Electronic Supplementary Information (ESI)

Synthesis and crystal structure of double-three ring (D3R)-type cage siloxanes modified with dimethylsilanol groups

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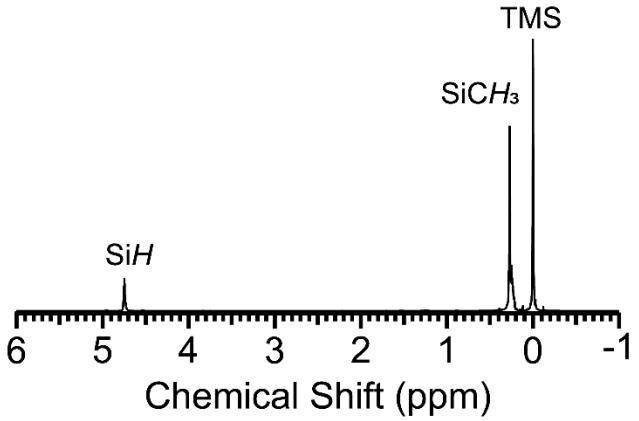

Figure S1 ^{1}H NMR spectra of the $CDCl_3$ solution of dimethylsilylated D3R siloxane.

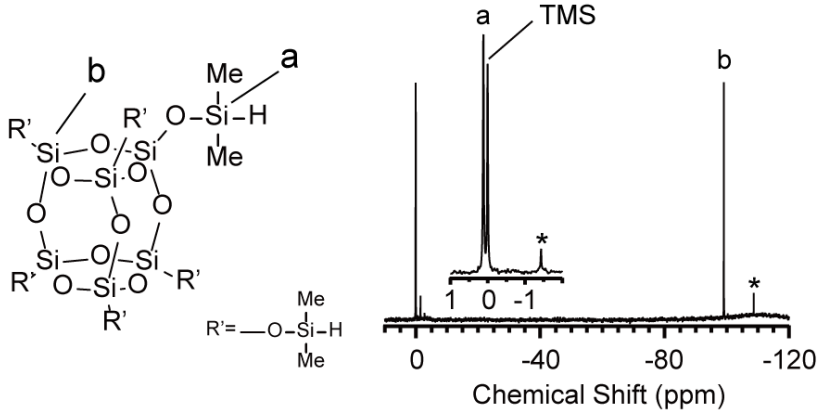

Figure S2 ^{29}Si NMR spectrum of the $CDCl_3$ solution of **2**. (*: the signals assigned to dimethylsilylated D4R siloxane)

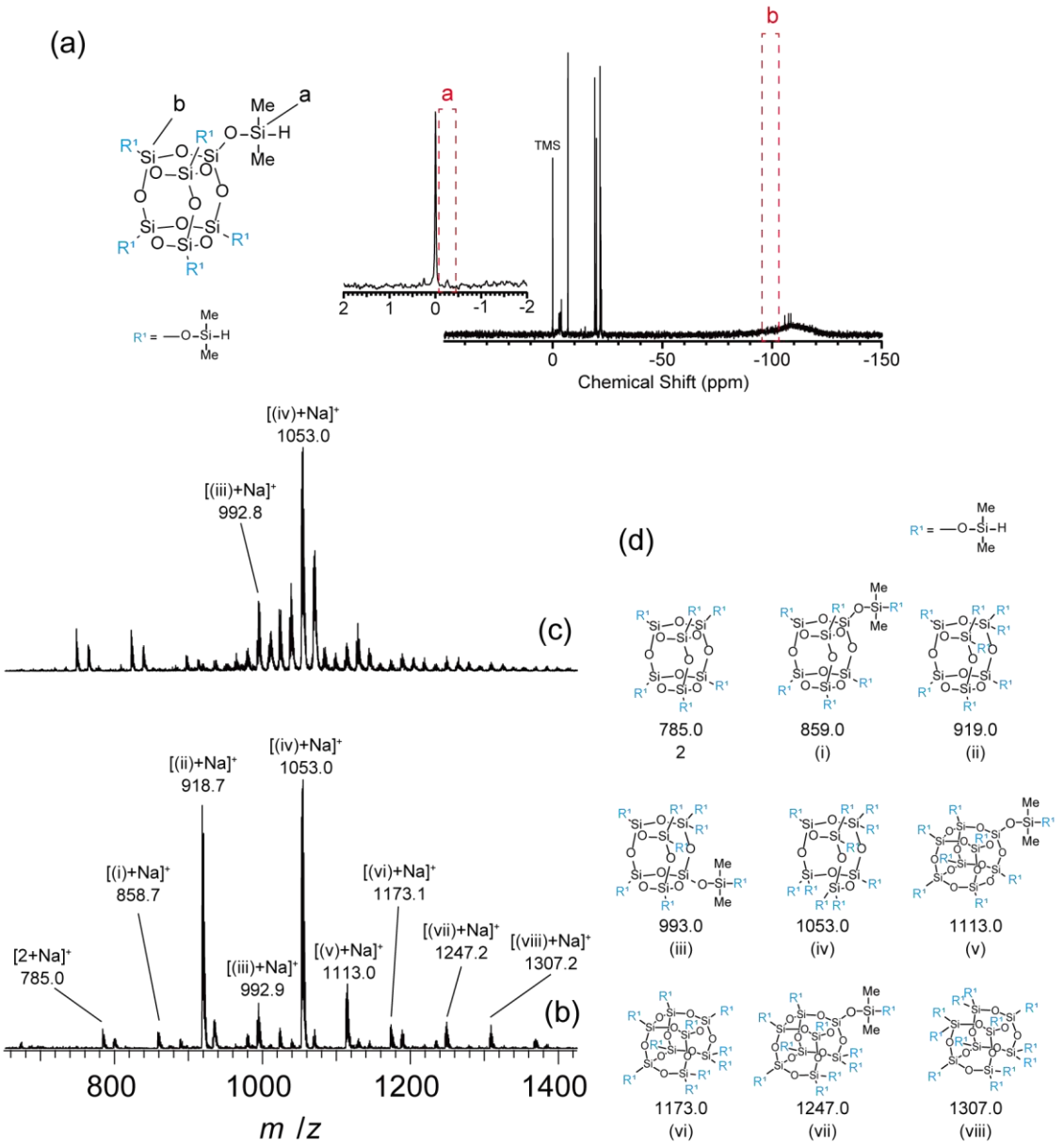

Figure S3 (a) ^{29}Si NMR spectrum of the $CDCl_3$ solution of the product of dimethylsilylation of **1** at room temperature. (b,c) MALDI-TOF mass spectra the product of dimethylsilylation of **1** at (b) –94 °C and (c) room temperature. (d) Proposed structures and calculated molecular weight of Na adduct assigned to each peak.

Note: in the Figure S3b, the peak assigned to **2** is much smaller than those of other byproducts. The reason for the small intensity of the peak due to **2** is the instability of **2**. Even though **2** mainly exists, it is difficult to detect the species in the mass analysis.

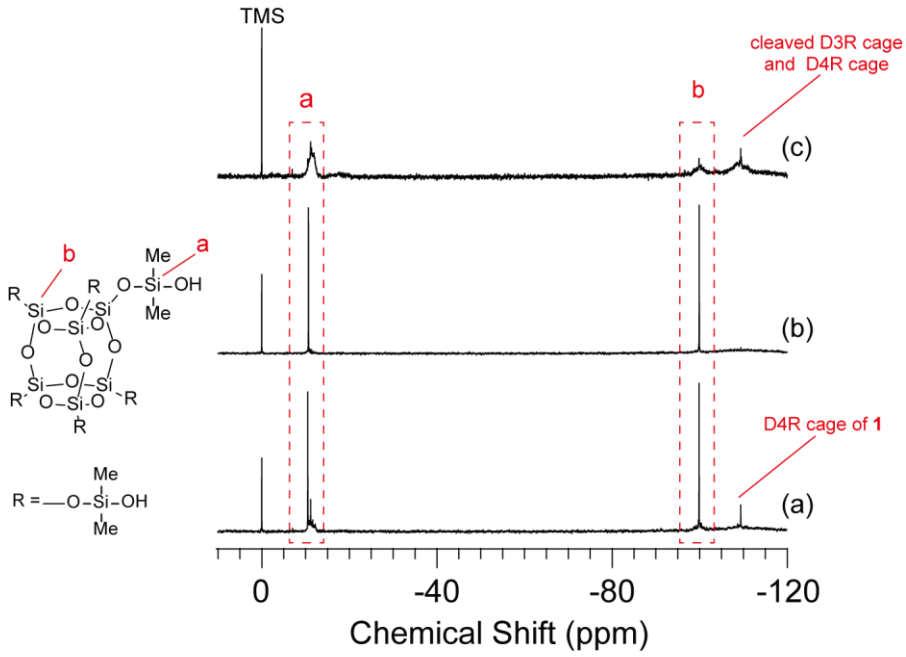

Figure S4 ^{29}Si NMR spectra of the THF-d_8 solutions of **2** (a) before recrystallization, (b) recrystallized from THF-toluene-hexane solution, and (c) obtained by solvent removal at 40 °C.

Note: In the synthetic process of **3**, the solvent evaporation at 40 °C after the reaction resulted in deterioration of the D3R cage, though the solvent evaporation at 0 °C gave soluble solids. We suppose that this is attributed to the attack of silanol groups. Bassindale *et al.* reported that deterioration of D3R cage occurs during the purification by silica gel column chromatography.[1)] Therefore, the silanol groups of **3** tend to deteriorate the D3R cage at high concentration unless the temperature of the solution is sufficiently low.

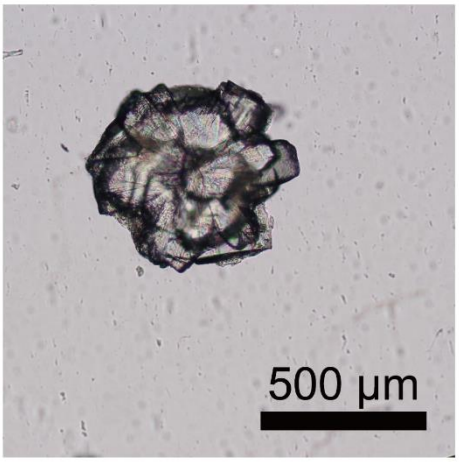

Figure S5 Optical microscope image of the crystal of **3**.

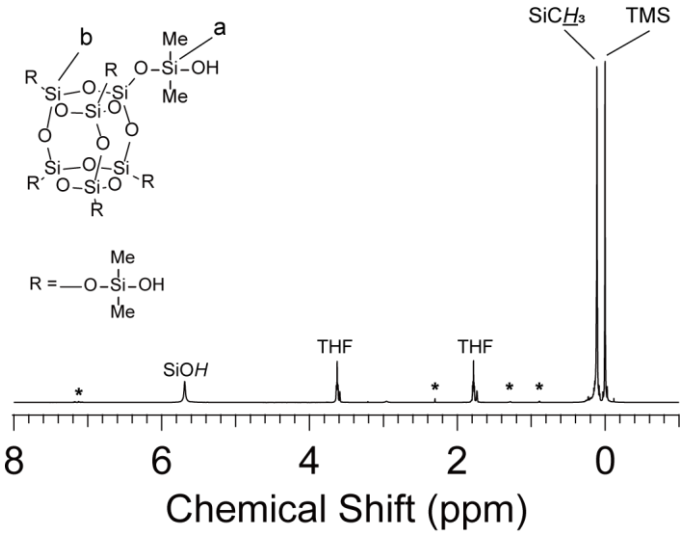

Figure S6 ^{1}H NMR spectra of the THF-d_8 solution of **3** recrystallized from the THF-toluene-hexane solution (*: the signals assigned to solvent molecules or impurities; THF, water, and toluene).

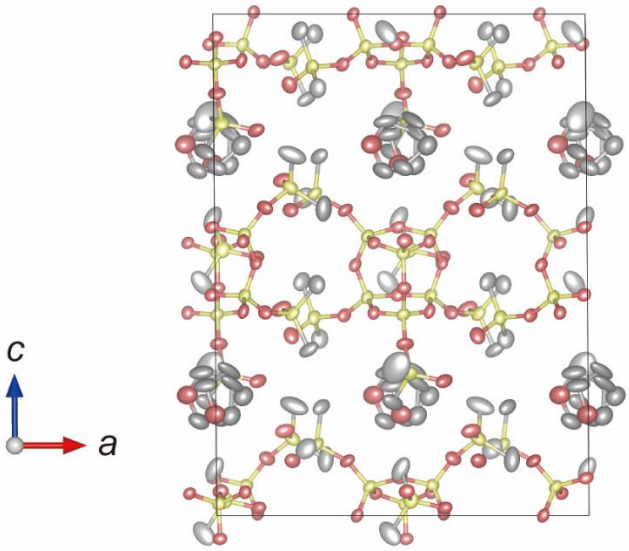

Figure S7 Structural model of the crystal of **3** containing disordered THF molecules (two probable orientations) with thermal ellipsoids drawn at the 50% probability. Hydrogen atoms are omitted for clarity (Atom colors: Yellow, Si; Gray, C; Red, O). The occupancies of the two types of THF molecules were 59.9% and 40.1%.

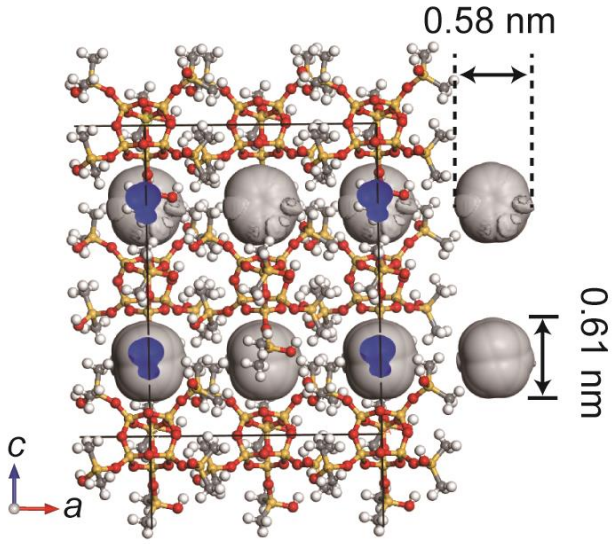

Figure S8 Connolly surface of the crystal of **3** viewed along the *b* axis (probe diameter: 0.4 nm). Atom colors: Yellow; Si, Gray; C, Red; O, and White; H.

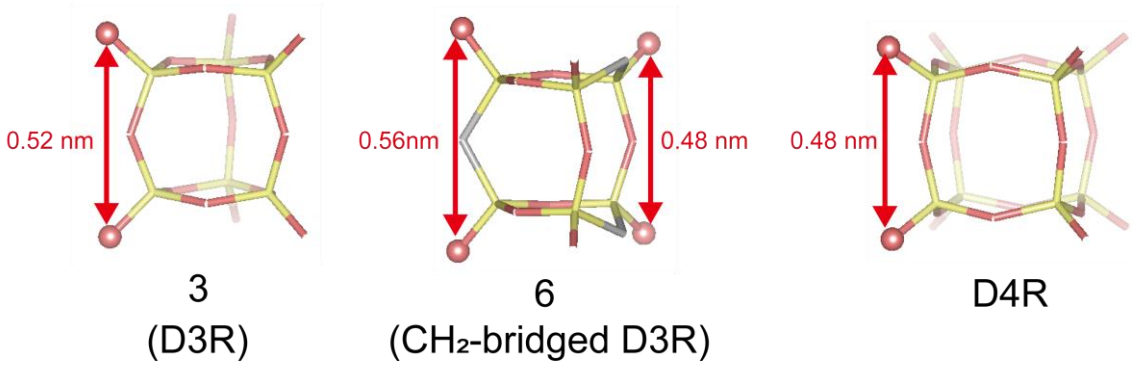

Figure S9 the distance between the oxygen atoms attached directly to the cage of **3**, **6**, and D4R siloxane[2)] modified with dimethylsilanol groups. Atom colors: Yellow; Si, Red; O, and Gray, C.

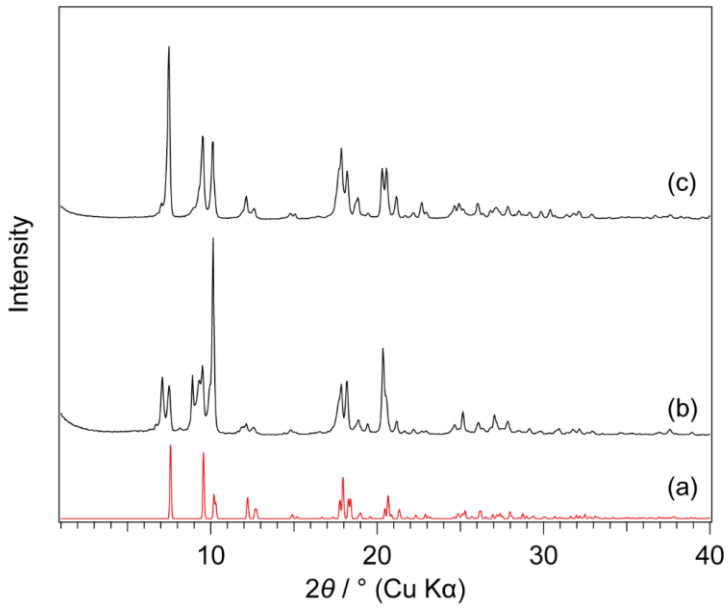

Figure S10 XRD patterns of the crystals of **6**. (a) a simulated pattern from the structural model using Crystaldiffract software. (b) the crystal obtained by recrystallization from THF-toluene-hexane. (c) the crystal obtained by recrystallization from THF-hexane solution.

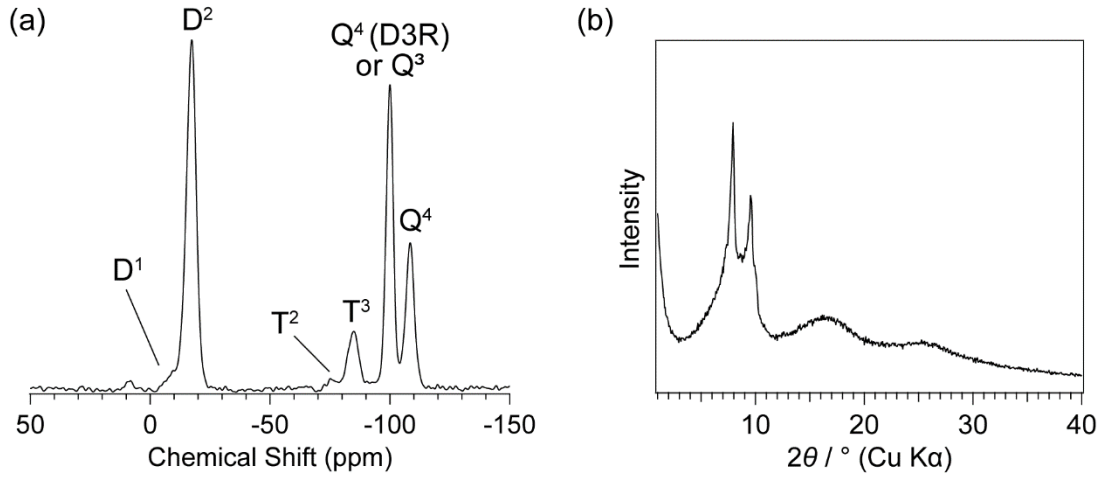

Figure S11 (a) Solid-state ^{29}Si MAS NMR spectrum and (b) XRD pattern of the product obtained by silylation of the molecular crystal of **6**.

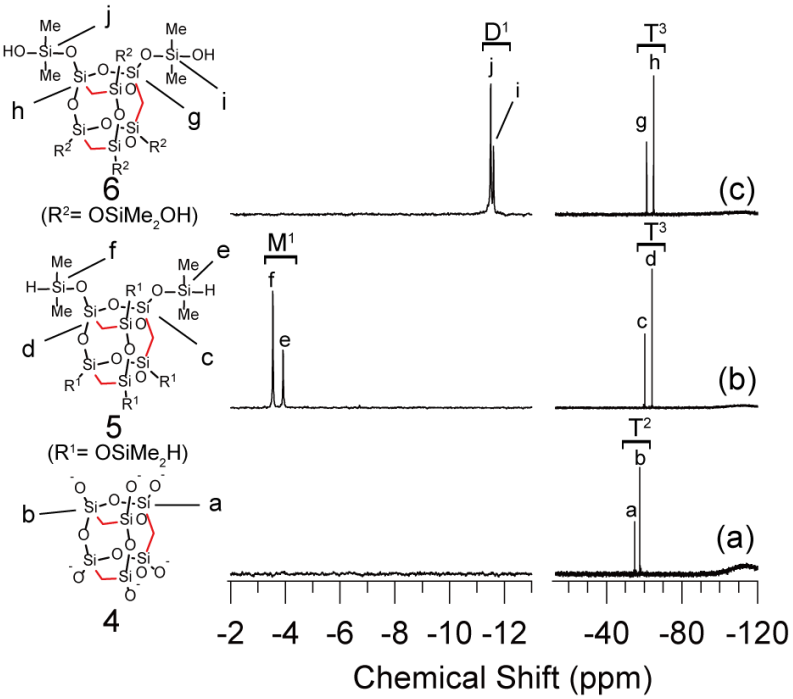

Figure S12 Liquid-state ^{29}Si NMR spectra of (a) methanol-d_4 solution of the compound **4**, (b) $CDCl_3$ solution of the compound **5** and (c) acetone-d_6 solution of compound **6**.

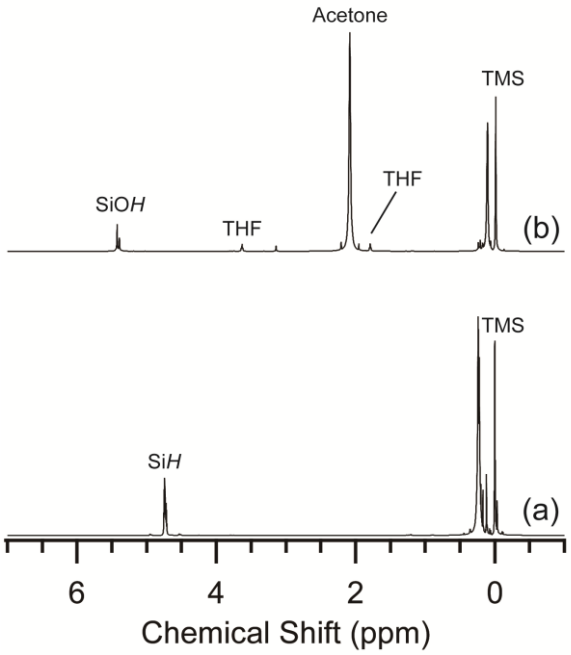

Figure S13 Liquid-state ^{1}H NMR spectra of (a) $CDCl_3$ solution of the compound **5** and (b) acetone-d_6 solution of compound **6**.

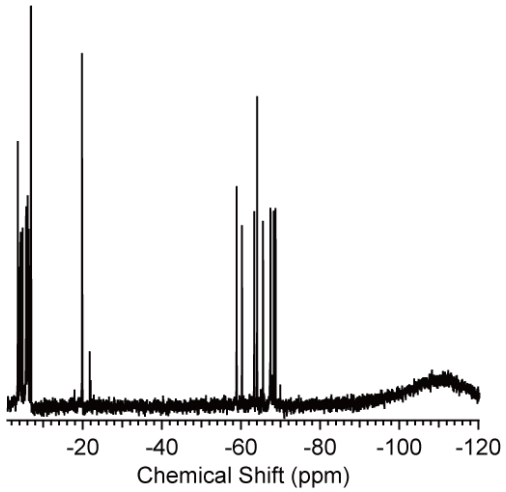

Figure S14 Liquid-state ^{29}Si NMR spectra the product of dimethylsilylation of cage oligomer **4** at room temperature.

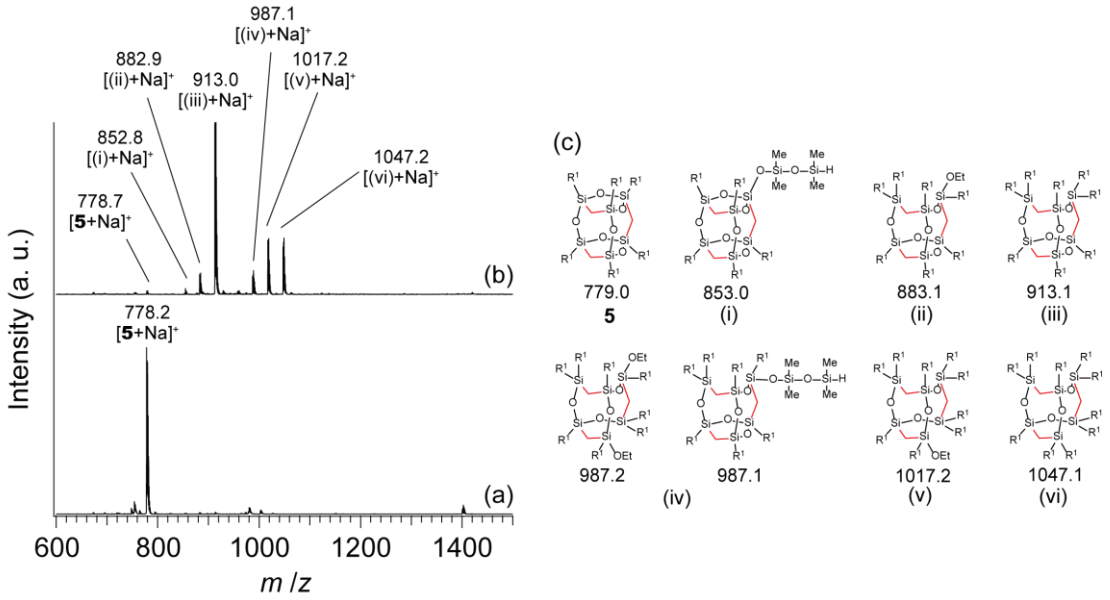

Figure S15 (a) MALDI–TOF MS spectra of (a) **5** and (b) **4** after dimethylsilylation at room temperature and (c) proposed structures and calculated molecular weight of Na adduct assigned to each peak.

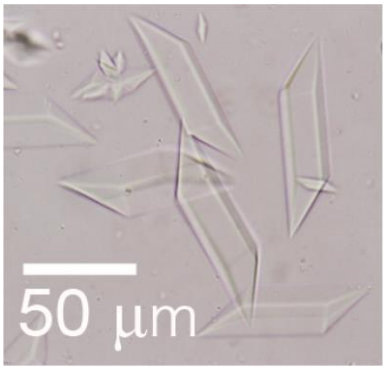

Figure S16 Optical microscope image of the crystal of **6**.

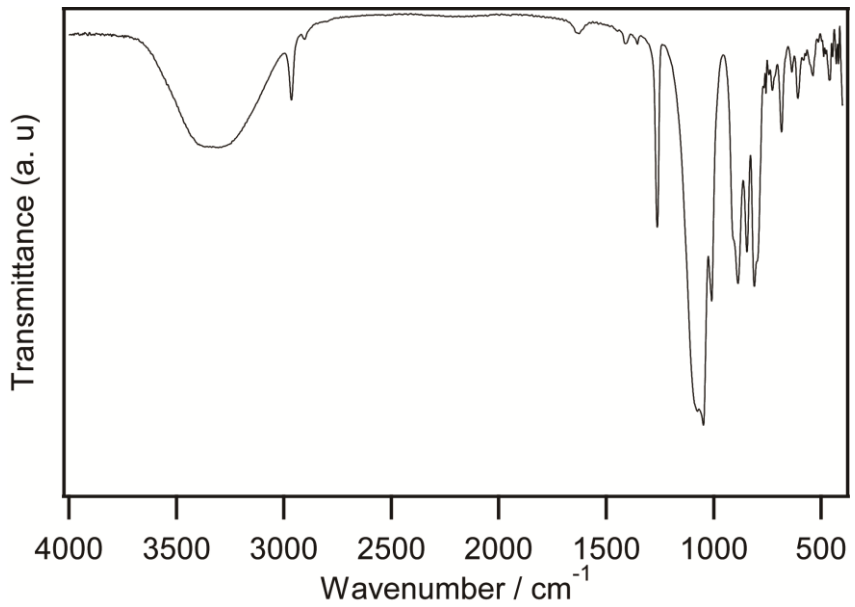

Figure S17 FT-IR spectrum of **6**.

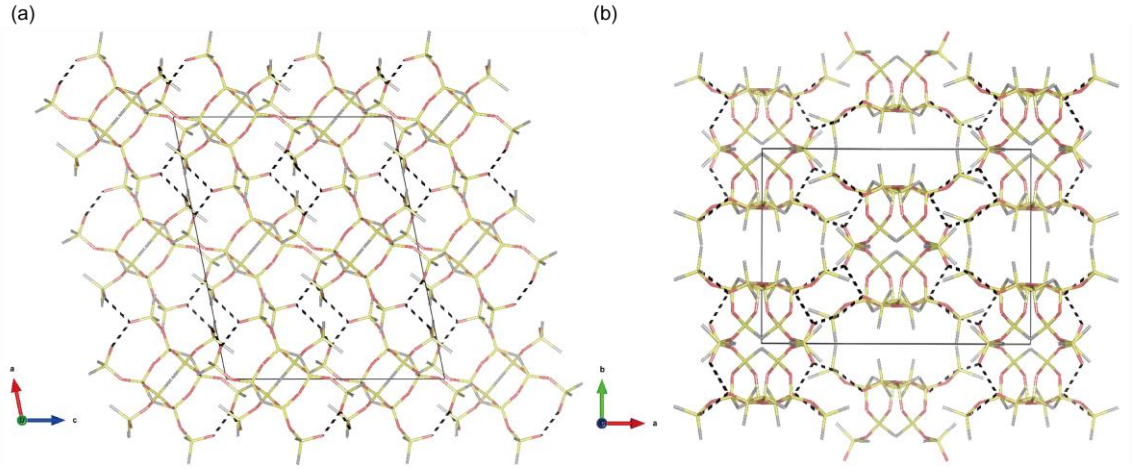

Figure S18 Structural model of the crystal of **6** viewed from (a) *b* and (b) *c* axes. Hydrogen atoms are omitted for clarity. Atom colors: Yellow; Si, Red; O, and Gray, C.

References

1) A. R. Bassindale, I. A. MacKinnon, M. G. Maesano and P. G. Taylor, *Chem. Commun.* 2003, 1382.

2) N. Sato, Y. Kuroda, H. Wada, A. Shimojima and K. Kuroda, *Chem. Eur. J.* 2018, **24**, 17033.