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Controlled formation of ordered coordination polymeric networks using silsesquioxane building blocks

This work describes the formation of ordered coordination polymers using polyhedral oligomeric silsesquioxanes (POSS). In our group, we have exploited the cage-structure of POSS as building blocks and fabricated unique ordered materials. We are trying to create a new function by making strictly defined structures.

In this report, we synthesized ordered coordination polymers using polyhedral oligomeric silsesquioxanes (POSS) as a building block. A POSS with eight carboxylic terminals was coordinated with copper ions at various temperatures, forming polymeric networks. This novel coordination polymer has a long-range ordered structure.

Polyhedral oligomeric silsesquioxanes (POSS) have a unique cage-like structure with the general formula RSiO$_{1.5}$ and have been used in a wide range of applications as hybrid materials. In recent years, several efforts have been made to exploit POSS as a building block for synthesising ordered materials, and some schemes have been proposed. As one of the most accepted schemes, POSS were first tethered with chemical moieties and then self-assembled/crosslinked to form higher-order structures via intermolecular interactions. For example, Shimojima et al. synthesised porous materials by modifying POSS terminals with an alkyl group or dimethylsilanol groups. Chu et al. prepared POSS with 8 acetamido-pyridine terminals and made an electroluminescent material. Huang et al. modified tetrakis(4-azidophenyl)methane terminals with hydrophilic or hydrophobic POSS cages and formed self-assembling materials. Recently, Janeta et al. synthesised several imino functionalized POSS and obtained well-defined crystals. We also employed a POSS with propylammonium groups as an interlayer for the fabrication of crystalline layered perovskite materials.

Coordinate bonds are known to form extended networks with well-defined geometries and have been widely used for metal–organic coordination polymers. In these coordination polymers, organic ligands are typically coordinated to metal centres. While many organic ligands have been used in a wide range of applications as hybrid materials, they are limited by their flexibility and functionality. POSS, on the other hand, offer a unique combination of rigidity and functionality, making them ideal for the fabrication of coordination polymers.
temperatures above 80 °C, CP100 exhibits a plate-like shape similar to CP60 and CP80, but has smaller and more randomly-formed particles than CP60 and CP80. These changes in shape are possibly related to the degree of coordinate bond formation.

Powder X-ray diffraction (PXRD) patterns of the obtained coordination polymers were analysed for the investigation of their crystalline nature (Fig. 2). The PXRD pattern of S-POSS exhibits sharp peaks ranging from 18° to 25°, which is presumably related to the POSS cages (approximately 5 Å). The pattern of CP45 shows peaks similar to that of S-POSS as well as peaks appearing at angles lower than 15°, especially at 7.7° ($d = 11.5$ Å). For CP60 and CP80, the peaks from 3° to 15° are predominant while those in the range 18°–25° are attenuated except for that at 22.3° ($d = 3.98$ Å). In particular, a sharp peak at 3.8° corresponds to a $d$-spacing of 23.3 Å, nearly equivalent to the size of S-POSS (24 Å, see also Fig. S1 in the ESI†).

Therefore, the results clearly suggest the formation of long-range ordered networks of S-POSS. The pattern of CP100 is almost the same as those of CP60 and CP80 except for the noticeable diffused bands observed in the range 10°–25°, ascribed to amorphous materials. Although we have not been able to thoroughly refine these patterns, we speculate that the crystalline structures of CP60 and CP80 are orthorhombic (see Fig. S2 in the ESI†).

Fourier transform infrared (FTIR) spectra were measured for further understanding the coordinate bond formation. Major peaks and their assignments are presented in Fig. 3. The spectra of coordination polymers show some characteristic differences from that of S-POSS through the coordination reaction to Cu$^{2+}$. The bands of the carboxyl group (1197 and 1695 cm$^{-1}$) that clearly appear in the S-POSS spectrum are attenuated for CP45 and are not present for CP60, CP80, and CP100. Meanwhile, a band at 1588 cm$^{-1}$ newly appears for CP45 and is intensified for CP60, CP80, and CP100. Furthermore, the peak at 1427 cm$^{-1}$ is slightly shifted to 1438 cm$^{-1}$ with an increase in the reaction temperature. In addition, the S-POSS itself is intact in the coordination polymers from the solid-state NMR results (see Fig. S3 in the ESI†). Accordingly, the Si–O–Si stretching peak
Results infer that the carboxyl groups of S-POSS ligands form a bridging bidentate coordination to Cu atoms.23,24,27 As for the carboxylate groups that newly appeared for CP60, CP80, and CP100 (1588 and 1438 cm⁻¹), the gap between the asymmetric and symmetric bands, Δν, is 150 cm⁻¹. These results infer that the carboxyl groups of S-POSS ligands form a bridging bidentate coordination to Cu atoms.23,24,27-29

Furthermore, inductively coupled plasma (ICP) data were collected for all coordination polymers to obtain the fraction of the Cu and Si species. The Cu and Si weight fractions obtained from the ICP data are presented in Table 1. Based on these numbers, the Si/Cu ratio and X were calculated. The Cu fraction increases with an increase in the reaction temperature, while the Si/Cu ratio markedly varies with the reaction temperature. The degree of the network formation between the carboxylate terminals and Cu²⁺ is sensitive to the reaction temperature, which is in good agreement with the previous results. For the CP60 and CP80 cases, the Si/Cu ratio is approximately 2. This indicates that two carboxylate ligands are bound to each copper on average with the formula [Si₈O₁₂(C₇H₁₁NO₃)₈][Cu²⁺]₄. From the FTIR results, the carboxylate ligands form a bridging bidentate coordination to Cu²⁺ cations. Accordingly, four carboxylate terminals on POSS appear to be coordinated to two copper metals and form paddle-wheel units.28 This is also supported by the UV-vis spectra (see Fig. S4 in the ESI†). For CP45 at Si/Cu = 10.6, the coordinate bond formation is incomplete whereas the coordination polymer has partially random networks in the structure in the case of CP100 at Si/Cu = 0.867.

Thermogravimetric analysis (TGA) of S-POSS and all coordination polymers was conducted to confirm their thermal stabilities (Fig. 4). CP45 exhibited a step-wise mass loss, which is quite different from that of S-POSS and the other coordination polymers. This indicates that it is a mixture of components and contains an insufficient coordination network formation. CP60, CP80, and CP100 were thermally decomposed around 230 °C. Importantly, the weight fraction at 500 °C was approximately 31.3% for CP60, 33.1% for CP80, and 41.5% for CP100. This trend is consistent with the ICP data.

From the results of FE-SEM, PXRD, FTIR, ICP, and TGA when the coordinate bond formation is incomplete at a low reaction temperature (45 °C), CP45 retains the nature of S-POSS. At a high reaction temperature (100 °C), CP100 contains the random polymeric network. The desired crystalline polymeric network can be obtained only at suitable temperatures between 60 °C and 80 °C. This temperature dependence is interpreted in the following way. When water was added to S-POSS dissolved in DMF in the absence of Cu²⁺, S-POSS was partially precipitated within 30 min in our experimental procedure because of the low solubility of S-POSS in water. Accordingly, when S-POSS in DMF and Cu²⁺ in water were mixed, two competing reactions were involved: the precipitation through the removal of DMF solvated around S-POSS and the coordinate bond formation between Cu²⁺ and S-POSS. Therefore, a precise reaction temperature control is required for making crystalline coordination polymers.

In addition, we conducted nitrogen sorption measurements at 77 K for all coordination polymers (see Fig. S5 in the ESI†). The results indicated that the polymers adsorbed a minimal

<table>
<thead>
<tr>
<th>Materials</th>
<th>Cu</th>
<th>Si</th>
<th>Si/Cu ratio</th>
<th>X⁺</th>
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</thead>
<tbody>
<tr>
<td>CP45</td>
<td>2.45</td>
<td>11.5</td>
<td>10.6</td>
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<tr>
<td>CP60</td>
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<td>9.89</td>
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<tr>
<td>CP80</td>
<td>12.3</td>
<td>11.1</td>
<td>2.05</td>
<td>3.90</td>
</tr>
<tr>
<td>CP100</td>
<td>21.3</td>
<td>8.17</td>
<td>0.867</td>
<td>9.22</td>
</tr>
</tbody>
</table>

a X with the chemical formula [Si₈O₁₂(C₇H₁₁NO₃)₈][Cu²⁺]₄.

Fig. 3 Fourier transform infrared (FTIR) spectra of S-POSS and coordination polymers in the range from 1000 to 1800 cm⁻¹. Major peaks are as follows: Si–O–Si stretching vibration of the POSS cage (1103 cm⁻¹); C–O and C=O stretching vibrations of the carboxyl group (1197 and 1695 cm⁻¹); the asymmetric stretching band of the carboxylate group (1427 cm⁻¹); and the N–H bending and C=O stretch bands of the amide group (1544 and 1643 cm⁻¹). The symmetric stretching band of the carboxylate group is largely overlapped by the amide bands at 1643 cm⁻¹. Peaks appear only in coordination polymers: the symmetric and asymmetric stretching bands of the carboxylate group (1438 and 1588 cm⁻¹).

Table 1 Inductively coupled plasma (ICP) data of coordination polymers
amount of nitrogen molecules. Although the obtained coordination polymers have a long-range ordered network similar to typical coordination polymers with organic ligands, they are almost non-porous. We speculate that this is caused by the strong interaction between the amide groups and the length of the S-POSS side chains. The side chain having a C₃H₅N₃O₃ chemical formula (approximately 10 Å) is relatively long compared to the POSS cage (approximately 5 Å). Therefore, the S-POSS side chains are close to each other, which results in their non-porous structure (see Fig. S1 in the ESI).

In conclusion, we developed a synthetic method for coordination polymers with a long-range ordered structure using POSS and copper chloride. We conducted a detailed study of the formation of coordination networks between S-POSS ligands at various reaction temperatures. We also confirmed the structural and chemical identity of the prepared materials through FE-SEM, PXRD, FTIR, and ICP analyses. Finally, we demonstrated that a POSS with 8 terminal groups can be employed as a ligand for coordination polymers.

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Notes and references