Supporting Information

Anion-π interaction inside the polyanionic $Mo_{132}O_{372}$ cage with hydrophobic inner space

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I. Experimental

A. Materials

Ammonium acetate (97%), ammonium molybdate tetrahydrate (99%), anisole (99%), benzene (99%), chlorobenzene (99%), hydrazinium sulfate (99%), methyl benzoate (98%), nitrobenzene (99%), and phenol (99%) were obtained from FUJIFILM Wako Pure Chemical Corporation. Deuterium oxide (98%) and cyclohexanecarbonitrile (98%) were purchased from Sigma-Aldrich. Acetic acid (99%) and acetophenone (99%) were obtained from Nakalai Tesuque. Benzonitrile (99%), 2-phenylacetonitrile (98%), dimethyl sulfone (99%), phenylacetylene (98%), styrene (99%) and toluene (99.5%), were obtained from Tokyo Chemical Industry. All reagents were used as received. Milli-Q water was obtained on a Milli-Q Advantage system. $(NH_4)_{42}[Mo_{132}O_{372}(H_2O)_{72}(CH_3COO)_{30}]$ (**1**) was prepared according to the procedure reported by Müller *et al.*[1]

B. Measurements and methods

^{1}H and ^{1}H DOSY NMR spectra were collected in D_2O at ambient temperature on a Bruker Avance 300 MHz spectrometer and the chemical shifts (in ppm) were referenced to internal HDO (δ 4.79). Diffusion coefficients in the DOSY spectra were calculated by using Dynamics Center software (v. 2.6.2) or Bruker Topspin (v. 4.1.4). Calculation of mono-substituted benzenes was conducted using a Winmoster package V10[2] containing GAMESS[3] and MOPAC[4] softwares. Geometry optimization and electrostatic potential calculation were conducted using the density functional theory method at the B3LYP level with basis sets 6-31G*. Molecular volumes were estimated on MOPAC.

C. Guest inclusion experiments

Typically, **1** (14 mg (0.61 μmol)) was dissolved in 590 μL D_2O containing dimethyl sulfone (DMSO2, internal standard, 2.0 mM) in a microtube, and then organic guest (120 μmol) was added. After being vortexed for 30 s, the mixture was transferred to an NMR tube and kept in dark at room temperature for 96 hours, and then was subjected to ^{1}H and DOSY NMR analyses. The trapped amounts of the guests were estimated based on the internal standard (δ 3.15).

II. Results

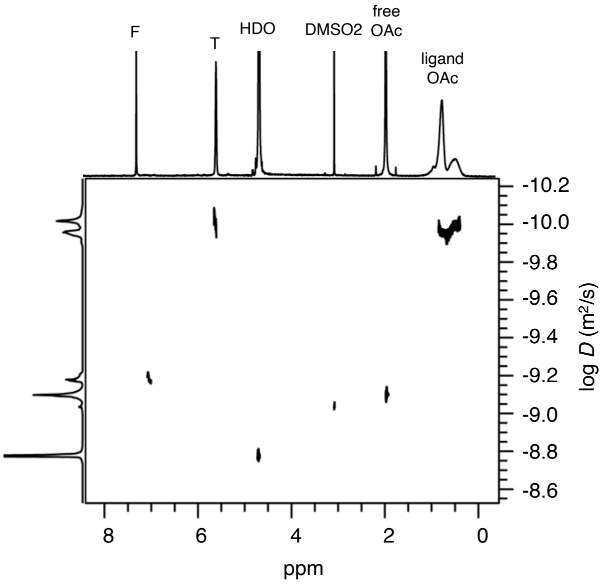


Figure S1a. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat benzene (200 molar equiv) for 96 h at room temperature.

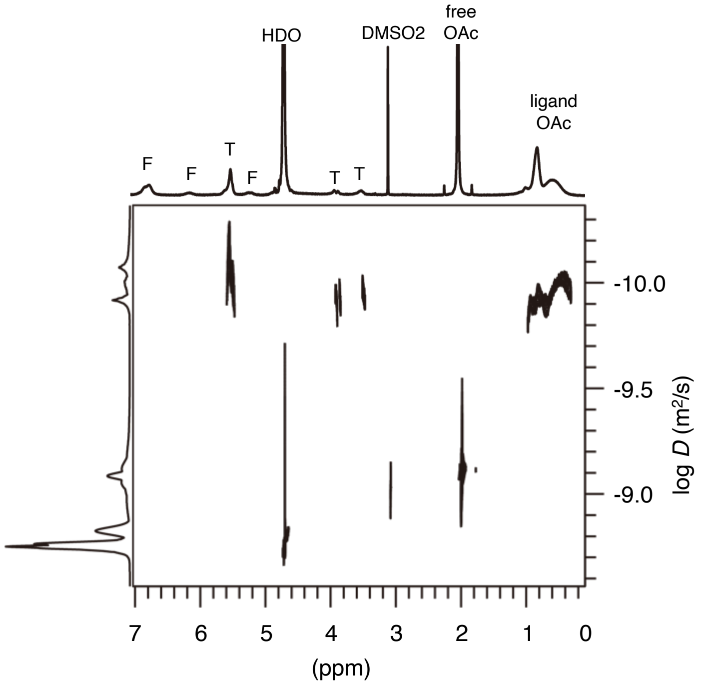


Figure S1b. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat styrene (200 molar equiv) for 96 h at room temperature.

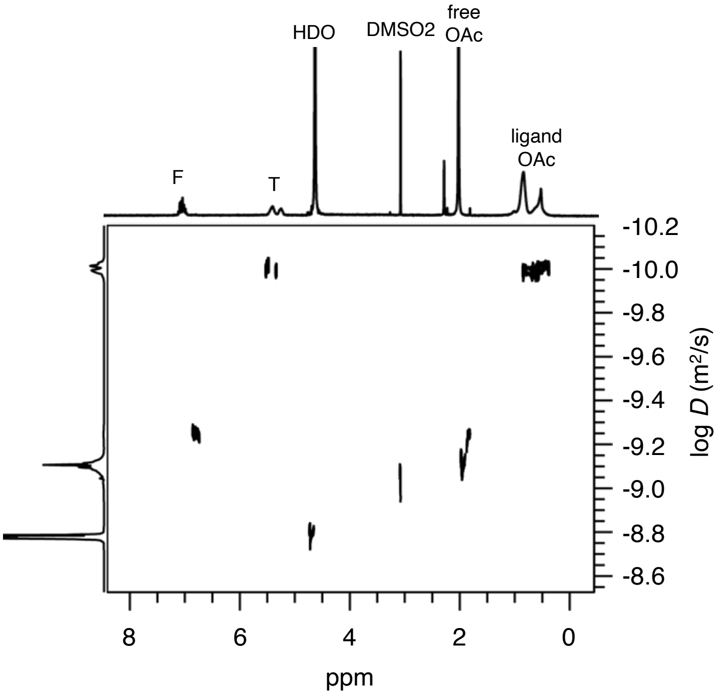


Figure S1c. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat toluene (200 molar equiv) for 96 h at room temperature.

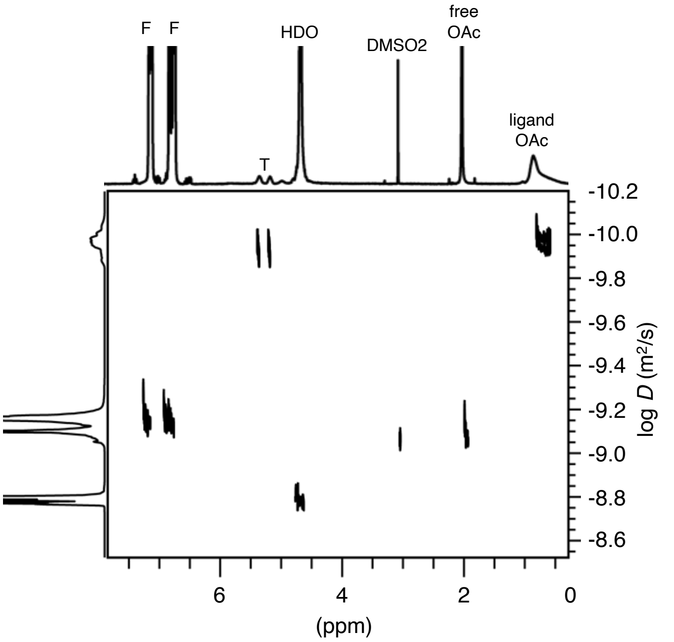


Figure S1d. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat phenol (200 molar equiv) for 96 h at room temperature.

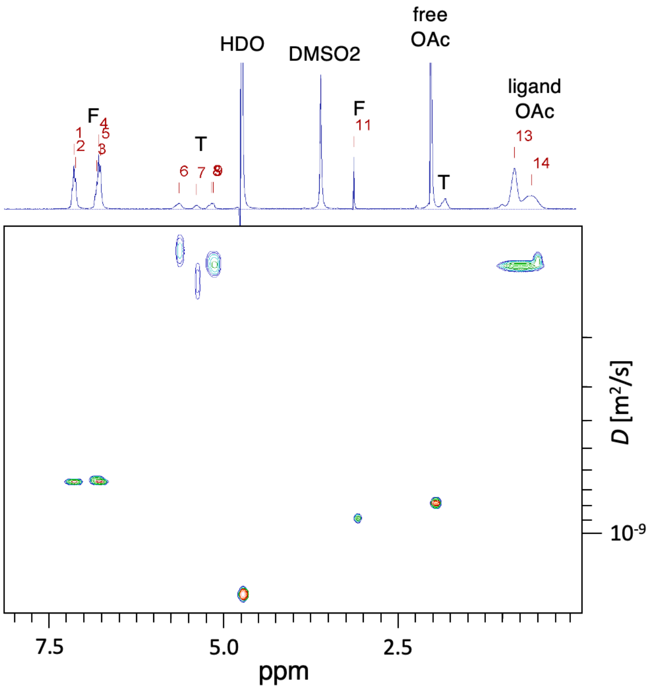


Figure S1e. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat anisole (200 molar equiv) for 96 h at room temperature.

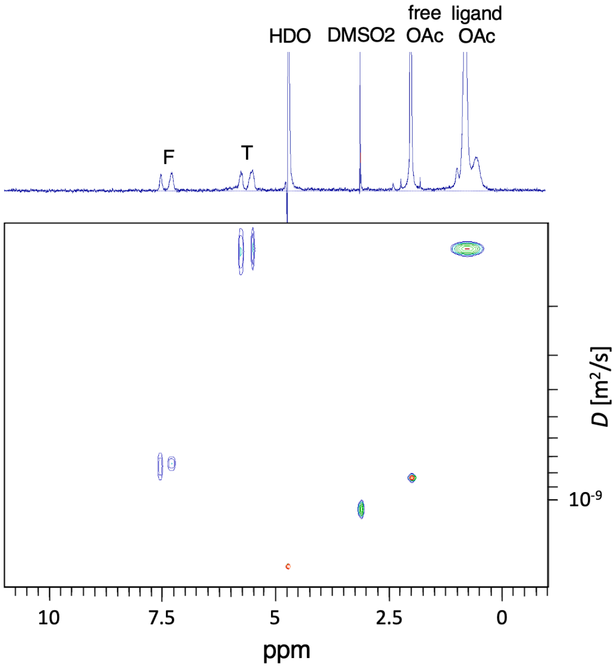


Figure S1f. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat bromobenzene (200 molar equiv) for 96 h at room temperature.

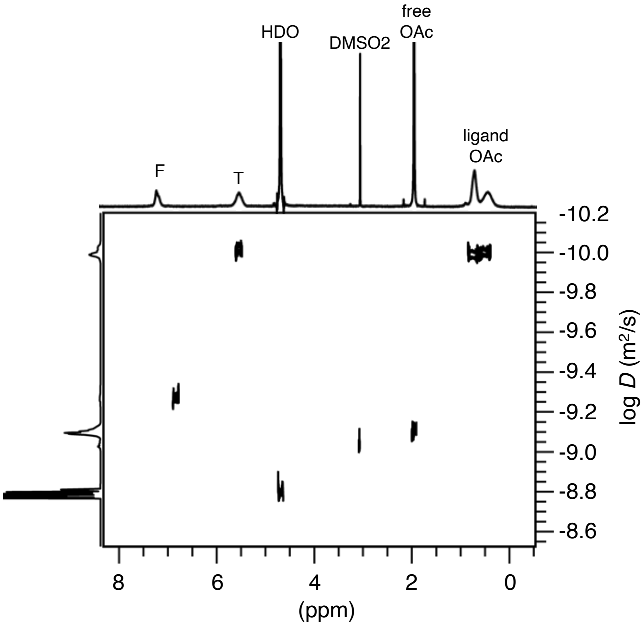


Figure S1g. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat chlorobenzene (200 molar equiv) for 96 h at room temperature.

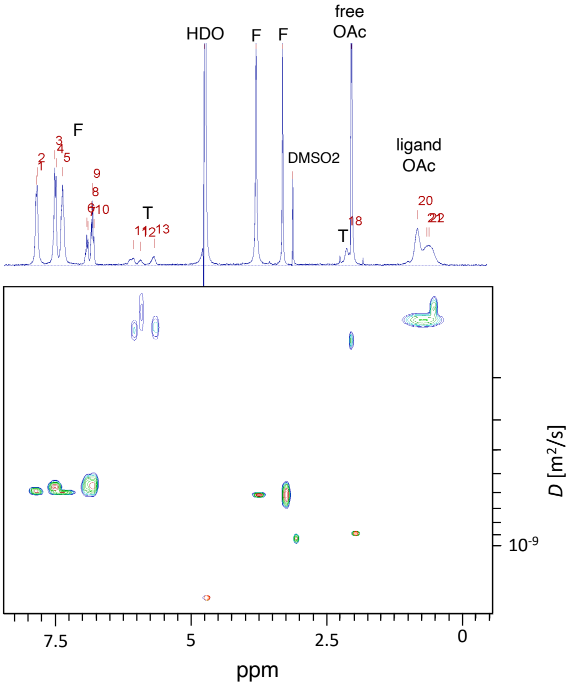


Figure S1h. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat methyl benzoate (200 molar equiv) for 96 h at room temperature.

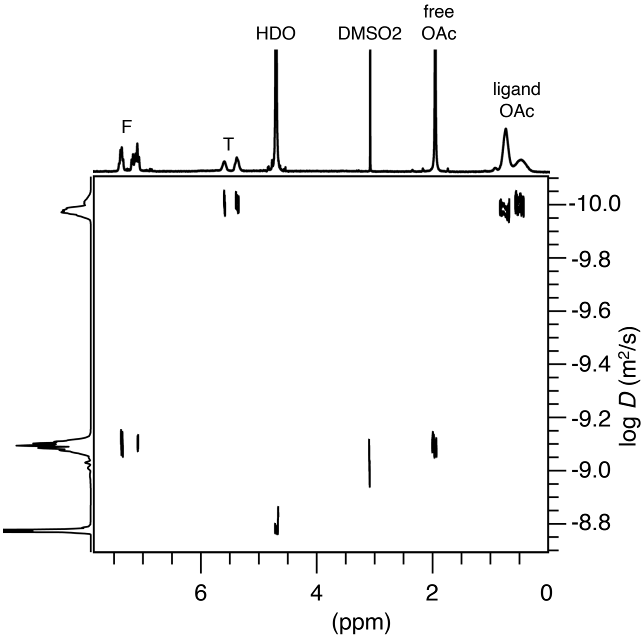


Figure S1i. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat fluorobenzene (200 molar equiv) for 96 h at room temperature.

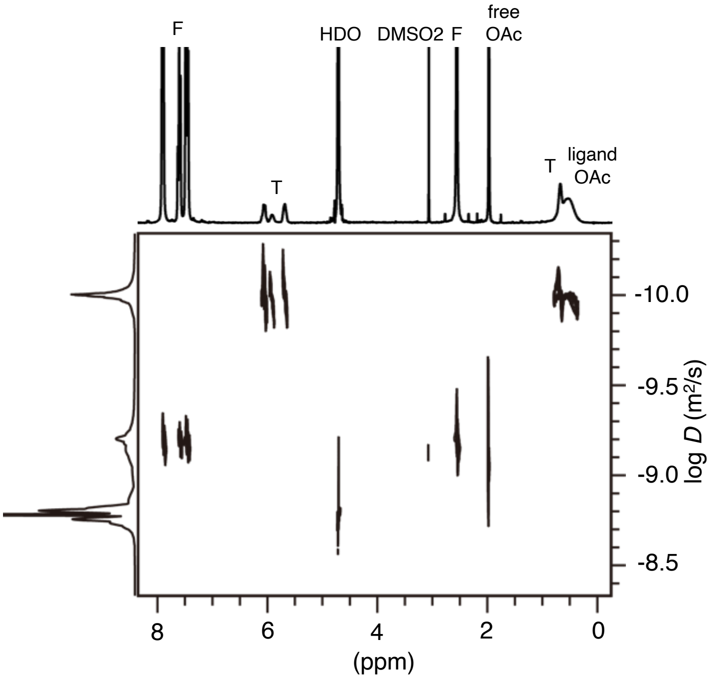


Figure S1j. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat acetophenone (200 molar equiv) for 96 h at room temperature.

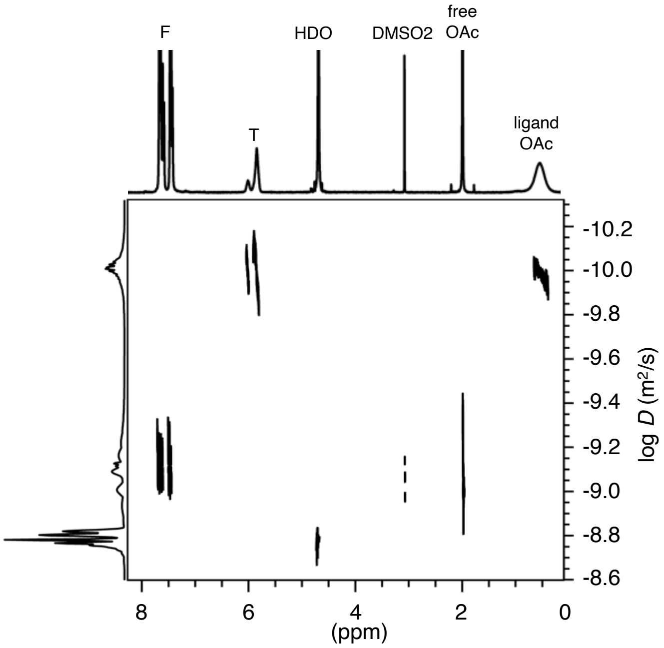


Figure S1k. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat benzonitrile (200 molar equiv) for 96 h at room temperature.

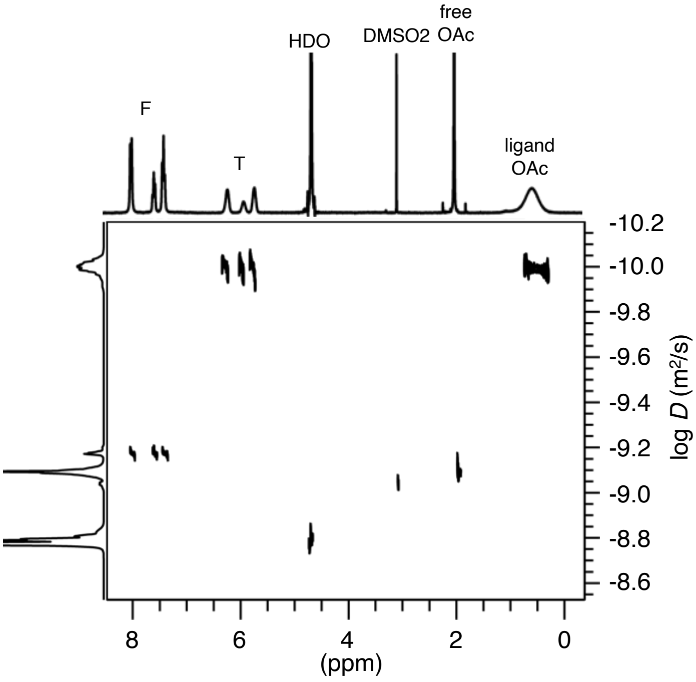


Figure S1l. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat nitrobenzene (200 molar equiv) for 96 h at room temperature.

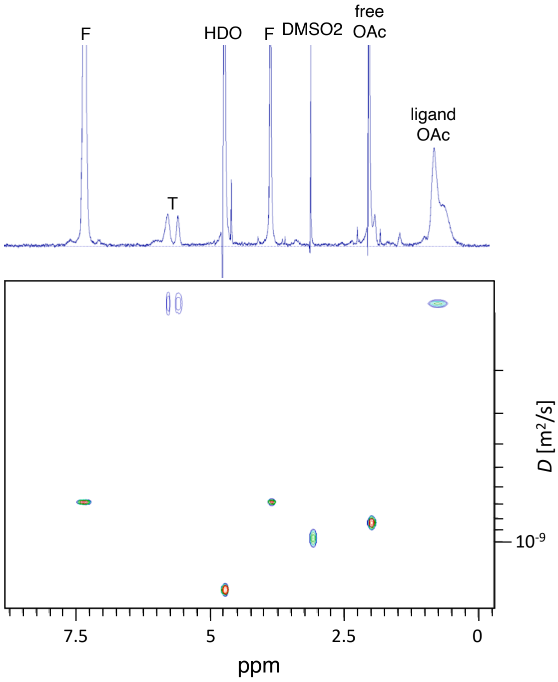


Figure S1m. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat 2-phenylacetonitrile (200 molar equiv) for 96 h at room temperature.

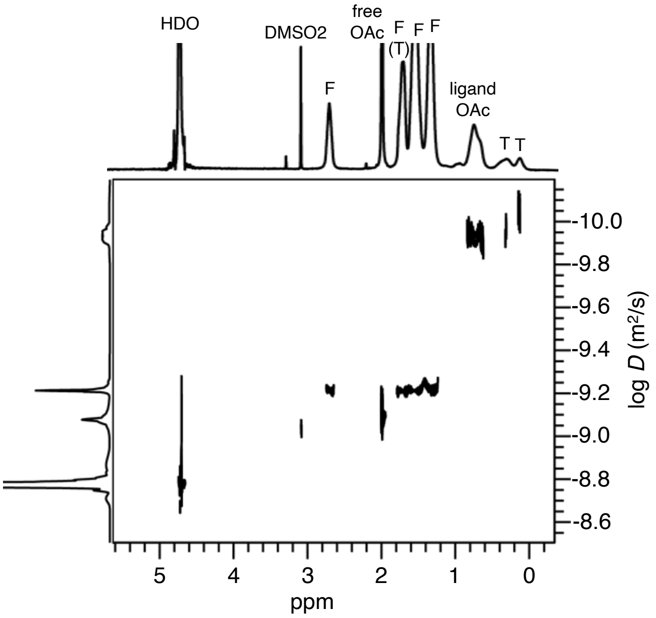


Figure S1n. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat cyclohexanecarbonitrile (200 molar equiv) for 96 h at room temperature.

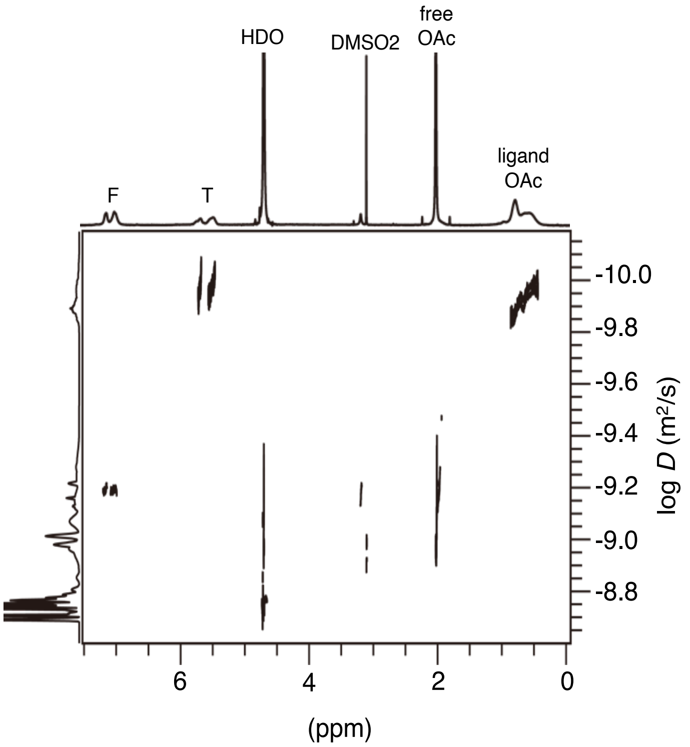


Figure S1o. ^{1}H-DOSY spectrum of the mixture after **1** (0.1 mM in D_2O) was treated with neat phenylacetylene (200 molar equiv) for 96 h at room temperature.

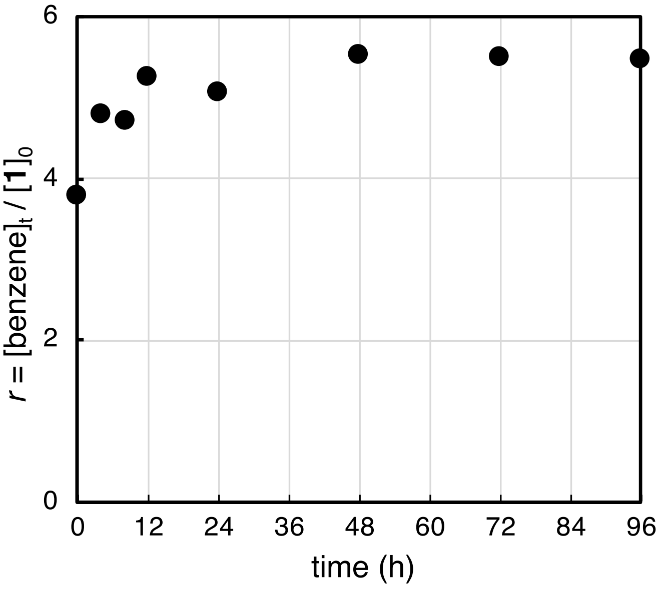


Figure S2. Time course of inclusion of benzene into the inner space of **1**.

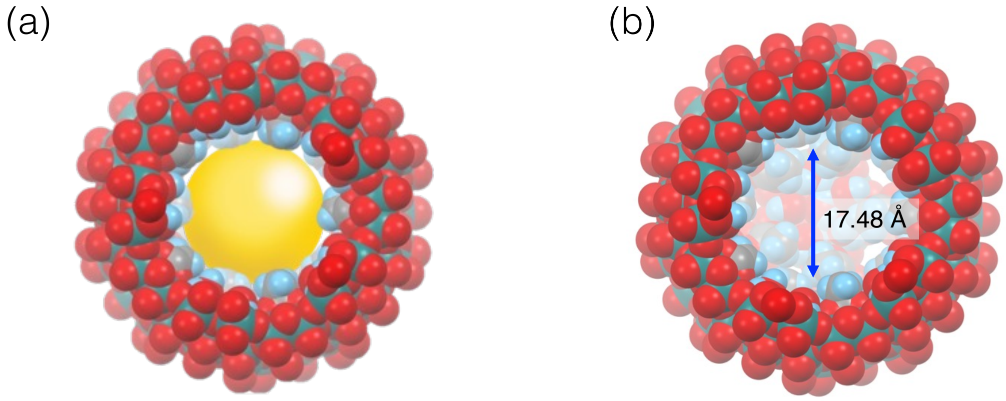
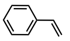
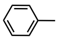
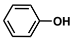
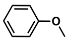
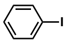
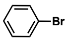
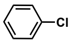
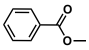
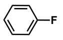
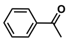
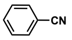
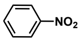


Figure S3. Cross-section views of **1** showing the inner void sphere (yellow) (a) and its diameter (b).

Table S1. Octanol/water partition coefficients (log P), dipole moments (μ), and molecular volumes of the guests, and amounts trapped within one molecule of **1** ($r = [\mathrm{G}]_\mathrm{t} / [\mathbf{1}]_0$), guest-occupying volumes, and volume% when **1** was treated with neat guest (200 molar equiv) for 96 h at room temperature.

	log P [a]	μ [a]	molecular volume (Å^3) [b]	$r = [\mathrm{G}]_\mathrm{t} / [\mathbf{1}]_0$	occupied volume (Å^3) [c]	occupied volume% [c]
	2.1	0	83.8	5.6	469.5	30
	3.1	0.1	101.0	4.0	404.0	26
	2.7	0.4	100.4	4.2	421.2	27
	1.5	1.2	97.8	5.5	507.3	33
	2.1	1.4	108.0	5.3	372.2	37
	3.3	1.7	107.7	3.2	344.6	16
	3.0	1.7	101.8	5.8	590.4	38
	2.8	1.7	97.8	7.0	684.8	44
	2.1	1.9	127.6	6.4	816.6	53
	2.3	1.7	88.8	9.1	808.1	52
	1.6	3.1	120.0	10.0	1200.0	77
	1.6	4.2	101.4	12.6	1419.9	92
	1.9	4.2	106.6	13.7	1460.0	94

[a] ref. 5. [b] Estimated from the molecular structures optimized by MOPAC calculation (ref. 4). [c] Based on the estimated volume of inner void sphere (1550.4 Å^3, Fig. S3).

References

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2. Winmostar V10, X-Ability Co. Ltd., Tokyo, Japan, **2022**.
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