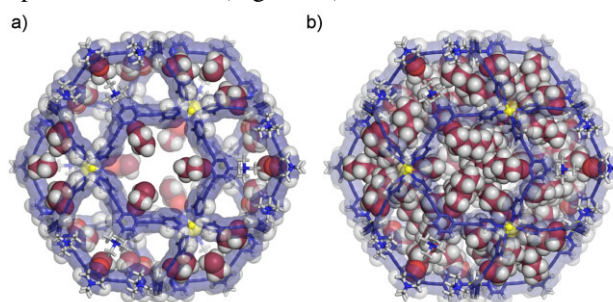


Figure 2 The X-ray crystal structure of **2**. Counter ions and solvent molecules are omitted for clarity.

Complexes **2a–c** provide a 5 nm hydrophobic phase localized and isolated from the polar solvent. The well-known hydrophobic dye, Nile red, was examined as a guest because of the poor solubility in aqueous solvents and its solvatochromatic property suitable for estimating the hydrophobicity of the local environment. The solubility and solvatochromatic behavior of Nile red clearly show that the properties of hydrophobic interior of **2a–c** vary with the alkyl chain length. The maximum absorption wavelength (λ_{max}) of dissolved Nile red in spheres was underwent a bathochromic shift in the order of **2a**<**2b**<**2c** (576, 555, and 552 nm, respectively), in good agreement with the solvatochromism of Nile red that shows bathochromic shifts in nonpolar media. The number of Nile red contained in spheres **2a–c** was calculated to be 2, 10, and 12 molecules, respectively.

References

[1] K. Suzuki *et al.*, *Angew. Chem. Int. Ed.*, 47, 5780, 1638 (2009).

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