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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.

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 $[\mathrm{RSiO}_{3/2}]_n$ 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 $\mathrm{R_7Si_7O_9(OH)_3}$ (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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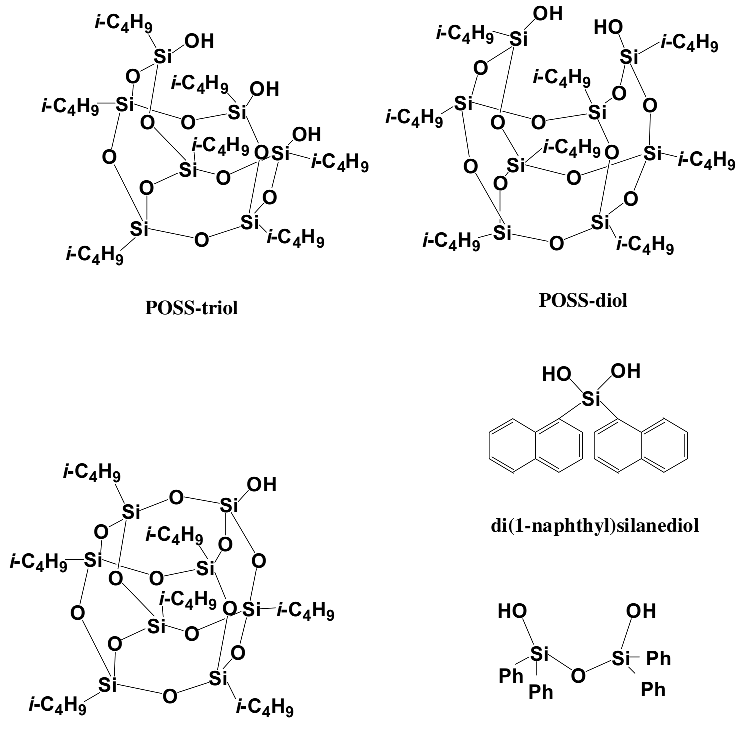


POSS-triol

POSS-diol

di(1-naphthyl)silanediol

POSS-mono-ol

1, 1, 3, 3 - tetraphenyl -1, 3 - disiloxane

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.

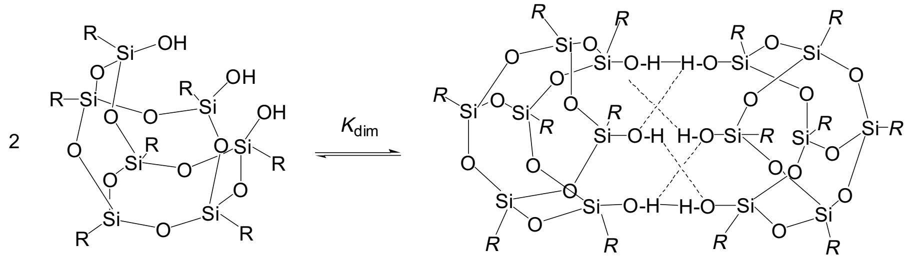
2. Results and discussion

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 ($K_{\mathrm{dim}} = 270\ \mathrm{mol^{-1}\ dm^3}$ 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].

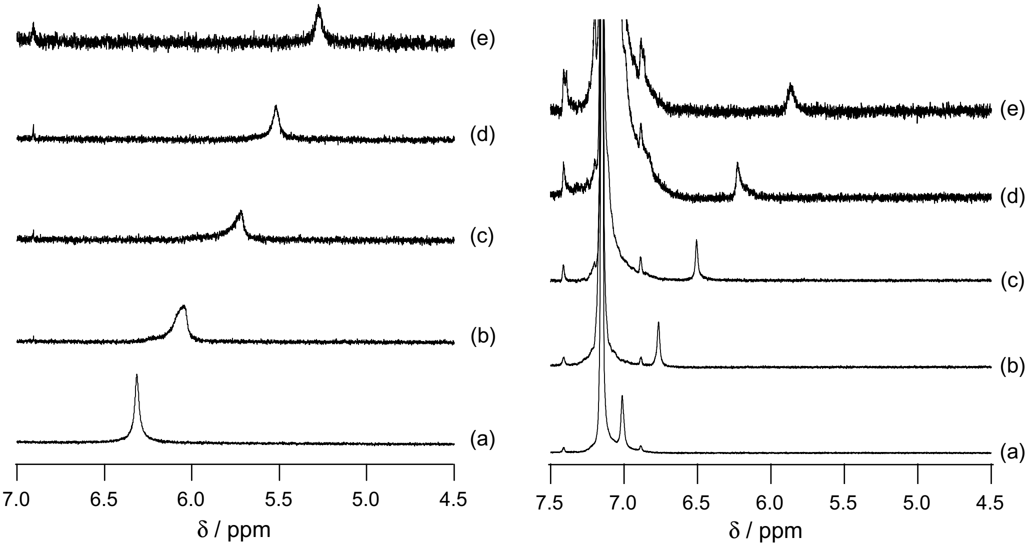
In this paper, firstly we use ^{1}H NMR dilution experiment and FTIR spectra to investigate the hydrogen bond existing in three different types of incompletely condensed silsesquioxanes (POSS-triol, POSS-diol and POSS-mono-ol). POSS-triol, POSS-diol and POSS-mono-ol (R = *iso*-Bu) were prepared following 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 ($5.0–0.625 \times 10^{-3}$ $\mathrm{mol\ dm^{-3}}$) caused virtually no shift ($\Delta\delta \leqslant 0.1$ ppm) (see supplementary material) indicating that intermolecular dimerization is negligible at least in our experimental concentration range in $CDCl_3$. As we know, for POSS-triol, there existed a dynamic equilibrium between a single molecule and an intermolecular hydrogen-bonded dimer (Scheme 2). The equilibrium was investigated by ^1H NMR dilution experiment in different solvents, *i.e.* $CDCl_3$, C_6D_6, DMSO-d_6, and acetonitrile-d_3. Results showed that POSS-triol did not dissolve in acetonitrile-d_3 within the dilution experimental concentration. The ^1H NMR chemical shifts of silanol appeared at 6.3 ppm and did not move whether the concentration of POSS-triol decreased or increased in DMSO-d_6 ([POSS-triol]: 0.625×10^{-3}–$1.0 \times 10^{-2}\ mol\ dm^{-3}$). These results implied that POSS-triol dimer could not form in DMSO-d_6 due to strong hydrogen bond with DMSO molecule. Therefore, it was impossible to determine the dimerization constants in DMSO-d_6. The ^1H NMR chemical shift variation could be obviously observed in $CDCl_3$ and C_6D_6 as shown in Fig. 1. With decreasing concentration of POSS-triol, POSS-triol dimer gradually dissociated to form single POSS-triol, which embodied that the OH signal shifted to the upfield. The dimerization constants were calculated by non-linear least squares curve fitting of ^1H NMR titration data above ($K_{dim} = 174\ mol^{-1}\ dm^3$ in $CDCl_3$ and $1075\ mol^{-1}\ dm^3$ in C_6H_6, respectively) as shown in Fig. 2 [19]. This implied that stronger intermolecular hydrogen bond could be formed in less polar solvents, such as chloroform and benzene. The results of ESI-MS of POSS-triol in acetonitrile also showed that POSS-triol had two existing forms in solution, monomeric form ($m/z = 771.2$ for $[M-H_3O]^-$ and 789.2 for $[M-H]^-$) and hydrogen-bonded dimer ($m/z = 1580.7$ for $[2M-H]^-$), as shown in Fig. 5.

Solution FTIR spectrum was also used to investigate the equilibrium between single POSS-triol and intermolecular hydrogen bonded dimer. Unfortunately, the characteristic wavenumber change of silanol OH could not be observed in the spectrum because of the strong intermolecular hydrogen bond (see Fig. 3).

We also investigated POSS-mono-ol, POSS-diol and POSS-triol in the solid-state and solution state (0.1 M, 0.05 M and 0.025 M in CCl_4) by FTIR spectra. For POSS-mono-ol, in CCl_4 solution, the silanol group is truly isolated ($3680\ cm^{-1}$), whereas in the solid state it also



Scheme 2. The equilibrium between single POSS-triol and POSS-triol dimer.



(1) **(2)**

Fig. 1. ^1H NMR dilution experiment in $CDCl_3$ (1) and in C_6D_6 (2). [POSS-triol] = 1.0×10^{-2} (a), 5.0×10^{-3} (b), 2.5×10^{-3} (c), 1.25×10^{-3} (d), 6.25×10^{-4} (e) $mol\ dm^{-3}$.

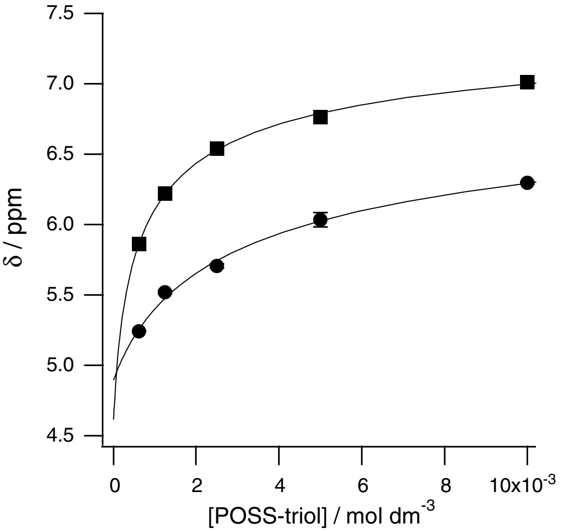


Fig. 2. Chemical shift changes of OH protons of in $CDCl_3$ (closed circles) and C_6D_6 (closed squares).

shows an intermolecularly mono-hydrogen-bonded vibration at 3500 cm^{-1}, which was ascribed to a dimeric structure, most probably in the crystalline phase. For POSS-triol, whether in solid or in solution, the silanol group stretching vibration appeared at about 3200 cm^{-1}, which is a characteristic vibration of poly-hydrogen-bonded silanols, and it suggests that even in solution POSS-triol can also form strongly hydrogen-bonded dimeric structure. The above results were in good agreement with the report by Duchateau *et al* [17a]. As for POSS-diol, in the solid state, characteristic stretching vibration appeared at about 3150 cm^{-1}, which implied that POSS-diol forms poly-hydrogen-bond and maybe dimeric structure. But in the solution, POSS-diol was accompanied with a shift of the silanol stretching vibration to almost 3300 cm^{-1} ($\Delta\lambda = 200$ cm^{-1}), ascribing to the intramolecular mono-hydrogen bond. It should be pointed out that the characteristic absorptions of POSS-triol, POSS-diol or POSS-mono-ol did not shift with decreasing concentration (see supplementary material). Based on the above results, it is clear that in solution state there exists intermolecular hydrogen bond in POSS-triol, intramolecular mono-hydrogen bond in POSS-diol, and no hydrogen bond in POSS-mono-ol.

It is interesting to investigate the effects of the hydrogen bond in POSS silanols on the complex ability with anion. To elucidate the anion complexation ability of three different POSS silanols, ^1H NMR titrations with tetrabutylammonium salts of anions such as Cl^-, Br^-, and AcO^- were investigated in $CDCl_3$. Fig. 4 showed the ^1H NMR spectral changes of POSS-triol upon the addition of Cl^-. It was found that with increasing concentration of Cl^-, the signals for OH in the POSS-triol shifted to the downfield, indicating the hydrogen bond formation of silanol with Cl^-. However, the value of OH chemical shift change was not large, indicating that POSS-triol had stronger tendency to form dimer, and there existed two equilibriums for POSS-triol, as shown in Scheme 3. The spectral changes could be fitted onto the 1:1 binding isotherm; the association constant (K_{11}) was then calculated to be 107 mol^{-1} dm^3 by nonlinear least squares curve fitting analysis. Electrospray ionization mass spectra (ESI-MS, negative mode) of POSS-triol in the presence and absence of tetramethylammonium chloride were measured in

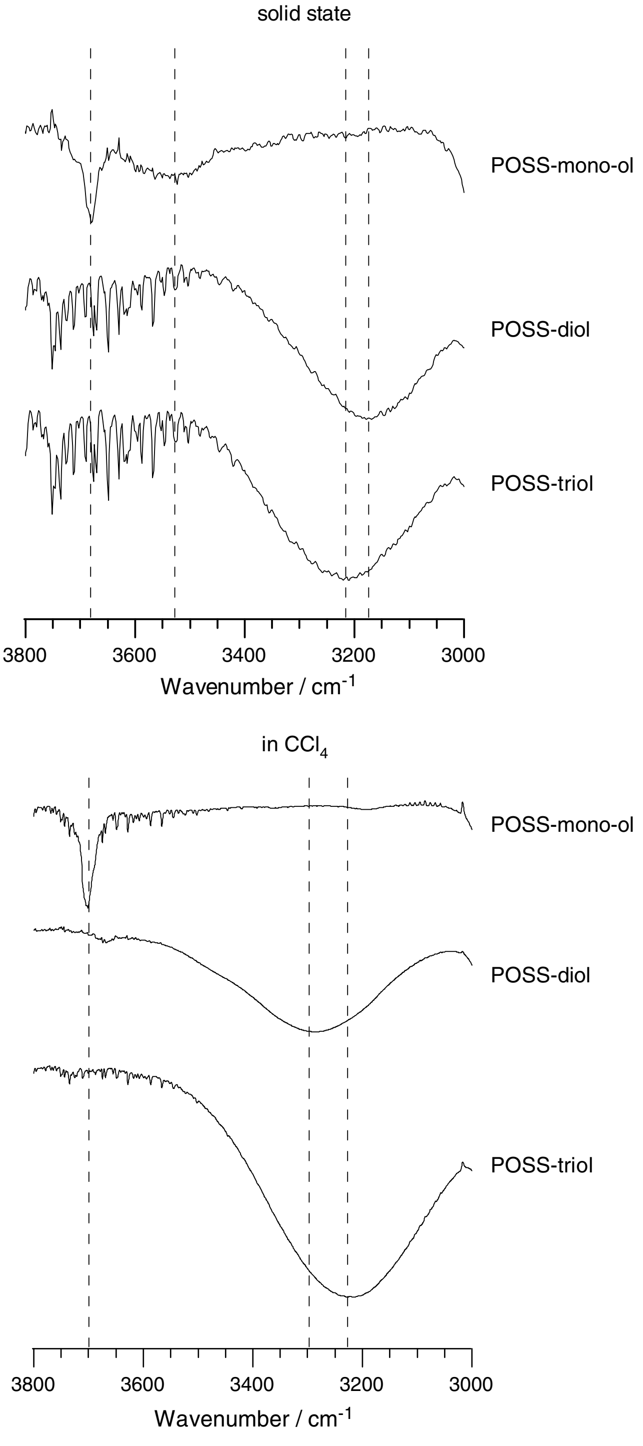


Fig. 3. FTIR spectra of POSS-triol, POSS-diol and POSS-mono-ol in solid state and solution (CCl_4, 0.1 M).

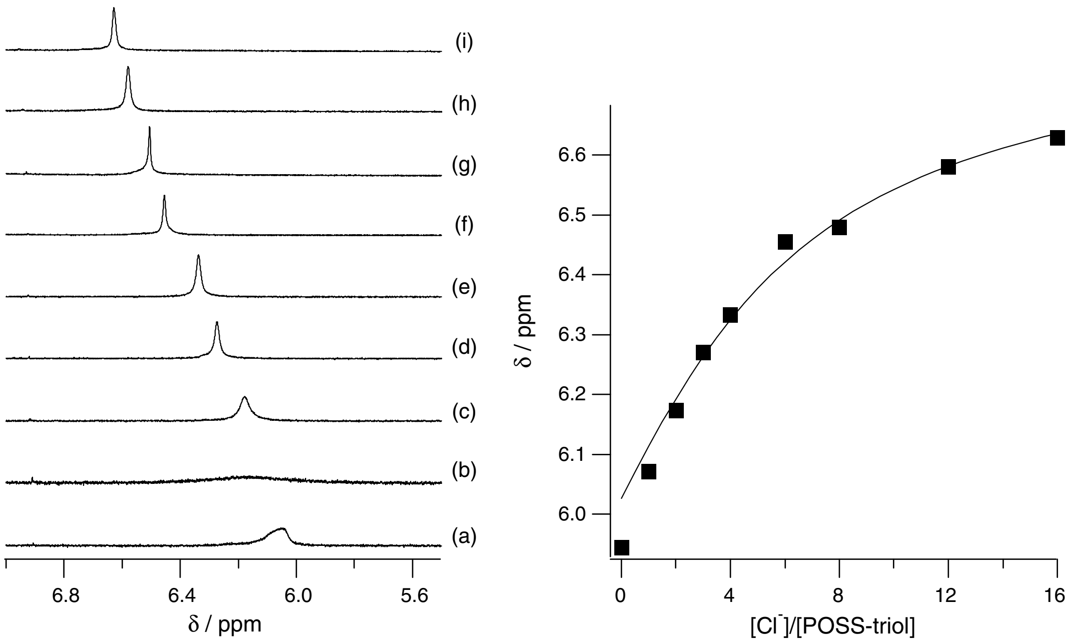
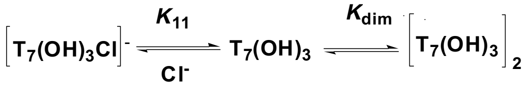


Fig. 4. Partial ^{1}H NMR spectra of POSS-triol in the absence (a) and the presence of 1 (b), 2 (c), 3 (d), 4 (e), 6 (f), 8 (g), 12 (h) and 16 (i) equiv. of tetrabutylammonium chloride in $CDCl_3$ at 298 K. [POSS-triol] = 5.0×10^{-3} mol dm^{-3}.



Scheme 3. The equilibria between single POSS-triol and POSS-triol dimer and complex with Cl^-.

MeCN, as shown in Fig. 5. Ion peaks corresponding to 1:1 complex were clearly observed in good agreement with the isotope patterns in the presence of Cl^-, which suggest the 1:1 complex of POSS-triol with Cl^- formed in the solvent ($m/z = 825.6$). It should be pointed out that even in the absence of tetramethylammonium chloride, predominant 1:1 complex peak was also observed, which should be ascribed to the small quantity of Cl^- in the solution [11].

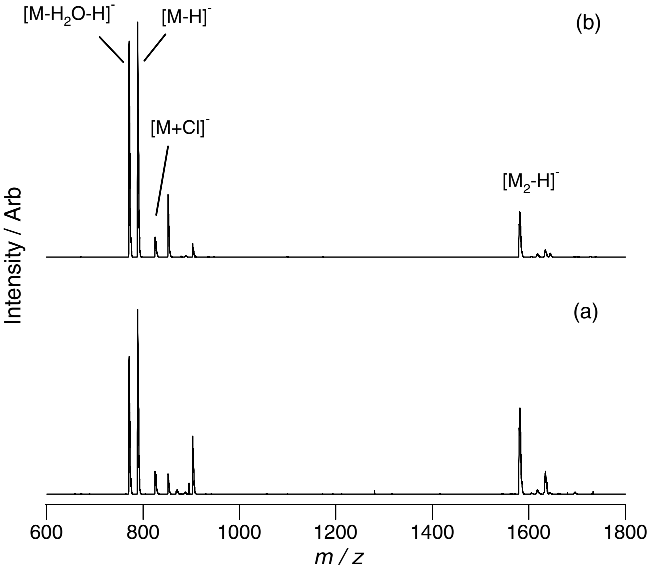


Fig. 5. ESI-MS (negative ion mode) of POSS-triol in the absence (a) and presence of tetramethylammonium chloride (b) in MeCN.

In the ^{1}H NMR titration experiment of POSS-triol with Br^-, OH signals also showed downfield shifts due to hydrogen bond with Br^-; however the change of the chemical shifts was so little that it was difficult to determine the association constant. This result suggests that POSS-triol has stronger complex ability with Cl^- relative to Br^-, and this could be explained by the larger charge density of Cl^- which resulted in the formation of stronger hydrogen bond. We also attempted to determine the association ability of POSS-triol with AcO^-; however, OH signal disappeared in the spectrum, which was ascribed to the stronger basicity of AcO^- and facile ion exchange of one proton of siloxy group on a POSS framework with AcO^- to form AcOH. And a stable anion formed which could be stabilized by the extensive hydrogen bond [13].

For di(1-naphthyl)silanediol and 1,1,3,3-tetraphenyl-1,3-disiloxane (Scheme 1), ^{1}H NMR dilution experiment at 5.0–0.625 × 10^{-3} mol dm^{-3} caused virtually no shift ($\Delta\delta \leqslant 0.05$ ppm) indicating that intermolecular dimerization or intramolecular hydrogen bond with another silanol oxygen atom are negligible, therefore both of them have good complex ability with anion [11]. The association constants for di(1-naphthyl)silanediol and 1,1,3,3-tetraphenyl-1,3-disiloxane with Cl^- were 144 and 377 mol^{-1} dm^3 in $CDCl_3$, respectively. For POSS-diol, dilution experiment also showed that intermolecular dimer was negligible. But different from above two disilanols, there exists intramolecular hydrogen bond between two silanol OH groups according to the spectrum of ^{1}H NMR of POSS-diol.

Fig. 6 showed the ^{1}H NMR spectral changes of POSS-diol upon the addition of Cl^-. It was found that with increasing concentration of Cl^-, the signals for OH in the POSS-diol also shifted to the downfield, indicating the hydrogen bond formation of silanol with Cl^- and destroying the intramolecular hydrogen bond between two silanol OH groups. The spectral changes could be fitted onto the 1:1 binding isotherm; the association constant (K_{11}) was then calculated to be 24.6 mol^{-1} dm^3 by nonlinear least squares curve fitting analysis, which implied that intramolecular hydrogen bond also unfavorably formed the host–guest complex. ESI-MS was also used to attempt to check the complex of POSS-diol with Cl^-, however POSS-diol was hard to ionize in the acetonitrile solution, and desired peaks could not be observed in the spectrum. It should be pointed that in ESI-MS spectrum of POSS-diol (in MeOH), in addition to the peak of POSS-diol ($m/z = 889.3$), the 1:1 complex of POSS-diol with Cl^- also appeared ($m/z = 925.1$), as shown in Fig. 7.

Although only one OH group exists in POSS-mono-ol, the complex ability of POSS-mono-ol with Cl^- was also investigated in order to compare with POSS-triol and POSS-diol. Fig. 8 showed the ^{1}H NMR spectral changes of POSS-mono-ol upon the addition of Cl^-. For POSS-mono-ol, large ratios of Cl^- and POSS-mono-ol (10, 50, 75 and 100 equiv.) should be chosen; the chemical shift was 3.14, 4.53, 5.05 and 5.58 ppm, respectively. It should be pointed out that when the ratio is 25, the chemical shift of OH overlapped with that of CH_2 which was linked with nitrogen atom in the Bu_4NCl. The association constant was determined to be 2.4 mol^{-1} dm^3 by nonlinear least square curve fitting analysis.

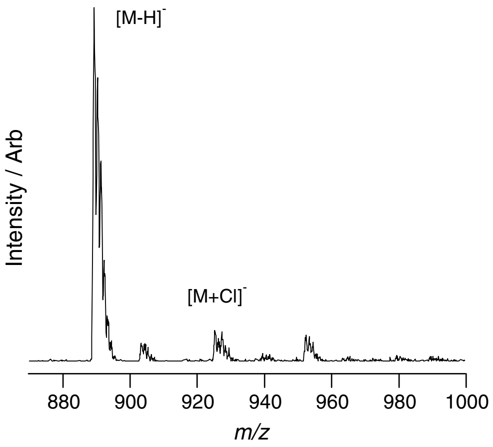


Fig. 7. ESI-MS (negative ion mode) of POSS-diol in MeOH.

From above, it is clear that the complex ability of POSS silanol with anion depends on the number of silanol OH group and hydrogen bonded interaction (intermolecular and intramolecular). For these types of three POSS silanols, the more OH groups, the more complexation ability; either intermolecular or intramolecular hydrogen bond unfavor the complex with anion.

POSS-triol crystallized as a hydrogen-bonded dimer (Fig. 9) [8c]. We also attempted to obtain the single crystal of complex of POSS-triol and Cl^-, but we failed. Even if the ratio of POSS-triol and Cl^- is 1:5 or higher, only the single crystal of POSS-triol dimer was obtained from the mixture, which further demonstrated that the intermolecular hydrogen bond between POSS-triol was stronger. Previously we reported that di(1-naphthyl)silanediol could not

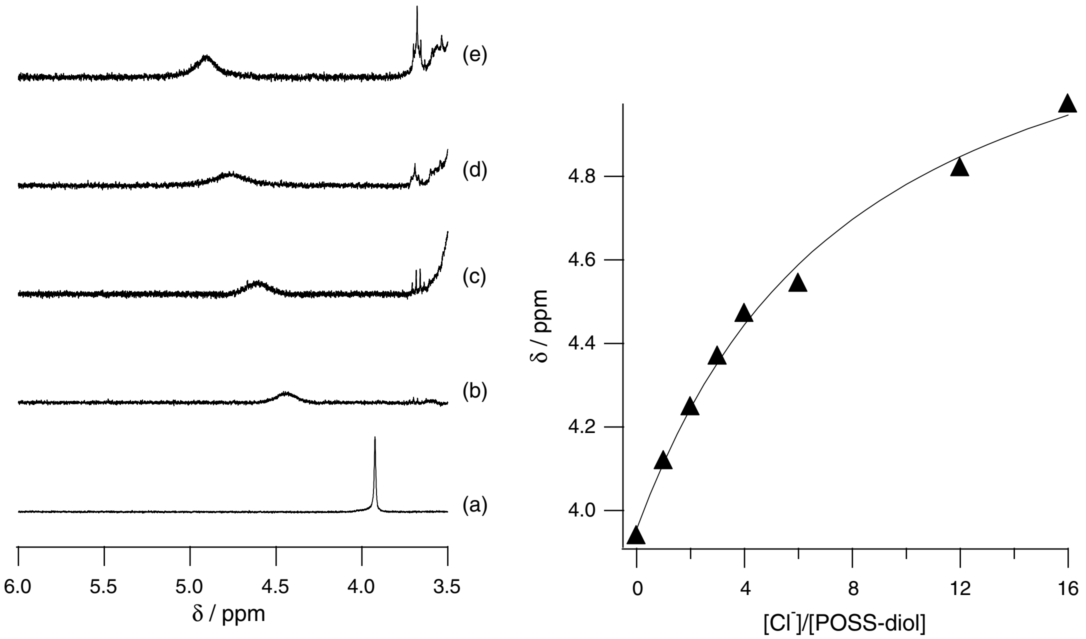


Fig. 6. Partial ^{1}H NMR spectra of POSS-diol in the absence (a) and the presence of 4 (b), 6 (c), 12 (d), 16 (e) equiv. of tetrabutylammonium chloride in $CDCl_3$ at 298 K. [POSS-diol] = 5.0×10^{-3} $mol\ dm^{-3}$.

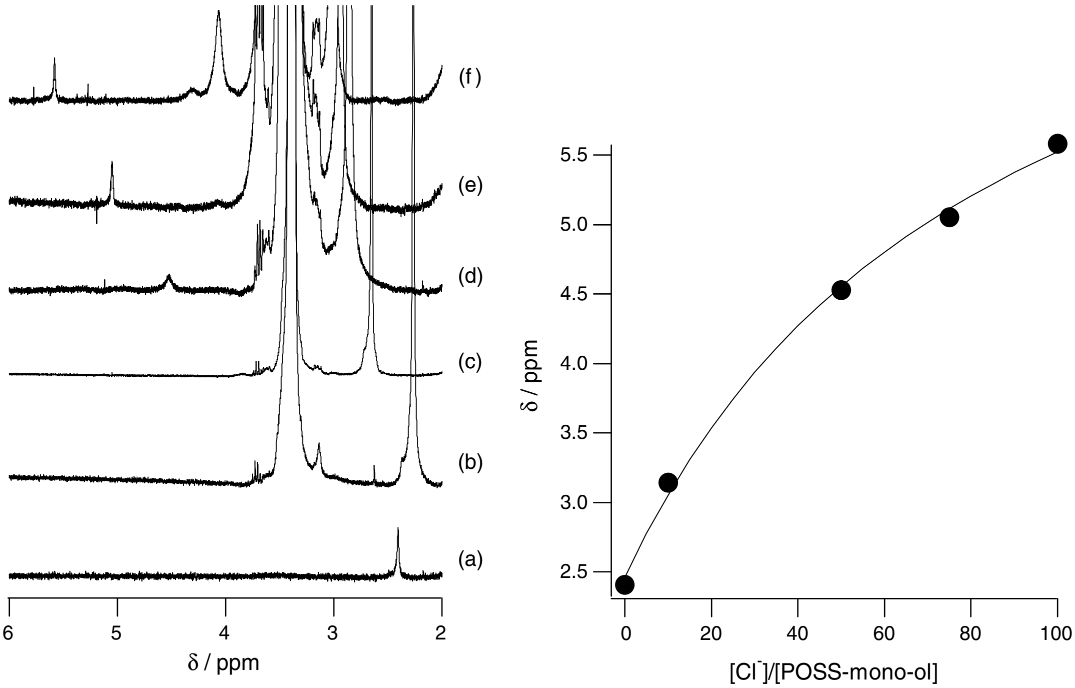


Fig. 8. Partial ^{1}H NMR spectra of POSS-mono-ol in the absence (a) and the presence of 10 (b), 25 (c), 50 (d), 75 (e), 100 (f) equiv. of tetrabutylammonium chloride in $CDCl_3$ at 298 K. [POSS-mono-ol] = 5.0×10^{-3} mol dm^{-3}.

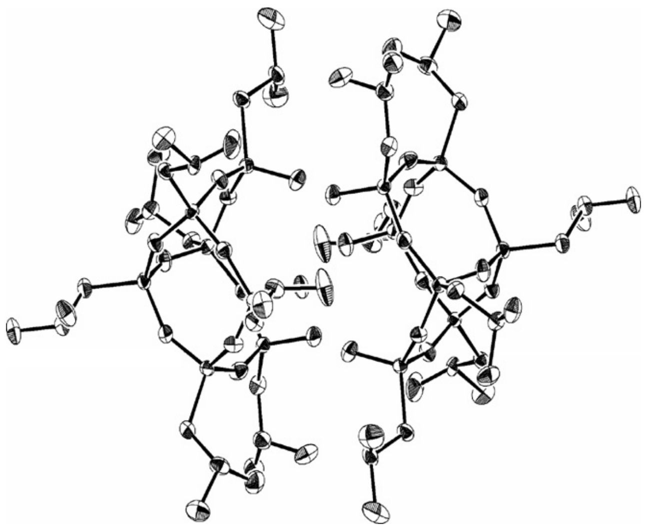


Fig. 9. ORTEP drawing (50% probability) of hydrogen bonded POSS-triol dimer. Hydrogen atoms are omitted for clarity.

form intermolecular hydrogen-bonded dimer in the solution because of weak intermolecular hydrogen bond, therefore the single crystal of di(1-naphthyl)silanediol with Cl$^-$ could be obtained [11a].

3. Conclusion

In conclusion, ^{1}H NMR dilution experiment and FTIR spectra were used to study the hydrogen-bonded interaction in POSS-triol, POSS-diol and POSS-mono-ol. The results showed that POSS-diol and POSS-mono-ol could not form dimer in the solution and there existed a dynamic equilibrium between single molecule and hydrogen-bonded dimer for POSS-triol; the dimerization constants (K_{dim}) of POSS-triol were 174 mol^{-1} dm^3 in $CDCl_3$ and 1075 mol^{-1} dm^3 in C_6H_6, respectively, by ^{1}H NMR dilution experiment. The association constants (K_{11}) of POSS-triol, POSS-diol and POSS-mono-ol with Cl$^-$ were 107, 24.6 amd 2.4 mol^{-1} dm^3, respectively, by nonlinear least square curve fitting analysis. Results showed for POSS silanols that with intermolecular or intramolecular hydrogen bond unfavorably formed the complex with anion.

4. Experimental

4.1. General procedures

All reagents used were of analytical grade. ^{1}H NMR spectra were measured on a JEOL AL300 (300 MHz) and referenced to tetramethysilane as an internal standard. FTIR spectra were measured with a SHIMADZU FTIR-8700 at room temperature (25 °C). The sample was granulated, and the powder was mixed with KBr pellets to press into the small flasks for measurements; solution FTIR spectra was determined in CCl_4. Electrospray ionization mass spectra (ESI-MS) were recorded on an Applied Biosystems/MDS-Sciex API-100 spectrometer. Single-crystal X-ray crystallography of POSS-triol was measured on a Rigaku RAXIS-IV++ imaging plate diffractometer with graphite-monochromated Mo Kα radiation. Data were collected and processed using the CrystalClear program (Rigaku).

4.2. ^{1}H NMR titrations

A solution of POSS silanol (5.0×10^{-3} mol dm^{-3}) in $CDCl_3$ was prepared in an NMR tube. Aliquots of a stock solution of anions (tetrabutylammonium salts) dissolved in a solution of POSS silanol (5.0×10^{-3} mol dm^{-3}) in $CDCl_3$ were added and the spectrum were recorded repeatedly. Each measurement was at least duplicated. The association constant was calculated from the chemical shifts of silanol OH by a self-written nonlinear least-square-fitting program.

4.3. X-ray crystallography

4.3.1. Crystal data for POSS-triol

Crystal data of POSS-triol: $C_{28}H_{66}O_{12}Si_7$, $Mw = 791.42$, Crystal Dimensions $0.30 \times 0.20 \times 0.20$ mm, monoclinic, $P2_1/n$ (#14), $a = 14.086(4)$ Å, $b = 21.300(10)$ Å, $c = 14.725(5)$ Å, $\beta = 100.316(4)°$, $V = 4346(3)$ Å^3, $Z = 4$, $D_{calc} = 1.209$ g/cm^3, $T = 123$ K, $F(0\,0\,0) = 1712.00$, (Mo Kα) = 2.687 cm^{-1}, $R = 0.100$, $wR_2 = 0.229$ (all data).

Acknowledgement

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Appendix A. Supplementary material

CCDC 65192 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.01.027.

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