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Nanoscopic structure of hydrophilic and hydrophobic molecules in artificial clathrate hydrates

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ABSTRACT

We introduce one-dimensional nanotube water-cluster crystal $[Ru(H_2bim)_3]_2\{trimesate\}_2$ $(H_2O)_{30}\cdot\{tetrahydrofuran\}_3$ as a gas container, and describe from TGA measurements and DFT calculations that the $(H_2O)_{36}\cdot$cluster confines two or three hydrophilic and hydrophobic molecules. It is confirmed in DFT calculations that the $(H_2O)_{36}$ cluster as abstracted from the water-cluster crystal has weaker H-bond energies and longer H-bond distance among water molecules than the H-bonding in the $(H_2O)_{24}$ cavity of hydrates in nature. The cluster has weak repulsion interactions with the organic molecules as quest ones. Experimentally, we investigate the dynamic behavior of the organic molecules in the polyhedral hydrate $(H_2O)_{36}$-cluster in the temperature range of 173–277 K for ^{2}H NMR observables (spin-lattice relaxation times and line shapes).

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1. Introduction

The first carbon nanotubes were found out by Russian investigators [1], although the research effort remained unnoticed. Later, single-walled carbon nanotubes were observed in the type of hollow tubes of rolled up graphite sheets synthesized with a chemical vapor-growth technique [2], and recognized to show images of a nanotube with a solitary graphene wall [3]. In around 2000, carbon nanotubes advanced explosively as materials with extraordinary properties that make them ideal building blocks for nano-electromechanical devices and so on [4,5]. One of the more interesting applications proposed for carbon nanotubes are as storage media for fluids and solids. Particular interest is their potential for fuel gas storage, especially hydrogen [6].

Recently, we are also deeply interested in producing nanotube water-cluster containers for gases in atmosphere, and have synthesized one-dimensional nanotube cluster crystal, $[Ru(H_2bim)_3]_2$-$\{trimesate\ (TMA)\}_2\cdot(H_2O)_{30}$ -$\{tetrahydrofuran\ (THF)\}_3$ (*A*), with polyhedral hydrate cavity, $(H_2O)_{36}$, consisted of $4^4 6^{10} 7^4$ at 253 K in Fig. 1 [7]. The nanotube crystal changes into a disordered $4^4 6^4 7^8 8^2$ at 90 K of thirty-six H_2O units. The polyhedral water units include three THF molecules in the center of the periodic units as the THF hydrates stabilized under ambient temperature and pressure. The structure of clathrate hydrate can be stabilized at moderate temperature and low pressure by introducing an organic molecule such as a THF molecule. In order to investigate the possibility of some other organic solvent molecules (OSM)s including in the water nanotube-like cluster (WNT), we will prepare the other crystal with hydrophilic 1, 4 dioxane (Diox) in the same synthetic method as *A*-like crystal [7]. The crystal structures are also constructed from the same structure as *A*, and the organic molecule exists at the center of the periodic units of WNT. The crystal can be dealt with a uniform interface, since it is a single crystal and has one-dimensional uniform pore.

Experimentally, NMR is a very powerful tool for probing porous materials to measure molecular level dynamic and static information. In NMR observables (relaxation times, spectral line shapes, chemical shieldings), the relaxation time is an indicator of the local molecular motions, and the line shape exhibits isotropic or anisotropic characteristics in the pore of the crystal, respectively. For carbon and silica nanotubes, there are considerably several important studies using NMR chemical shieldings [8,9] and NMR relaxations [10]. Some investigators have performed interesting analysis of C-13 chemical shieldings for carbon nanotubes from the DFT calculations [11,12]. We are also able to use the relaxation time and line shape to characterize motions of OSMs in cavities of the

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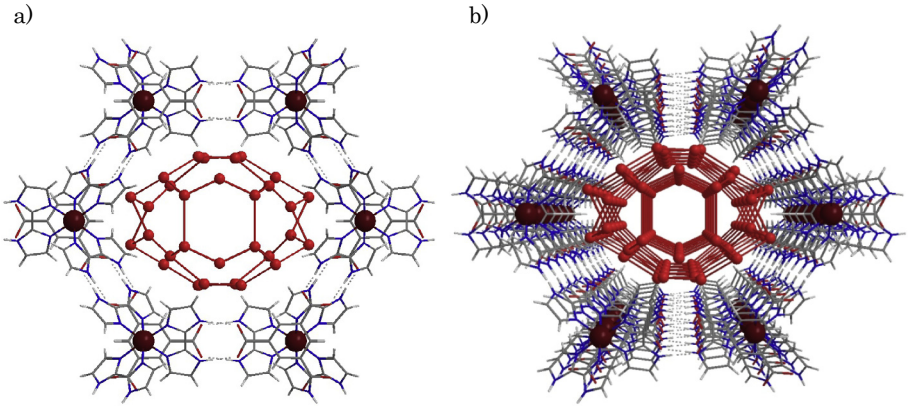

Fig. 1. First layer and one-dimensional structures in $[Ru^{III}(H_2bim)_3\ (TMA)]_2 \cdot 3THF \cdot 30H_2O\}_n$ nanopore, a)First layer structure, b) one-dimensional structure.

one-dimensional nanotube cluster crystals. The NMR T_1 and line shape measurements of the molecules in ^2H_2O-cluster cavity are employed to probe the change of water structure around hydrophobic and hydrophilic OSMs during the organic molecular hydrate formation and dissociation to understand the role of the molecules and hydrate interface. Then, we can investigate the dynamic and static behaviors of hydrophilic and hydrophobic molecules [(THF, Diox), and (cyclohexane (cHex), n-hexane (nHex))], respectively as quest ones in $(H_2O)_{36}$-cluster cavities as abstracted from the WNT crystal with measurements of spin-lattice relaxation times and resonance line shapes using ^2H solid NMR method. In order to discuss static behavior between the guest solvent molecule and the $(H_2O)_{36}$-cluster in the nanopore, we perform DFT calculations of the static interaction system in GAUSSIAN 09 [13] software, and confirm that the $(H_2O)_{36}\cdot$cluster confines two or three OSMs for hydrophilic and hydrophobic ones, respectively.

Quantum chemical calculation method has an important role for the theoretical study of the static behavior of the hydrates, and our previous works [14,15] of gas hydrates in cubic structures I ($5^{12}6^2$ and 5^{12} polyhedral units) in nature [16–18] provided the information on static behavior of guest molecules (CH_4 and CO_2) in $(H_2O)_{20}$ and $(H_2O)_{24}$ cluster cavities from the nanometer-scopic viewpoint. The calculated carbon NMR chemical shifts of CO_2 and CH_4 in gas, and in the two cluster cavities are in considerably good

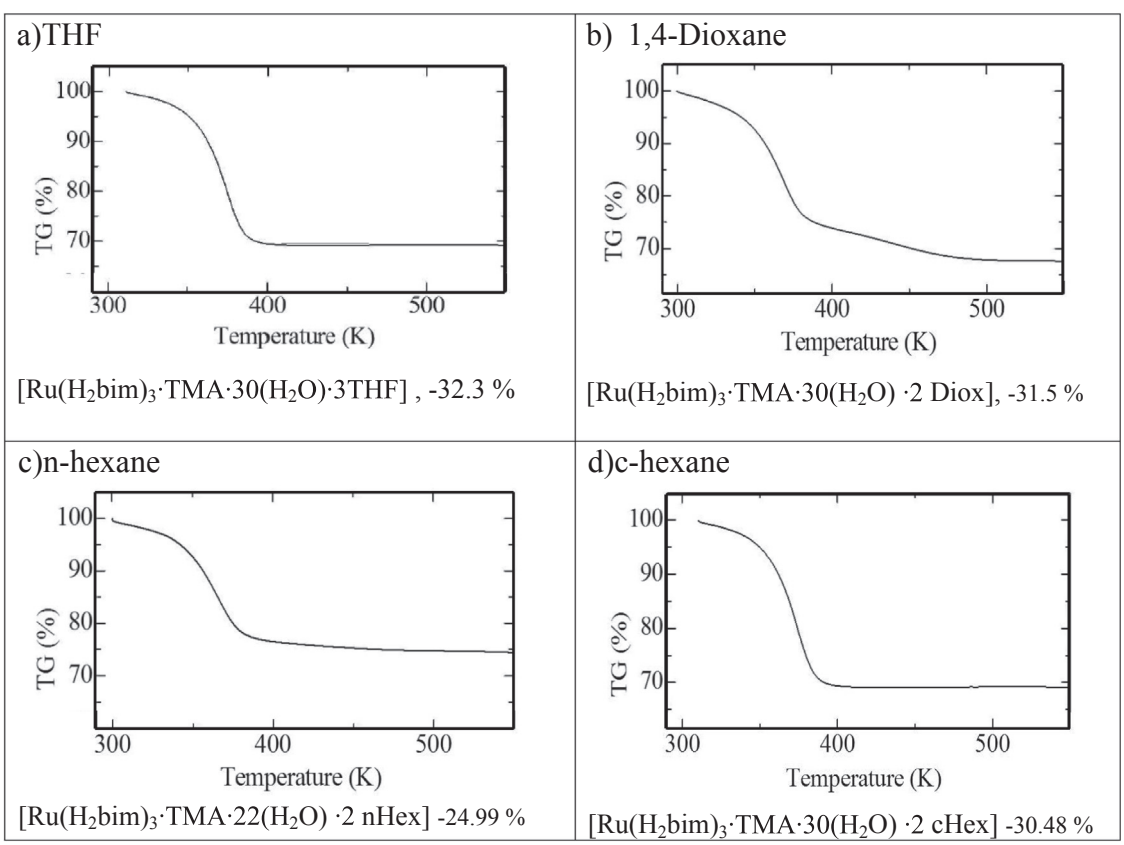

Fig. 2. Thermal gravimetric analysis of THF, 1, 4-dioxane (Diox), n-hexane (nHex), and c-hexane (cHex) confined in one-dimensional nanotube-cluster, $[Ru(H_2bim)_3]_2$- {trimesate (TMA)}$_2$- $(H_2O)_{30}$-(nOSM).

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