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A spectroscopic investigation of incompletely condensed polyhedral oligomeric silsesquioxanes (POSS-mono-ol, POSS-diol and POSS-triol): Hydrogen-bonded interaction and host–guest complex

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Abstract

^{1}H NMR dilution experiment and FTIR were used to investigate the hydrogen bonded interaction in three different types of incompletely condensed silsesquioxanes (POSS-mono-ol, POSS-diol and POSS-triol). For POSS-triol, there existed a dynamic equilibrium between single molecule and hydrogen-bonded dimer, and the dimerization constants (K_{dim}) of POSS-triol in different solvents were determined by ^{1}H NMR dilution experiment. In addition, based on hydroxy group which acted as hydrogen bond donors, the possibility of three POSS silanols as anion receptors to form host–guest complexes was also explored in this paper.
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Keywords: Supramolecular chemistry; POSS silanol; Hydrogen bond; Host–guest complex

1. Introduction

Silsesquioxane is the general name for a family of molecular siloxanes with the formula $[RSiO_{3/2}]_n$ and closely related compounds [1]. Random, ladder and cage structures are known for these compounds, of which the latter are the most familiar. Incompletely condensed silsesquioxanes containing Si–OH groups have gained considerable attention in recent years; these compounds have been shown to be effective homogeneous mimics for zeolites as well as amorphous and mesoporous silica which contain surface silanol sites. And many of these have been proved to be excellent starting materials for the preparation of a number of hetero- and metallasiloxanes [2]. The leading representative of these incompletely condensed silsesquioxanes is the trisilanol $R_7Si_7O_9(OH)_3$ (denoted as POSS-triol, Scheme 1). POSS-triol has an increasing number of applications in the fields of inorganic/organic hybrid materials [3], as homogeneous models for silica supports [4], as ligands for single-site polymerization catalysts [5] and even as chiral phosphate ligands [6]. To further extend the applications of incompletely condensed silsesquioxanes beyond POSS-triol, two other POSS silanols (POSS-diol and POSS-mono-ol, Scheme 1) are also chosen to use as anion receptors in this paper.

Hydrogen bond is one of the most important non-covalent interactions in supramolecular chemistry. Recently, host–guest complexes based on hydrogen bonded interaction (intermolecular and intramolecular) are widely investigated [7]. For example, the hydrogen-donating effects of NH's of amide, sulfonamide, urea, and thiourea on anion binding have been reported [8]. Organosilanols can extend the range of useful building blocks for supramolecular chemistry. Some complexes based on silanols also have been reported; even fluoride ion could be encapsulated in cage silsesquioxanes [9]. However, the vast potential of organosilanols in molecular recognition needs further exploit for application in supramolecular chemistry.

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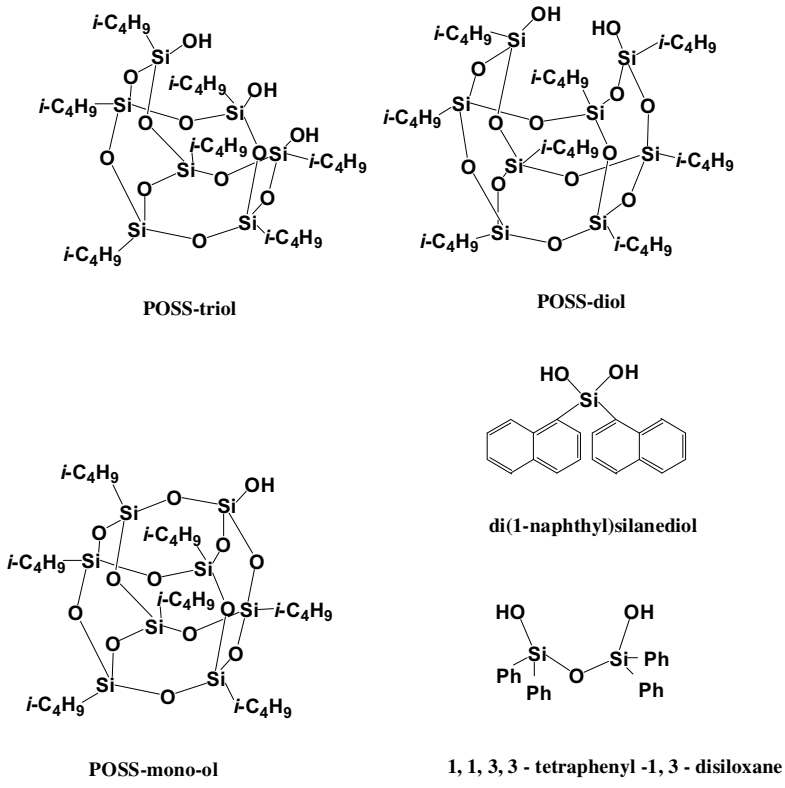

Scheme 1. The structure of different silanols.

A novel silanol of 1,3,5-$(HOiPr_2Si)_3C_6H_3$ could co-crystallize with 4,4′-bipyridine (bpy), (*E*)-bis(4-pyridyl)ethylene (bpe), 4,4′-azo-pyridine (azpy) and bis(4-pyridyl)acetylene (bpa) those exhibit similar supramolecular motifs featuring 2D grid networks of O–H···O(H)Si and O–H···N hydrogen bonds reported by Beckmann et al. [10]. Now one of the current research efforts in our group addresses the possibility of various different silanols as anion receptors. Two different silanols that could be used as anion receptors have been successfully reported by our group [11]. It is well known that POSS silanols own rigid cage structure and hydroxy groups, which will be a help for the usage as anion receptors. As a part of the program, this work investigates the possibility of three different POSS silanols as anion receptors. To the best of our knowledge, this is the first report on incompletely condensed silsesquioxanes as anion receptors.

2. Results and discussion

At first, it seems necessary to investigate the hydrogen bond in POSS-triol, POSS-diol and POSS-mono-ol. Brown and Vogt reported that POSS-triol (R = cyclohexyl) could form a stable dimer in which all of the hydroxy groups formed hydrogen bonds and dimerization constants were determined ($K_{dim} = 270\ mol^{-1}\ dm^3$ in benzene at 25 °C). However, the authors did not give the details about the method the dimerization constants were determined [12]. Later Feher and co-workers reported that POSS-triol existed in hydrogen-bonded dimer by single crystal X-ray diffraction [4a]. They also reported that POSS-triol could form a remarkably stable anion by the extensive hydrogen bond, which was formally derived from deprotonation of POSS-triol [13]. Gun'ko et al. reported that pyridine could react with POSS-triol dimer to form pyridinium salt consisted of separated dimeric hydrogen-bonded silsesquioxane anions and pyridinium cations, in which the deprotonated anionic trisilanol was stabilized by dimerization *via* multiple hydrogen bonds [14]. Pietsching reported that the deprotonated disiloxanetetrol formed a dimeric structure in the solid state, which was stabilized by hydrogen bond and potassium-aryl interactions [15]. Krijimen's group successfully used FTIR data and DFT calculations of incompletely condensed silsesquioxanes as references for FTIR assignments of hydroxy clusters in zeolite structure [16]. Duchateau et al. reported that POSS-triol could be partially silylated to afford vicinal, geminal disilanols or monosilanols and investigated the hydrogen bond of these different types of incompletely condensed silsesquioxanes in detail [17].

In this paper, firstly we use ^1H NMR dilution experiment and FTIR spectra to investigate the hydrogen bond existing in three different types of incompletely condensed silsesquioxanes (POSS-triol, POSS-diol and POSS-mono-ol). POSS-triol, POSS-diol and POSS-mono-ol (R = *iso*-Bu) were prepared following the literature [5b,18]. In order to reduce the effect of water on experimental results, analytical grade solvents were chosen (Purity ⩾ 99.8%). Dilution of POSS-mono-ol and POSS-diol ($5.0–0.625 \times 10^{-3}$ mol dm^{-3}) caused virtually no shift ($\Delta\delta \leqslant 0.1$ ppm) (see

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