Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information for

Controlled Formation of Ordered Coordination Polymeric Networks using Silsesquioxane Building Blocks

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This PDF file includes:

Experimental Details:

Supplementary Results: Figs. S1 to S5.

Experimental Details:

Materials. All chemicals were used without further purification. Methanol, hydrochloric acid (HCl), copper(II) chloride, 2-hydrate ($CuCl_2 \cdot 2H_2O$), chloroform, N,N-dimethylformamide (DMF) and succinic acid anhydride were purchased from Kishida Chemical Co. (Osaka, Japan). 3-Aminopropyltriethoxysilane was purchased from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan). Water used in all the experiments was prepared using a Milli-Q Ultrapure Water System (Direct-Q, Millipore, Billerica, MA).

Characterization of coordination polymers. The microstructures of coordination polymers were observed using a field emission scanning electron microscope (FE–SEM) at an acceleration voltage of 0.8 kV (SU-9000, Hitachi High-Technologies, Japan). Powder X-ray diffraction (PXRD) patterns were collected using a Bruker D–8 diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm, 40 kV, 40 mA). Fourier transform infrared spectrometer equipped with a diamond ATR accessory (Nicolet 6700 and Smart Orbit, Thermo Fisher Scientific, USA). Inductively coupled plasma (ICP) was measured using atomic emission spectrometer (SPS-7800, SII Nanotechnology Inc., Japan). Thermogravimetric analysis (TGA) was carried out using TG/DTA 6200 (SII Nano Technology, Tokyo, Japan) at the heating rate of 1 °C/min with an air flow rate of 200 ml/min. Solid-state NMR spectra were measured at 12.5 kHz, using a Bruker AVANCE-400 spectrometer equipped with a 4 mm magic-angle spinning (MAS) probe. The Nitrogen (N_2) isotherms were measured at 77 K using a Belsorp−mini (BEL Japan Inc.).

Supplementary Results:

3D Structure of S−POSS

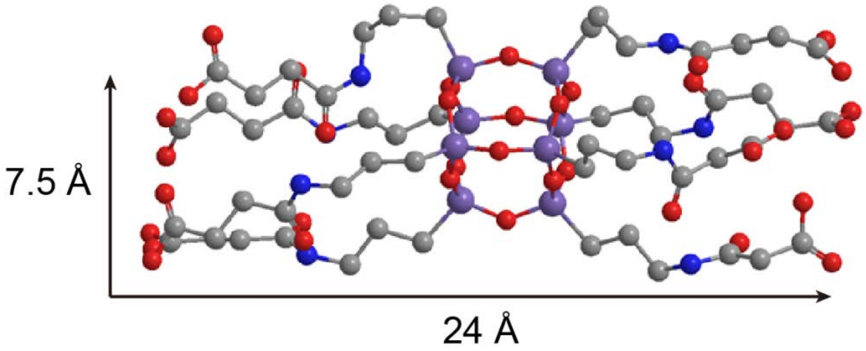

Fig. S1: 3D Structure of S−POSS. The graphic was generated with the MM2 energy minimization program in ChemBio3D Ultra (version 13.0).

Powder X-Ray diffraction pattern

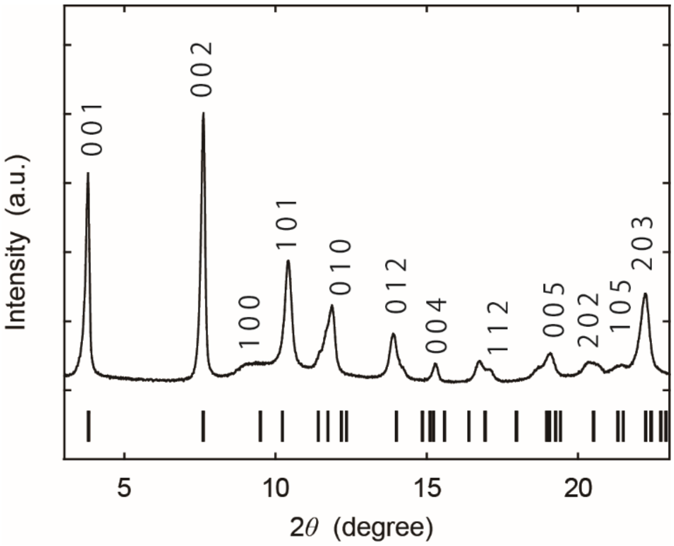

Fig. S2: The PXRD pattern of CP80 and the peak positions calculated using an orthorhombic lattice with a = 9.33 Å, b = 7.55 Å, c = 23.3 Å.

Solid-state NMR spectra.

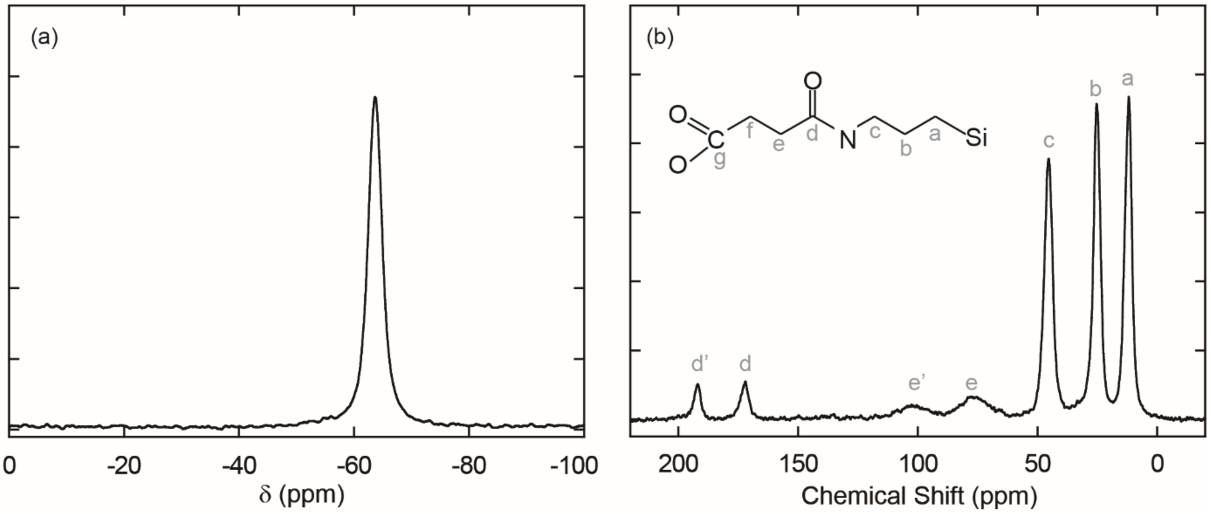

Fig. S3: Solid-state MAS NMR spectra of CP80: (a) ^{29}Si and (b) ^{13}C.

CP80 was characterized by ^{29}Si and ^{13}C magic angle spinning (MAS) NMR spectroscopy was measured with a spinning rate of 12.5 KHz at 30 °C. The ^{29}Si NMR spectrum revealed a sharp peak at -63.7ppm, suggesting the presence of the POSS cage in CP80. The peak position is nearly identical to that of the original S−POSS (-66.3ppm). The result indicates POSS cage remains virtually uninfluenced from the formation of network with metal centres (Fig. 4a). The ^{13}C NMR spectrum exhibits distinct and sharp signals: 11.2, 24.4, 44.8, 70.7, 103.4, 172.5, 192.2ppm. Peak assignments for all the carbons are shown in Fig. S3 except carboxylate carbon (“g”) and one adjacent to it (“f”). These two carbons are under influence of strong paramagnetic interaction of Cu^{2+} due to close proximity towards metal centres. This is also an evidence for the metal-carboxylate coordinate bond formation.

UV-vis Spectra.

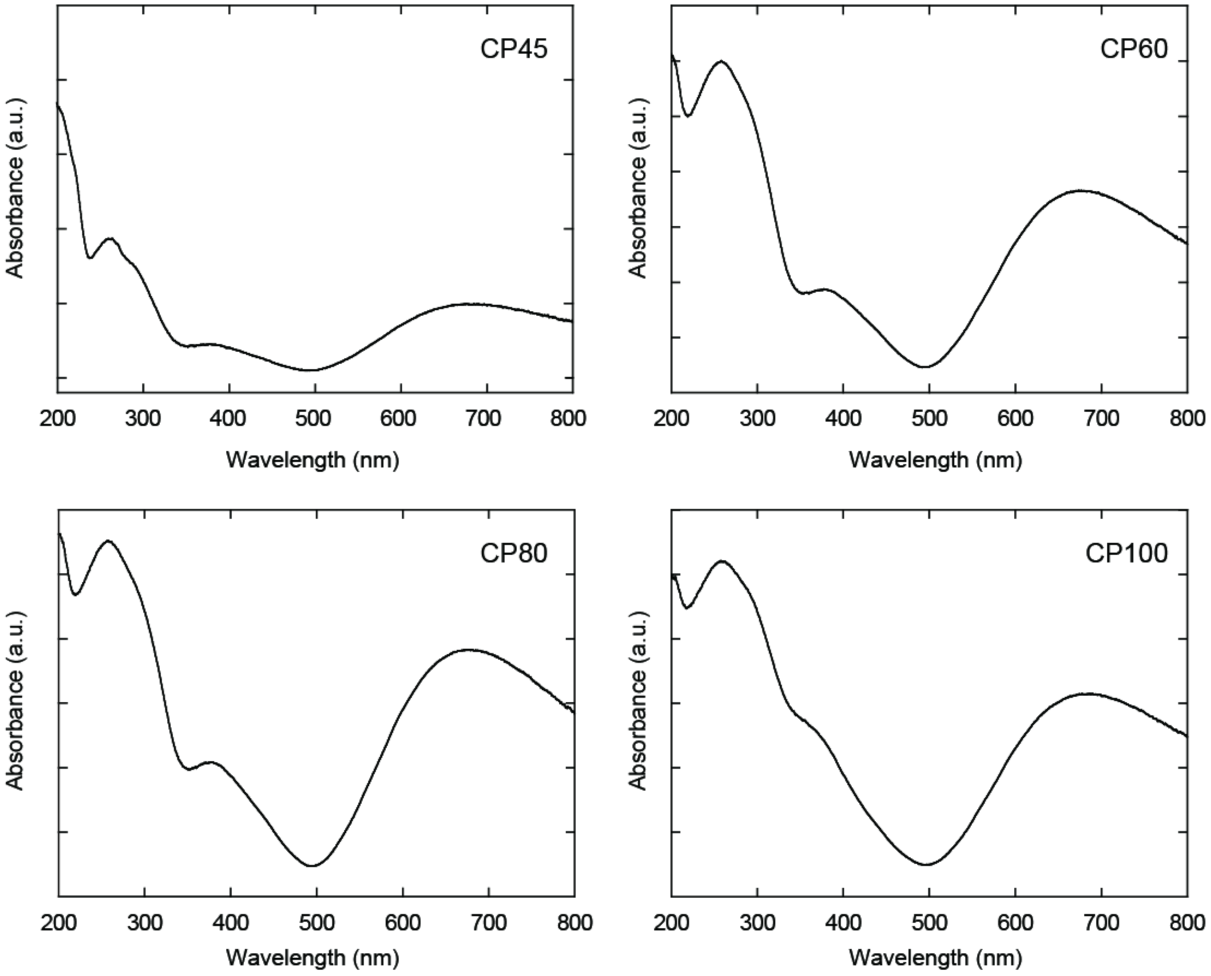

Fig. S4: UV-vis spectra of the obtained coordination polymers. The spectra were measured using a UV-vis spectrophotometer equipped with a diffuse reflectance accessory (UV-2450 Shimadzu, Japan).

N_2 sorption isotherms.

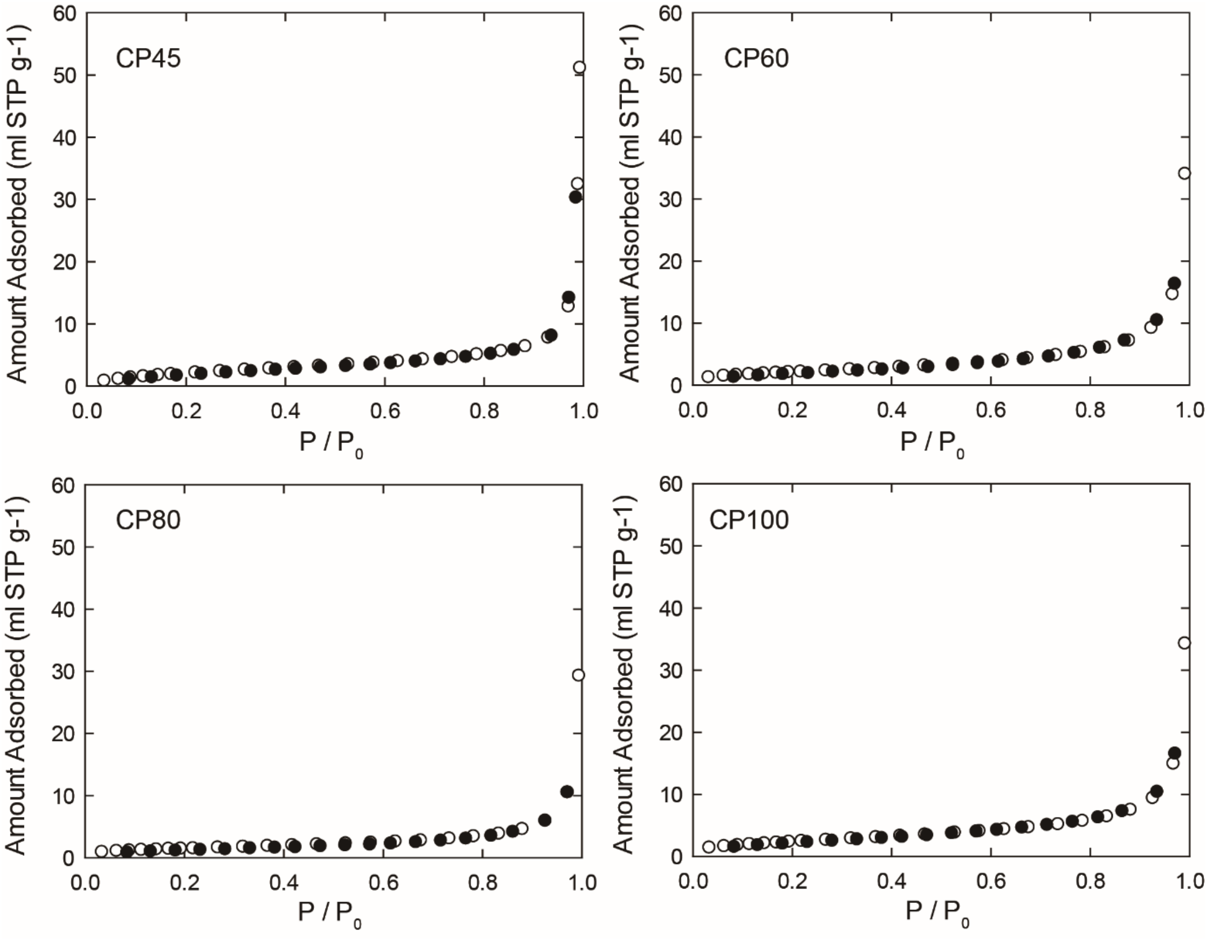

Fig. S5: N_2 sorption isotherms of the obtained coordination polymers at 77 K (open circles, adsorption; filled circles, desorption). The isotherms were measured using an adsorption apparatus (Belsorp-mini, BEL Japan Inc.).