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Supplementary Information

Self-Assembled Cage as an Endo-Template for Cyclophane Synthesis

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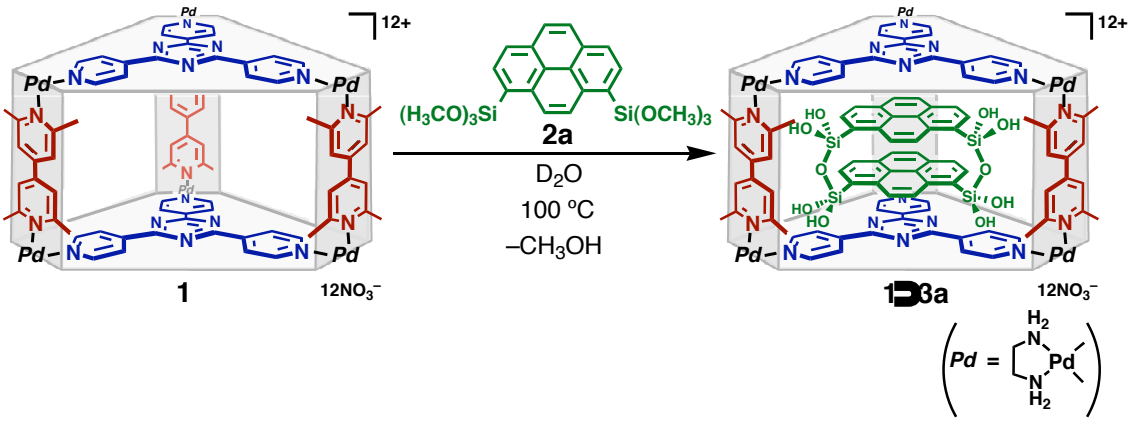
Contents

Materials and methods:

^{1}H, ^{13}C NMR, and 2D NMR spectra were recorded on a Bruker DRX-500 spectrometer equipped with a 5 mm BBO Z-gradient probe, a Bruker AV-500 spectrometer equipped with a 5 mm BBI Z-gradient probe. ^{29}Si NMR and ^{1}H-^{29}Si HMBC spectra were measured on a JEOL JNM-ECA 300. TMS ($CDCl_3$ solution) in a capillary served as external standard (δ 0 ppm). IR measurements (ATR) were carried out using a DIGILAB Scimitar FTS-2000 instrument. UV-visible spectral data were recorded on a SHIMADZU UV-3150. LDI-TOFMS spectra were measured with Voyager DE-STR without matrix. Melting points were determined with a Yanaco MF-500 V micro melting point apparatus. Elemental analyses were performed on a Yanaco MT-6 at the Elemental Analysis Center of School of Science of the University of Tokyo. Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Sigma-Aldrich Co. Deuterated H_2O was acquired from Cambridge Isotope Laboratories, Inc. and used as supplied for the complexation reactions and NMR measurements.



Preparation of 1⊃3a. A mixture of cage **1** (14.9 mg, 5 μmol), **2a** (6.6 mg, 15 μmol) in D_2O (0.5 mL) was stirred at 100 °C for 20 h to give clear red solution. ^{1}H NMR analysis of the solution revealed the formation of **1⊃3a**. After filtration of the resulted orange solution, the resulting solution was dried by a freeze-drying equipment. **1⊃3a** was isolated as an orange powder (15.4 mg, 84% yield). ^{1}H NMR (500 MHz, D_2O, 300 K): δ 8.65 (br, 12H), 8.44 (br, 12H), 8.20 (br, 12H), 8.12 (d, J = 7.5 Hz, 4H), 8.12 (d, J = 7.5 Hz, 4H), 3.73 (s, 18H), 3.73 (s, 18H), 3.73 (s, 36H), (br, 12H), (br, 12H); ^{13}C NMR (125 MHz, D_2O, 300 K): δ 167.2 (C_q), 161.4 (C_q), 152.0 (*C*H), 146.3 (C_q), 143.5 (C_q), 132.4 (C_q), 131.1 (*C*H), 130.3 (C_q), 127.6 (*C*H), 127.2 (*C*H), 126.9 (C_q), 124.8

(*C*H), 122.7 (*C*H), 122.0 (*C*H), 120.1 (C_q), 47.5 (CH_2), 46.4 (CH_2), 26.1 (CH_3); DOSY (m^2/s): log*D* = –9.83; IR (KBr, cm^{-1}): 2427, 2353, 2337, 1615, 1520, 1385, 1213, 1058, 859, 808, 674; m.p.: ~230 ºC (decomposed); E.A. Calcd. for $C_{122}H_{144}N_{42}O_{46}Pd_6Si_4$• 23($H_2O$): C, 35.74; H, 4.67; N, 14.35. Found: C, 35.89; H, 4.42; N, 14.07.

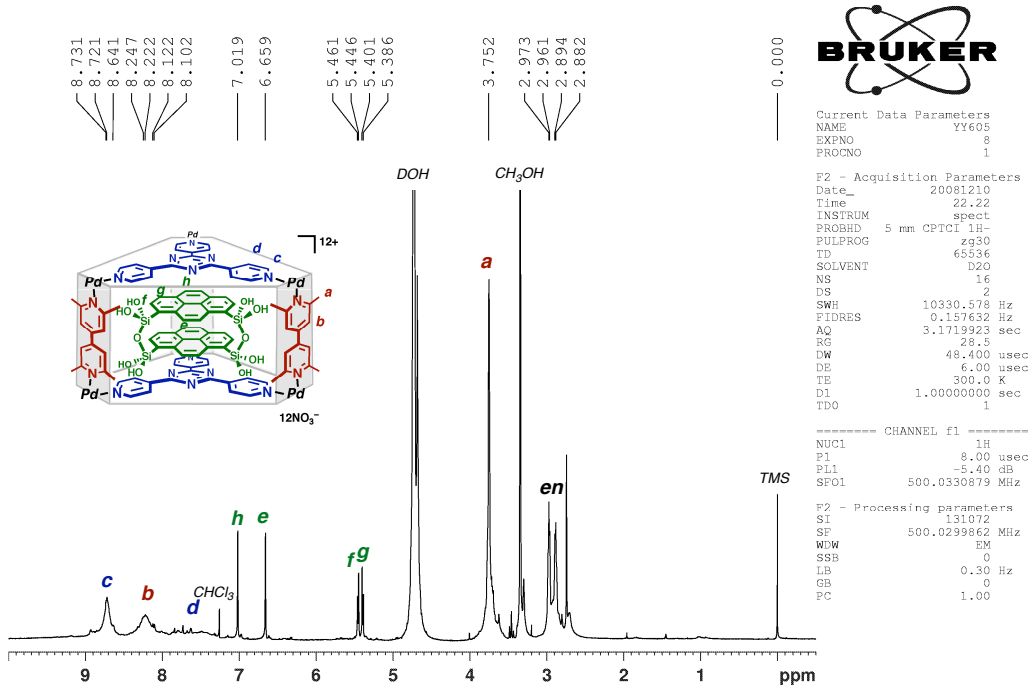


Fig. S1. ^{1}H NMR (500 MHz, D_2O, 300 K) spectrum of **1⊃3a**.

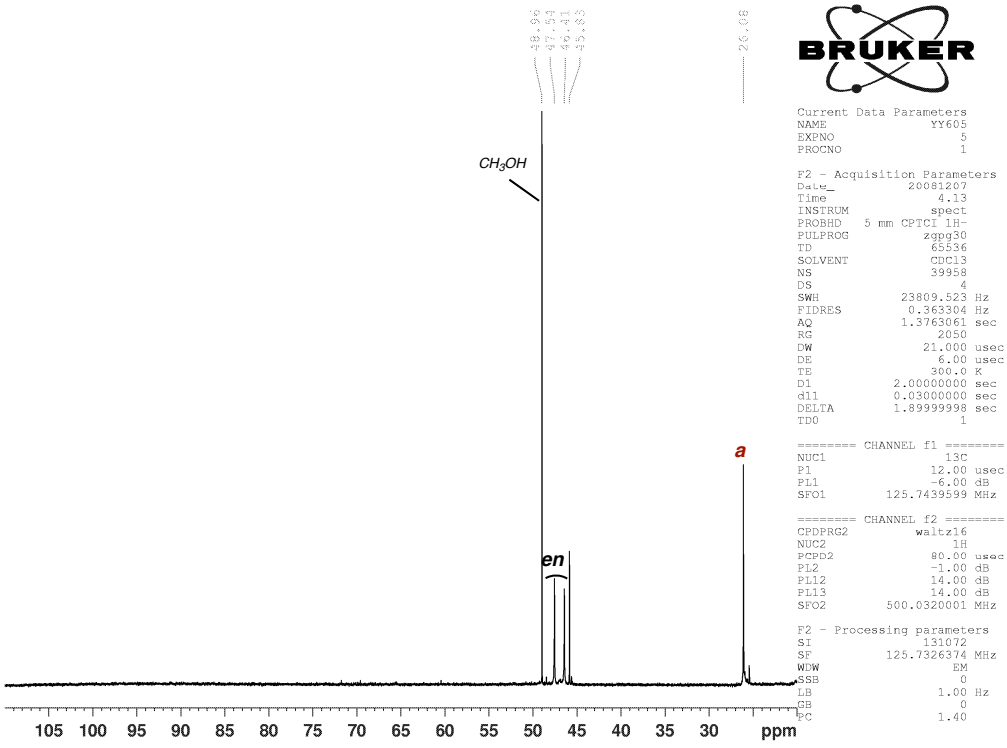


Fig. S2a. ^{13}C NMR (125 MHz, D_2O, 300 K) spectrum of **1⊃3a**.

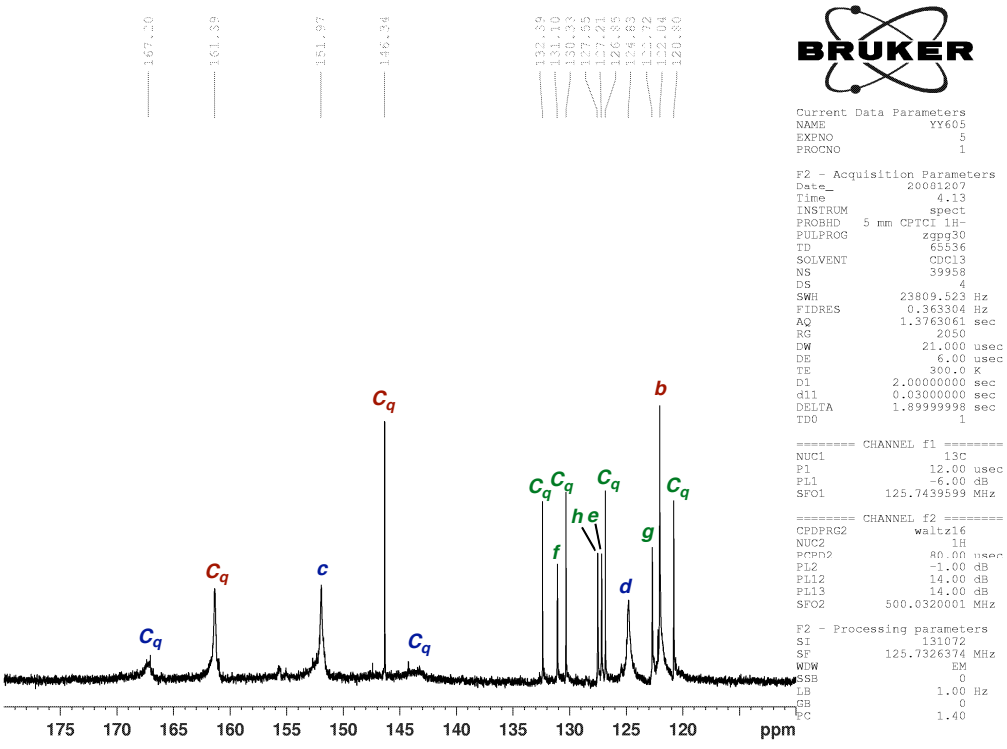


Fig. S2b. ^{13}C NMR (125 MHz, D_2O, 300 K) spectrum of **1⊃3a**.

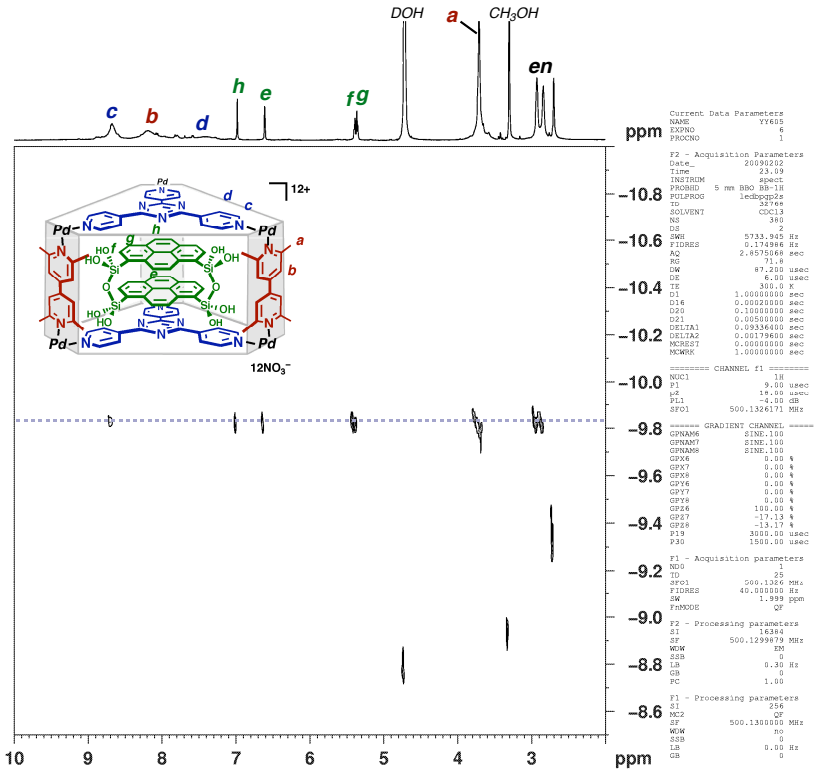


Fig. S3. ^{1}H DOSY (D_2O, 300 K) spectrum of **1**⊃**3a**.

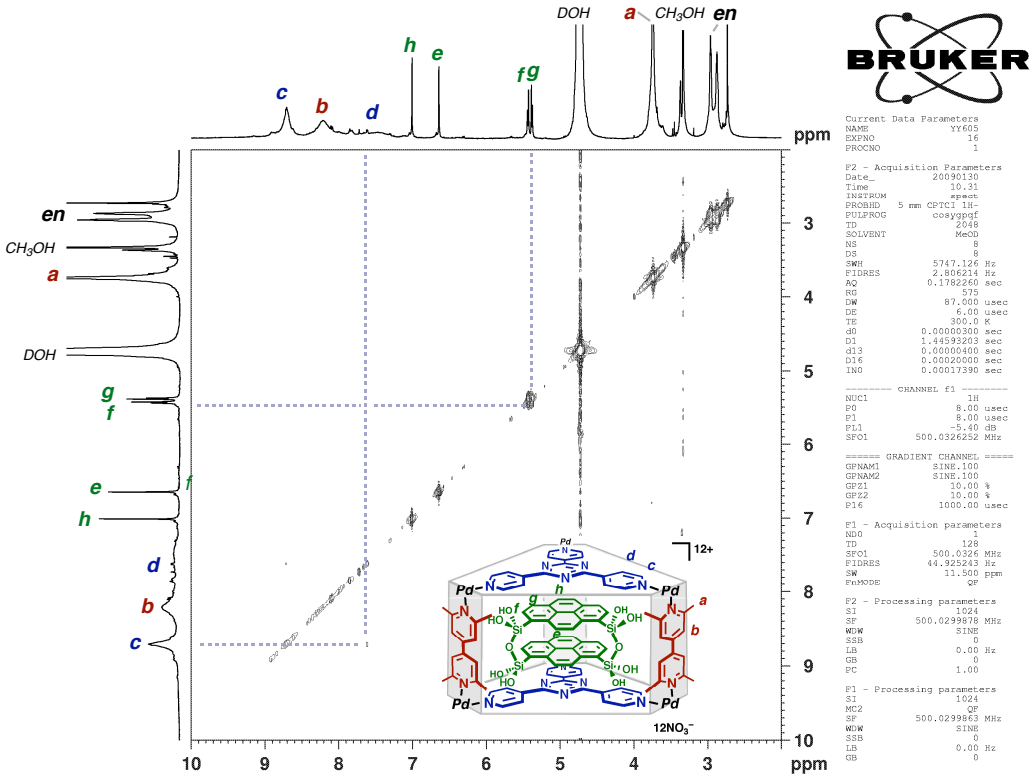


Fig. S4. ^{1}H-^{1}H COSY (D_2O, 300 K) spectrum of **1**⊃**3a**.

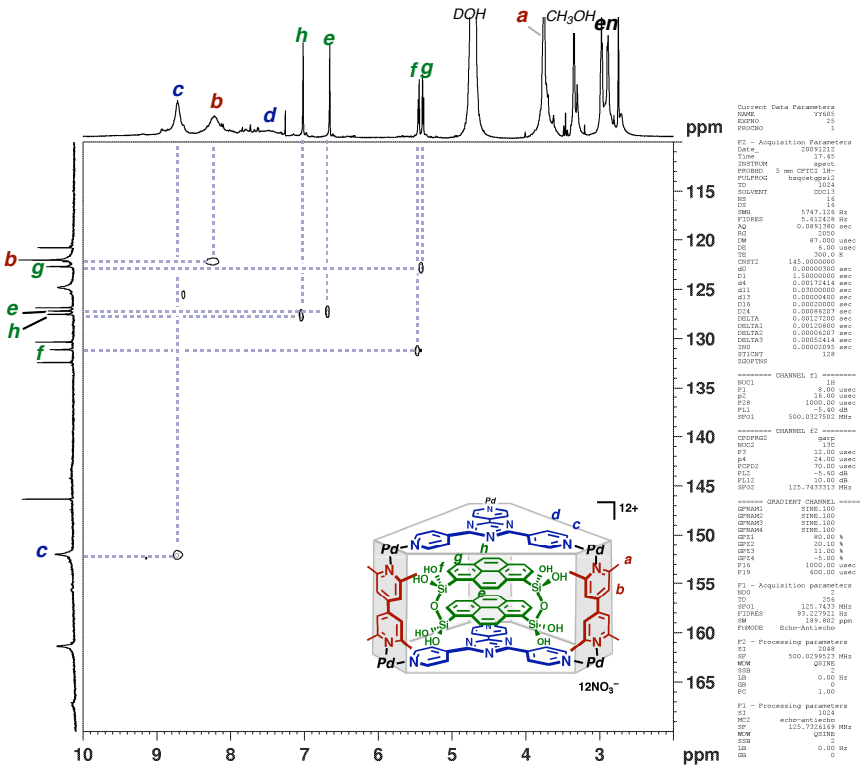


Fig. S5a. ^{1}H-^{13}C HSQC (D_2O, 300 K) spectrum of **1⊃3a**.

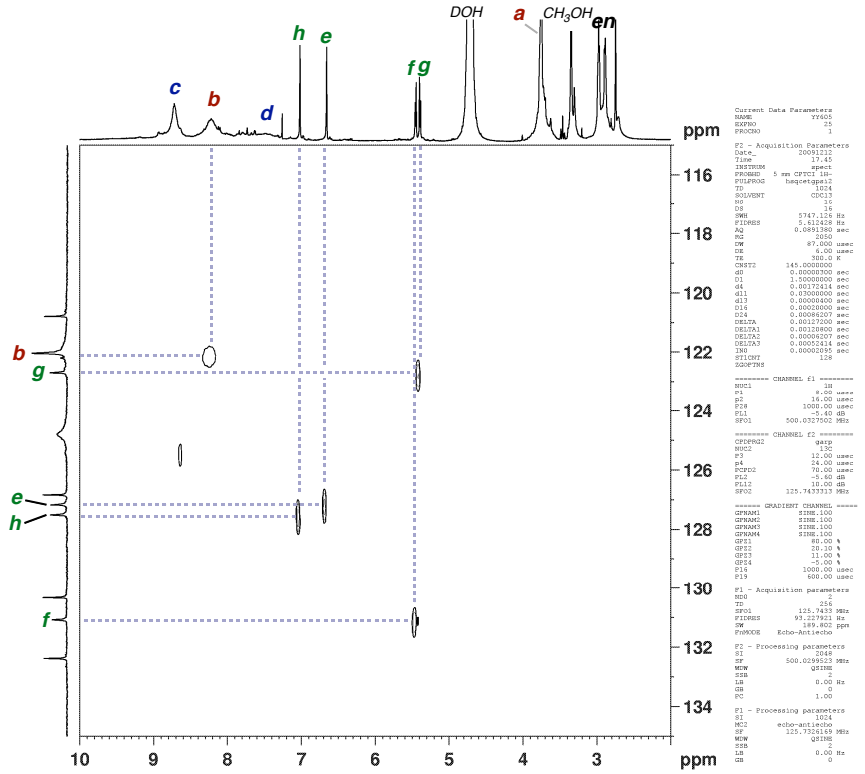


Fig. S5b. ^{1}H-^{13}C HSQC (D_2O, 300 K) spectrum of **1⊃3a**.

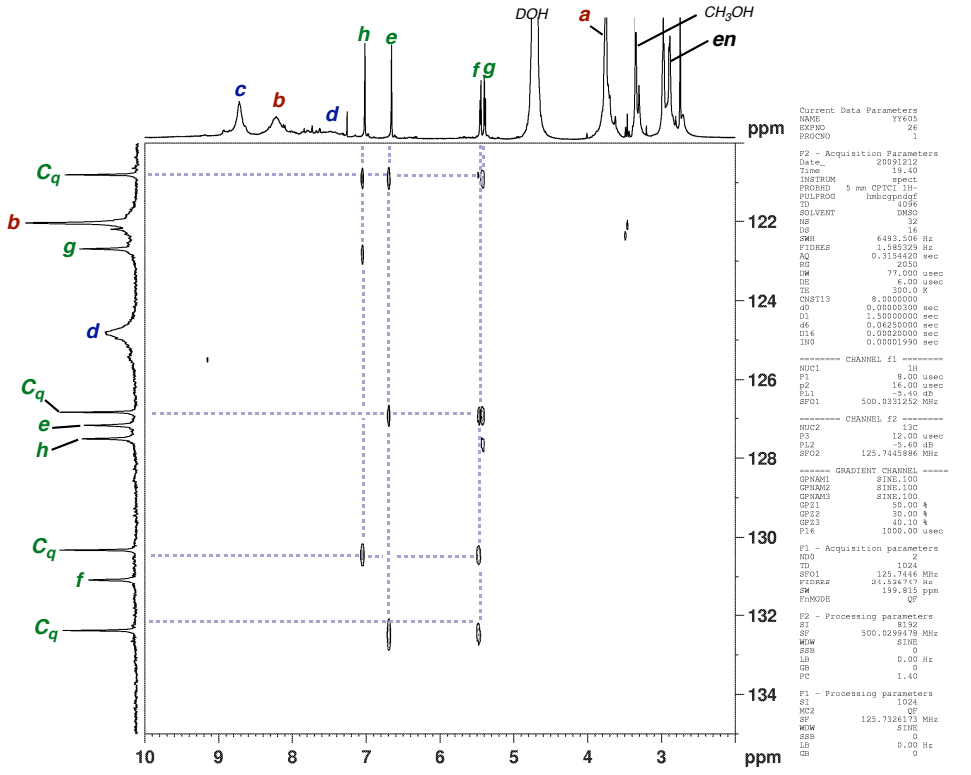


Fig. S6. ^{1}H-^{13}C HMBC (D_2O, 300 K) spectrum of **1⊃3a**.

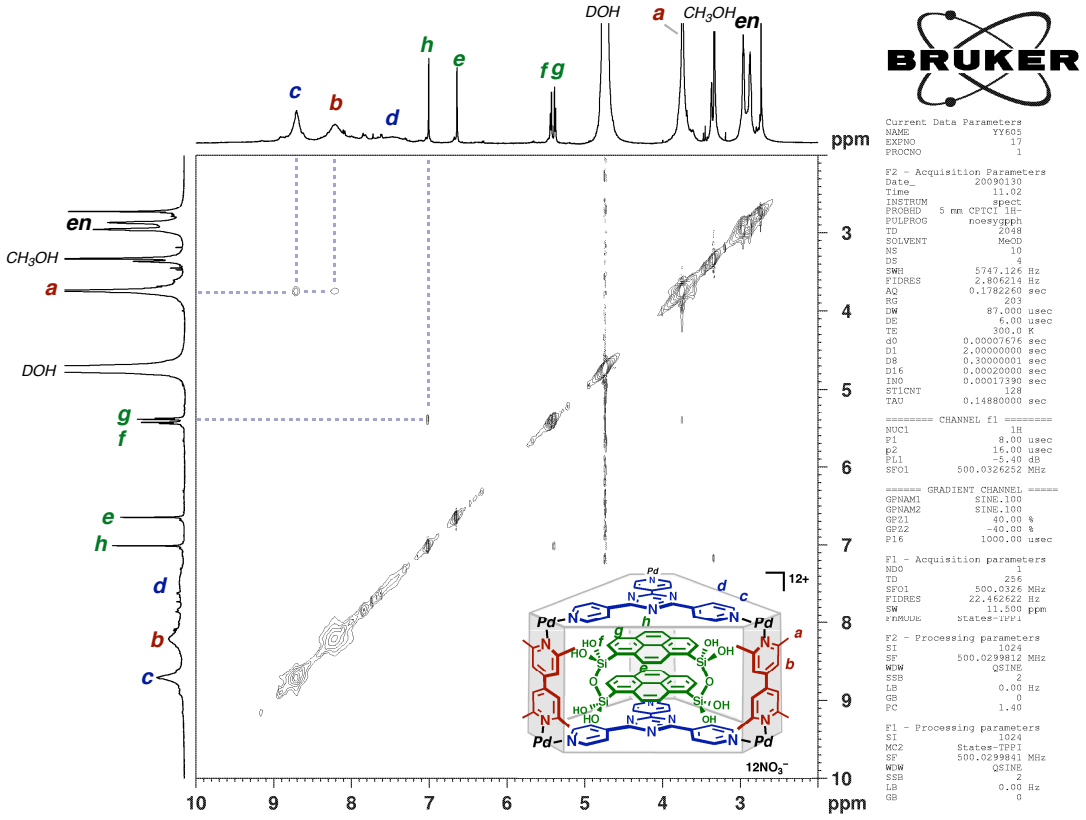
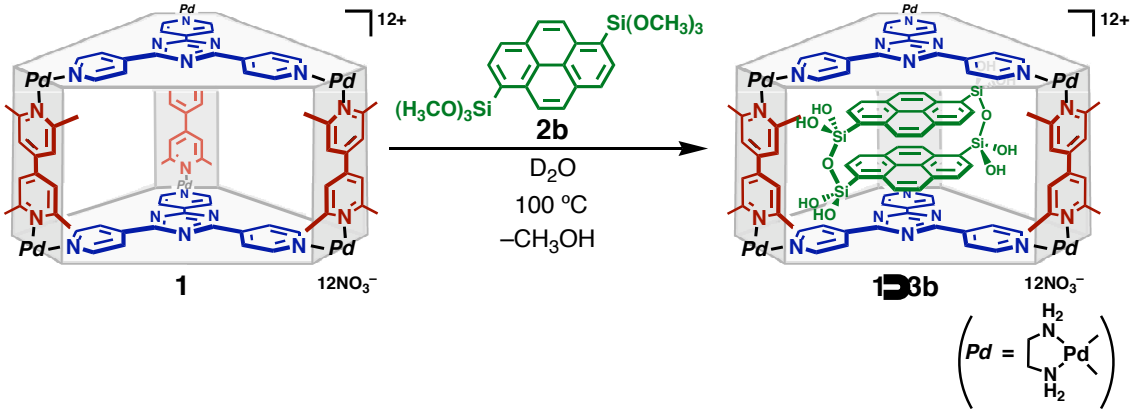


Fig. S7. ^{1}H-^{1}H NOESY (D_2O, 300 K) spectrum of **1⊃3a**.



Preparation of 1⊃3b. A mixture of cage **1** (14.9 mg, 5 μmol), **2b** (6.6 mg, 15 μmol) in D_2O (0.5 mL) was stirred at 100 °C for 20 h to give clear orange solution. ^{1}H NMR analysis of the solution revealed the formation of **1⊃3b**. After filtration of the resulted orange solution, the resulting solution was dried by a freeze-drying equipment. **1⊃3b** was isolated as an orange powder (15.3 mg, 83% yield). ^{1}H NMR (500 MHz, D_2O, 300 K): δ 8.65 (br, 12H), 8.44 (br, 12H), 8.20 (br, 12H), 8.12 (d, J = 7.5 Hz, 4H), 8.12 (d, J = 7.5 Hz, 4H), 3.73 (s, 18H), 3.73 (s, 18H), 3.73 (s, 36H), (br, 12H), (br, 12H); ^{13}C NMR (125 MHz, D_2O, 300 K): δ 167.1 (C_q), 161.6 (C_q), 161.1 (C_q), 152.1 (*C*H), 147.5 (C_q), 144.3 (C_q), 133.2 (C_q), 132.3 (*C*H), 129.5 (C_q), 127.6 (C_q), 127.2 (*C*H), 125.4 (*C*H), 125.0 (*C*H), 122.4 (*C*H), 122.2 (*C*H), 120.4 (C_q), 47.6 (CH_2), 46.5 (CH_2), 26.1 (CH_3); DOSY (m^2/s): log$D$ = –9.81; IR (KBr, cm^{-1}): 3403, 3086, 1607, 1575, 1550, 1521, 1384, 1100, 1087, 1059, 808, 523, 434; m.p.: ~230 ºC(decomposed).

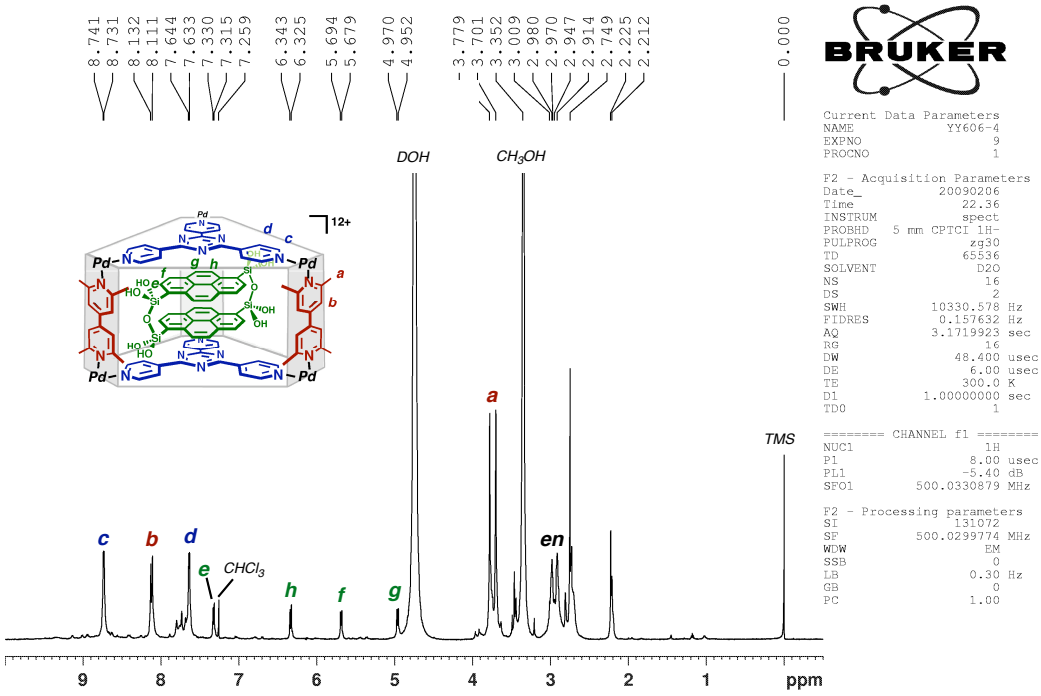


Fig. S8. ^{1}H NMR (500 MHz, D_2O, 300 K) spectrum of **1⊃3b**.

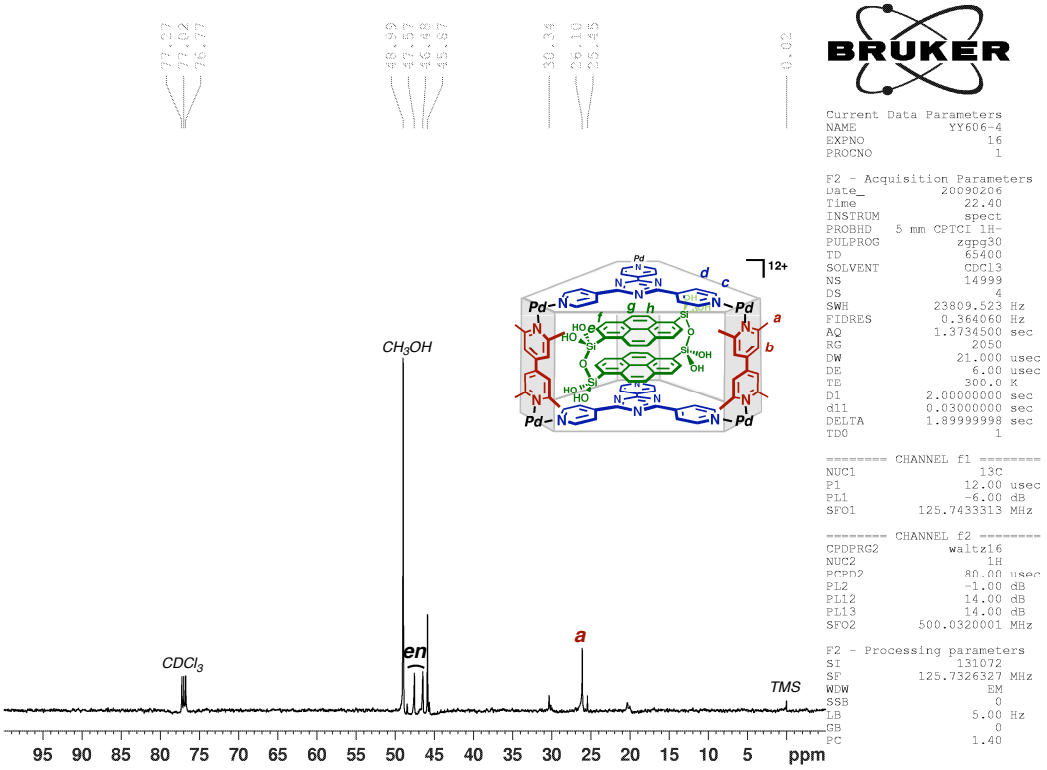


Fig. S9a. ^{13}C NMR (125 MHz, D_2O, 300 K) spectrum of **1⊃3b**.

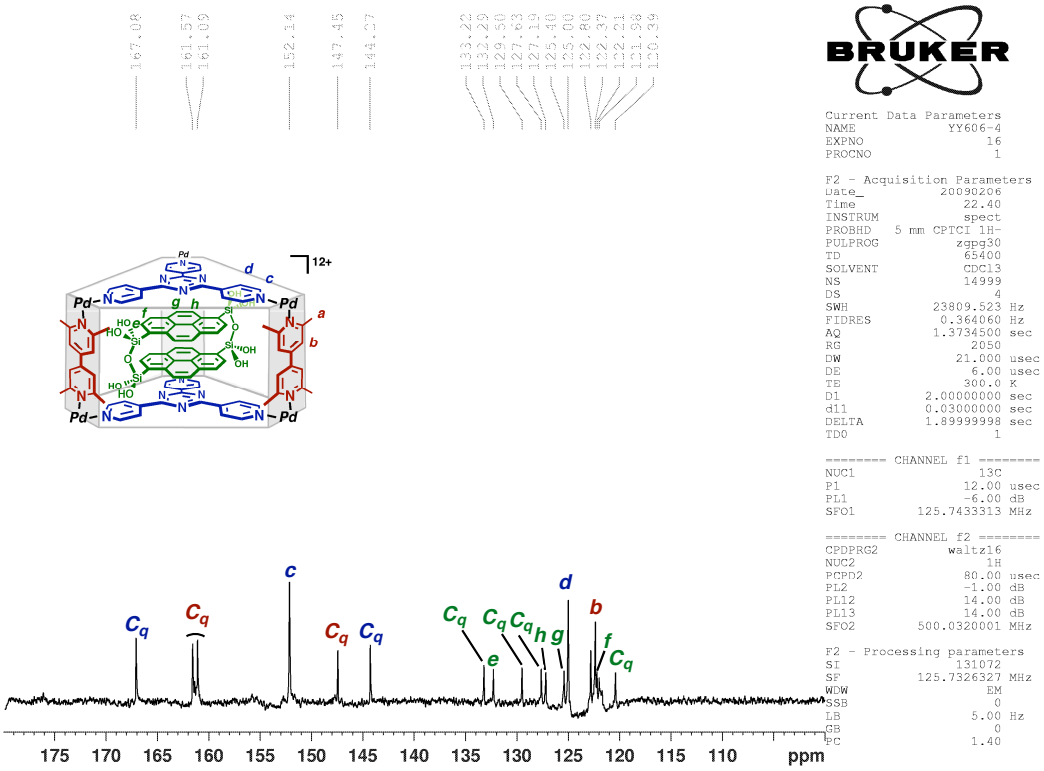


Fig. S9b. ^{13}C NMR (125 MHz, D_2O, 300 K) spectrum of **1⊃3b**.

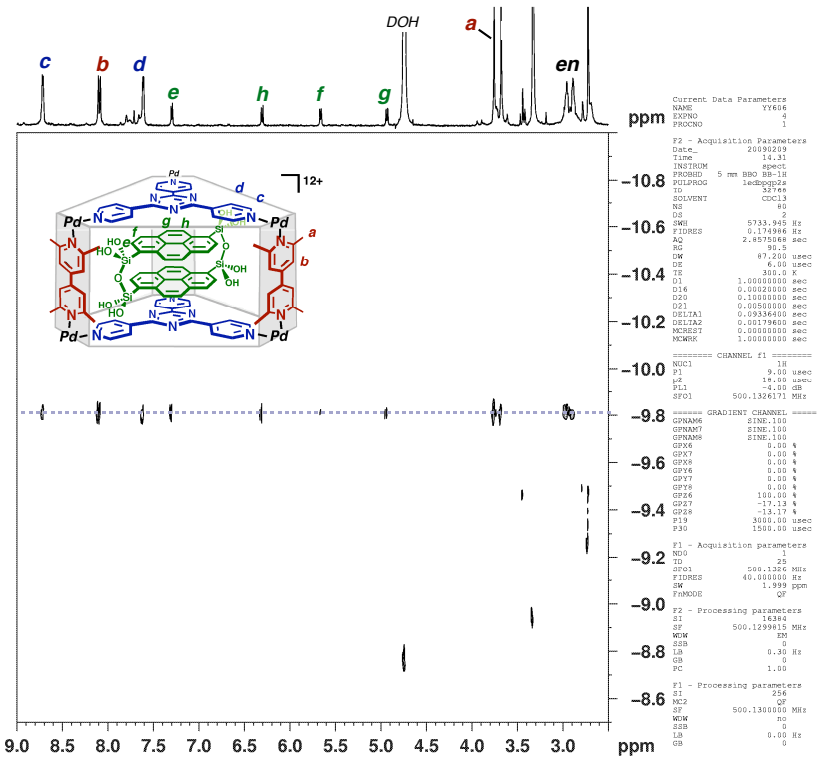


Fig. S10. ^{1}H DOSY (D_2O, 300 K) spectrum of **1⊃3b**.

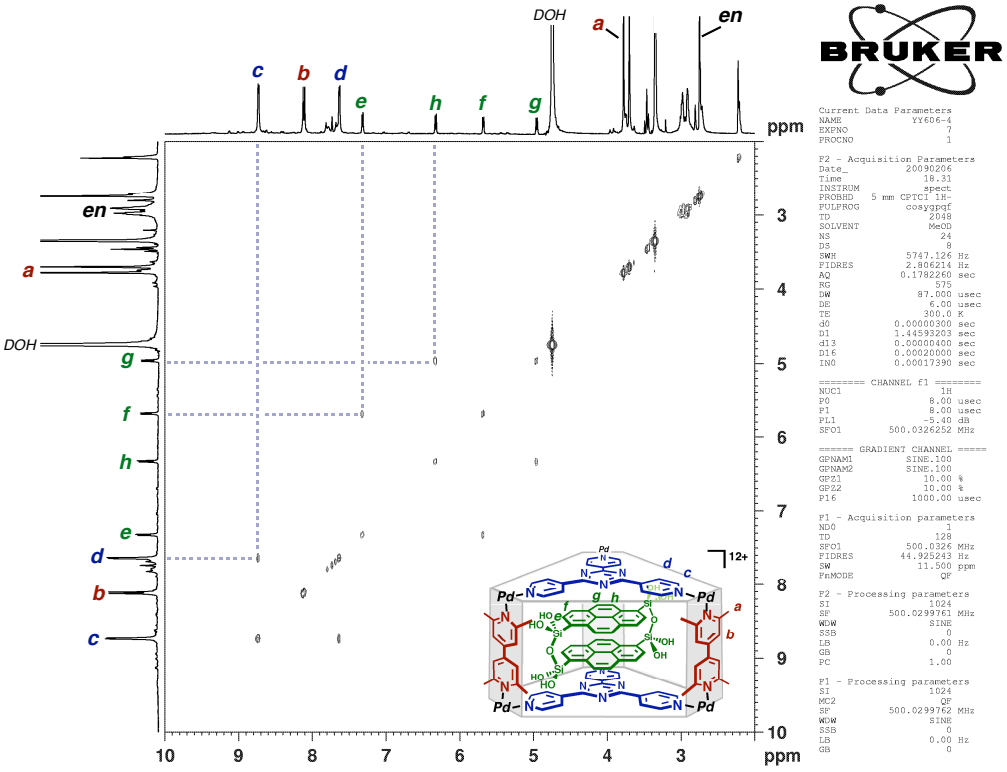


Fig. S11. ^{1}H-^{1}H COSY (D_2O, 300 K) spectrum of **1**⊃**3b**.

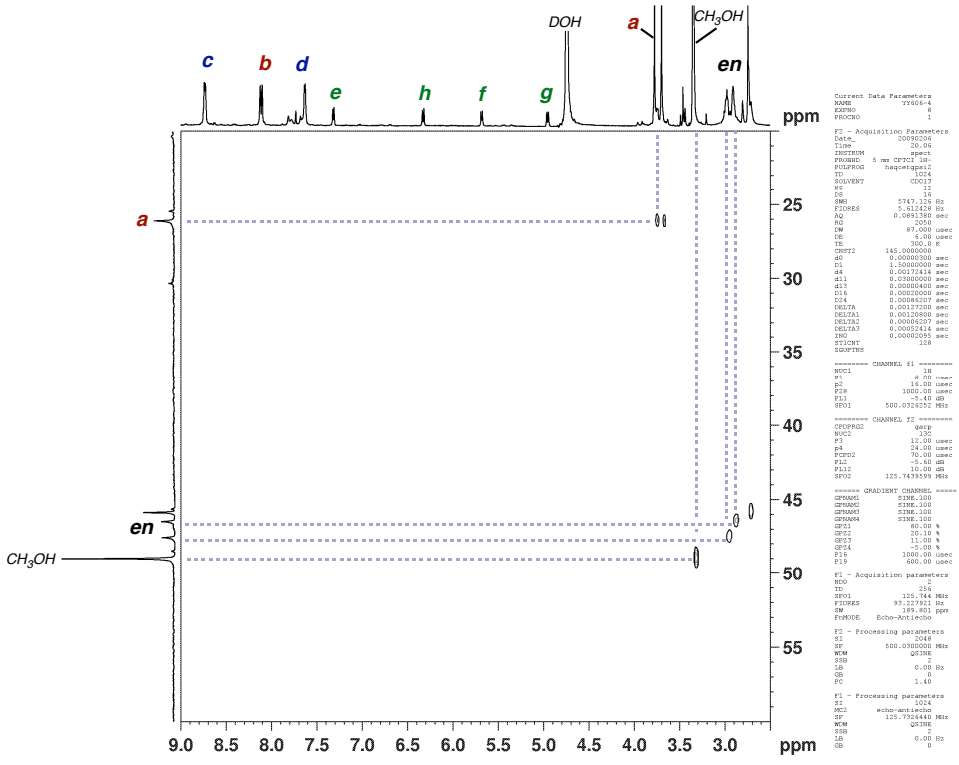


Fig. S12a. ^{1}H-^{13}C HSQC (D_2O, 300 K) spectrum of **1**⊃**3b**.

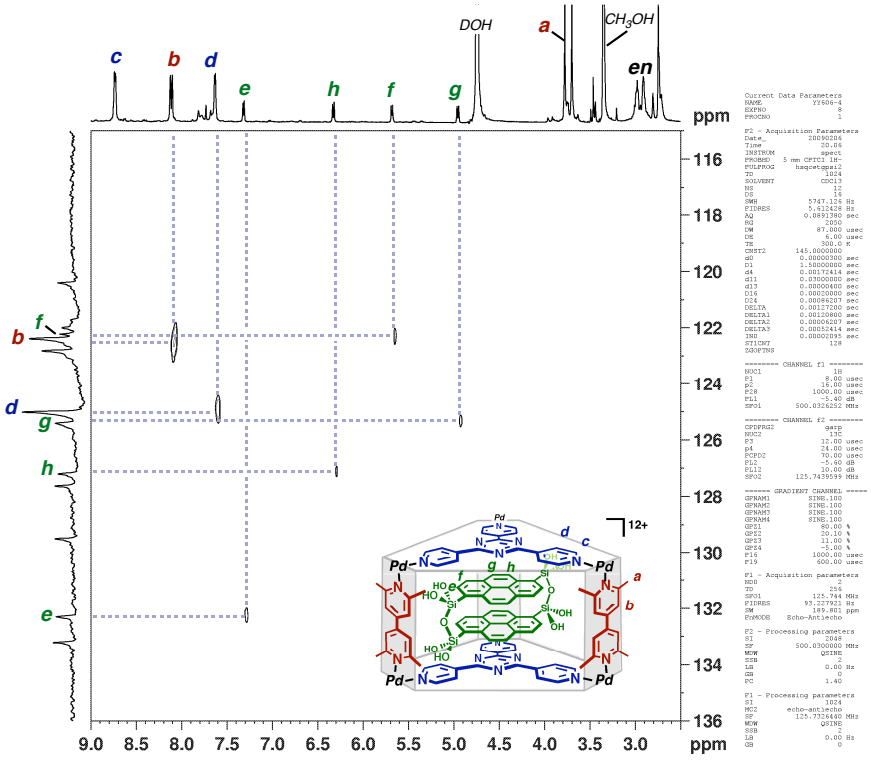


Fig. S12b. ^{1}H-^{13}C HSQC (D_2O, 300 K) spectrum of **1⊃3b**.

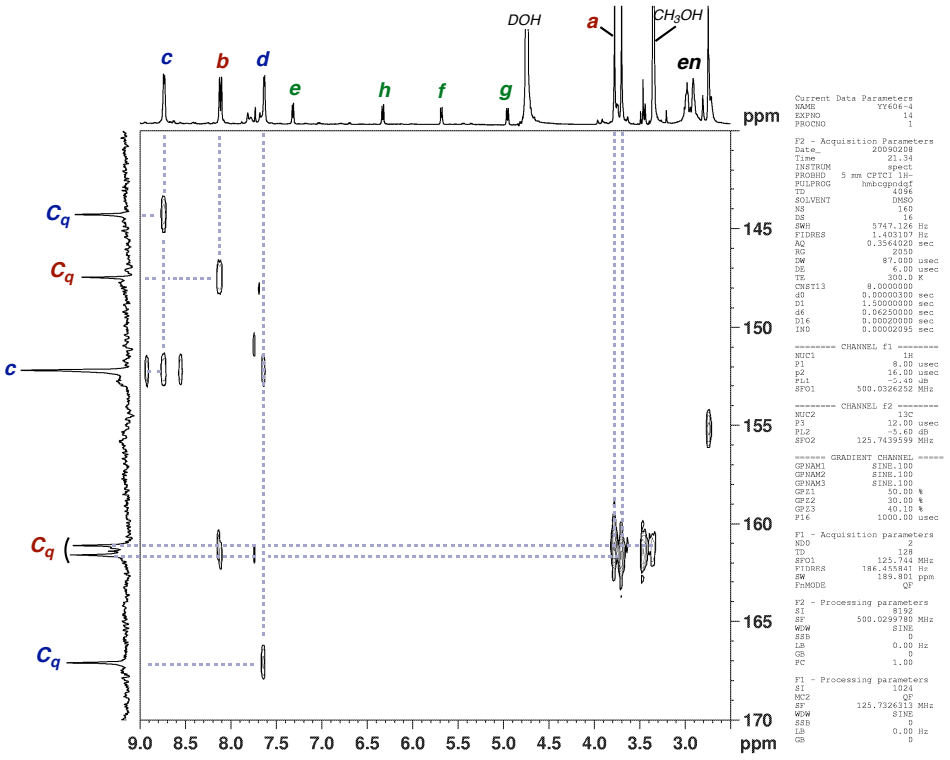


Fig. S13a. ^{1}H-^{13}C HMBC (D_2O, 300 K) spectrum of **1⊃3b**.

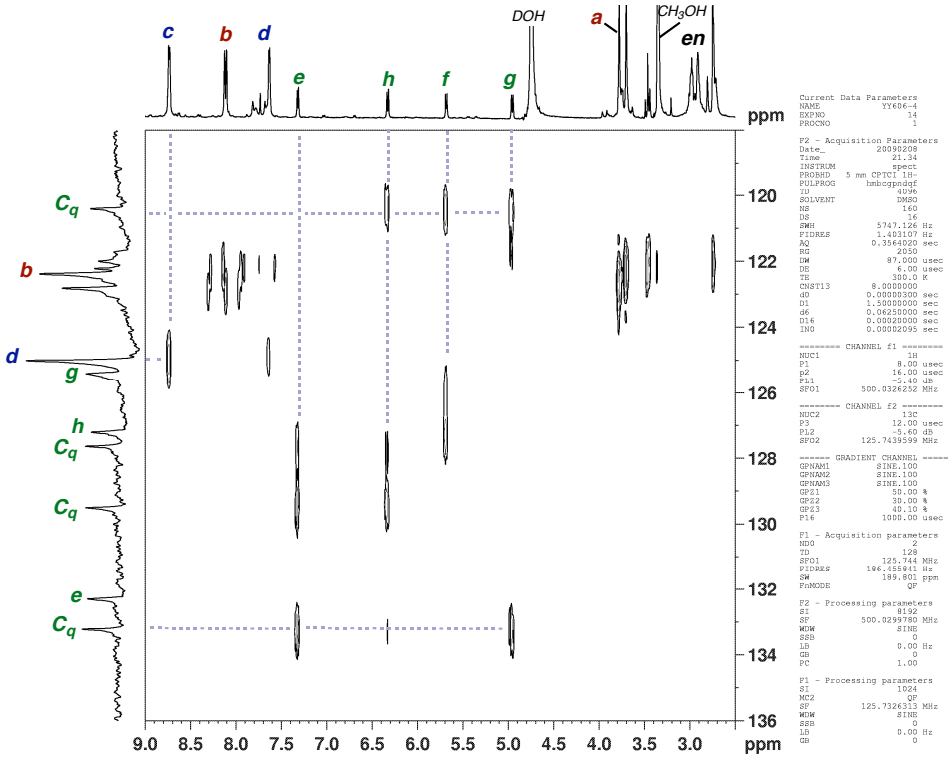


Fig. S13b. ^{1}H-^{13}C HMBC (D_2O, 300 K) spectrum of **1⊃3b**.

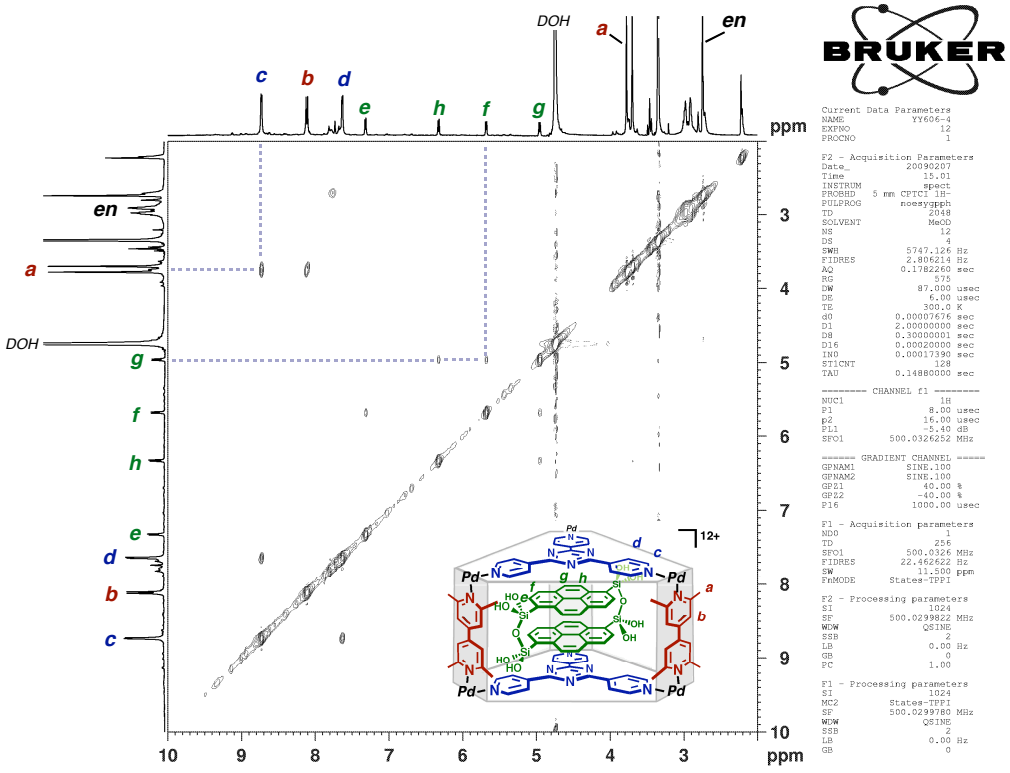


Fig. S14. ^{1}H-^{1}H NOESY (D_2O, 300 K) spectrum of **1⊃3b**.

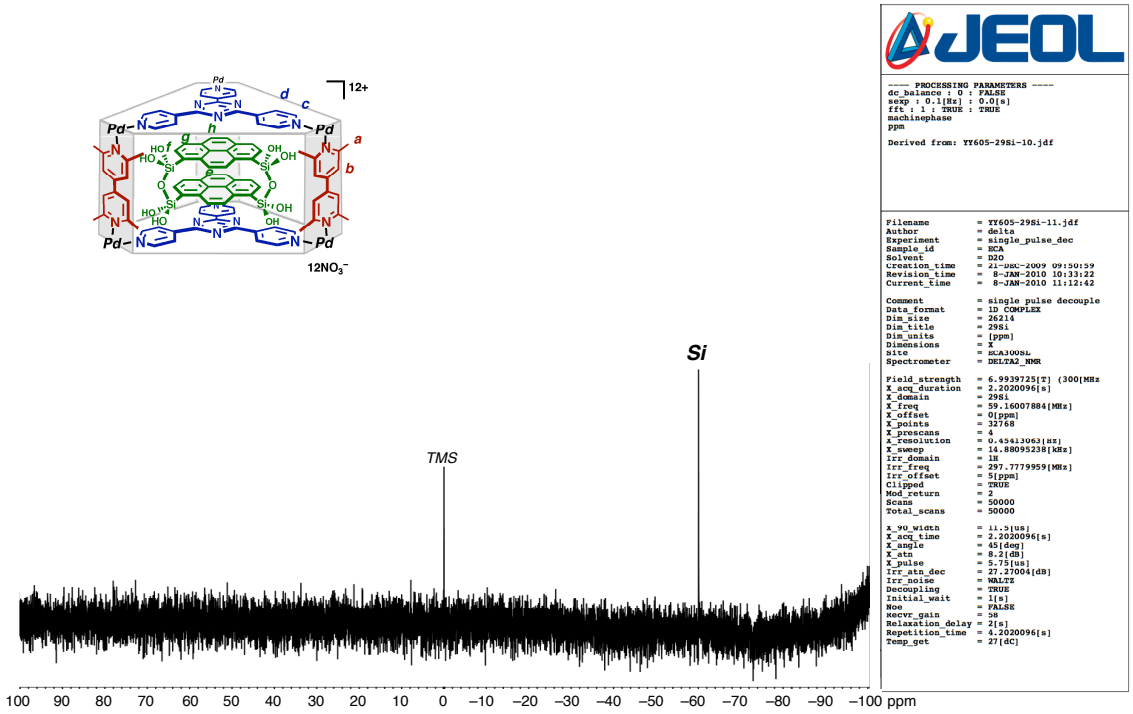


Fig. S15. ^{29}Si NMR (60 MHz, D_2O, 300 K) spectrum of **1⊃3a**.

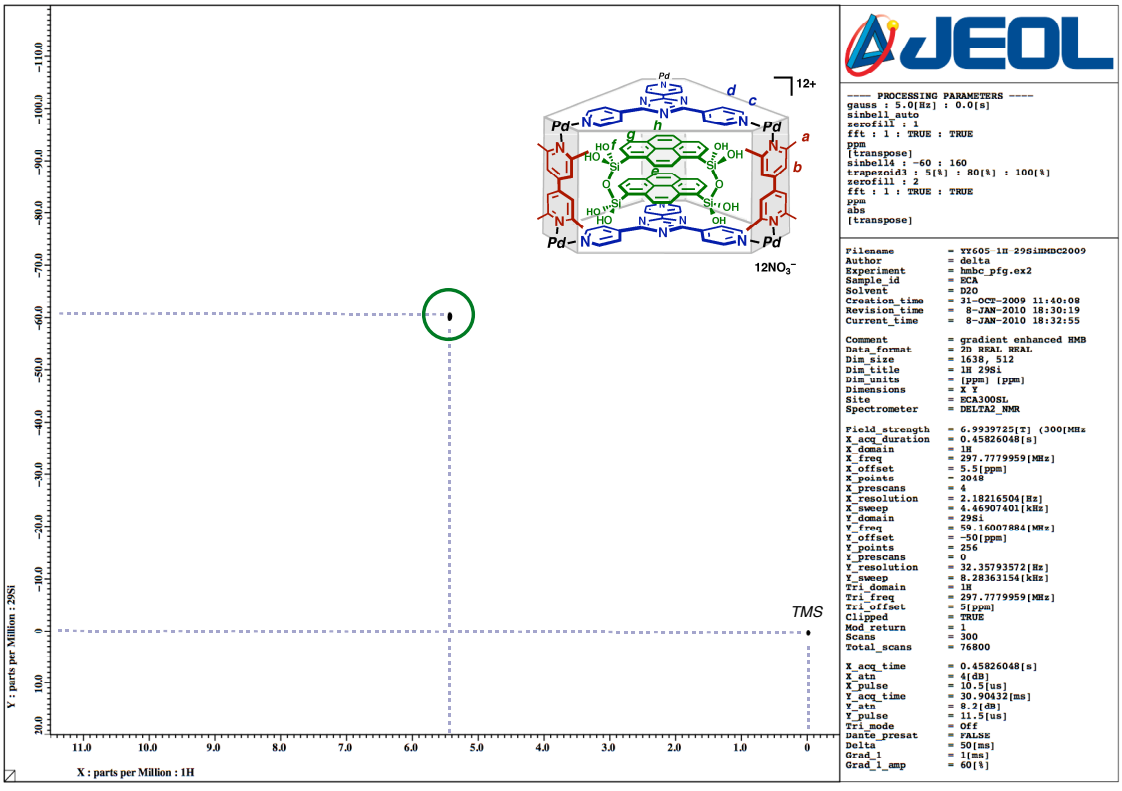


Fig. S16. ^{1}H-^{29}Si HMBC (D_2O, 300 K) spectrum of **1⊃3a**.

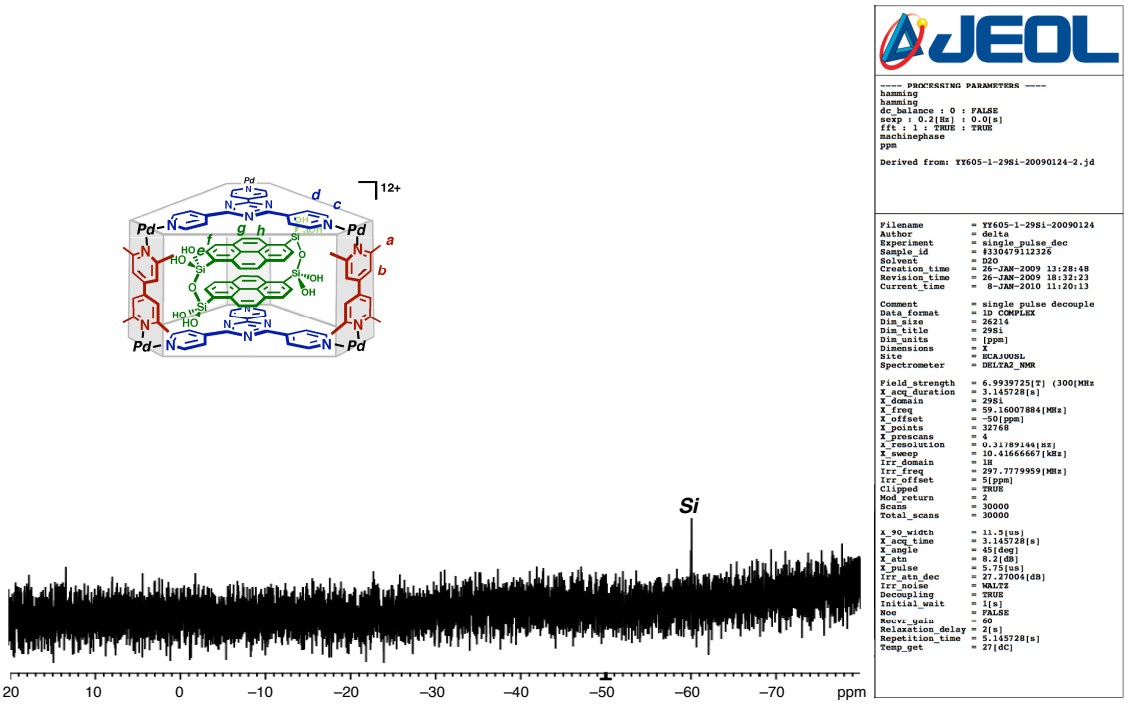


Fig. S17. ^{29}Si NMR (60 MHz, D_2O, 300 K) spectrum of **1⊃3b**.

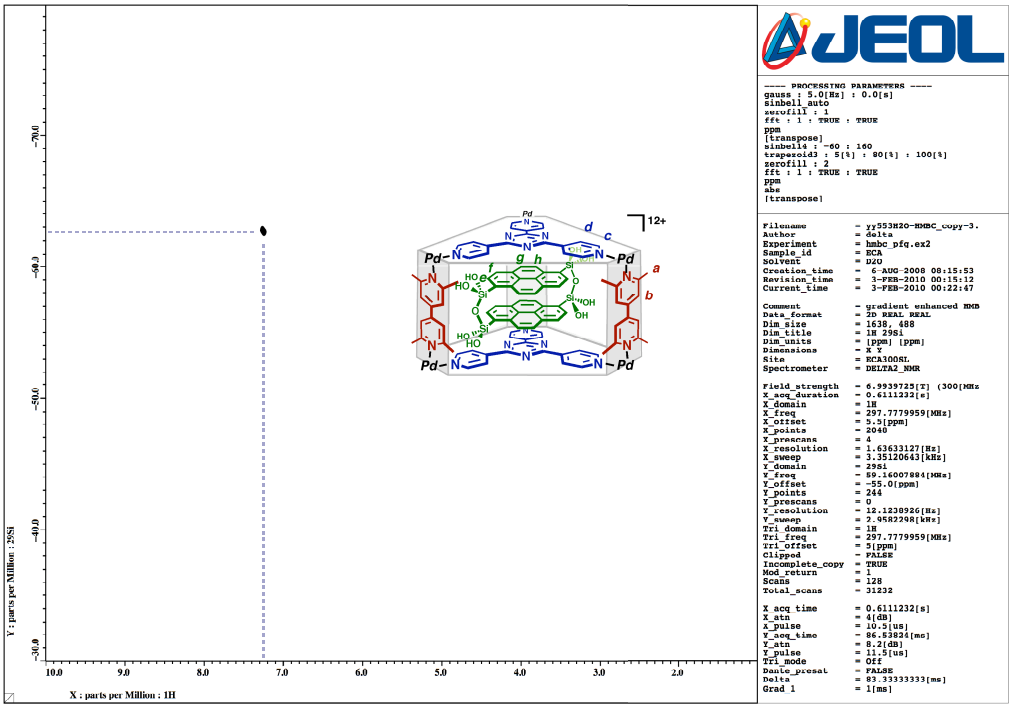


Fig. S18. ^{1}H-^{29}Si HMBC (D_2O, 300 K) spectrum of **1⊃3b**.

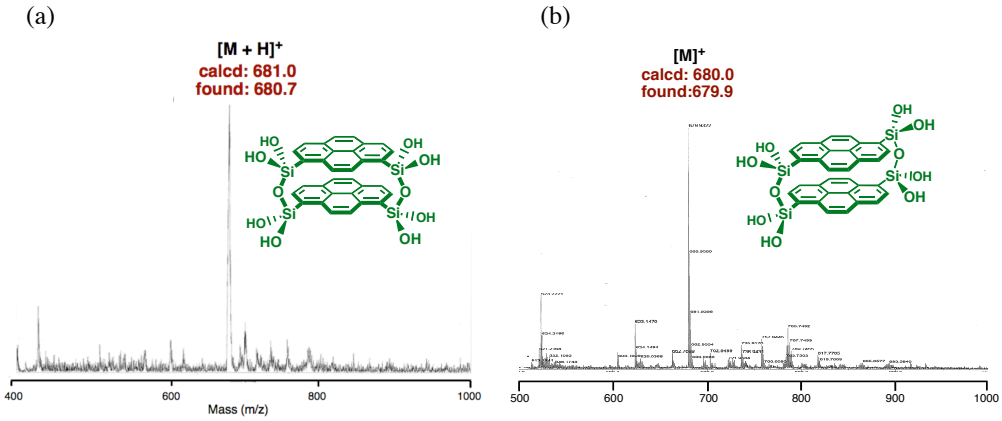


Fig. S19. LDI-MS spectra of (a) **3a** and (b) **3b**.

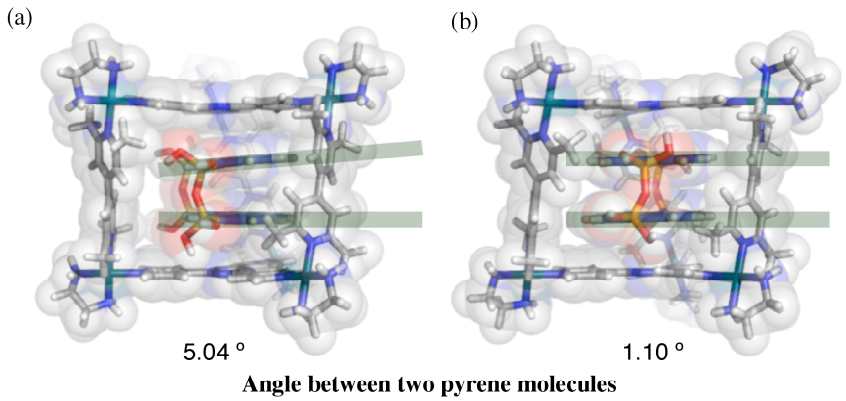


Fig. S20. Optimized structures (MM) of (a) **1⊃3a** and (b) **1⊃3b**.

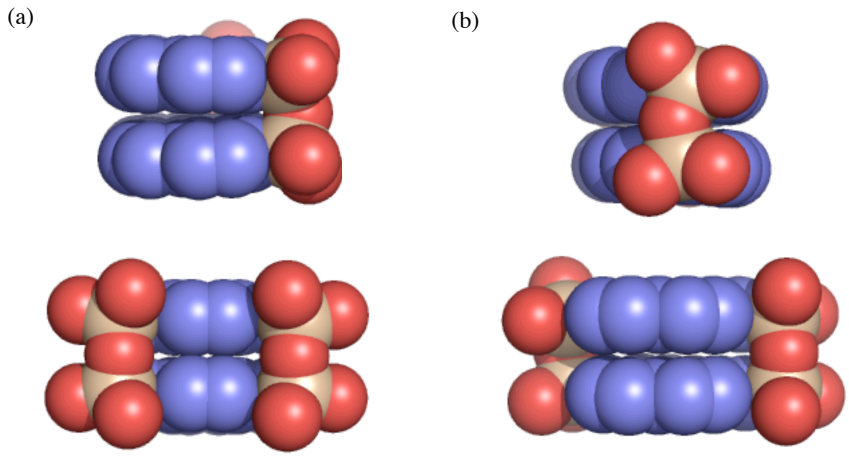


Fig. S21. Optimized structures (MM) focusing on (a) **3a** and (b) **3b** within the cavity of **1**. Hydrogen atoms of **3a** and **3b** were omitted for clarity.