Supporting Information

A Double-Walled Knotted Cage for Guest-Adaptive Molecular Recognition

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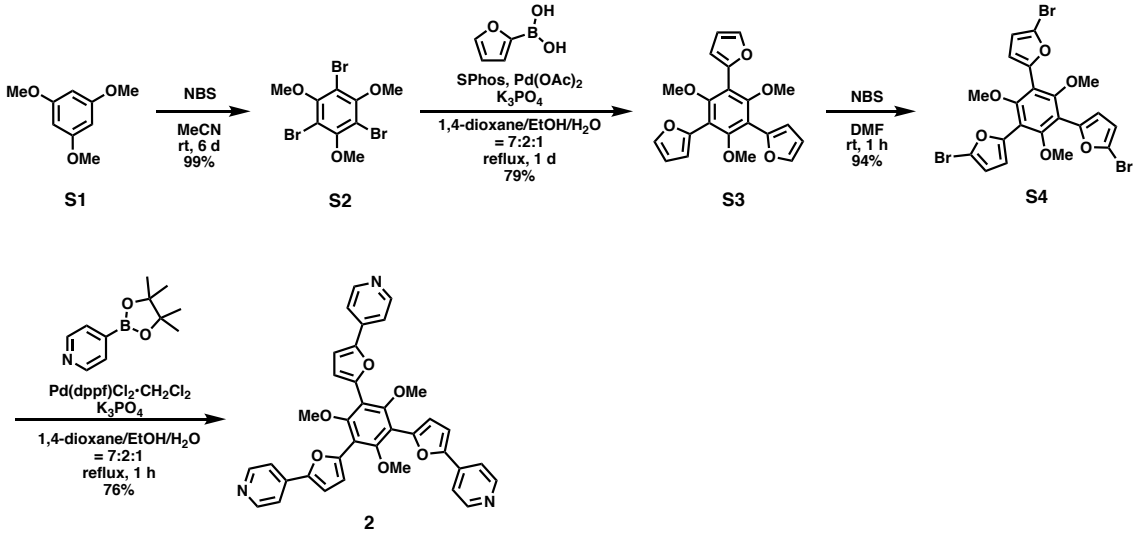
Contents

1. Materials and instrumentations

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III or a Bruker AVANCE 500 equipped with CP-TCI cryoprobe (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) at 300 K unless otherwise stated. TMS ($CDCl_3$ solution) in a capillary served as an internal standard for ^{1}H NMR (δ = 0 ppm). GC-MS data were obtained on an Agilent 5977B inert Mass selective Detector equipped with a 7820A Network GC system and an EI source. ESI-MS data were recorded on a Bruker maXis. The MALDI-TOF mass spectra were obtained using a Bruker Daltonics Autoflex Speed spectrometer with dithranol as the matrix. IR measurements were carried out using a DIGILAB Scimitar FTS-2000 instrument. Melting points were determined on a Stanford Research Systems OptiMelt. Elemental analyses were performed at the Elemental Analysis Center (School of Science, The University of Tokyo). Single crystal X-ray diffraction data were collected on a BRUKER APEX-II CCD rotating anode diffractometer equipped with focusing mirrors with MoK_{α} (λ = 0.71073 Å) radiation under cryogenic conditions, which are controlled with a cryostat system equipped with an N_2 generator (Japan Thermal Eng. Co., Ltd.) or a Synergy-S diffractometer (Rigaku Oxford Diffraction), which is equipped with a micro-focus CuK_{α} radiation source (λ = 1.5418 Å), a high-sensitive CCD detector, and a low temperature system using cold nitrogen stream (100 K). Solvents and reagents were purchased from TCI Co., Ltd., Wako Pure Chemical Industries Ltd., Kanto Chemical Co., Inc., and Sigma-Aldrich Co. and used without any further purification.

2. Synthesis and physical properties of ligand 2



1,3,5-Tribromo-2,4,6-trimethoxybenzene (S2)

A mixture of 1,3,5-trimethoxybenzene (**S1**, 5.00 g, 29.7 mmol) and *N*-bromosuccinimide (21.0 g, 118 mmol) in CH_3CN (50 mL) was stirred at room temperature for 6 d. The solvent was removed under reduced pressure, and EtOAc was added. The solution was washed with H_2O, $Na_2S_2O_4$ aq. and $NaHCO_3$ aq. The organic layer was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure to give 1,3,5-tribromo-2,4,6-trimethoxybenzene (**S2**) quantitatively as a white powder (11.9 g, 29.3 mmol, 99%).[S1]

Physical data of S2: white powder. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.89 (s, 9H, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.0 (*C*), 110.1 (*C*Br), 60.7 (*C*H$_3$). GC/MS (EI) *m*/*z*: 405.8 $[M]^+$.

1,3,5-Tris(2-furyl)-2,4,6-trimethoxybenzene (S3)

A mixture of 1,3,5-tribromo-2,4,6-trimethoxybenzene (**S2**, 5.01g, 12.3 mmol), 2-furylboronic acid (4.97 g, 44.5 mmol), $Pd(OAc)_2$ (280 mg, 1.23 mmol), SPhos (1.01 g, 2.47 mmol) and K_3PO_4 (13.0 g, 61.7 mmol) in a mixed solvent of 1,4-dioxane (28 mL), ethanol (8 mL) and H_2O (4 mL) was refluxed under Ar atmosphere for 19 h. $CHCl_3$ (80 mL) was added to the mixture and the organic layer was collected and washed with H_2O (100 mL×2) and brine (100 mL×2). The organic layer was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 98:2) to provide 1,3,5-tris(2-furyl)-2,4,6-trimethoxybenzene (**S3**) as a white crystalline powder (3.56 g, 9.72 mmol, 79%).[S2]

Physical data of S3: white crystalline powder. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.57 (t, J = 1.0 Hz, 3H, Ar*H*), 6.64 (dd, J = 0.8, 3.3 Hz, 3H, Ar*H*), 6.53 (dd, J = 1.8, 3.3 Hz, 3H, Ar*H*), 3.39 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 158.5 (*C*), 146.2 (*C*), 142.3 (*C*H), 116.1 (*C*), 111.1 (*C*H), 111.0 (*C*H), 61.2 (*C*H_3). GC/MS (EI) *m*/*z*: 366.1 $[M]^+$.

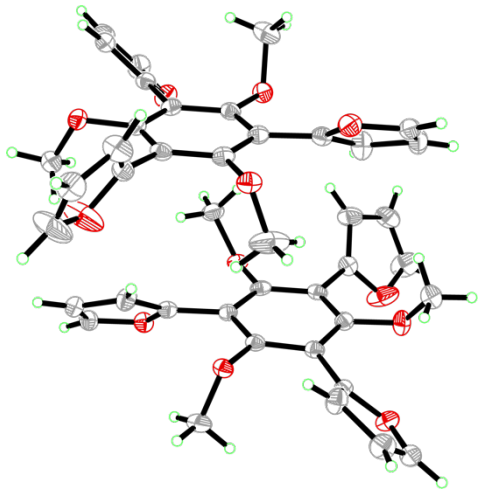


Figure S1. ORTEP drawing (50% probability ellipsoids) of the refinement structure of **S3** (CCDC reference number: 1984215).

1,3,5-Tris(5-bromofuran-2-yl)-2,4,6-trimethoxybenzene (S4)

A mixture of 1,3,5-tris(2-furyl)-2,4,6-trimethoxybenzene (**S3**, 1.00 g, 2.73 mmol) and *N*-bromosuccinimide (1.61 g, 9.04 mmol) in *N*,*N*-dimethylformamide (10 mL) was stirred at room temperature for 1 h. Et_2O (50 mL) and H_2O (150 mL) were added to the mixture and the organic layer was collected. The organic layer was washed with H_2O, $Na_2S_2O_4$ aq. and $NaHCO_3$ aq. then dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc = 9:1) to provide 1,3,5-tris(5-bromofuran-2-yl)-2,4,6-trimethoxybenzene (**S4**) as a white powder (1.55 g, 2.57 mmol, 94%).

Physical data of S4: white powder. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.60 (d, J = 3.0 Hz, 3H, Ar*H*), 6.44 (d, J = 3.0 Hz, 3H, Ar*H*), 3.48 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 158.8 (*C*), 148.1 (*C*), 121.8 (*C*), 115.6 (*C*), 114.1 (*C*H), 112.9 (*C*H), 61.7 (*C*H_3). IR (ATR, cm^{-1}): 2359, 2344, 2335, 2327, 2321, 1080, 1016, 956, 931, 776, 719, 666. m.p.: 125–126 ºC. MALDI–TOF–MS (ESI): calcd. for $[M]^+$: 599.8, found 599.6. Elemental analysis (%): calcd. for $C_{21}H_{15}Br_3O_6$: C 41.83, H 2.51, N: 0.00; found: C 41.94, H 2.70, N 0.00.

1,3,5-Tris(5-(prydine-4-yl)furan-2-yl)-2,4,6-trimethoxybenzene (2)

A mixture of 1,3,5-tris(5-bromofuran-2-yl)-2,4,6-trimethoxybenzene (**S4**, 511 mg, 0.847 mmol), 4-pyridylboronic acid pinacol ester (571 mg, 2.78 mmol), $Pd(dppf)Cl_2 \bullet CH_2Cl_2$ (206 mg, 0.252 mmol) and K_3PO_4 (891 mg, 4.20 mmol) in a mixed solvent of 1,4-dioxane (21 mL), ethanol (6 mL) and H_2O (3 mL) was refluxed under Ar atmosphere for 1 h. EtOAc (80 mL) was added to the mixture and filtered. The organic layer was washed with H_2O (100 mL×3) and extracted with 50 mM HCl aq (60 mL×2). The aqueous layer was neutralized with NaOH aq. and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The crude product was purified by recrystallization from EtOAc and *n*-hexane to provide 1,3,5-tris(5-(pyridine-4-yl)furan-2-yl)-2,4,6-trimethoxybenzene (**2**) as an off-white powder (385 mg, 0.644 mmol, 76%).

Physical data of 2: off-white powder. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.61 (d, J = 5.5 Hz, 6H, PyH_α), 7.58 (d, J = 5.5 Hz, 6H, PyH_β), 7.06 (d, J = 3.5 Hz, 3H, Ar*H*), 6.86 (d, J = 3.5 Hz, 3H, Ar*H*), 3.57 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 158.9 (*C*), 151.0 (*C*), 150.2 (*C*H), 147.6 (*C*), 117.7 (*C*H), 115.9 (*C*), 114.1 (*C*H), 110.4 (*C*H), 61.7 (*C*H_3). IR (ATR, cm^{-1}): 2973, 2935, 2363, 1592, 1455, 1080, 730, 712. m.p.: 168–169 ºC. HR–MS (ESI): calcd for $[M+H]^+$: 598.1973, found: 598.1998.

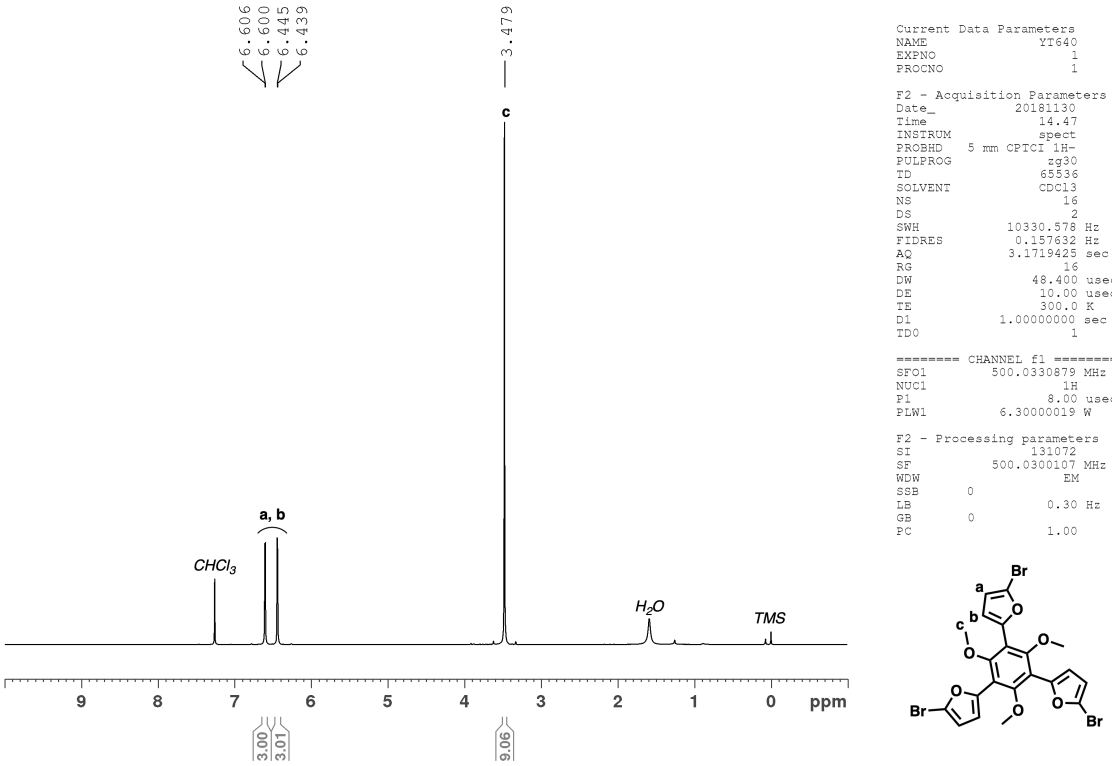


Figure S2. ^{1}H NMR spectrum (500 MHz, 300 K, $CDCl_3$) of **S4**.

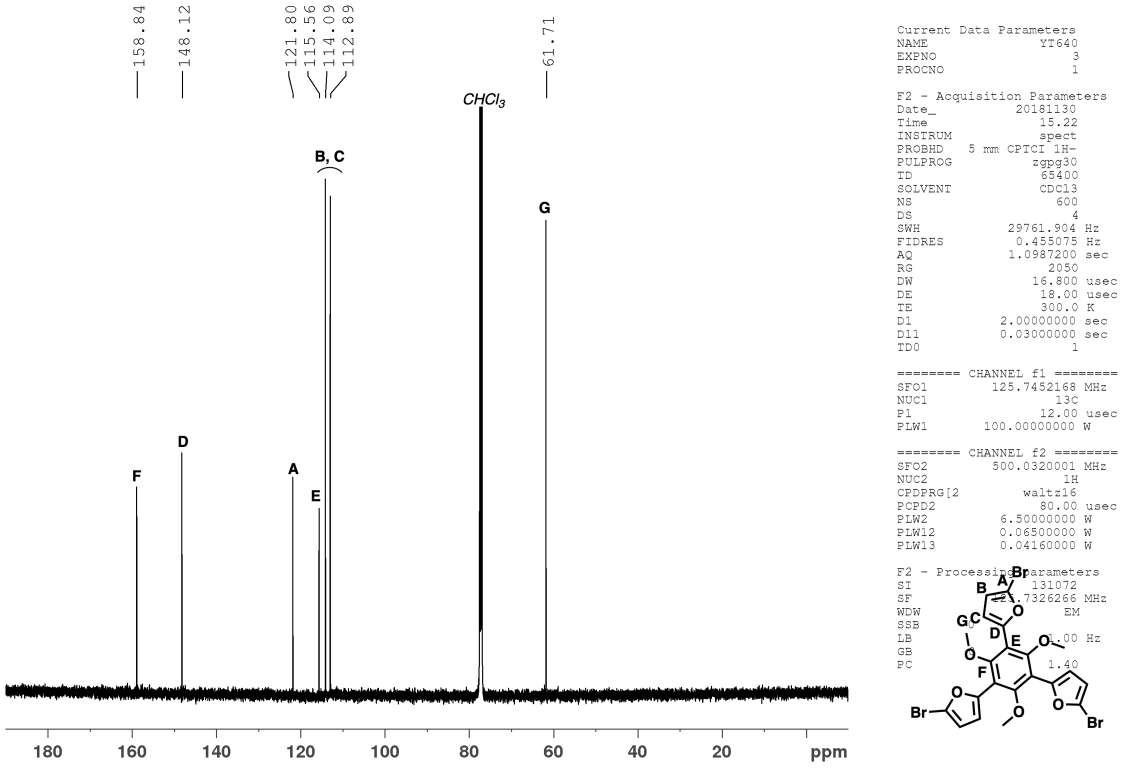


Figure S3. ^{13}C NMR spectrum (125 MHz, 300 K, $CDCl_3$) of **S4**.

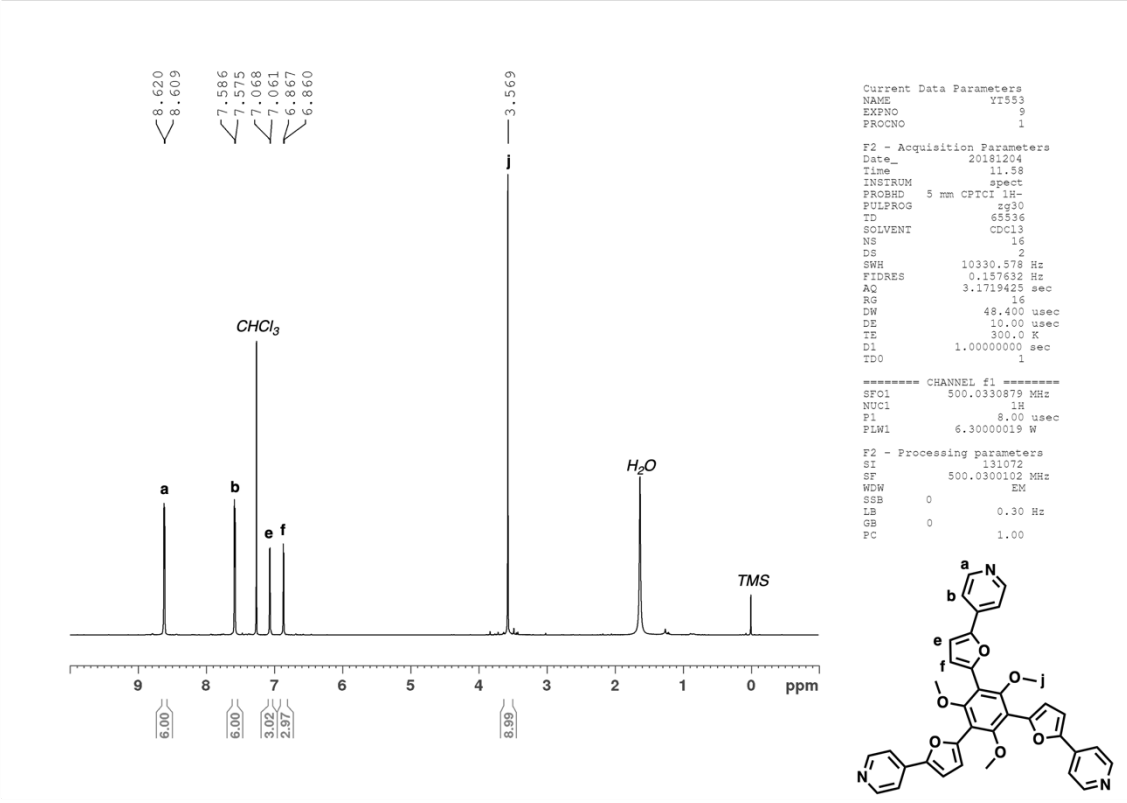


Figure S4. ^{1}H NMR spectrum (500 MHz, 300 K, $CDCl_3$) of **2**.

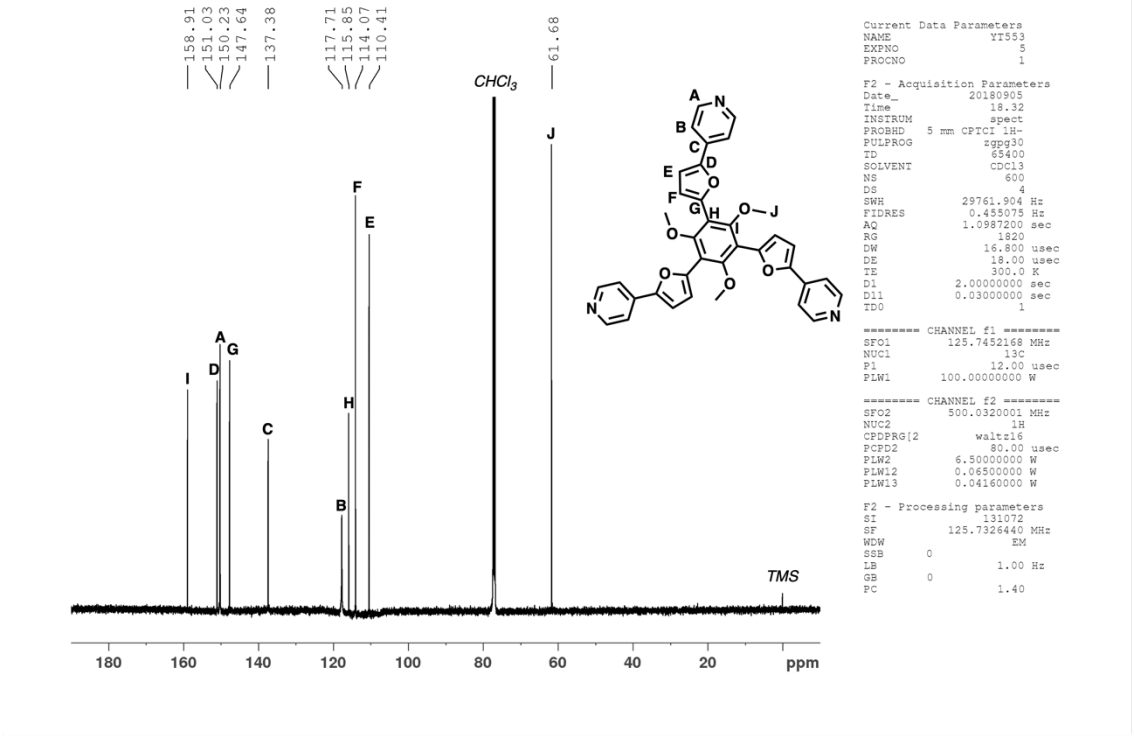
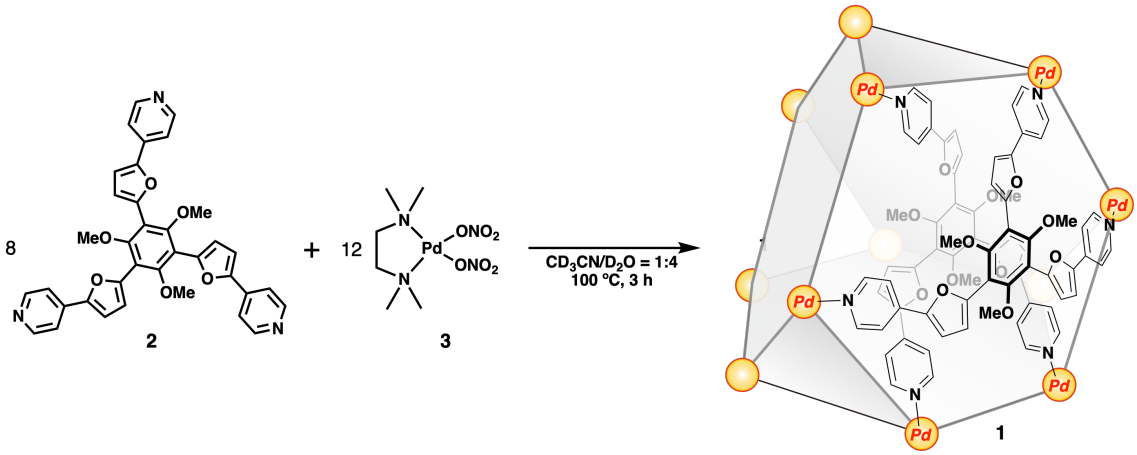


Figure S5. ^{13}C NMR spectrum (125 MHz, 300 K, $CDCl_3$) of **2**.

3. Synthesis and physical properties of cage 1



1,3,5-Tris(5-(prydine-4-yl)furan-2-yl)-2,4,6-trimethoxybenzene (**2**, 60.0 mg, 100 μmol) and (tmeda)Pd(ONO_2)$_2$ (**3**, 52.0 mg, 150 μmol) were added in acetonitrile-d_3/D_2O (5.0 mL, 1:4 v/v). After stirring at 100 ºC for 3 h, a trace amount of insoluble material was filtrated. The quantitative formation of cage **1** was confirmed by ^{1}H NMR spectroscopy.

Physical data of 1: ^{1}H NMR (acetonitrile-d_3/D_2O (1:4 v/v), 500 MHz): δ 10.16 (d, J = 5.5 Hz, 4H, Ar*H*), 10.09 (d, J = 6.0 Hz, 4H, Ar*H*), 9.68 (d, J = 6.0 Hz, 4H, Ar*H*), 9.62 (d, J = 6.0 Hz, 4H, Ar*H*), 9.58 (d, J = 6.0 Hz, 4H, Ar*H*), 9.54 (d, J = 6.0 Hz, 4H, Ar*H*), 9.50 (d, J = 6.0 Hz, 4H, Ar*H*), 9.38 (d, J = 6.0 Hz, 4H, Ar*H*), 9.35 (d, J = 6.0 Hz, 4H, Ar*H*), 9.24 (d, J = 4.5 Hz, 8H, Ar*H*), 9.11 (d, J = 6.0 Hz, 4H, Ar*H*), 8.21 (d, J = 5.5 Hz, 4H, Ar*H*), 7.81 (d, J = 5.5 Hz, 4H, Ar*H*), 7.70 (d, J = 5.5 Hz, 12H, Ar*H*), 7.66 (d, J = 5.5 Hz, 4H, Ar*H*), 7.65 (d, J = 5.5 Hz, 4H, Ar*H*), 7.60 (d, J = 5.5 Hz, 4H, Ar*H*), 7.56 (d, J = 5.5 Hz, 4H, Ar*H*), 7.54 (d, J = 5.5 Hz, 4H, Ar*H*), 7.45 (d, J = 5.5 Hz, 4H, Ar*H*), 7.17 (d, J = 3.5 Hz, 4H, Ar*H*), 7.11 (d, J = 5.0 Hz, 4H, Ar*H*), 7.07 (d, J = 3.5 Hz, 4H, Ar*H*), 7.05 (d, J = 4.0 Hz, 4H, Ar*H*), 6.78 (d, J = 3.5 Hz, 4H, Ar*H*), 6.77 (d, J = 4.0 Hz, 4H, Ar*H*), 6.61 (d, J = 3.5 Hz, 4H, Ar*H*), 5.88 (d, J = 3.5 Hz, 4H, Ar*H*), 5.80 (d, J = 3.0 Hz, 4H, Ar*H*), 5.36 (d, J = 3.0 Hz, 4H, Ar*H*), 5.33 (d, J = 3.0 Hz, 4H, Ar*H*), 4.92 (d, J = 3.5 Hz, 4H, Ar*H*), 4.46 (d, J = 3.0 Hz, 4H, Ar*H*), 3.92 (s, 12H, –O*Me*), 3.82 (s, 12H, –O*Me*), 3.62 (s, 12H, –O*Me*), 3.49 (s, 12H, –O*Me*), 3.49–3.23 (br, 40H, –CH_2–), 3.27 (s, 12H, –O*Me*), 3.26 (s, 12H, CH_3), 3.18 (s, 36H, CH_3), 3.07 (br, 8H, –CH_2–), 3.06 (s, 12H, CH_3), 3.04 (s, 12H, CH_3), 2.97 (s, 24H, CH_3), 2.94 (s, 24H, CH_3), 2.92 (s, 12H, CH_3), 2.91 (s, 12H, CH_3), 2.05 (s, 12H, –O*Me*); ^{13}C NMR (acetonitrile-d_3/D_2O (1:4 v/v), 125 MHz): δ 157.1 (*C*), 157.0 (*C*), 156.9 (*C*), 156.7 (*C*), 155.8 (*C*), 153.2 (*C*H), 152.6 (*C*H), 152.5 (*C*H), 151.9 (*C*H), 151.8 (*C*H), 151.6 (*C*H), 151.1 (*C*H), 151.1 (*C*H), 150.7 (*C*H), 150.0 (*C*), 149.5 (*C*), 149.0 (*C*), 148.7 (*C*), 148.5 (*C*), 148.1 (*C*), 147.9 (*C*), 147.6 (*C*), 147.5 (*C*), 147.4 (*C*), 147.1 (*C*), 140.4 (*C*), 140.3 (*C*), 139.6 (*C*), 139.2 (*C*), 121.2 (*C*H), 121.0 (*C*H), 120.9 (*C*H), 120.7 (*C*H), 120.6 (*C*H), 120.3 (*C*H), 120.2 (*C*H), 119.6 (*C*H), 116.7 (*C*), 116.1 (*C*H), 115.8 (*C*), 115.8 (*C*H), 115.6 (*C*H), 115.3 (*C*), 115.3 (*C*H), 114.9(*C*), 114.9 (*C*H), 114.4 (*C*H), 114.3 (*C*H), 114.1 (*C*H), 113.5 (*C*H), 112.5 (*C*H), 112.1 (*C*H), 111.9 (*C*), 111.8 (*C*H), 63.4 (–O*Me*), 63.2 (–CH_2–), 63.1 (–CH_2–), 62.9 (–CH_2–), 62.5 (–CH_2–), 61.5 (–O*Me*), 61.1 (–O*Me*), 61.1 (–O*Me*), 60.9 (–O*Me*), 59.2 (–O*Me*), 51.4 (CH_3), 51.2 (CH_3), 51.0 (CH_3), 50.9 (CH_3), 50.9 (CH_3), 50.7 (CH_3), 50.7 (CH_3), 50.5 (CH_3), 50.4 (CH_3). DOSY-NMR (acetonitrile-d_3/D_2O (1:4 v/v), m^2/s): D = 1.26 ×10^{-10}. IR (ATR, cm^{-1}): 2968, 2886, 2367, 2360, 2343, 2331, 1341, 1044, 811, 719, 656, 627, 560. m.p.: > 155 ºC

(decomposed). HR–MS (ESI): calcd. for $[(C_{36}H_{27}N_3O_6)_8(C_6H_{16}N_2Pd)_{12}(BF_4)_{16}]^{8+}$: 1105.1267, found: 1105.1280.

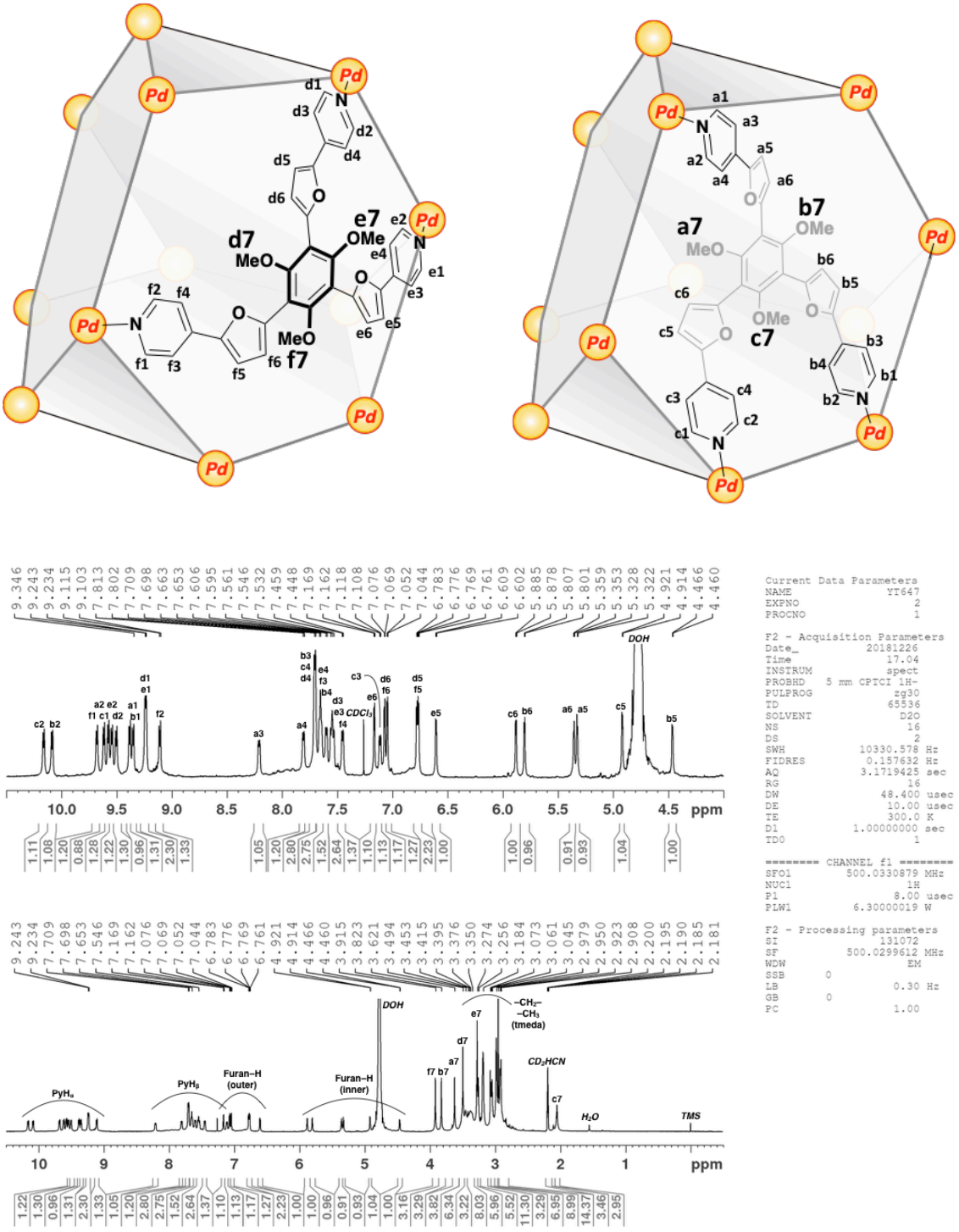



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Figure S6. ^{1}H NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1**.

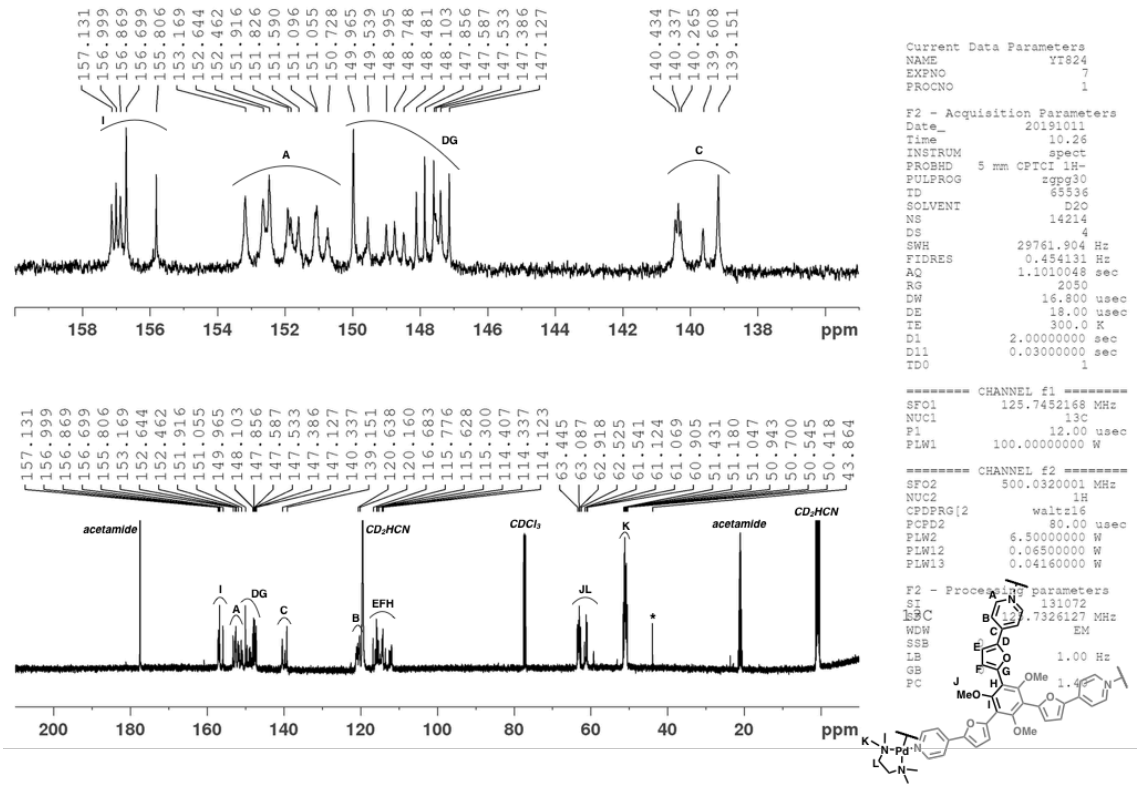


Figure S7. ^{13}C NMR spectrum (125 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1**.

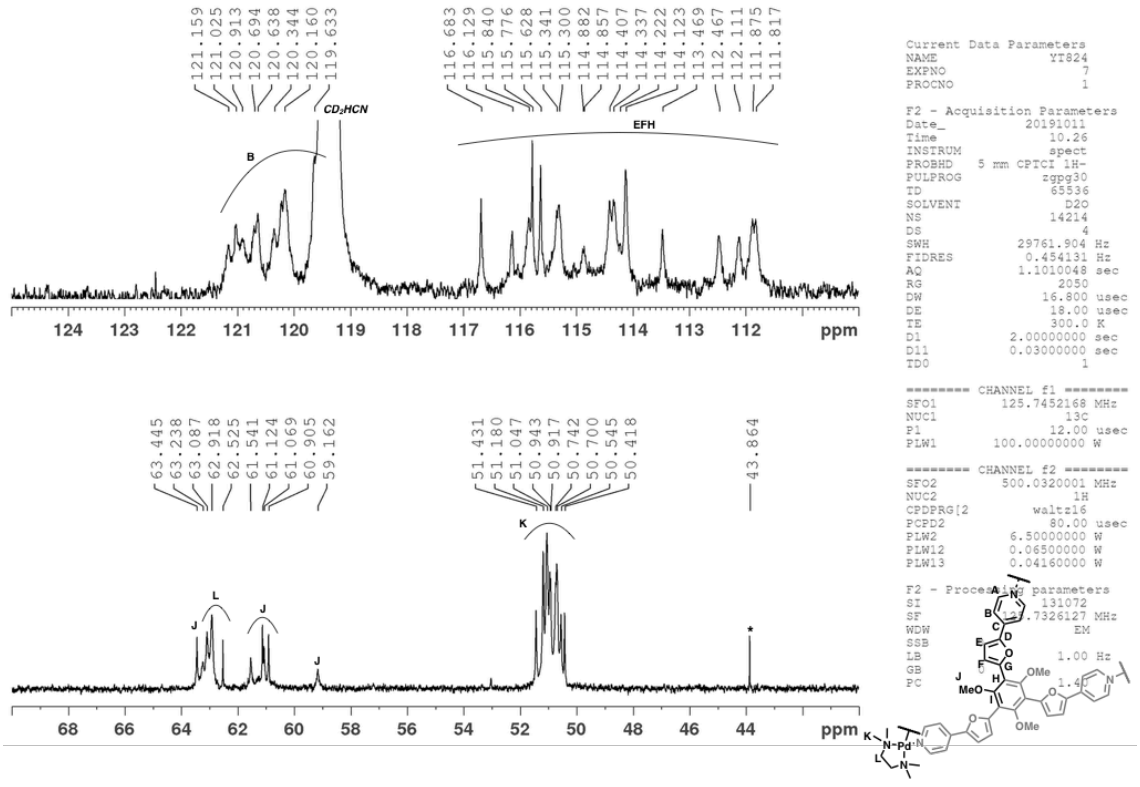


Figure S8. ^{13}C NMR spectrum (125 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1**.

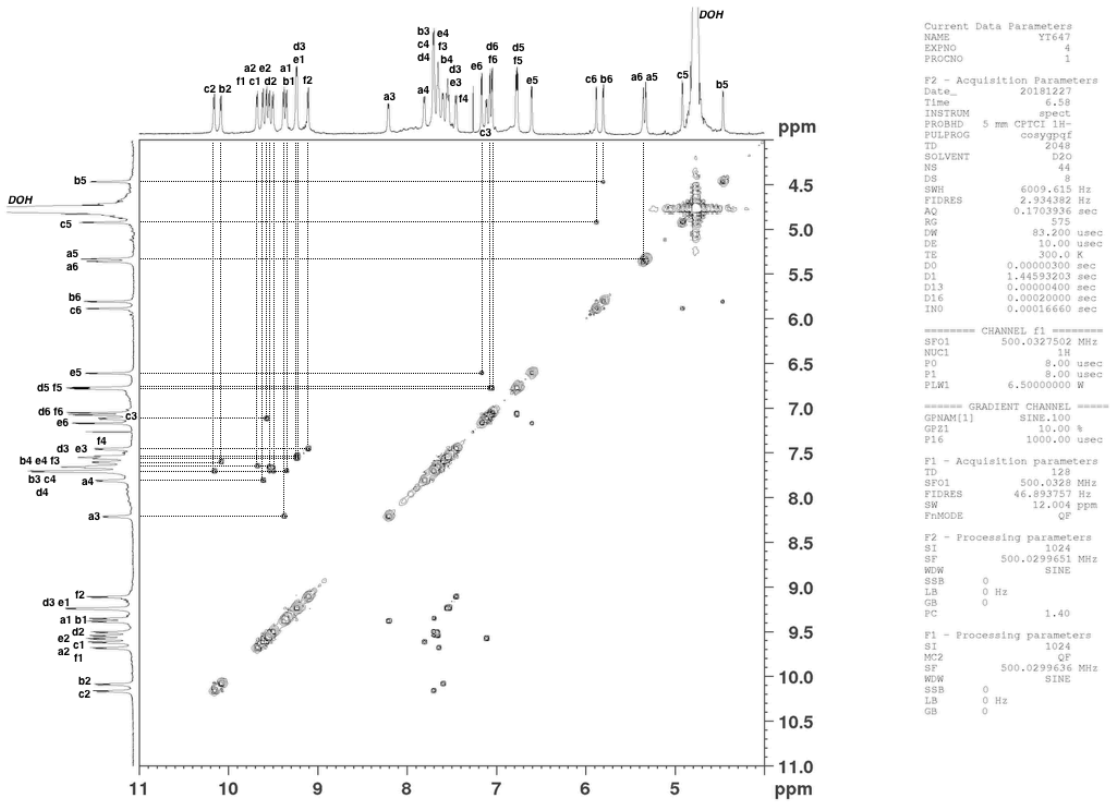


Figure S9. ^{1}H-^{1}H COSY NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1**.

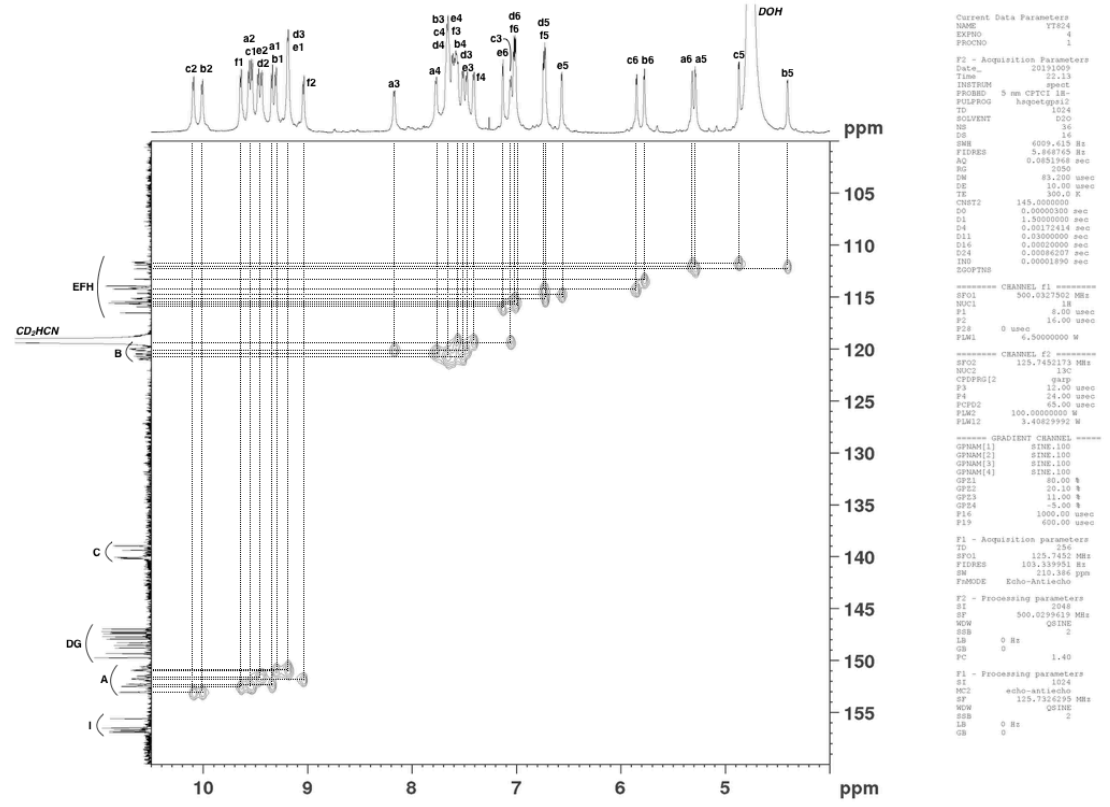


Figure S10. ^{1}H-^{13}C HSQC NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1**.

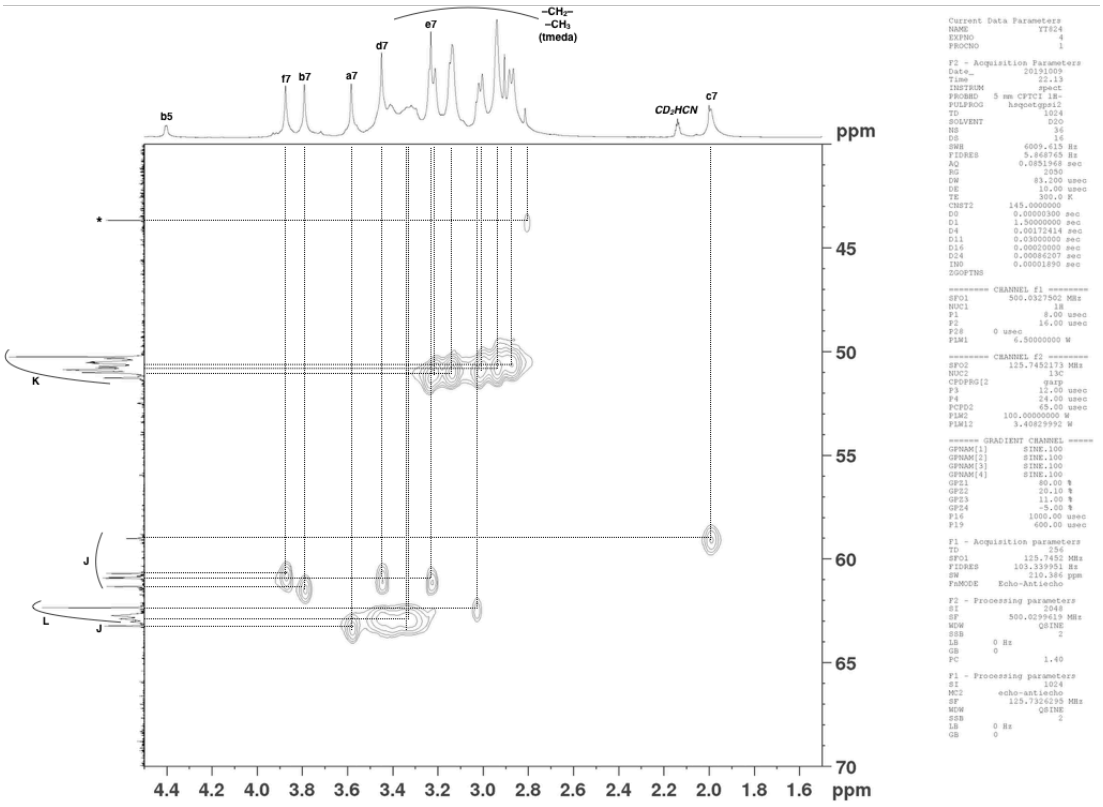


Figure S11. ^{1}H-^{13}C HSQC NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1**.

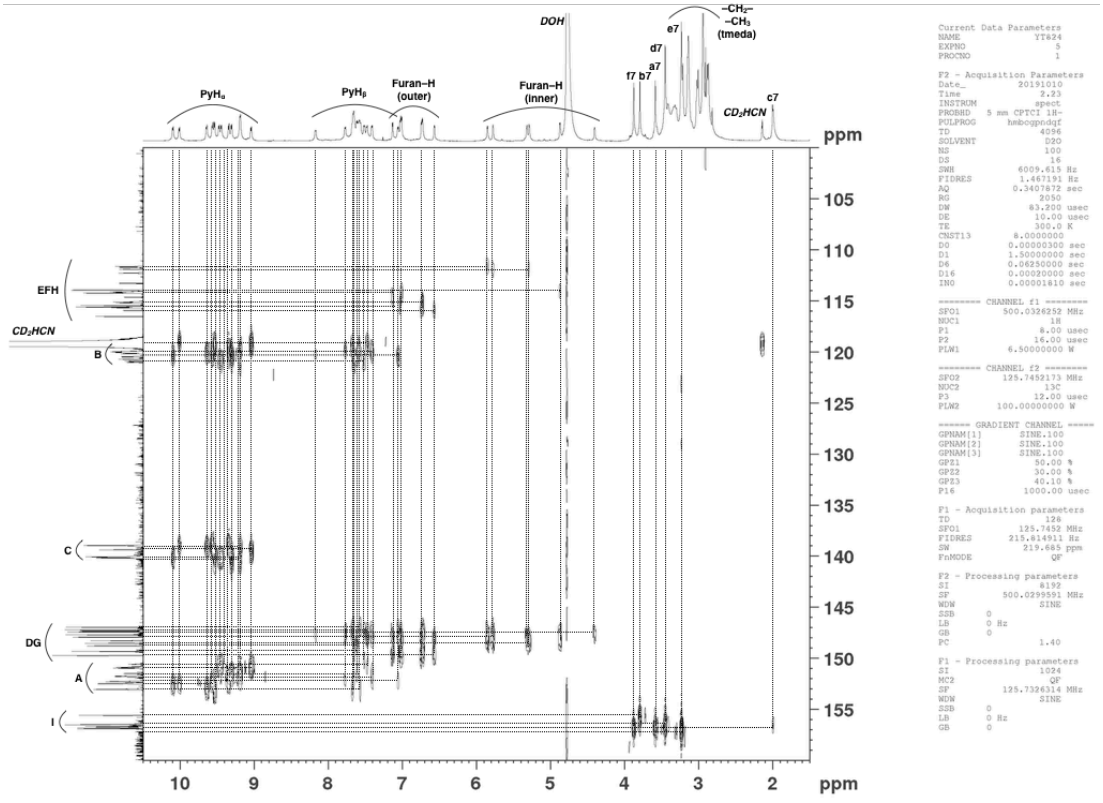


Figure S12. ^{1}H-^{13}C HMBC NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1**.

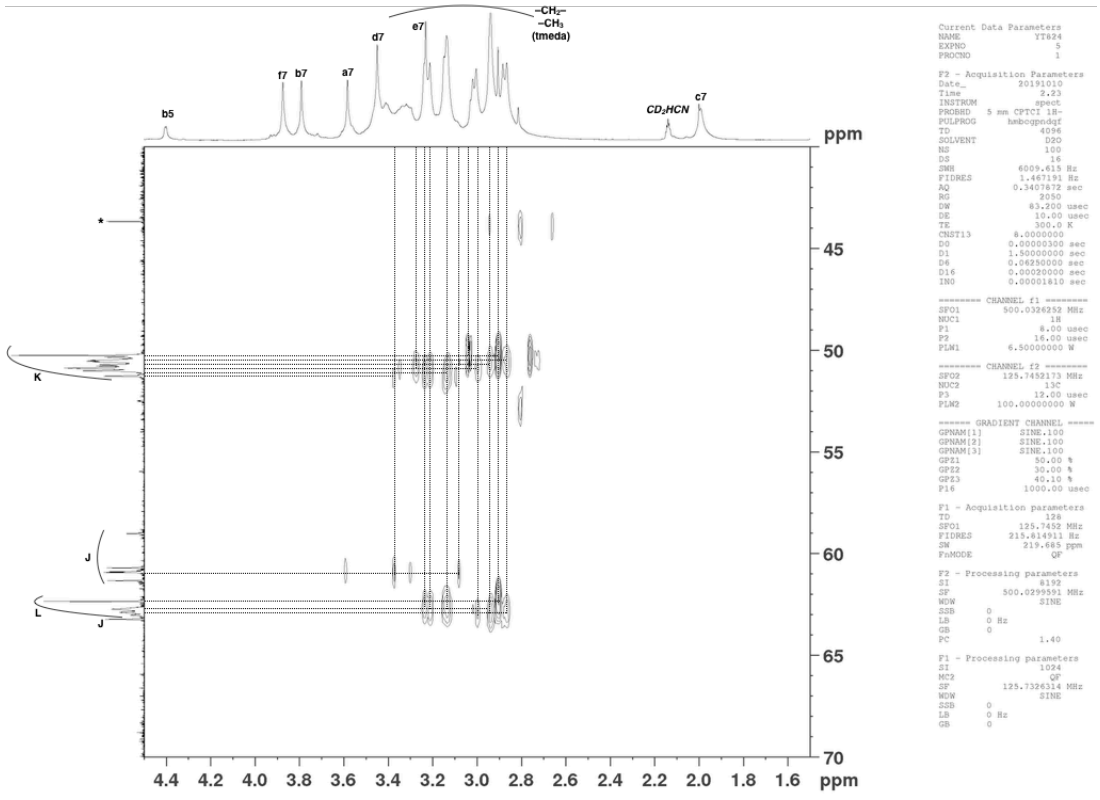


Figure S13. ^{1}H-^{13}C HMBC NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1**.

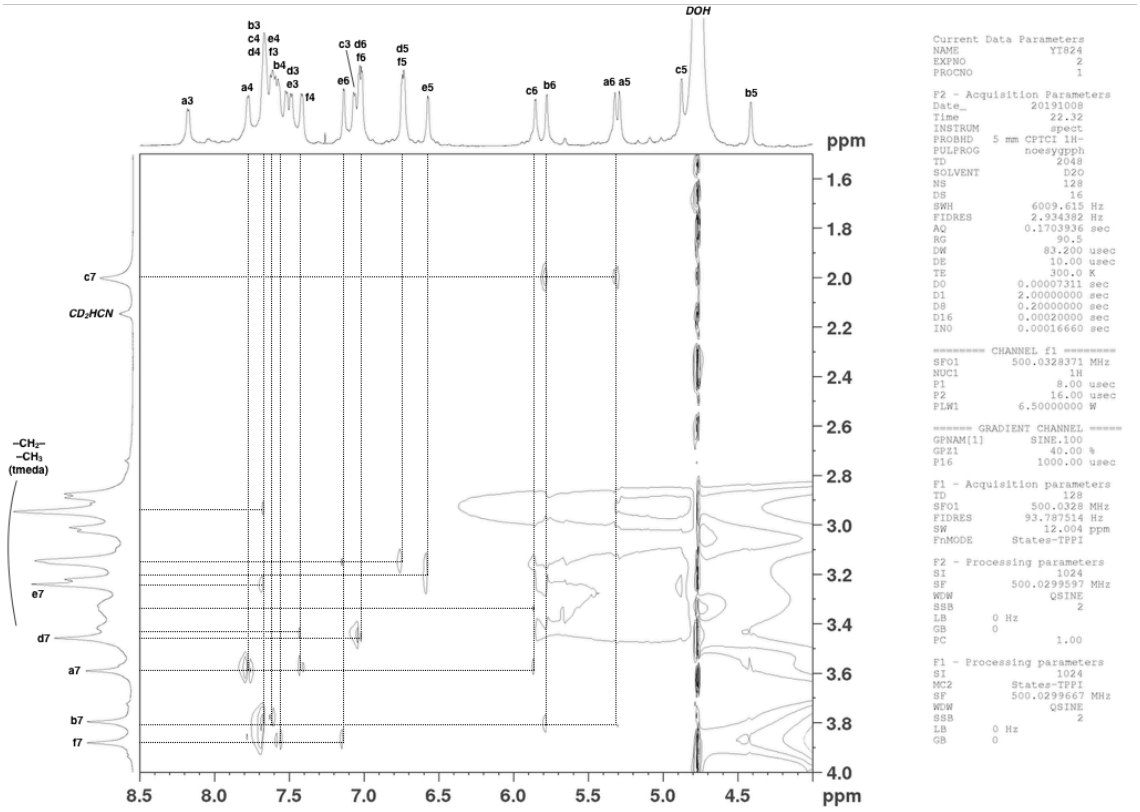


Figure S14. ^{1}H-^{1}H NOESY NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1**.

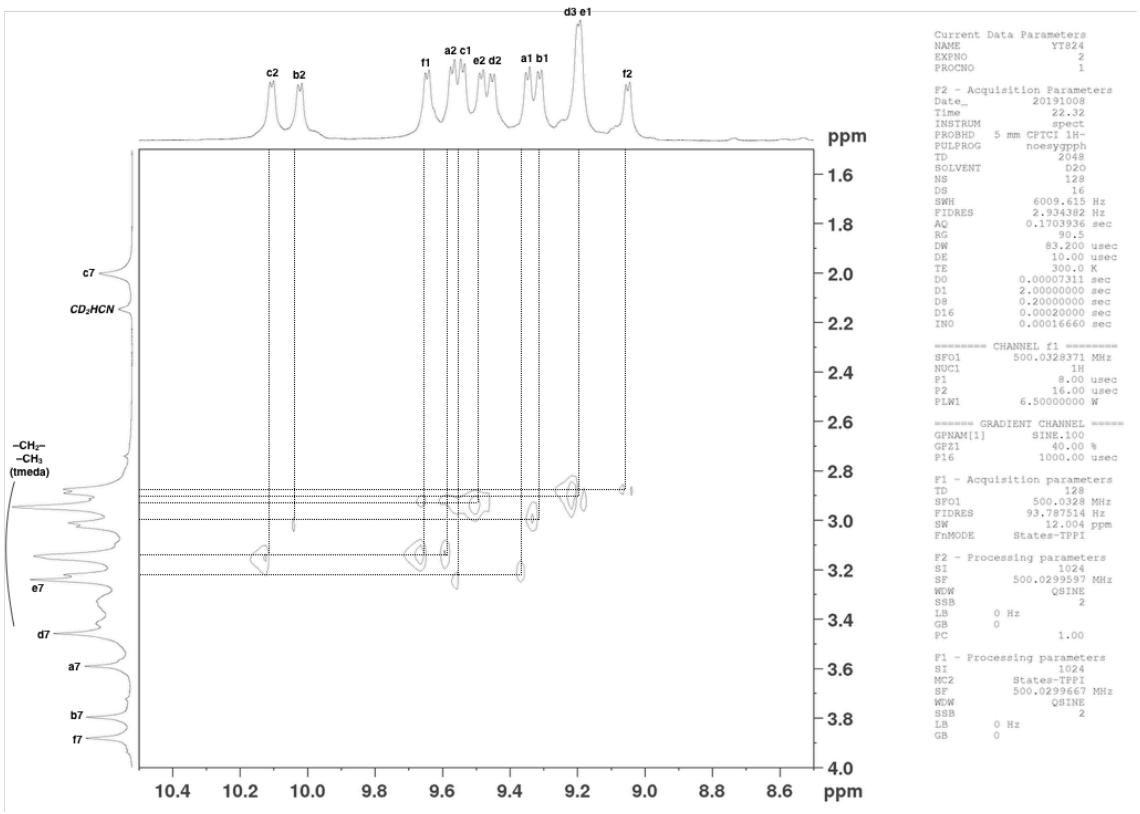


Figure S15. ^{1}H-^{1}H NOESY NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1**.

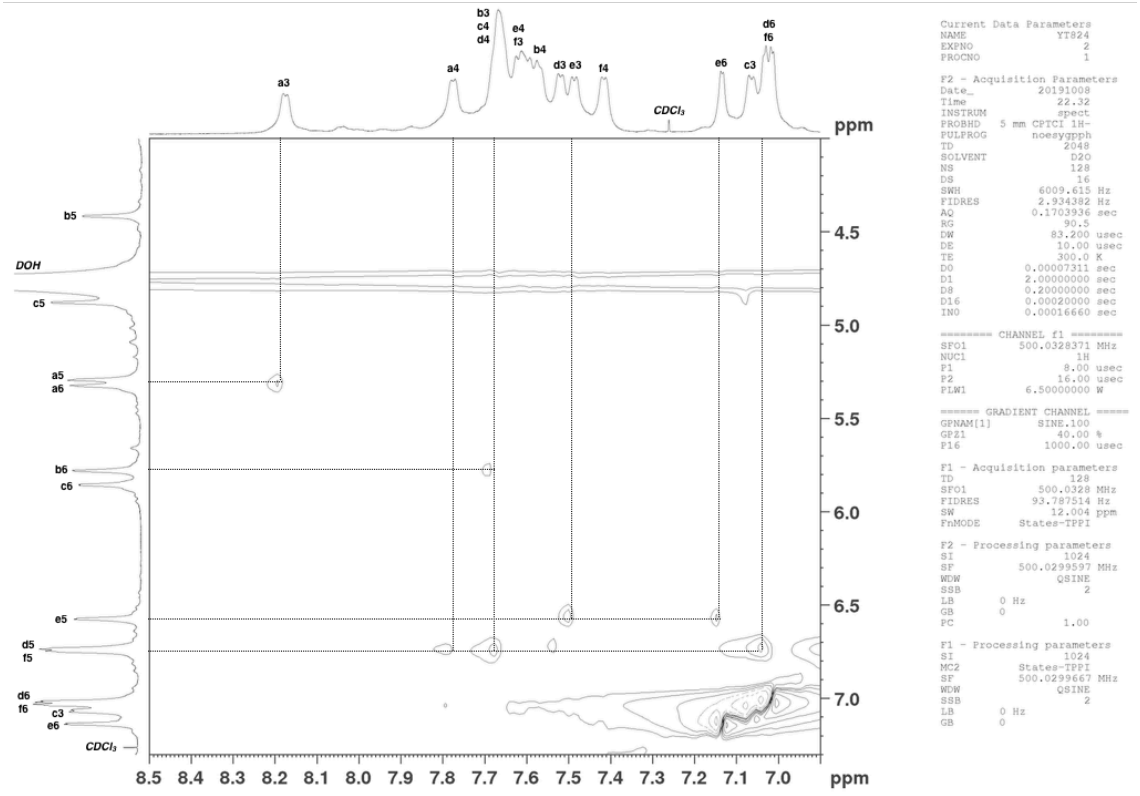


Figure S16. ^{1}H-^{1}H NOESY NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1**.

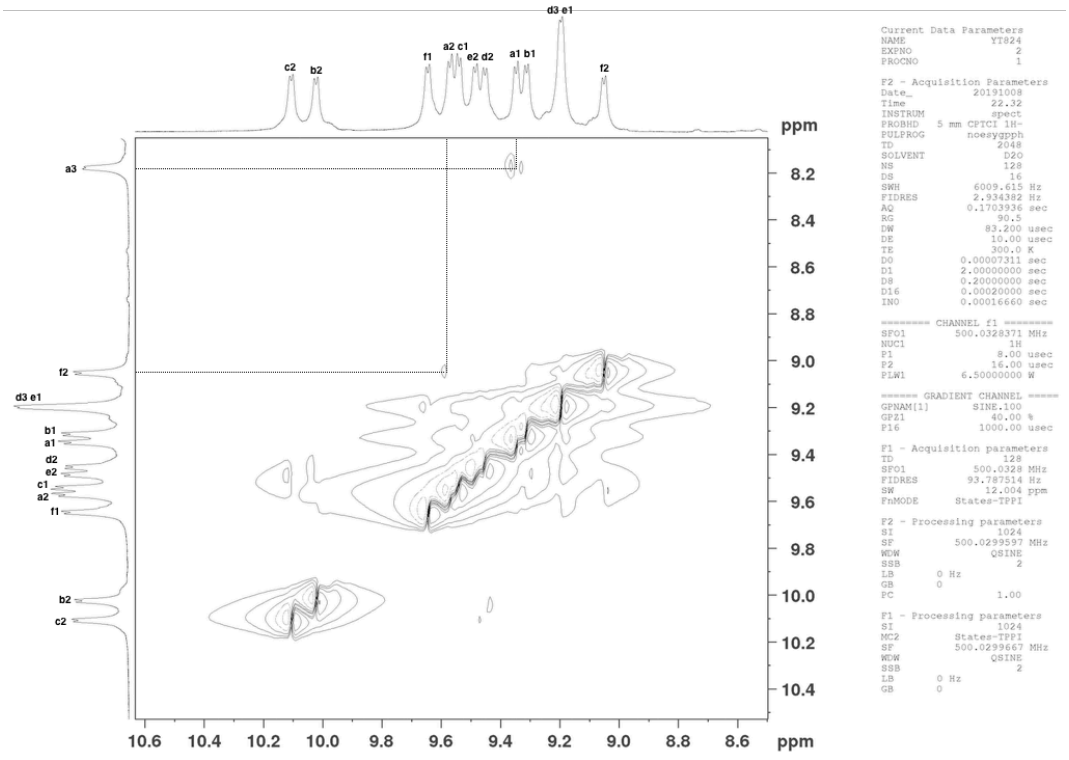


Figure S17. ^{1}H-^{1}H NOESY NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1**.

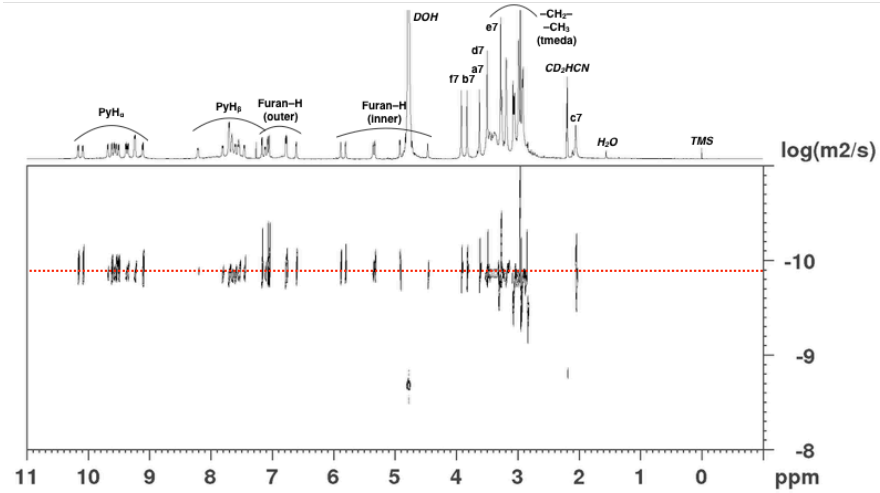


Figure S18. ^{1}H DOSY NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1**.

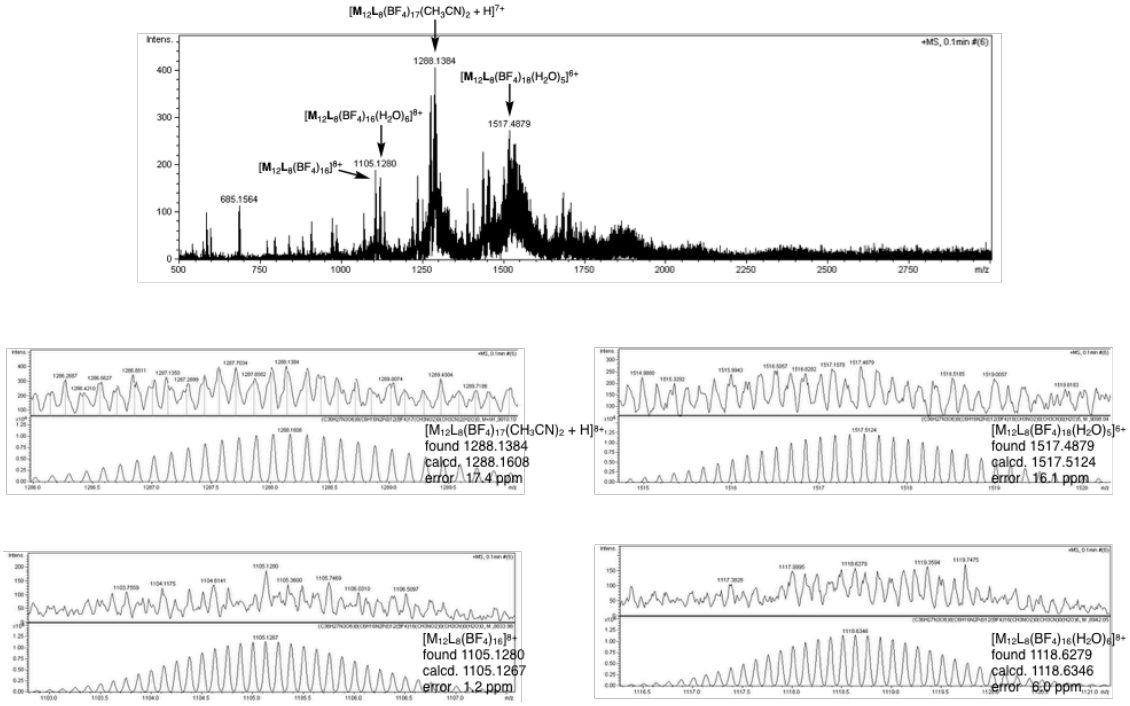
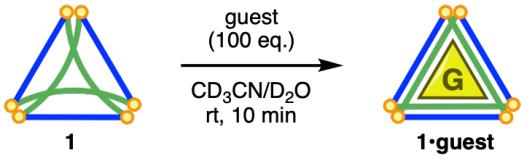


Figure S19. ESI-MS spectra of **1**.

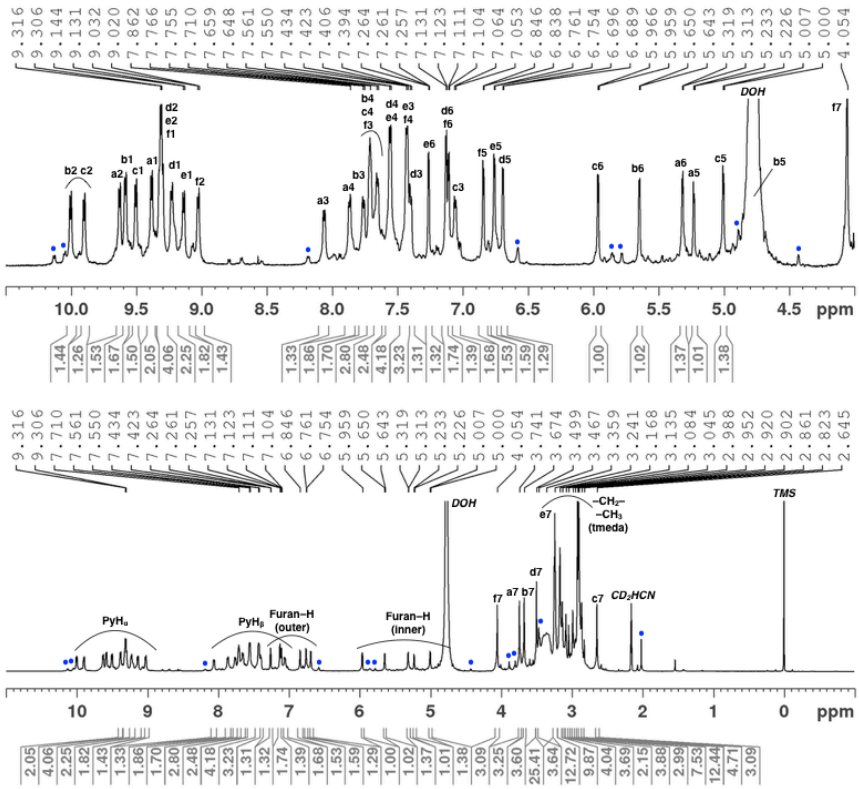
4. Inclusion experiments

General procedure



Dried powder of cage **1** (18.0 mg, 2.0 μmol) was dissolved in acetonitrile-d_3/D_2O (800 μL, 1:4 v/v). Guest molecule (100 eq.) was added to the solution and stirred at room temperature for 10 min. The formation of the inclusion complex was confirmed by ^{1}H NMR spectroscopy. The yields of the inclusion complex were determined by comparison of the integral ratio between the signals from empty cage **1** and the guest included cage **1•G**.

Physical data of 1•CCl_4: ^{1}H NMR (acetonitrile-d_3/D_2O (1:4 v/v), 500 MHz): δ 10.00 (d, J = 6.0 Hz, 4H, Ar*H*), 9.90 (d, J = 6.0 Hz, 4H, Ar*H*), 9.63 (d, J = 6.0 Hz, 4H, Ar*H*), 9.58 (d, J = 5.5 Hz, 4H, Ar*H*), 9.50 (d, J = 5.5 Hz, 4H, Ar*H*), 9.38 (d, J = 6.0 Hz, 4H, Ar*H*), 9.32 (d, J = 5.5 Hz, 8H, Ar*H*), 9.30 (d, J = 5.5 Hz, 4H, Ar*H*), 9.23 (d, J = 6.0 Hz, 4H, Ar*H*), 9.14 (d, J = 6.5 Hz, 4H, Ar*H*), 9.03 (d, J = 6.0 Hz, 4H, Ar*H*), 8.06 (d, J = 5.0 Hz, 4H, Ar*H*), 7.87 (d, J = 5.5 Hz, 4H, Ar*H*), 7.76 (d, J = 5.5 Hz, 4H, Ar*H*), 7.71 (br, 8H, Ar*H*), 7.65 (d, J = 5.5 Hz, 4H, Ar*H*), 7.56 (d, J = 5.5 Hz, 8H, Ar*H*), 7.43 (d, J = 5.5 Hz, 8H, Ar*H*), 7.40 (d, J = 6.0 Hz, 4H, Ar*H*), 7.26 (d, J = 3.5 Hz, 4H, Ar*H*), 7.13 (d, J = 4.0 Hz, 4H, Ar*H*), 7.11 (d, J = 3.5 Hz, 4H, Ar*H*), 7.06 (d, J = 5.5 Hz, 4H, Ar*H*), 6.84 (d, J = 4.0 Hz, 4H, Ar*H*), 6.76 (d, J = 3.5 Hz, 4H, Ar*H*), 6.69 (d, J = 3.5 Hz, 4H, Ar*H*), 5.96 (d, J = 3.5 Hz, 4H, Ar*H*), 5.65 (d, J = 3.5 Hz, 4H, Ar*H*), 5.32 (d, J = 3.0 Hz, 4H, Ar*H*), 5.23 (d, J = 3.5 Hz, 4H, Ar*H*), 5.00 (d, J = 3.5 Hz, 4H, Ar*H*), 4.05 (s, 12H, –O*Me*), 3.74 (s, 12H, –O*Me*), 3.67 (s, 12H, –O*Me*), 3.50 (s, 12H, –O*Me*), 3.50–3.27 (br, 40H, –CH_2–), 3.24 (s, 12H, –O*Me*), 3.24 (s, 12H, CH_3), 3.17 (s, 24H, CH_3), 3.14 (s, 12H, CH_3), 3.01 (s, 12H, CH_3), 3.05 (br, 8H, –CH_2–), 2.99 (s, 12H, CH_3), 2.92 (s, 24H, CH_3), 2.90 (s, 36H, CH_3), 2.86 (s, 12H, CH_3), 2.65 (s, 12H, –O*Me*); ^{13}C NMR (acetonitrile-d_3/D_2O (1:4 v/v), 125 MHz): δ 157.2 (*C*), 157.1 (*C*), 156.8 (*C*), 156.7 (*C*), 156.0 (*C*), 155.1 (*C*), 153.0 (*C*H), 152.7 (*C*H), 152.6 (*C*H), 151.9 (*C*H), 151.7 (*C*H), 151.1 (*C*H), 150.6 (*C*H), 150.2 (*C*), 150.1 (*C*), 150.0 (*C*), 149.9 (*C*), 149.6 (*C*), 149.4 (*C*), 148.0 (*C*), 148.0 (*C*), 147.6 (*C*), 147.2 (*C*), 147.2 (*C*), 147.1 (*C*), 140.6 (*C*), 140.1 (*C*), 139.9 (*C*), 139.3 (*C*), 139.2 (*C*), 120.9 (*C*H), 120.7 (*C*H), 120.3 (*C*H), 120.2 (*C*H), 119.9 (*C*H), 116.4 (*C*), 116.2 (*C*H), 116.0 (*C*), 115.8 (*C*H), 115.7 (*C*), 115.6 (*C*H), 115.4 (*C*H), 115.0 (*C*), 114.8 (*C*H), 114.6 (*C*H), 114.5 (*C*), 113.3 (*C*H), 112.5 (*C*H), 112.0 (*C*H), 111.8 (*C*H), 96.5 (*C*Cl_4), 95.7 (*C*Cl_4), 63.4 (–O*Me*), 63.1 (–CH_2–), 62.9 (–CH_2–), 62.6 (–CH_2–), 61.1 (–O*Me*), 61.0 (–O*Me*), 60.8 (–O*Me*), 51.5 (CH_3), 51.2(CH_3), 51.1 (CH_3), 51.1 (CH_3), 51.0 (CH_3), 50.8 (CH_3), 50.7 (CH_3), 50.6 (CH_3), 50.5 (CH_3).



Current Data Parameters
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PROCNO 1

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TD 65536
SOLVENT D2O
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 16
DW 48.400 usec
DE 10.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

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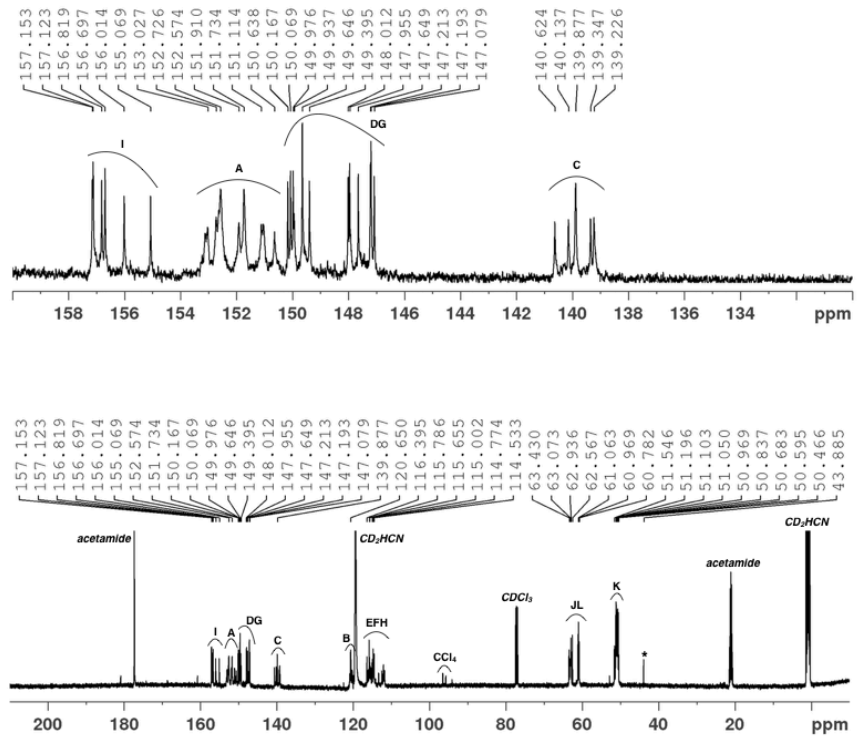
NUC1 1H
P1 8.00 usec
PLW1 6.30000019 W

F2 - Processing parameters
SI 131072
SF 500.0299601 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure S20. ^{1}H NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1•CCl$_4$**.



Current Data Parameters
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EXPNO 6
PROCNO 1

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INSTRUM spect
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PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 20000
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 1820
DW 16.800 usec
DE 18.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 125.7452168 MHz
NUC1 13C
P1 12.00 usec
PLW1 100.00000000 W

======== CHANNEL f2 ========
SFO2 500.0320001 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 6.50000000 W
PLW12 0.06500000 W
PLW13 0.04160000 W

F2 - Processing parameters
SI 131072
SF 125.7326130 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure S21. ^{13}C NMR spectrum (125 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1•CCl$_4$**.

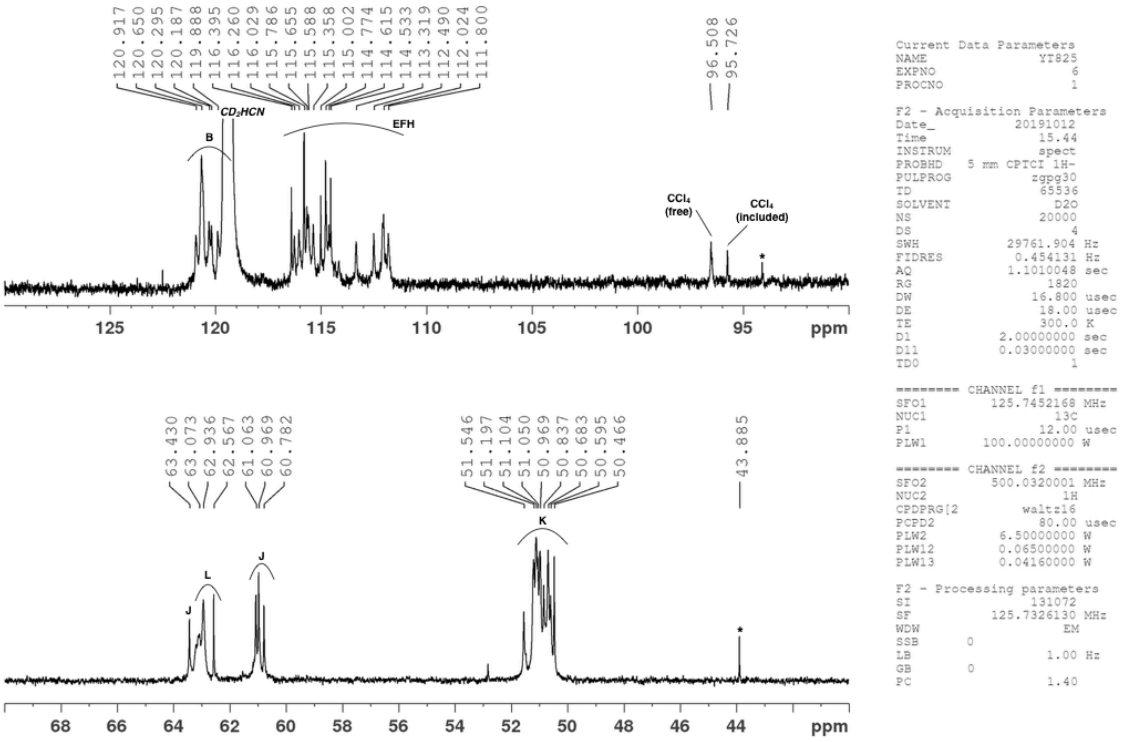


Figure S22. ^{13}C NMR spectrum (125 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1•CCl$_4$**.

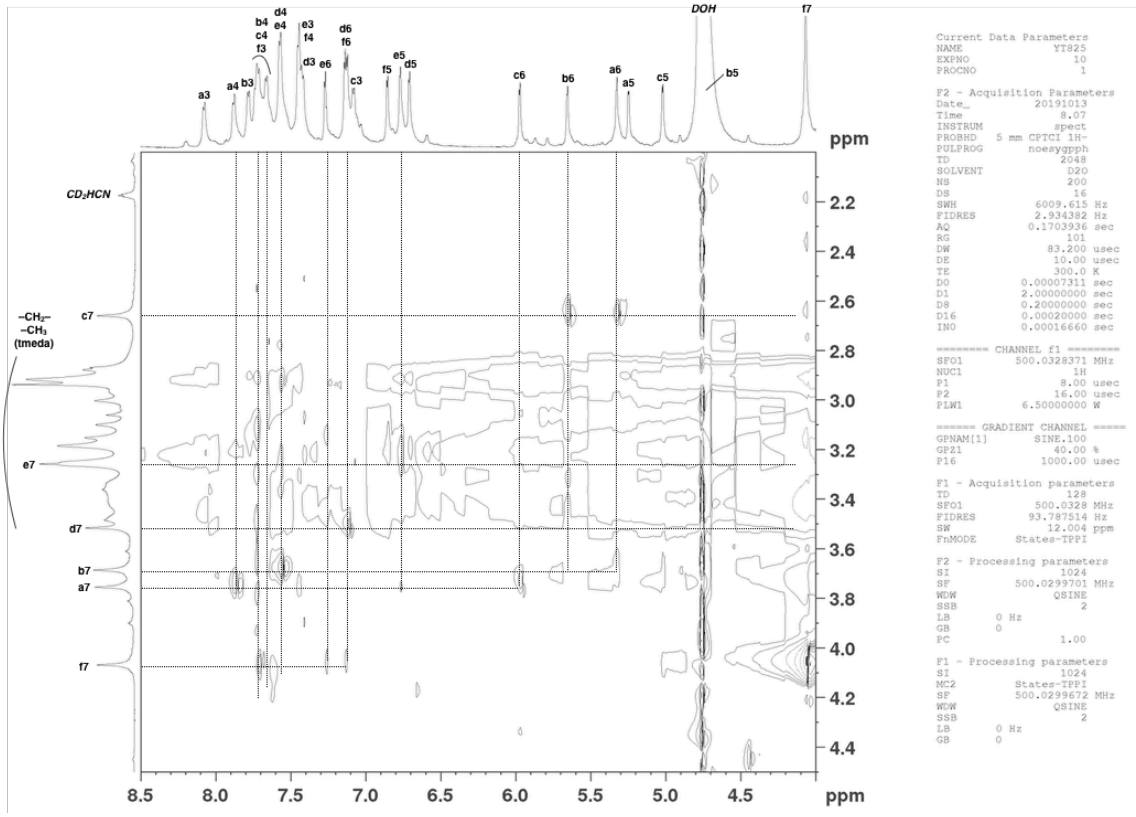
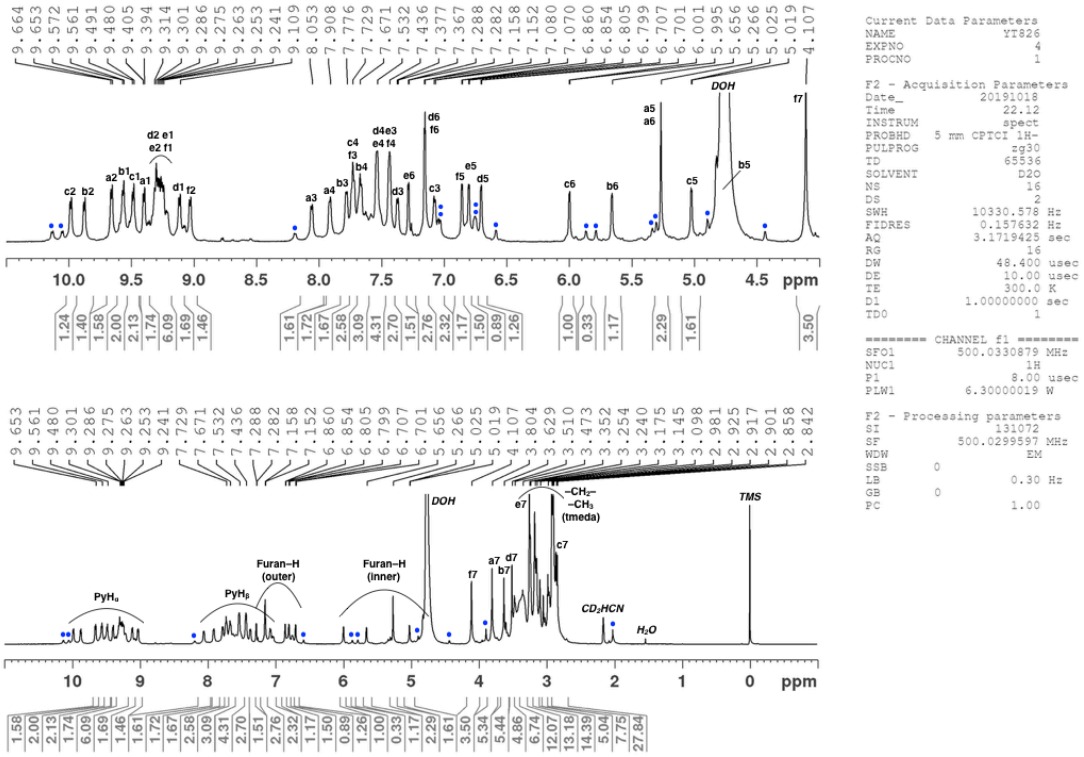


Figure S23. ^{1}H-^{1}H NOESY NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1•CCl$_4$**.

Physical data of 1•CBr_4: ^{1}H NMR (acetonitrile-d_3/D_2O (1:4 v/v), 500 MHz): δ 9.98 (d, J = 6.0 Hz, 4H, Ar*H*), 9.87 (d, J = 6.0 Hz, 4H, Ar*H*), 9.65 (d, J = 6.0 Hz, 4H, Ar*H*), 9.56 (d, J = 5.5 Hz, 4H, Ar*H*), 9.48 (d, J = 5.5 Hz, 4H, Ar*H*), 9.39 (d, J = 5.5 Hz, 4H, Ar*H*), 9.30 (d, J = 6.0 Hz, 4H, Ar*H*), 9.29 (d, J = 6.0 Hz, 4H, Ar*H*), 9.26 (d, J = 6.0 Hz, 4H, Ar*H*), 9.24 (d, J = 6.0 Hz, 4H, Ar*H*), 9.11 (d, J = 6.0 Hz, 4H, Ar*H*), 9.02 (d, J = 6.0 Hz, 4H, Ar*H*), 8.05 (d, J = 5.0 Hz, 4H, Ar*H*), 7.90 (d, J = 6.0 Hz, 4H, Ar*H*), 7.77 (d, J = 5.0 Hz, 4H, Ar*H*), 7.72 (d, J = 6.0 Hz, 4H, Ar*H*), 7.72 (d, J = 6.0 Hz, 4H, Ar*H*), 7.71 (d, J = 6.0 Hz, 4H, Ar*H*), 7.53 (d, J = 5.0 Hz, 8H, Ar*H*), 7.43 (d, J = 4.5 Hz, 8H, Ar*H*), 7.36 (d, J = 5.5 Hz, 4H, Ar*H*), 7.28 (d, J = 3.0 Hz, 4H, Ar*H*), 7.15 (d, J = 3.5 Hz, 8H, Ar*H*), 7.06 (d, J = 5.5 Hz, 4H, Ar*H*), 6.85 (d, J = 3.5 Hz, 4H, Ar*H*), 6.79 (d, J = 3.0 Hz, 4H, Ar*H*), 6.69 (d, J = 3.5 Hz, 4H, Ar*H*), 5.99 (d, J = 3.0 Hz, 4H, Ar*H*), 5.65 (d, J = 3.0 Hz, 4H, Ar*H*), 5.26 (s, 8H, Ar*H*), 5.01 (d, J = 3.5 Hz, 4H, Ar*H*), 4.10 (s, 12H, –O*Me*), 3.80 (s, 12H, –O*Me*), 3.62 (s, 12H, –O*Me*), 3.50 (s, 12H, –O*Me*), 3.48–3.27 (br, 40H, –CH_2–), 3.24 (s, 12H, –O*Me*), 3.23 (s, 12H, CH_3), 3.17 (s, 24H, CH_3), 3.14 (s, 12H, CH_3), 3.09 (s, 12H, CH_3), 3.04 (br, 8H, –CH_2–), 2.97 (s, 12H, CH_3), 2.92 (s, 24H, CH_3), 2.91 (s, 12H, CH_3), 2.89 (s, 24H, CH_3), 2.85 (s, 12H, CH_3), 2.83 (s, 12H, –O*Me*); ^{13}C NMR (acetonitrile-d_3/D_2O (1:4 v/v), 125 MHz): δ 157.1 (*C*), 156.8 (*C*), 156.7 (*C*), 156.1 (*C*), 154.8 (*C*), 153.0 (*C*H), 152.8 (*C*H), 152.6 (*C*H), 152.5 (*C*H), 151.9 (*C*H), 151.7 (*C*H), 151.1 (*C*H), 150.2 (*C*), 150.1 (*C*), 150.0 (*C*), 149.9 (*C*), 147.9 (*C*), 147.7 (*C*), 147.2 (*C*), 147.1 (*C*), 146.9 (*C*), 140.6 (*C*), 140.1 (*C*), 140.0 (*C*), 139.7 (*C*), 139.4 (*C*), 139.3 (*C*), 120.7 (*C*H), 120.5 (*C*H), 120.4 (*C*H), 120.4 (*C*H), 120.2 (*C*H), 119.8 (*C*H), 116.5 (*C*), 116.2 (*C*H), 116.0 (*C*H), 115.8 (*C*H), 115.7 (*C*), 115.5 (*C*H), 115.3(*C*), 115.1 (*C*), 114.8 (*C*H), 114.6 (*C*H), 113.3 (*C*H), 112.4 (*C*), 112.0 (*C*H), 111.8 (*C*), 63.4 (–O*Me*), 63.2 (–O*Me*), 63.1 (–O*Me*), 62.9 (–O*Me*), 62.6 (–O*Me*), 61.2 (–O*Me*), 61.1(–O*Me*), 61.0(–O*Me*), 61.0(–O*Me*), 60.9 (–O*Me*), 60.8 (–O*Me*), 51.5 (*C*H_3), 51.2 (*C*H_3), 51.1 (*C*H_3), 51.0 (*C*H_3), 50.9 (*C*H_3), 50.9 (*C*H_3), 50.7 (*C*H_3), 50.6 (*C*H_3), 50.5 (*C*H_3), –27.5 (*C*Br_4), –32.5 (*C*Br_4).

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PROCNO                    1

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TD                   65536
SOLVENT                D2o
NS                       16
DS                        2
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1719425 sec
RG                       16
DW                  48.400 usec
DE                  10.00 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
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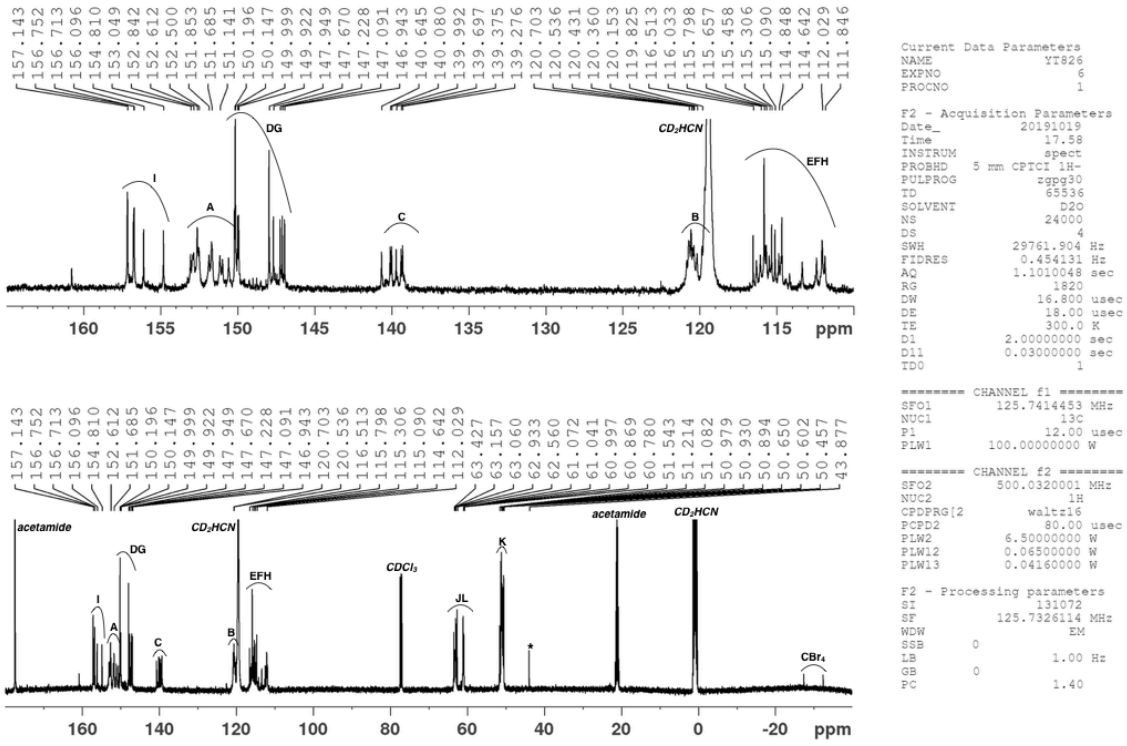
NUC1                     1H
P1                    8.00 usec
PLW1           6.30000019 W

F2 - Processing parameters
SI                   131072
SF             500.0299597 MHz
WDW                      EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

Figure S24. ^{1}H NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1•CBr$_4$** (signals from empty cage **1** are denoted by blue dots).

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EXPNO                     6
PROCNO                    1

F2 - Acquisition Parameters
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INSTRUM              spect
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PULPROG             zgpg30
TD                   65536
SOLVENT                D2O
NS                   24000
DS                        4
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ               1.1010048 sec
RG                     1820
DW                  16.800 usec
DE                  18.00 usec
TE                  300.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1          125.7414453 MHz
NUC1                     13C
P1                   12.00 usec
PLW1         100.00000000 W

======== CHANNEL f2 ========
SFO2          500.0320001 MHz
NUC2                     1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2            6.50000000 W
PLW12           0.06500000 W
PLW13           0.04160000 W

F2 - Processing parameters
SI                   131072
SF            125.7326114 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

Figure 25. ^{13}C NMR spectrum (125 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1•CBr$_4$** (a signal from impurity is denoted by an asterisk).

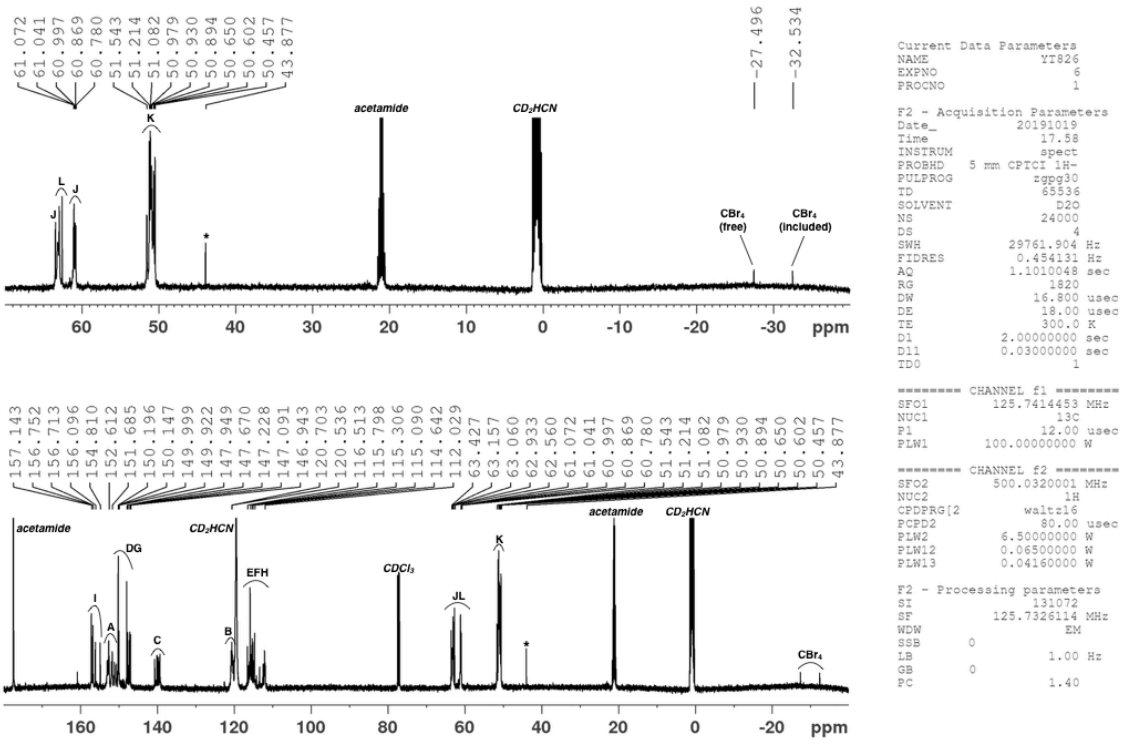


Figure S26. ^{13}C NMR spectrum (125 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1•CBr$_4$** (a signal from impurity is denoted by an asterisk).

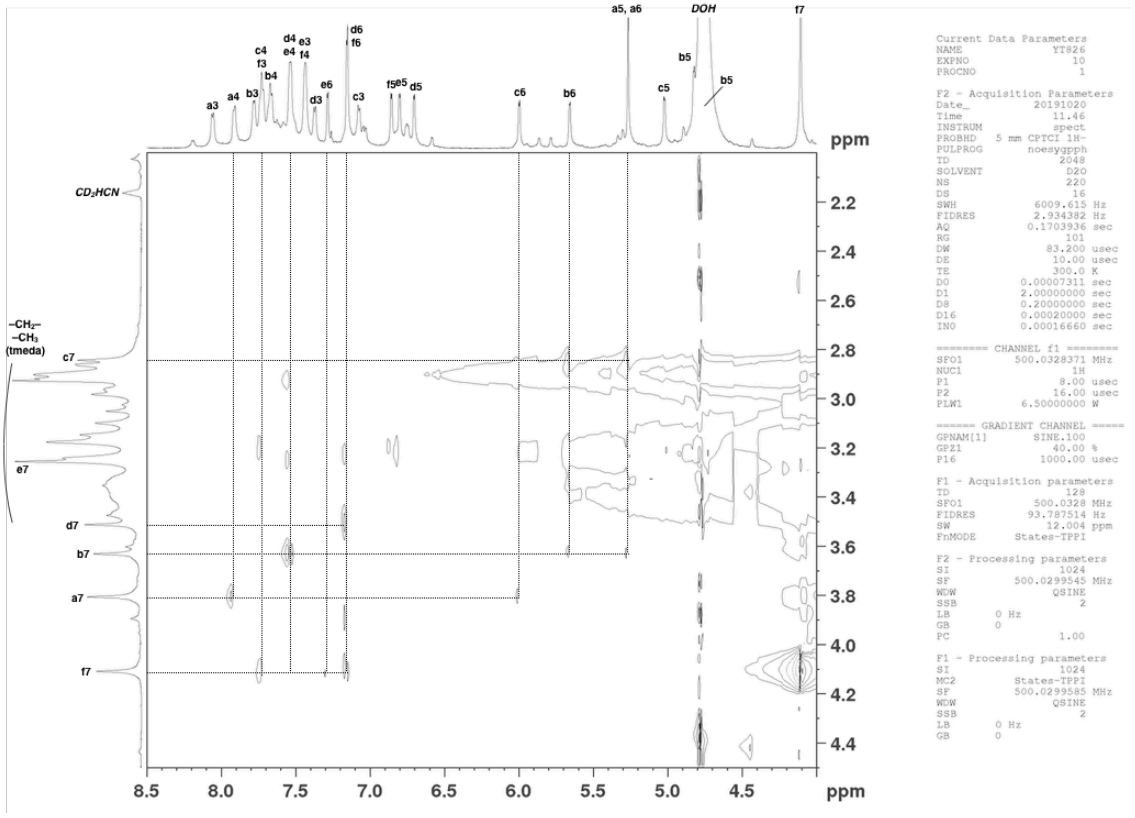


Figure S27. ^{1}H-^{1}H NOESY NMR spectrum (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of **1•CBr$_4$**.

Physical data of 1•$CHBr_3$: ^{1}H NMR (acetonitrile-d_3/D_2O (1:4 v/v), 500 MHz): δ 10.05 (d, J = 5.0 Hz, 4H, Ar*H*), 9.97 (d, J = 5.0 Hz, 4H, Ar*H*), 9.63 (d, J = 6.0 Hz, 4H, Ar*H*), 9.61 (d, J = 5.0 Hz, 4H, Ar*H*), 9.52 (d, J = 5.5 Hz, 4H, Ar*H*), 9.41 (d, J = 6.0 Hz, 4H, Ar*H*), 9.39 (d, J = 5.5 Hz, 4H, Ar*H*), 9.38 (d, J = 5.0 Hz, 4H, Ar*H*), 9.30 (d, J = 5.5 Hz, 4H, Ar*H*), 9.26 (d, J = 6.0 Hz, 4H, Ar*H*), 9.16 (d, J = 5.5 Hz, 4H, Ar*H*), 9.08 (d, J = 5.0 Hz, 4H, Ar*H*), 8.06 (d, J = 5.0 Hz, 4H, Ar*H*), 7.86 (d, J = 5.5 Hz, 4H, Ar*H*), 7.78 (d, J = 4.5 Hz, 4H, Ar*H*), 7.71 (d, J = 5.5 Hz, 4H, Ar*H*), 7.69 (d, J = 5.0 Hz, 4H, Ar*H*), 7.63 (d, J = 5.5 Hz, 4H, Ar*H*), 7.59 (br, 8H, Ar*H*), 7.51 (d, J = 5.5 Hz, 4H, Ar*H*), 7.45 (d, J = 6.0 Hz, 4H, Ar*H*), 7.43 (d, J = 6.0 Hz, 4H, Ar*H*), 7.21 (br, 4H, Ar*H*), 7.11 (br, 12H, Ar*H*), 6.82 (d, J = 3.0 Hz, 4H, Ar*H*), 6.74 (d, J = 3.0 Hz, 4H, Ar*H*), 6.73 (d, J = 3.0 Hz, 4H, Ar*H*), 5.94 (br, 4H, Ar*H*), 5.72 (br, 4H, Ar*H*), 5.36 (br, 4H, Ar*H*), 5.21 (br, 4H, Ar*H*), 4.98 (br, 4H, Ar*H*), 4.07 (s, 12H, –O*Me*), 3.72 (s, 12H, –O*Me*), 3.71 (s, 12H, –O*Me*), 3.50 (s, 12H, –O*Me*), 3.48–3.30 (br, 40H, –CH_2–), 3.27 (s, 12H, –O*Me*), 3.23 (s, 12H, CH_3), 3.16 (s, 24H, CH_3), 3.14 (s, 12H, CH_3), 3.07 (s, 12H, CH_3), 3.04 (s, 12H, CH_3), 2.99 (br, 8H, –CH_2–), 2.92 (s, 24H, CH_3), 2.91 (s, 24H, CH_3), 2.88 (s, 24H, CH_3), 2.58 (s, 12H, –O*Me*).

Physical data of 1•CH_2I_2: ^{1}H NMR (acetonitrile-d_3/D_2O (1:4 v/v), 500 MHz): δ 9.98 (d, J = 5.5 Hz, 4H, Ar*H*), 9.91 (d, J = 5.5 Hz, 4H, Ar*H*), 9.59 (d, J = 5.5 Hz, 8H, Ar*H*), 9.54 (d, J = 5.5 Hz, 4H, Ar*H*), 9.52 (d, J = 5.0 Hz, 4H, Ar*H*), 9.35 (br, 4H, Ar*H*), 9.33 (d, J = 6.0 Hz, 4H, Ar*H*), 9.26 (d, J = 6.0 Hz, 4H, Ar*H*), 9.23 (d, J = 5.5 Hz, 4H, Ar*H*), 9.12 (d, J = 6.0 Hz, 4H, Ar*H*), 9.02 (d, J = 5.5 Hz, 4H, Ar*H*), 8.03 (d, J = 5.0 Hz, 4H, Ar*H*), 7.83 (d, J = 5.5 Hz, 4H, Ar*H*), 7.76 (d, J = 6.0 Hz, 4H, Ar*H*), 7.34 (br, 4H, Ar*H*), 7.64 (br, 8H, Ar*H*), 7.56 (br, 12H, Ar*H*), 7.40 (br, 8H, Ar*H*), 7.16 (br, 4H, Ar*H*), 7.08 (br, 12H, Ar*H*), 6.78 (br, 4H, Ar*H*), 6.73 (br, 4H, Ar*H*), 6.69 (br, 4H, Ar*H*), 5.88 (br, 4H, Ar*H*), 5.73 (br, 4H, Ar*H*), 5.34 (br, 4H, Ar*H*), 5.17 (br, 4H, Ar*H*), 4.24 (br, 4H, Ar*H*), 4.05 (br, 4H, Ar*H*), 3.98 (s, 12H, –O*Me*), 3.72 (s, 12H, –O*Me*), 3.69 (s, 12H, –O*Me*), 3.41–3.26 (br, 40H, –CH_2–), 3.22 (s, 12H, CH_3), 3.20 (s, 12H, CH_3), 3.13 (s, 24H, CH_3), 3.04 (s, 12H, CH_3), 2.99 (br, 8H, –CH_2–), 2.97 (s, 12H, CH_3), 2.93 (s, 12H, CH_3), 2.89 (s, 36H, CH_3), 2.85 (s, 24H, CH_3), 2.46 (s, 12H, –O*Me*).

Inclusion of $CHCl_3$, $(CHCl_2)_2$, and trimethylsilyl acetylene (TMSA) were carried out with 1.25 mM solution of **1** in acetonitrile-d_3/D_2O (800 μL, 1:4 v/v).

Physical data of 1•$CHCl_3$: ^{1}H NMR (acetonitrile-d_3/D_2O (1:4 v/v), 500 MHz): δ 10.14 (br, 4H, Ar*H*), 10.07 (br, 4H, Ar*H*), 9.65 (d, J = 5.0 Hz, 8H, Ar*H*), 9.56 (d, J = 5.0 Hz, 4H, Ar*H*), 9.50 (br, 4H, Ar*H*), 9.46 (br, 4H, Ar*H*), 9.40 (d, J = 5.0 Hz, 4H, Ar*H*), 9.35 (d, J = 5.0 Hz, 4H, Ar*H*), 9.27 (d, J = 5.0 Hz, 4H, Ar*H*), 9.22 (br, 4H, Ar*H*), 9.12 (d, J = 5.5 Hz, 4H, Ar*H*), 8.14 (br, 4H, Ar*H*), 7.74 (br, 8H, Ar*H*), 7.69 (br, 12H, Ar*H*), 7.64 (br, 8H, Ar*H*), 7.55 (br, 4H, Ar*H*), 7.50 (br, 4H, Ar*H*), 7.46 (br, 4H, Ar*H*), 7.29 (br, 4H, Ar*H*),

7.20 (br, 4H, Ar*H*), 7.14 (d, *J* = 6.5 Hz, 4H, Ar*H*), 7.10 (br, 4H, Ar*H*), 6.97 (br, 4H, Ar*H*), 5.93 (br, 4H, Ar*H*), 5.75 (br, 4H, Ar*H*), 5.37 (br, 4H, Ar*H*), 5.28 (br, 4H, Ar*H*), 4.99 (br, 4H, Ar*H*), 4.42 (br, 4H, Ar*H*), 3.99 (s, 12H, –O*Me*), 3.77 (s, 12H, –O*Me*), 3.68 (s, 12H, –O*Me*), 3.47–3.32 (br, 40H, –CH_2–), 3.30 (s, 12H, –O*Me*), 3.28 (s, 12H, CH_3), 3.27 (s, 12H, CH_3), 3.19 (br, 24H, CH_3), 3.03 (s, 12H, CH_3), 2.99 (br, 8H, –CH_2–), 2.83 (s, 36H, CH_3), 2.47 (br, 12H, –O*Me*).

Physical data of 1•($CHCl_2$)$_2$: ^{1}H NMR (acetonitrile-d_3/D_2O (1:4 v/v), 500 MHz): δ 10.02 (d, *J* = 6.0 Hz, 4H, Ar*H*), 9.94 (d, *J* = 6.0 Hz, 4H, Ar*H*), 9.65 (d, *J* = 6.0 Hz, 8H, Ar*H*), 9.59 (d, *J* = 6.0 Hz, 8H, Ar*H*), 9.51 (d, *J* = 6.5 Hz, 4H, Ar*H*), 9.40 (d, *J* = 6.0 Hz, 4H, Ar*H*), 9.30 (d, *J* = 5.5 Hz, 4H, Ar*H*), 9.27 (d, *J* = 5.5 Hz, 4H, Ar*H*), 9.14 (d, *J* = 6.0 Hz, 4H, Ar*H*), 9.08 (d, *J* = 5.5 Hz, 4H, Ar*H*), 8.05 (d, *J* = 5.0 Hz, 4H, Ar*H*), 7.89 (d, *J* = 5.5 Hz, 4H, Ar*H*), 7.80 (d, *J* = 6.5 Hz, 4H, Ar*H*), 7.71 (d, *J* = 6.0 Hz, 8H, Ar*H*), 7.56 (br, 12H, Ar*H*), 7.50 (d, *J* = 5.0 Hz, 4H, Ar*H*), 7.45 (d, *J* = 6.0 Hz, 4H, Ar*H*), 7.40 (d, *J* = 5.5 Hz, 4H, Ar*H*), 7.22 (d, *J* = 3.5 Hz, 4H, Ar*H*), 7.13 (d, *J* = 3.0 Hz, 12H, Ar*H*), 6.82 (d, *J* = 3.5 Hz, 4H, Ar*H*), 6.75 (d, *J* = 3.5 Hz, 4H, Ar*H*), 6.74 (d, *J* = 3.5 Hz, 4H, Ar*H*), 6.01 (d, *J* = 4.0 Hz, 4H, Ar*H*), 5.69 (d, *J* = 4.0 Hz, 4H, Ar*H*), 5.33 (d, *J* = 3.5 Hz, 4H, Ar*H*), 5.23 (d, *J* = 3.5 Hz, 4H, Ar*H*), 5.03 (d, *J* = 3.5 Hz, 4H, Ar*H*), 4.03 (s, 12H, –O*Me*), 3.74 (s, 12H, –O*Me*), 3.70 (s, 12H, –O*Me*), 3.50 (s, 12H, –O*Me*), 3.44–3.30 (br, 40H, –CH_2–), 3.26 (s, 12H, –O*Me*), 3.23 (s, 12H, CH_3), 3.17 (s, 12H, CH_3), 3.15 (s, 24H, CH_3), 3.08 (s, 12H, CH_3), 3.06 (s, 12H, CH_3), 2.98 (br, 8H, –CH_2–), 2.95 (s, 12H, CH_3), 2.92 (s, 24H, CH_3), 2.90 (s, 24H, CH_3), 2.87 (s, 12H, CH_3), 2.85 (s, 24H, CH_3), 2.60 (s, 12H, –O*Me*).

Physical data of 1•TMSA: ^{1}H NMR (acetonitrile-d_3/D_2O (1:4 v/v), 500 MHz): δ 10.02 (d, *J* = 6.0 Hz, 4H, Ar*H*), 9.95 (d, *J* = 6.0 Hz, 4H, Ar*H*), 9.60 (d, *J* = 5.5 Hz, 8H, Ar*H*), 9.53 (d, *J* = 5.5 Hz, 8H, Ar*H*), 9.44 (d, *J* = 6.0 Hz, 4H, Ar*H*), 9.31 (d, *J* = 5.5 Hz, 12H, Ar*H*), 9.16 (d, *J* = 6.0 Hz, 4H, Ar*H*), 9.13 (d, *J* = 6.0 Hz, 4H, Ar*H*), 8.00 (d, *J* = 5.5 Hz, 4H, Ar*H*), 7.92 (d, *J* = 5.5 Hz, 4H, Ar*H*), 7.89 (d, *J* = 5.0 Hz, 4H, Ar*H*), 7.73 (d, *J* = 6.5 Hz, 4H, Ar*H*), 7.68 (d, *J* = 6.5 Hz, 8H, Ar*H*), 7.59 (d, *J* = 4.5 Hz, 8H, Ar*H*), 7.55 (br, 4H, Ar*H*), 7.52 (d, *J* = 6.0 Hz, 4H, Ar*H*), 7.41 (d, *J* = 5.0 Hz, 4H, Ar*H*), 7.23 (d, *J* = 3.5 Hz, 4H, Ar*H*), 7.20 (d, *J* = 5.0 Hz, 4H, Ar*H*), 7.15 (d, *J* = 4.5 Hz, 8H, Ar*H*), 6.85 (d, *J* = 4.0 Hz, 4H, Ar*H*), 6.81 (d, *J* = 3.5 Hz, 4H, Ar*H*), 6.76 (d, *J* = 4.0 Hz, 4H, Ar*H*), 6.07 (d, *J* = 3.5 Hz, 4H, Ar*H*), 5.70 (d, *J* = 3.0 Hz, 4H, Ar*H*), 5.42 (d, *J* = 3.5 Hz, 4H, Ar*H*), 5.19 (br, 4H, Ar*H*), 5.02 (d, *J* = 3.0 Hz, 4H, Ar*H*), 4.93 (d, *J* = 3.5 Hz, 4H, Ar*H*), 4.73 (d, *J* = 3.5 Hz, 4H, Ar*H*), 4.05 (s, 12H, –O*Me*), 3.69 (s, 12H, –O*Me*), 3.55 (s, 12H, –O*Me*), 3.49 (s, 12H, –O*Me*), 3.44−3.31 (br, 40H, –CH_2–), 3.28 (s, 12H, –O*Me*), 3.27 (s, 12H, CH_3), 3.25 (s, 12H, CH_3), 3.17 (s, 12H, CH_3), 3.16 (s, 24H, CH_3), 3.10 (s, 12H, CH_3), 3.02 (s, 12H, CH_3), 2.99 (br, 8H, –CH_2–), 2.97 (s, 12H, CH_3), 2.93 (s, 12H, CH_3), 2.91 (s, 24H, CH_3), 2.89 (s, 12H, CH_3), 2.67 (s, 12H, –O*Me*), –0.61 (s, 1H, C*H*), –2.35 (s, 9H, CH_3).

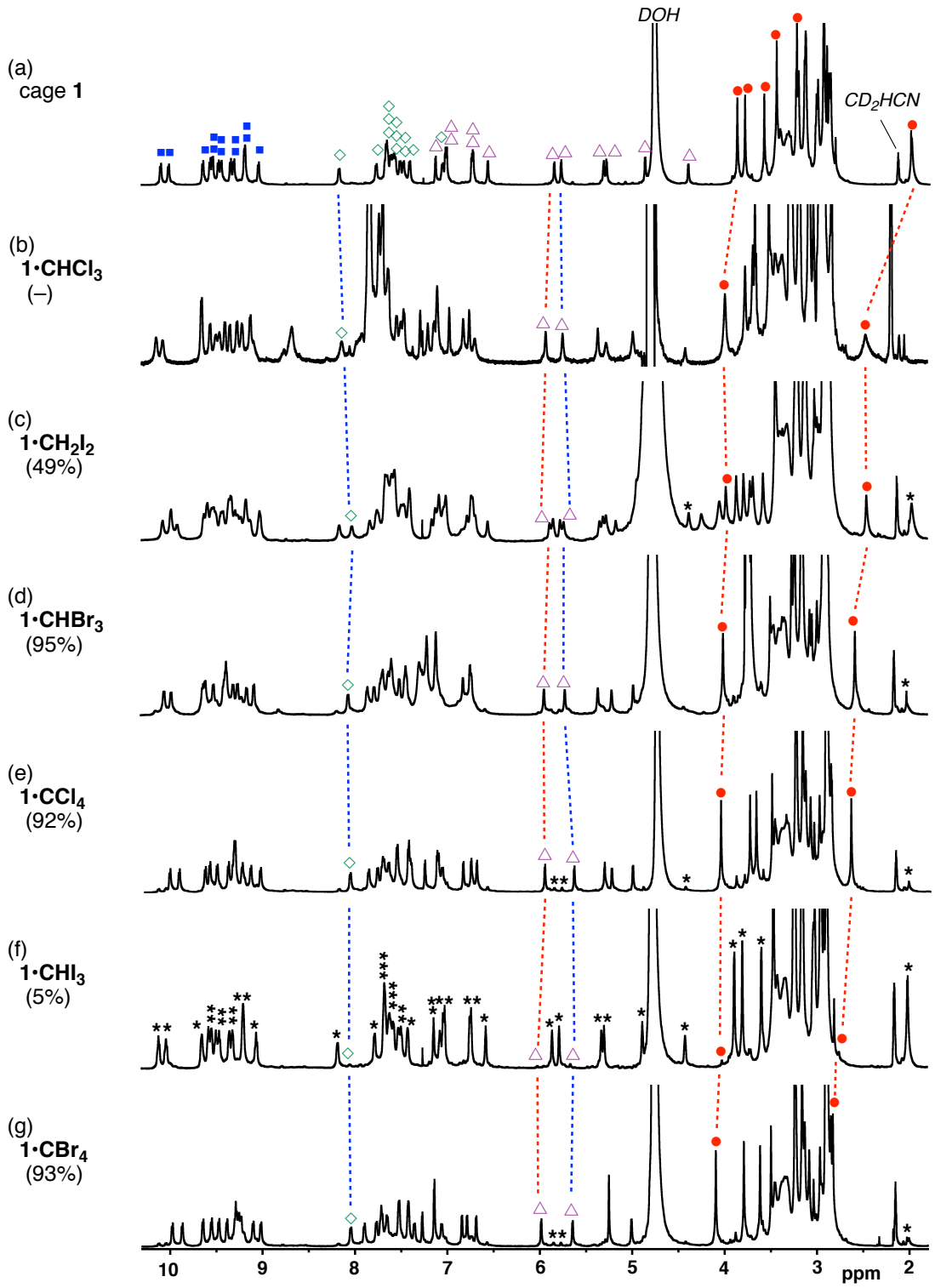


Figure S28. ^{1}H NMR spectra (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of (a) **1**, (b) **1•CHCl$_3$**, (c) **1•CH$_2$I$_2$**, (d) **1•CHBr$_3$**, (e) **1•CCl$_4$**, (f) **1•CHI$_3$**, and (g) **1•CBr$_4$**. Chloroform and diiodomethane showed fast exchange in acetonitrile-d_3/D_2O (1:4 v/v) to show broad signals of the cage.

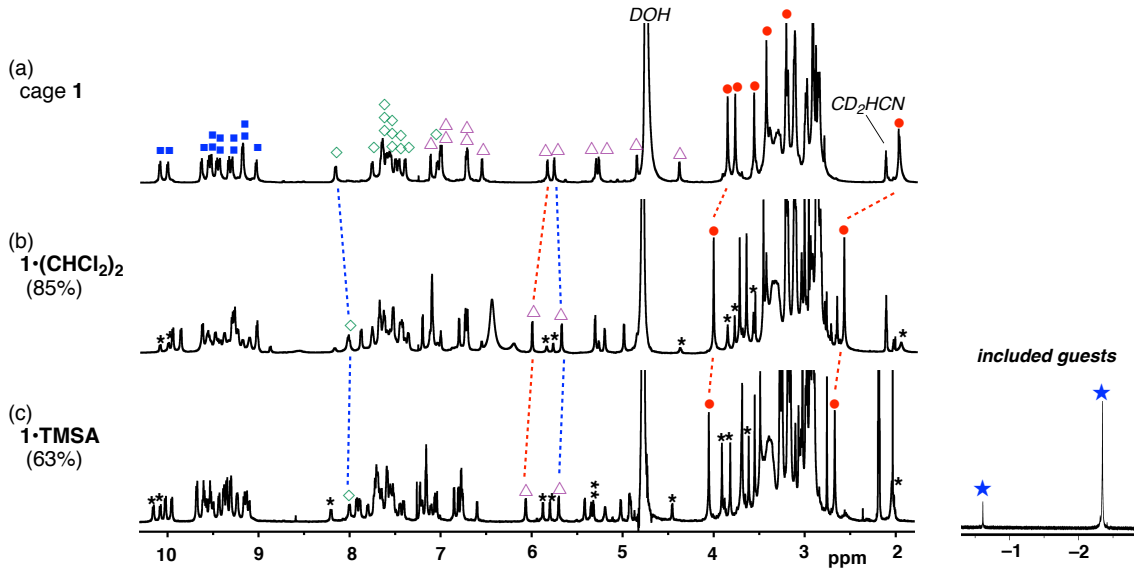


Figure S29. ^{1}H NMR spectra (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) of (a) **1**, (b) **1•(CHCl$_2$)$_2$**, and (c) **1•TMSA**.

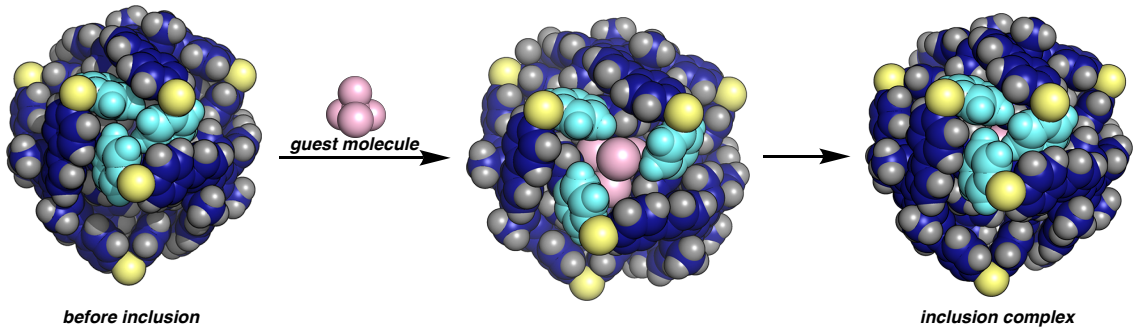


Figure S30. Proposed mechanism of inclusion

Inclusion experiments in D_2O

General procedure

Dried powder of cage **1** (18.0 mg, 2.0 μmol) was dissolved in D_2O (800 μL). Guest molecule (100 eq.) was added to the solution and stirred at room temperature for 10 min. The formation of the inclusion complex was confirmed by ^{1}H NMR spectroscopy. The yields of the inclusion complex were determined by comparison of the integral ratio between the signals from empty cage **1** and the guest included cage **1•G**.

Physical data of 1: ^{1}H NMR (D_2O, 500 MHz): δ 9.92 (d, J = 6.0 Hz, 4H, Ar*H*), 9.80 (d, J = 6.0 Hz, 4H, Ar*H*), 9.57 (d, J = 6.0 Hz, 4H, Ar*H*), 9.46 (d, J = 6.0 Hz, 4H, Ar*H*), 9.44 (d, J = 6.5 Hz, 4H, Ar*H*), 9.29 (d, J = 6.0 Hz, 4H, Ar*H*), 9.27 (d, J = 6.5 Hz, 4H, Ar*H*), 9.26 (d, J = 6.0 Hz, 4H, Ar*H*), 9.22 (d, J = 6.0 Hz, 4H, Ar*H*), 9.10 (d, J = 6.0 Hz, 4H, Ar*H*), 9.08 (d, J = 6.5 Hz, 4H, Ar*H*), 8.87 (d, J = 6.0 Hz, 4H, Ar*H*), 8.14 (d, J = 5.0 Hz, 4H, Ar*H*), 7.70 (d, J = 5.0 Hz, 4H, Ar*H*), 7.63 (d, J = 5.0 Hz, 4H, Ar*H*), 7.59 (d, J = 5.0 Hz, 4H, Ar*H*), 7.52 (d, J = 6.5 Hz, 8H, Ar*H*), 7.51 (d, J = 5.0 Hz, 4H, Ar*H*), 7.44 (d, J = 6.0 Hz, 4H, Ar*H*), 7.42 (d, J = 6.5 Hz, 4H, Ar*H*), 7.33 (d, J = 5.0 Hz, 4H, Ar*H*), 7.32 (d, J = 5.0 Hz, 4H, Ar*H*), 7.07 (d, J = 3.5 Hz, 4H, Ar*H*), 6.94 (d, J = 4.0 Hz, 4H, Ar*H*), 6.92 (d, J = 4.0 Hz, 8H, Ar*H*), 6.66 (d, J = 3.5 Hz, 4H, Ar*H*), 6.64 (d, J = 3.5 Hz, 4H, Ar*H*), 6.48 (d, J = 3.5 Hz, 4H, Ar*H*), 5.81 (d, J = 3.5 Hz, 4H, Ar*H*), 5.75 (d, J = 3.5 Hz, 4H, Ar*H*), 5.29 (d, J = 3.5 Hz, 4H, Ar*H*), 5.20 (d, J = 3.5 Hz, 4H, Ar*H*), 4.76 (d, J = 3.5 Hz, 4H, Ar*H*), 4.23 (d, J = 3.5 Hz, 4H, Ar*H*), 3.78 (s, 12H, –O*Me*), 3.76 (s, 12H, –O*Me*), 3.51 (s, 12H, –O*Me*), 3.43–3.21 (br, 40H, –CH_2–), 3.35 (s, 12H, –O*Me*), 3.18 (s, 12H, CH_3), 3.14 (s, 12H, –O*Me*), 3.13 (s, 12H, CH_3), 3.08 (br, 8H, –CH_2–), 3.05 (s, 24H, CH_3), 2.94 (s, 12H, CH_3), 2.93 (s, 12H, CH_3), 2.89 (s, 24H, CH_3), 2.87 (s, 24H, CH_3), 2.82 (s, 12H, CH_3), 2.77 (s, 12H, CH_3), 1.76 (s, 12H, –O*Me*).

Physical data of 1•CCl_4: ^{1}H NMR (D_2O, 500 MHz): δ 9.77 (d, J = 6.0 Hz, 4H, Ar*H*), 9.63 (d, J = 5.5 Hz, 4H, Ar*H*), 9.51 (d, J = 6.0 Hz, 4H, Ar*H*), 9.49 (d, J = 5.5 Hz, 4H, Ar*H*), 9.41 (d, J = 5.5 Hz, 4H, Ar*H*), 9.30 (d, J = 6.0 Hz, 4H, Ar*H*), 9.20 (d, J = 6.0 Hz, 4H, Ar*H*), 9.15 (br, 12H, Ar*H*), 9.02 (d, J = 6.0 Hz, 4H, Ar*H*), 8.85 (d, J = 6.0 Hz, 4H, Ar*H*), 7.98 (d, J = 4.5 Hz, 4H, Ar*H*), 7.80 (d, J = 5.0 Hz, 4H, Ar*H*), 7.66 (d, J = 5.0 Hz, 4H, Ar*H*), 7.61 (br, 12H, Ar*H*), 7.45 (d, J = 5.0 Hz, 8H, Ar*H*), 7.33 (d, J = 5.0 Hz, 4H, Ar*H*), 7.27 (d, J = 5.0 Hz, 4H, Ar*H*), 7.26 (d, J = 5.0 Hz, 4H, Ar*H*), 7.20 (d, J = 3.0 Hz, 4H, Ar*H*), 7.05 (d, J = 3.0 Hz, 4H, Ar*H*), 6.99 (d, J = 3.0 Hz, 4H, Ar*H*), 6.90 (d, J = 4.5 Hz, 4H, Ar*H*), 6.76 (d, J = 3.0 Hz, 4H, Ar*H*), 6.69 (d, J = 3.0 Hz, 4H, Ar*H*), 6.58 (d, J = 3.0 Hz, 4H, Ar*H*), 5.91 (d, J = 3.5 Hz, 4H, Ar*H*), 5.60 (d, J = 2.5 Hz, 4H, Ar*H*), 5.25 (d, J = 3.0 Hz, 4H, Ar*H*), 5.14 (d, J = 2.5 Hz, 4H, Ar*H*), 4.91 (d, J = 3.5 Hz, 4H, Ar*H*), 4.63 (d, J = 3.0 Hz, 4H, Ar*H*), 3.98 (s, 12H, –O*Me*), 3.68 (s, 12H, –O*Me*), 3.62 (s, 12H, –O*Me*), 3.39 (s, 12H, –O*Me*), 3.35–3.20 (br, 40H, –CH_2–), 3.17 (s, 12H, CH_3), 3.16 (s, 12H, –O*Me*), 3.09 (s, 12H, CH_3), 3.07 (s, 12H, CH_3), 3.04 (s, 12H, CH_3), 3.00 (s, 12H, CH_3), 2.90 (br, 8H, –CH_2–), 2.84 (s, 12H, CH_3), 2.83 (s, 12H, CH_3), 2.81 (s, 36H, CH_3), 2.78 (s, 24H, CH_3), 2.58 (s, 12H, –O*Me*).

Physical data of 1•$CHBr_3$: ^{1}H NMR (D_2O, 500 MHz): δ 9.82 (d, J = 6.0 Hz, 4H, Ar*H*), 9.70 (d, J = 5.5 Hz, 4H, Ar*H*), 9.52 (d, J = 5.5 Hz, 8H, Ar*H*), 9.43 (d, J = 6.0 Hz, 4H, Ar*H*), 9.30 (d, J = 5.0 Hz, 4H, Ar*H*), 9.20 (d, J = 6.0 Hz, 4H, Ar*H*), 9.18 (d, J = 5.0 Hz, 8H, Ar*H*), 9.14 (d, J = 5.5 Hz, 4H, Ar*H*), 9.04 (d, J = 6.0 Hz, 4H, Ar*H*), 8.90 (d, J = 5.5 Hz, 4H, Ar*H*), 7.99 (d, J = 5.0 Hz, 4H, Ar*H*), 7.80 (d, J = 5.0 Hz, 4H, Ar*H*), 7.65 (d, J = 6.0 Hz, 4H, Ar*H*), 7.63 (d, J = 5.5 Hz, 4H, Ar*H*), 7.59 (d, J = 5.5 Hz, 8H, Ar*H*), 7.49 (d, J = 5.5 Hz, 4H, Ar*H*), 7.48 (d, J = 6.0 Hz, 4H, Ar*H*), 7.35 (d, J = 5.0 Hz, 4H, Ar*H*), 7.34 (d, J = 6.0 Hz, 4H, Ar*H*), 7.31 (d, J = 5.5 Hz, 4H, Ar*H*), 7.15 (d, J = 3.5 Hz, 4H, Ar*H*), 7.04 (d, J = 3.5 Hz, 4H, Ar*H*), 6.99 (d, J = 4.0 Hz, 4H, Ar*H*), 6.97 (d, J = 5.5 Hz, 4H, Ar*H*), 6.74 (d, J = 3.5 Hz, 4H, Ar*H*), 6.66 (d, J = 3.0 Hz, 4H, Ar*H*), 6.64 (d, J = 3.5 Hz, 4H, Ar*H*), 5.88 (d, J = 3.0 Hz, 4H, Ar*H*), 5.68 (d, J = 3.0 Hz, 4H, Ar*H*), 5.30 (d, J = 3.5 Hz, 4H, Ar*H*), 5.13 (d, J = 3.0 Hz, 4H, Ar*H*), 4.89 (d, J = 3.0 Hz, 4H, Ar*H*), 4.63 (d, J = 3.5 Hz, 4H, Ar*H*), 3.94 (s, 12H, –O*Me*), 3.39 (s, 12H, –O*Me*), 3.38–3.20 (br, 40H, –CH_2–), 3.17 (s, 12H, CH_3), 3.16 (s, 12H, –O*Me*), 3.14 (s, 12H, CH_3), 3.07 (s, 24H, CH_3), 3.05 (s, 12H, CH_3), 3.00 (br, 8H, –CH_2–), 2.91 (s, 12H, CH_3), 2.86 (s, 12H, CH_3), 2.84 (s, 12H, CH_3), 2.83 (s, 24H, CH_3), 2.82 (s, 12H, CH_3), 2.80 (s, 12H, CH_3), 2.52 (s, 12H, –O*Me*).

Physical data of 1•CBr_4: ^{1}H NMR (D_2O, 500 MHz): δ 9.85 (d, J = 6.0 Hz, 4H, Ar*H*), 9.72 (d, J = 6.0 Hz, 4H, Ar*H*), 9.59 (d, J = 6.0 Hz, 4H, Ar*H*), 9.51 (d, J = 5.5 Hz, 4H, Ar*H*), 9.43 (d, J = 6.0 Hz, 4H, Ar*H*), 9.35 (d, J = 6.0 Hz, 4H, Ar*H*), 9.24 (d, J = 6.5 Hz, 4H, Ar*H*), 9.17 (d, J = 6.0 Hz, 4H, Ar*H*), 9.16 (d, J = 6.0 Hz, 8H, Ar*H*), 9.04 (d, J = 6.5 Hz, 4H, Ar*H*), 8.92 (d, J = 5.5 Hz, 4H, Ar*H*), 8.00 (d, J = 5.0 Hz, 4H, Ar*H*), 7.87 (d, J = 4.5 Hz, 4H, Ar*H*), 7.69 (d, J = 4.5 Hz, 8H, Ar*H*), 7.65 (d, J = 6.0 Hz, 4H, Ar*H*), 7.63 (d, J = 6.0 Hz, 4H, Ar*H*), 7.47 (d, J = 5.0 Hz, 8H, Ar*H*), 7.38 (d, J = 6.0 Hz, 4H, Ar*H*), 7.33 (d, J = 5.0 Hz, 4H, Ar*H*), 7.28 (d, J = 5.5 Hz, 4H, Ar*H*), 7.24 (d, J = 3.5 Hz, 4H, Ar*H*), 7.10 (d, J = 4.0 Hz, 4H, Ar*H*), 7.08 (d, J = 4.0 Hz, 4H, Ar*H*), 6.97 (d, J = 4.0 Hz, 4H, Ar*H*), 6.81 (d, J = 3.5 Hz, 4H, Ar*H*), 6.75 (d, J = 3.5 Hz, 4H, Ar*H*), 6.64 (d, J = 3.5 Hz, 4H, Ar*H*), 5.97 (d, J = 3.5 Hz, 4H, Ar*H*), 5.63 (d, J = 3.0 Hz, 4H, Ar*H*), 5.22 (d, J = 3.5 Hz, 4H, Ar*H*), 5.20 (d, J = 3.5 Hz, 4H, Ar*H*), 4.96 (d, J = 3.5 Hz, 4H, Ar*H*), 4.71 (d, J = 4.0 Hz, 4H, Ar*H*), 4.06 (s, 12H, –O*Me*), 3.76 (s, 12H, –O*Me*), 3.56 (s, 12H, –O*Me*), 3.44 (s, 12H, –O*Me*), 3.42–3.23 (br, 40H, –CH_2–), 3.20 (s, 12H, CH_3), 3.19 (s, 12H, –O*Me*), 3.18 (s, 12H, CH_3), 3.12 (s, 24H, CH_3), 3.08 (s, 12H, CH_3), 3.04 (s, 12H, CH_3), 2.97 (br, 8H, –CH_2–), 2.93 (s, 24H, CH_3), 2.86 (s, 48H, CH_3), 2.80 (s, 12H, –O*Me*).

Physical data of 1•CH_2I_2: ^{1}H NMR (D_2O, 500 MHz): δ 9.80 (d, J = 5.5 Hz, 4H, Ar*H*), 9.71 (d, J = 6.0 Hz, 4H, Ar*H*), 9.52 (d, J = 5.5 Hz, 4H, Ar*H*), 9.50 (d, J = 6.5 Hz, 4H, Ar*H*), 9.43 (d, J = 6.5 Hz, 4H, Ar*H*), 9.30 (d, J = 5.5 Hz, 4H, Ar*H*), 9.18 (d, J = 5.5 Hz, 12H, Ar*H*), 9.14 (d, J = 5.5 Hz, 4H, Ar*H*), 9.03 (d, J = 6.0 Hz, 4H, Ar*H*), 8.90 (d, J = 6.0 Hz, 4H, Ar*H*), 7.98 (d, J = 5.5 Hz, 4H, Ar*H*), 7.79 (d, J = 5.0 Hz, 4H, Ar*H*), 7.63 (d, J = 5.5 Hz, 8H, Ar*H*), 7.56 (d, J = 6.5 Hz, 8H, Ar*H*), 7.50 (d, J = 7.0 Hz, 8H, Ar*H*), 7.48 (d, J = 7.0 Hz, 4H, Ar*H*), 7.36 (d, J = 6.0 Hz, 4H, Ar*H*), 7.31(d, J = 6.5 Hz, 4H, Ar*H*), 7.13 (d, J = 3.5 Hz, 4H, Ar*H*), 7.03 (d, J = 3.5 Hz, 4H, Ar*H*), 7.00 (d, J = 3.0 Hz, 8H, Ar*H*), 6.72 (d, J = 3.0 Hz, 4H, Ar*H*), 6.66 (d, J = 3.0 Hz, 4H, Ar*H*), 6.64 (d, J = 3.0 Hz, 4H, Ar*H*), 5.84 (d, J = 3.0 Hz, 4H, Ar*H*), 5.70 (d, J = 3.0 Hz, 4H, Ar*H*), 5.29 (br, 4H, Ar*H*), 5.12 (d, J = 3.0 Hz, 4H, Ar*H*), 4.88 (d, J = 3.0 Hz, 4H, Ar*H*), 4.66 (d, J = 3.0 Hz, 4H, Ar*H*), 3.92 (s, 12H, –O*Me*), 3.67 (s, 12H, –O*Me*), 3.64 (s, 12H, –O*Me*), 3.47 (s, 12H, –O*Me*) , 3.33–3.21 (br, 40H, –CH_2–), 3.16 (s, 12H, –O*Me*), 3.16 (s, 12H, CH_3), 3.13 (s, 12H, CH_3), 3.06 (s, 24H, CH_3), 3.04 (s, 24H, CH_3), 2.97 (br, 8H, –CH_2–), 2.90 (s, 12H, CH_3), 2.85 (s, 12H, CH_3), 2.83 (s, 12H, CH_3), 2.81 (s, 12H, CH_3), 2.79 (s, 24H, CH_3), 2.41 (s, 12H, –O*Me*).

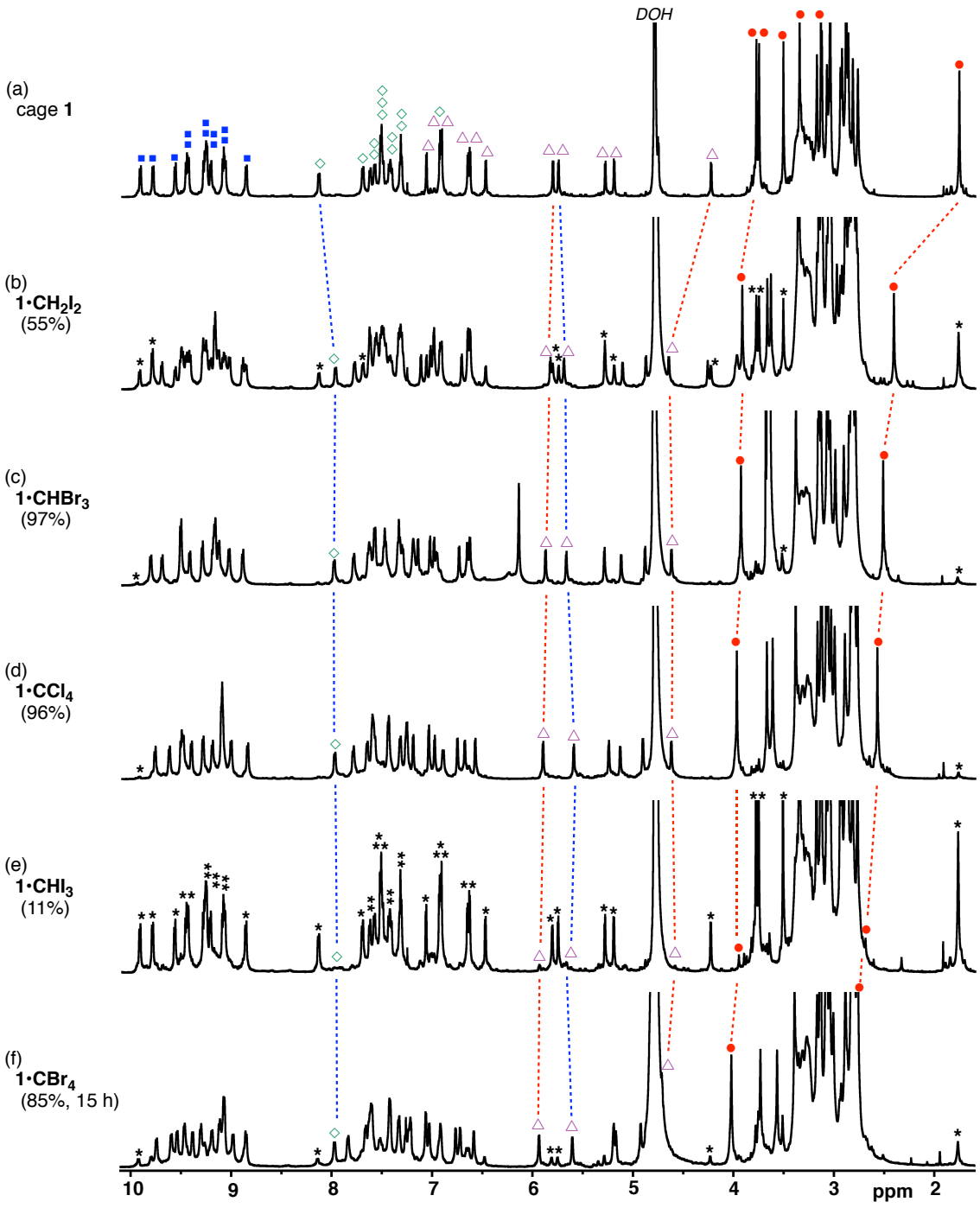


Figure S31. ^{1}H NMR spectra (500 MHz, 300 K, D_2O) of (a) **1**, (b) **1•CH_2I_2**, (c) **1•$CHBr_3$**, (d) **1•CCl_4**, (e) **1•CHI_3**, and (f) **1•CBr_4**.

5. X-ray crystallographic analyses of cage 1, 1•CCl_4, and S3

Procedures for crystallization

Cage 1

An CH_3CN/H_2O (1:4 v/v) solution of cage **1** was stood at 50 ºC and solvents were allowed to evaporate. After 10 days, a single crystal suitable for X-ray diffraction analysis was obtained.

Inclusion complex 1•CCl_4

Sat. $NaBF_4$ aq. was added the CH_3CN/H_2O (1:4 v/v) solution of cage **1**. The obtained precipitate was washed with water and dried under reduced pressure. Cage **1'** in which the counter anions were exchanged from NO_3^- to BF_4^- was dissolved in CH_3CN, an excess amount of CCl_4 was added, and the mixture was stirred at room temperature for 10 min. An excess amount of NH_4BF_4 was then added to the solution. The solution was stood at room temperature and the solvent were allowed to evaporate. After 1 day, a single crystal suitable for X-ray diffraction analysis was obtained.

Table S1 Crystal data and structural refinement for **1**, **1**•CCl_4, and **S3**

	1	**1**•CCl_4	**S3**
Identification code	i-42d	ht1419d	p-1
CCDC number	1971564	1971565	1984215
Empirical formula	$C_{713.58}H_{804.32}N_{114.89}O_{350.35}Pd_{24}$	$C_{724}H_{819}B_{48}Cl_8F_{192}N_{97}O_{110}Pd_{24}$	$C_{21}H_{18}O_6$
Formula weight	19148.69	19643.62	366.35
Temperature	90(2) K	100.01(10) K	90(2) K
Wavelength	0.71073 Å	1.54178 Å	0.71073 Å
Crystal system	Tetragonal	Monoclinic	Triclinic
Space group	*I*-42d	$P2_1/n$	*P*-1
Unit cell dimensions	$a = b = 40.908(11)$ Å $c = 28.479(8)$ Å $\alpha = \beta = \gamma = 90°$	$a = 35.2184(4)$ Å $b = 33.4270(4)$ Å $c = 37.3137(4)$ Å $\alpha = \gamma = 90°$ $\beta = 95.8588(10)°$	$a = 10.020(2)$ Å $b = 11.554(2)$ Å $c = 16.035(3)$ Å $\alpha = 74.125(3)°$ $\beta = 84.067(3)°$ $\gamma = 85.833(3)°$
Volume	47657(28) $Å^3$	43698.0(9) $Å^3$	1774.2(6) $Å^3$
Z	2	2	4
Density (calculated)	1.334 Mg/m^3	1.493 Mg/m^3	1.372 Mg/m^3
Absorption coefficient	0.533 mm^{-1}	5.072 mm^{-1}	0.101 mm^{-1}
F(000)	19547	19860	768
Crystal size	0.14× 0.12 × 0.09 mm^3	0.07× 0.04 × 0.03 mm^3	0.28 × 0.11 × 0.04 mm^3
Theta range for data	0.996 to 26.460°	2.249 to 62.384°	1.325 to 28.313°
Index ranges	$-51 \leqq h \leqq 51$, $-51 \leqq k \leqq 51$, $-35 \leqq l \leqq 35$	$-40 \leqq h \leqq 39$, $-36 \leqq k \leqq 38$, $-42 \leqq l \leqq 38$	$-13 \leqq h \leqq 13$, $-15 \leqq k \leqq 15$, $-20 \leqq l \leqq 15$
Reflection collected	247406	248790	14382
Independent reflections	24590 [$R_{int} = 0.1389$]	68906 [$R_{int} = 0.1391$]	8192 [$R_{int} = 0.0314$]
Completeness	99.9% ($\theta = 25.242°$)	99.2% ($\theta = 62.384°$)	98.9% ($\theta = 25.242°$)
Max. and min. transmission	0.7454 and 0.4738	1.00000 and 0.33030	0.7457 and 0.5879
Refinement method		Full-matrix least-squares on F^2	
Data / restraints / parameters	4590 / 1034 / 1803	68906 / 2715 / 6128	8192 / 0 / 493
Goodness-of-fit on F^2	1.013	0.979	1.053
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0858$, $wR_2 = 0.2218$	$R_1 = 0.0905$, $wR_2 = 0.2412$	$R_1 = 0.0678$, $wR_2 = 0.1853$
R indices (all data)	$R_1 = 0.1422$, $wR_2 = 0.2719$	$R_1 = 0.2005$, $wR_2 = 0.3146$	$R_1 = 0.1000$, $wR_2 = 0.2057$
Absolute structure parameter	0.144(10)	–	–
Largest diff. peak and hole	0.967 and –0.513 e•$Å^{-3}$	1.754 and -0.984 e•$Å^{-3}$	0.600 and -0.309 e.$Å^{-3}$

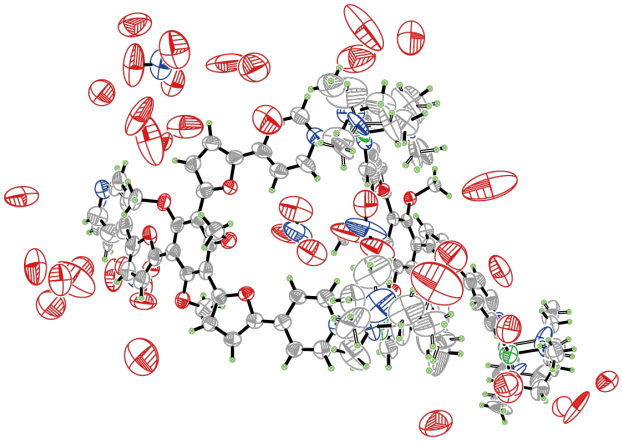


Figure S32. ORTEP drawings (50% probability ellipsoids) of the refinement structure of **1**.

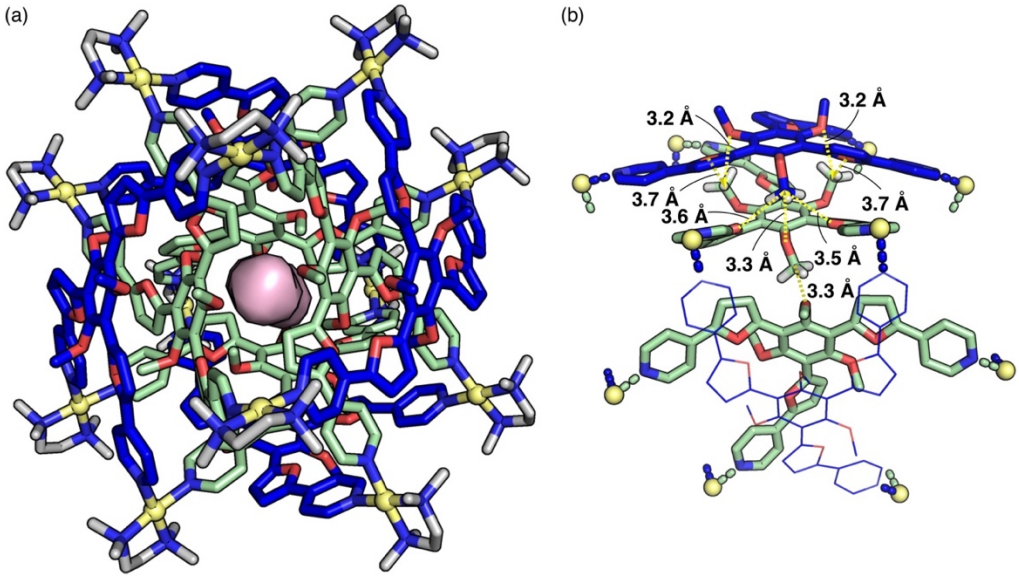


Figure S33. (a) Crystal structure of cage **1** (the pink object represents the cavity). (b) Hydrogen bonds between ligands of cage **1**. Hydrogen atoms, solvent molecules and anions were omitted for clarity.

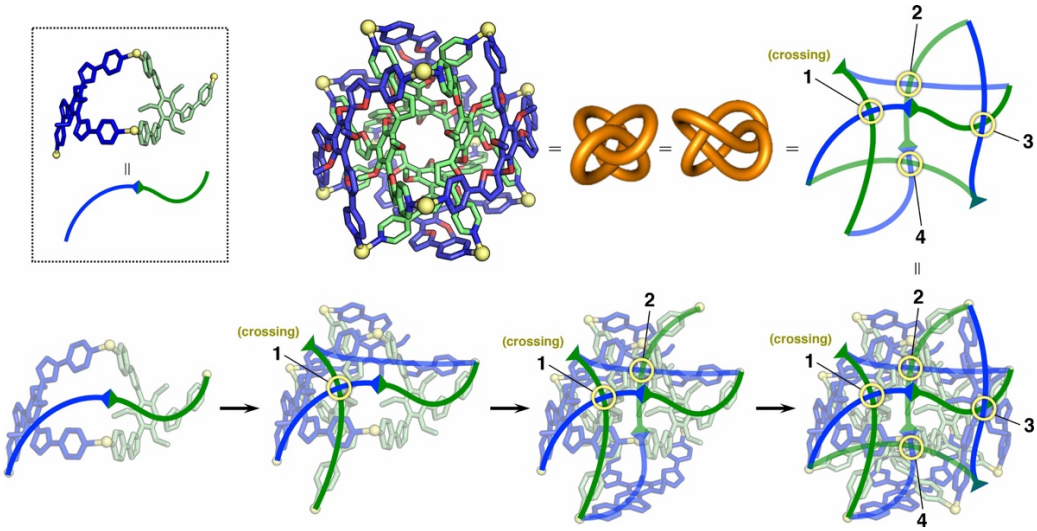


Figure S34. Schematic representation of the figure-eight (4_1) knot topology of cage **1**.[S3]

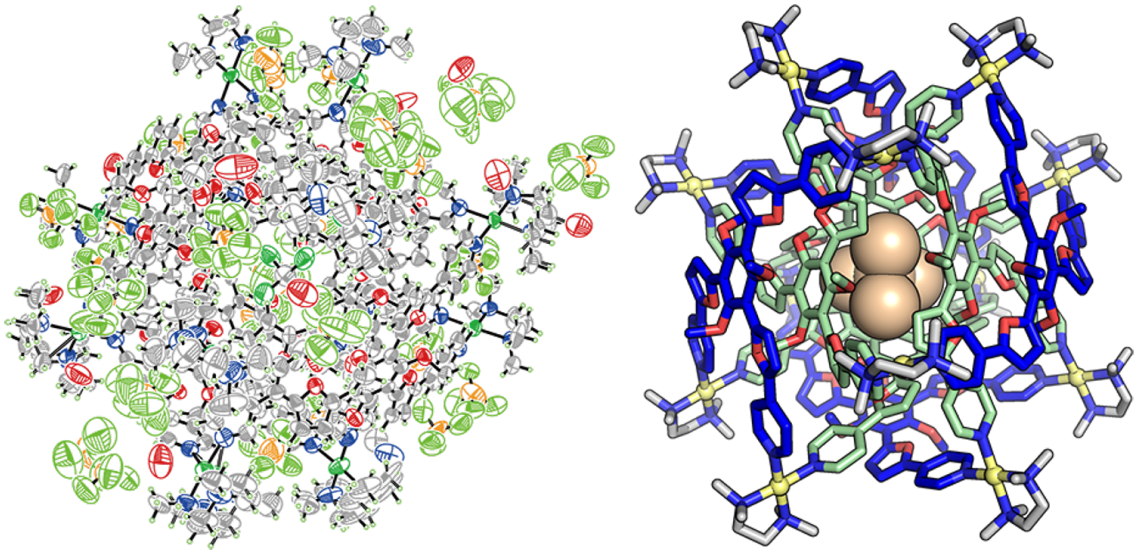


Figure S35. Crystal structure of **1•CCl$_4$**. ORTEP drawings (50% probability ellipsoids) of the refinement structure of **1•CCl$_4$** (left) and a stick model of **1•CCl$_4$** (right, the orange object represents CCl_4 in the cavity. Hydrogen atoms, solvent molecules and anions were omitted for clarity).

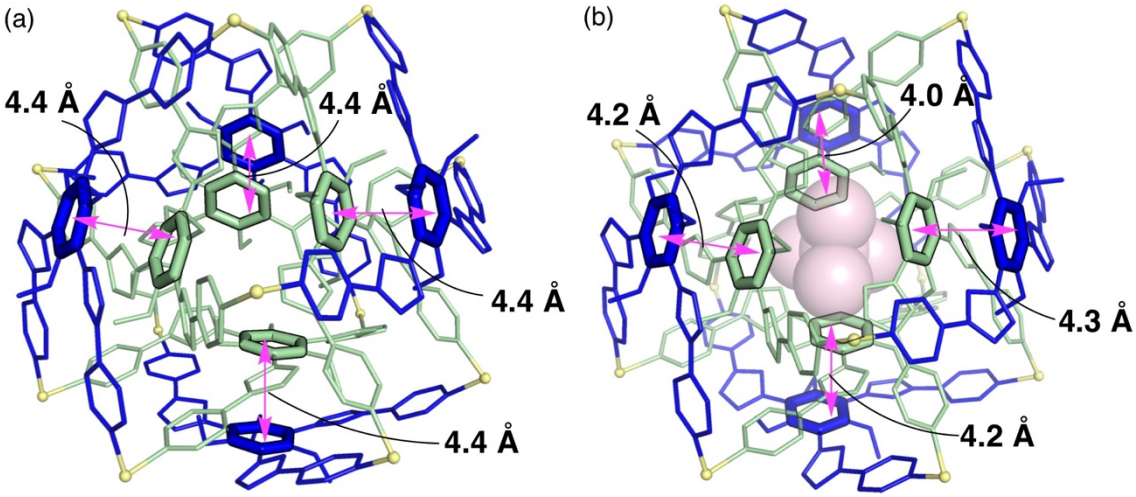
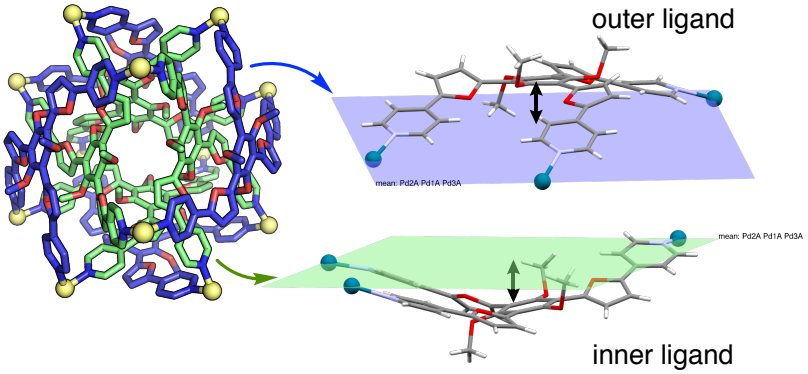


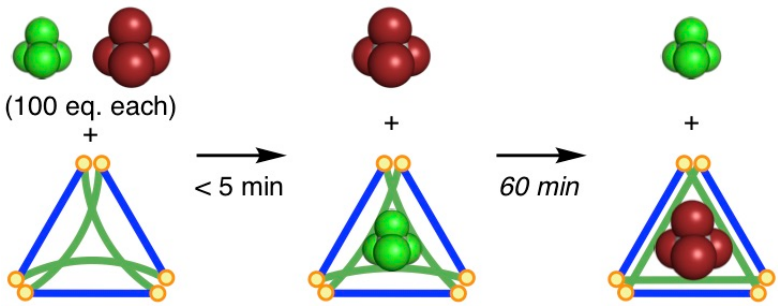
Figure S36. Distances between the benzene rings of outer and inner ligands in (a) cage **1** and (b) **1•CCl$_4$**. The distances were estimated with the averages of distances between six carbon atoms on a benzene ring of an inner ligand and the least-squares plane with six carbon atoms on the benzene ring of the correspondent outer ligand.



empty **1**	**1•CCl_4**
	2.46 Å
	2.23 Å
	2.49 Å
	2.49 Å
2.38 Å	**ave. 2.41 Å**
	1.84 Å
	2.01 Å
	1.71 Å
	1.82 Å
2.10 Å	**ave. 1.85 Å**

Figure S37. The averaged distances between the carbon atoms on the benzene core of the ligand and the plane passing through three Pd atoms connected to the ligand.

6. Sequential guest binding



Dried powder of cage **1** (18.0 mg, 2.0 μmol) was dissolved in acetonitrile-d_3/D_2O (800 μL, 1:4 v/v). Guest molecules (CCl_4 and CBr_4, 100 eq. each to cage **1**) were added to the solution and ^{1}H NMR was measured immediately. ^{1}H NMR measurements were repeated after every 5-minute stirring until the total stirring time reached 60 min. The yields of the inclusion complex were determined by comparison of the integral ratios among the signals from empty cage **1**, **1•CCl_4** and **1•CBr_4**.

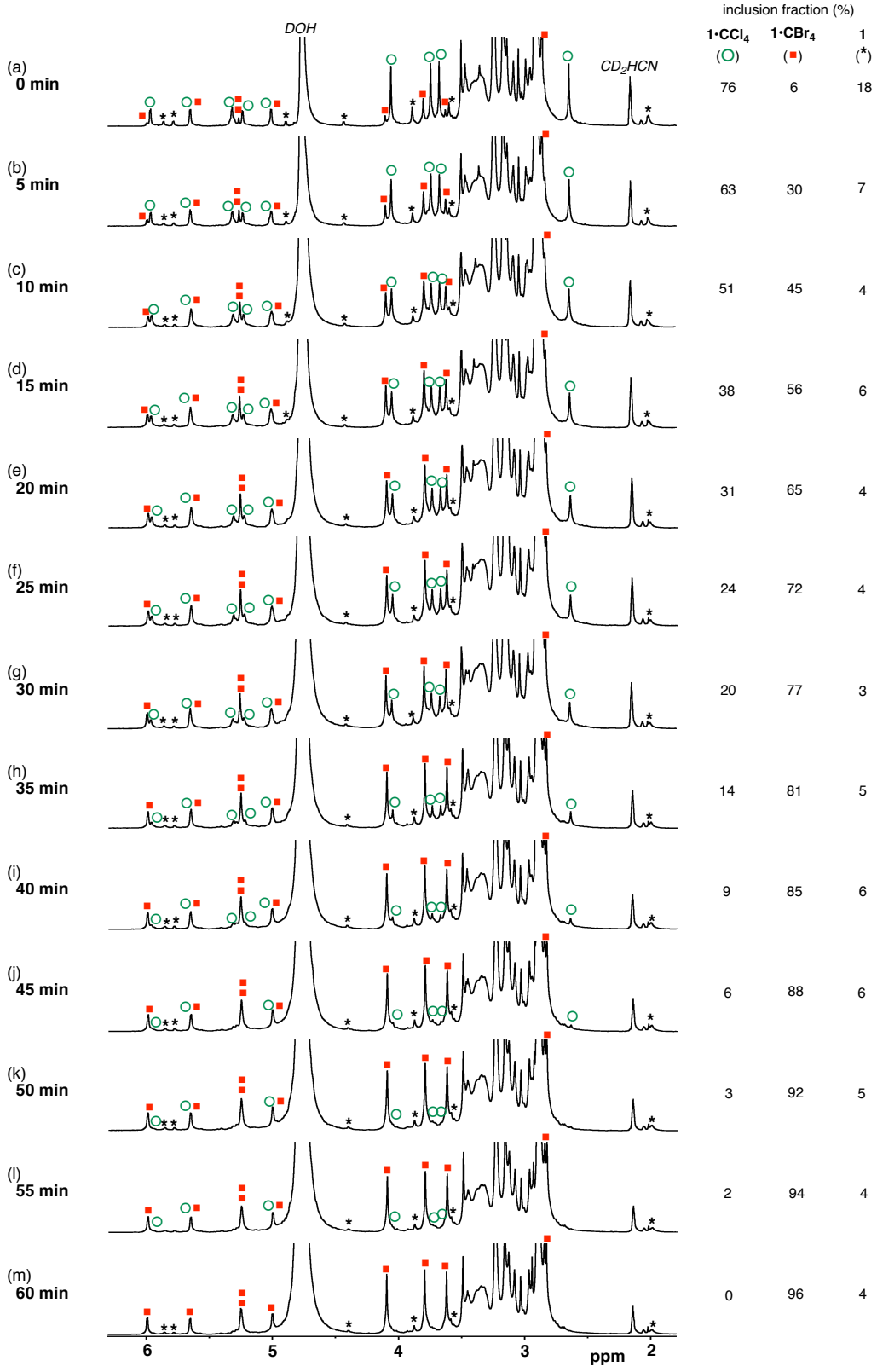


Figure S38. ^{1}H NMR spectra (500 MHz, 300 K, acetonitrile-d_3/D_2O (1:4 v/v)) during the sequential binding.

References

[S1] E. Kiehlmannand, and R. W. Lauen, *Can*. *J*. *Chem*. **1989**, *67*, 335–344.

[S2] K. R. Idzik, R. Beckert, E. Tauscher, Pr. Ledwon, S. Golba, M. Lapkowski, P. Rapta, L. Dunsch, and J. Frydel, *Mater*. *Sci*. *Forum*., **2010**, *663-665*, 876–879.

[S3] The 3D models of the figure-eight knot topology were drawn by KnotPlot Version 1.0 (https://knotplot.com/).