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Supporting Information for

Thermal ring-opening polymerization of an unsymmetrical silicon-bridged [1]ferrocenophane in coordination nanochannels

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### Materials

All the reagents and solvents were commercially available and used as received without further purification.  $[Al(OH)(2,6-naphthalenedicarboxylate)]_n$  (1a),<sup>1</sup>  $[La(1,3,5-benzenetrisbenzoate)]_n$  (1b),<sup>2</sup> and  $[Al_8(OH)_{12}(1,3,5-benzene tricarboxylate)_3]_n$  (1c)<sup>3</sup> were prepared according to previously described methods. Unsymmetrically substituted [1]ferrocenophane monomer Fe( $\eta$ -C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>SiMePh (FM) was synthesized according to the reported procedure.<sup>4</sup>

#### Measurements

The X-ray powder diffraction (XRPD) data were collected using a Rigaku SmartLab X-ray diffractometer employing CuK $\alpha$  radiation and samples were measured by using flat-bed sample holder. The IR spectra were measured by attenuated total reflection method using a Thermo Scientific Nicolet iS5. MALDI-TOF MS spectra were recorded in the linear positive mode on a mass spectrometer (BRUKER DALTONICS, Ultraflex III). 2,5-Dihydroxybenzoic acid was used as a matrix. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a JEOL A-500 and 600, respectively. Curve fitting using nonlinear least-squares method was performed using FT-NMR Data Processing Ver. 3.5. The thermogravimetric (TG) analysis was carried out from room temperature to 500 °C at a heating rate of 10 °C min<sup>-1</sup> using a Rigaku Instrument Thermo Plus TG8120 in a N<sub>2</sub> atmosphere. The scanning electron microscopy-energy-dispersive X-ray (SEM-EDX) measurements were conducted by using a JEOL JED-2300 detector in a JEOL JSM-5600 at an accelerating voltage of 30 kV. Samples were placed on a conducting carbon tape attached by SEM grid, and then coated with platinum. The adsorption isotherms of  $N_2$ at 77 K were measured by BELSORP-mini equipment. Before the adsorption measurements, the sample was treated under reduced pressure ( $<10^{-2}$  Pa) at 403 K for 12 Gel permeation chromatography (GPC) measurements on the resulting h. poly(ferrocenylsilane) were performed in THF at 40 °C on two linear-type KF-804L that were connected to a SHIMADZU LC-20AD precision pump and a SHIMADZU RID-10A refractive index detector. The columns were calibrated against standard Electrochemistry experiments were carried out using a polystyrene samples. VersaSTAT4 potentiostat with a glassy carbon working electrode, a Pt counter electrode, and an Ag/AgCl (KCl saturated) reference electrode. We prepared polymer solutions (0.5 mM) in CH<sub>2</sub>Cl<sub>2</sub> with tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte. Peak currents were found to be proportional to the square root of the scan rate over the range studied (50 to 1000 mV S<sup>-1</sup>), which indicates that charge transfer is similar to a semiinfinite linear diffusion process.

## Synthesis of PFMPS using 1.

The host compound 1 (1a; 0.28 g, 1b; 0.10 g, 1c; 0.18 g) was dried by heating at 130 °C under vacuum (0.21 kPa) for 4 h. Dried 1 was immersed in a benzene solution (1.0 mL) of FM (50, 44, and 70 mg for 1a, 1b, and 1c, respectively) at room temperature to incorporate FM into the pores of 1. Feed ratio of FM in 1 was determined from the mass decrease rate of as-synthesized 1 including solvent molecules (Figure S1), avoiding the over loading of the monomer in the host matrices. Benzene was removed by N<sub>2</sub> flow at room temperature. The resulting 1 $\supset$ FM (1a $\supset$ FM; 0.33 g, 1b $\supset$ FM; 0.14 g, 1c $\supset$ FM; 0.25 g) was heated in an evacuated and sealed flask at 130 °C for 48 h. The resulting product was washed with MeOH repeatedly to remove any unreacted FM. To isolate PFMPS from the channels, the resulting product was stirred in 0.5 M aqueous sodium ethylenediaminetetraacetate solution (10 mL) for 1 day to decompose the host framework. The solid obtained was separated by filtration and then dissolved in THF. This THF solution was poured into MeOH for reprecipitation. The precipitate was washed several times with MeOH and dried under reduced pressure at room temperature, providing PFMPS (16, 21, and 42 mg from 1a, 1b, and 1c, respectively).

# **Bulk polymerization of FM monomer**

**FM** (100 mg, 0.33 mmol) was polymerized in an evacuated, sealed flask at 130 °C for 1 h. After dissolving in THF, the obtained polymer was reprecipitated in MeOH. The precipitate was washed several times with MeOH and dried under reduced pressure at room temperature (91 mg, 91%).



**Figure S1.** (a) TGA profile of **FM** and **PFMPS**. Iron residues are left after the heating to 500 °C. TG profile of (b) **1a**, (c) **1b**, and (d) **1c** before and after the polymerization of **FM**. The weight loss up to 100 °C observed for the host PCPs corresponds to the removal of solvent, such as water and MeOH, used for the PCP preparation. These solvents were removed by evacuation of the host at 130 °C under the reduced pressure.



Figure S2. XRPD patterns of 1, FM,  $1 \supset$  FM, and  $1 \supset$  PFMPS (a; 1a, b; 1b, and c; 1c). A characteristic peak for crystalline FM was not observed in the XRPD patterns of  $1 \supset$  FM, indicating no leakage of FM from 1. XRPD patterns of  $1 \supset$  PFMPS and 1 were almost same, indicating that the nanochannel structure of 1 was maintained during the polymerization.



Figure S3. (a) SEM image and (b-d) EDX elemental mapping of  $1a \supset PFMPS$ . (e) SEM image and (f-h) EDX elemental mapping of  $1b \supset PFMPS$ . (i) SEM image and (j-l) EDX elemental mapping of  $1c \supset PFMPS$ . No heterogeneous distribution of elements was observed in the series of corresponding EDX images, indicating that the polymerization of FM proceeded only inside the channels of 1.



Figure S4. Nitrogen adsorption isotherms of (a) 1a, (b) 1b, and (c) 1c before and after the polymerization of FM at 77 K. After the polymerization of FM, the adsorption capacity of 1 was drastically decreased, indicating formation of PFMPS inside the nanochannels of 1.



**Figure S5.** IR spectra of **PFMPS** obtained from bulk, **1a**, **1b**, and **1c**. IR spectra of the **PFMPS** obtained from **1** showed the bands almost the same as those obtained from bulk polymerization.<sup>5</sup>



**Figure S6**. (a) <sup>1</sup>H and (b) <sup>13</sup>C NMR spectra ( $C_6D_6$ ) of **PFMPS** obtained from **1a**, **1b**, and **1c**, and bulk (\* corresponds to spinning sidebands.). Peaks for the trace amount of water in  $C_6D_6$  were found at 0.4 ppm in the <sup>1</sup>H NMR spectra. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **PFMPS** showed peaks for phenyl (Ph), cyclopentadienyl (Cp), and methyl (Me) parts.<sup>4a</sup> In addition, the ratio of integration value of these peaks in <sup>1</sup>H NMR spectra was appropriate for the formation of **PFMPS**.



**Figure S7**. Curve fitting using nonlinear least-squares method for the typical <sup>1</sup>H spectrum ( $C_6D_6$ ) of methyl moiety in **PFMPS** obtained from **1a**. Tacticity was calculated from the integral ratio of the peaks corresponding to mm, mr, and rr triads.



**Scheme S1.** Plausible mechanism for the formation of linear and cyclic PFS during thermal ring-opening polymerization. Induced by nucleophilic attack at the bridging silicon atom, ring-opening polymerization proceeds *via* Si-Cp bond cleavage generating a Cp anion. Backbiting reactions also occur when the Cp anion chain end attacks Si-Cp bond on the polymer main chain, resulting in the formation of cyclic polymers.<sup>4b,6</sup>



**Figure S8**. Cyclic voltammograms of a 0.5 mM  $CH_2Cl_2$  solution with tetrabutylammonium hexafluorophosphate as a supporting electrolyte of **PFMPS** obtained from **1a** (red), **1b** (blue), **1c** (green), and bulk (black) at scan rates of 50 mV/s at 25 °C.<sup>7</sup>

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