

Supporting Information

Self-assembly of conformation-adaptive dihydrophenazine-based coordination cages

Meng-Xiang Wu,^{‡a} Qiong-Yan Hong,^{‡a} Minghui Li,^a Wei-Ling Jiang,^a Bin Huang,^a Shuai Lu,^b Heng Wang,^b Hai-Bo Yang,^a Xiao-Li Zhao*^a and Xueliang Shi*^a

^aSchool of Chemistry and Molecular Engineering, Shanghai Key Laboratory of Green Chemistry and Chemical Processes, East China Normal University, 3663 N, Zhongshan Road, Shanghai 200062, China.

Email: xlzhao@chem.ecnu.edu.cn; xlshi@chem.ecnu.edu.cn

^bCollege of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, Guangdong 518055, China.

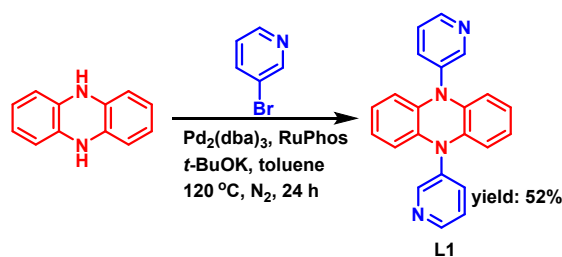
Contents

1 General.....	2
2 Synthesis and characterization.....	2
3 Additional figures and table.....	5
4 NMR and mass spectra	6
5 Single crystal data	19
6 Reference	20

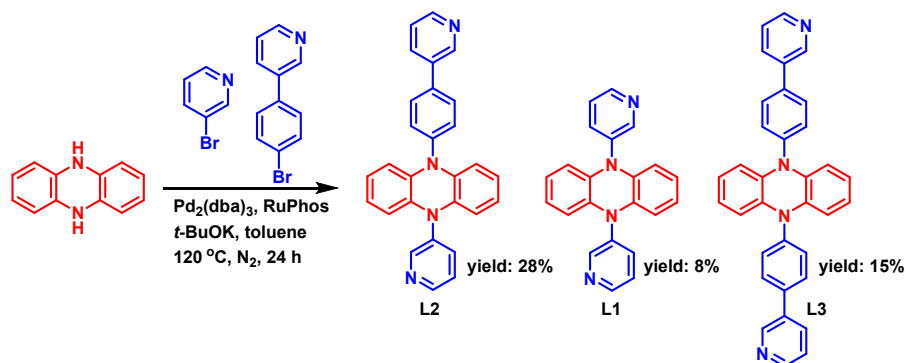
1 General

All experimental materials were acquired from Adamas Reagent Co., Ltd. (Shanghai, China), Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and Energy Chemical Co., Ltd. (Shanghai, China). All solvents (analytical grade) were obtained from commercial suppliers. Silica gel (200–300 mesh) was used to perform chromatography. The ^1H NMR, ^{13}C NMR and 2D NMR (DOSY) spectra were obtained using the Bruker 400 MHz spectrometer; moreover, tetramethylsilane (TMS) or solvent peaks were used as an internal standard. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet. High-resolution analysis (HRMS) were performed using an (Thermo QE focus LC/MS system). ESI-MS spectra were recorded with a Waters Synapt G2 mass spectrometer. UV-vis spectra were recorded in a quartz cell (light path 10 mm) on a Shimadzu UV2700 UV-visible spectrophotometer. Cyclic voltammetry (CV) was recorded on a Bio-Logic SAS SP-150 spectrometer in dichloromethane or acetonitrile containing *n*-Bu₄NPF₆ (0.1 M) as supporting electrolyte at a scan rate of 50 mV/s at room temperature. The CV cell has a glassy carbon electrode, a Pt wire counter electrode, and an Ag/Ag⁺ reference electrode. The potential was calibrated against the ferrocenium / ferrocene (Fc⁺/Fc) couple. The single crystals were measured on Rigaku XtaLAB PRO MM003-DS dual system with a Cu micro-focus source ($\lambda = 1.54184 \text{ \AA}$) and BL17B beamline at Shanghai Synchrotron Radiation Facility. Geometry structure optimized on GFN2-xTB by xtb-6.6.0 program.^{1,2}

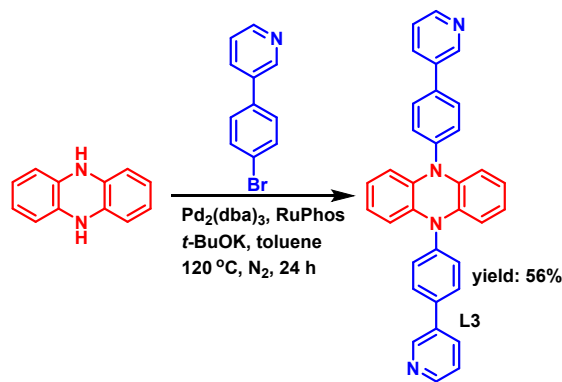
2 Synthesis and characterization



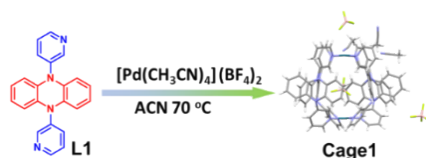
L1 was prepared according to the method reported by our previous work.³ A mixture of 2,5-dihydrophenazine (546.6 mg, 3.0 mmol), 3-bromopyridine (1042.8 mg, 6.6 mmol), Pd₂(dba)₃ (137.4 mg, 0.15 mmol), RuPhos (134.1 mg, 0.30 mmol) and *t*-BuOK (841.6 mg, 7.5 mmol) in toluene (20.0 mL) was stirred at 120 °C under N₂ atmosphere for 24 hours. After cooling to room temperature, the mixture was evaporated under reduced pressure, and the residue was washed by water (20.0 mL x 3) and ethyl acetate (3.0 mL), the residue was then purified by column chromatography on silica gel (eluent: chloroform) to give **L1** (524.6 mg) as a slight yellow solid in 52% yield. ^1H NMR (400 MHz, DMSO-*d*₆) δ (ppm) 8.74 (dd, $J = 4.8 \text{ Hz}, 1.5 \text{ Hz}, 2\text{H}$), 8.64 (d, $J = 2.5 \text{ Hz}, 2\text{H}$), 8.01–7.98 (m, 2H), 7.75–7.72 (m, 2H), 6.36–6.34 (m, 4H), 5.55–5.53 (m, 4H).



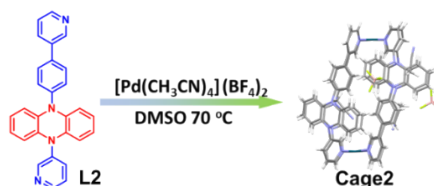
A mixture of 2,5-dihydrophenazine (546.6 mg, 3.0 mmol), 3-bromopyridine (1042.8 mg, 3.3 mmol), 3-(4-bromophenyl)pyridine (825.3 mg, 3.3 mmol), Pd₂(dba)₃ (137.4 mg, 0.15 mmol), RuPhos (134.1 mg, 0.30 mmol), and *t*-BuOK (841.6 mg, 7.5 mmol) in toluene (20.0 mL) was stirred at 120 °C under N₂ atmosphere for 24 hours. After cooling to room temperature, the mixture was evaporated under reduced pressure, and the residue was washed by water (20.0 mL x 3) and ethyl acetate (3.0 mL), the residue was then purified by column chromatography on silica gel (eluent: chloroform) to give **L2** as a slight yellow solid in 28% yield. In addition, **L1** (81.0 mg) and **L3** (218.5 mg) were also obtained. ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm) 9.01 (d, *J* = 2.4 Hz, 1H), 8.76 (dd, *J* = 7.8 Hz, 1.5 Hz, 1H), 8.66 (d, *J* = 2.3 Hz, 1H), 8.63 (d, *J* = 4.8 Hz, 1.6 Hz, 1H), 8.21 (dt, *J* = 8.0 Hz, 2.1 Hz, 1H), 8.05–8.00 (m, 3H), 7.73 (br, 1H), 7.56–7.52 (m, 3H), 6.34 (br, 4H), 5.65 (br, 2H), 5.53 (br, 2H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 178.6, 149.4, 149.0, 148.5, 138.0, 135.8, 134.5, 130.2, 123.8. HR-ESI-MS: *m/z* calculated for C₂₈H₂₀N₄ (M⁺): 412.1688, found: 412.1684.



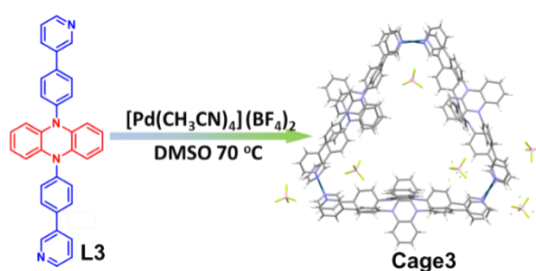
A mixture of 2,5-dihydrophenazine (546.6 mg, 3.0 mmol), 3-(4-bromophenyl)pyridine (1650.7 mg, 6.6 mmol), Pd₂(dba)₃ (137.4 mg, 0.15 mmol), RuPhos (134.1 mg, 0.30 mmol), and *t*-BuOK (841.6 mg, 7.5 mmol) in toluene (20.0 mL) was stirred at 120 °C under N₂ atmosphere for 24 hours. After cooling to room temperature, the mixture was evaporated under reduced pressure, and the residue was washed by water (20.0 mL x 3) and ethyl acetate (3.0 mL), the residue was then purified by column chromatography on silica gel (eluent: chloroform) to give **L3** (820.5 mg) as a slight yellow solid in 56% yield. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 8.94 (d, *J* = 2.4 Hz, 2H), 8.65 (d, *J* = 4.7 Hz, 2H), 7.98 (dt, *J* = 8.21 Hz, 1.7 Hz, 3H), 7.94 (br, 3H), 7.52 (br, 3H), 7.45–7.41 (m, 3H), 6.32 (br, 4H), 5.72 (br, 4H). HR-ESI-MS: *m/z* calculated for C₃₄H₂₄N₄ (M⁺): 488.2001, found: 488.1996.



Cage1 was prepared according to the method reported by our previous work.¹ A mixture of **L1** (15.6 mg, 46.4 μmol) and $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (10.3 mg, 23.2 μmol) in acetonitrile (0.7 mL) was stirred at 70 °C overnight. After cooling to room temperature, diethyl ether (10 mL) was added into it to obtain the crude product, and the precipitate was washed by toluene (4 mL) and diethyl ether (4 mL) and dried under reduced pressure to obtain a yellow solid in 92%. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ (ppm) 9.12 (d, $J = 2.4$ Hz, 8H), 8.62 (d, $J = 5.6$ Hz, 8H), 8.55–8.52 (m, 8H), 7.85–7.82 (m, 8H), 6.41 (br, 16H), 6.09 (br, 16H).



A mixture of **L2** (20.8 mg, 50.4 μmol) and $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (11.2 mg, 25.2 μmol) in dimethyl sulfoxide (1.0 mL) was stirred at 70 °C overnight. After cooling to room temperature, diethyl ether (10.0 mL) was added into it to obtain the crude product, and the precipitate was washed by toluene (4.0 mL) and diethyl ether (4.0 mL) and dried under reduced pressure to obtain a brown solid in 89%. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ (ppm) 9.58 (s, 4H), 9.48–9.47 (d, $J = 5.5$ Hz, 4H), 9.13–9.10 (m, 4H) 8.44–8.35 (m, 8H), 8.16–7.88 (m, 20H), 7.45–7.37 (m, 8H), 6.48–6.44 (m, 8H), 6.10–6.03 (m, 8H), 5.90–5.84 (m, 8H), 5.19–5.16 (m, 4H), 4.51–4.48 (m, 4H). ESI-MS: calcd for [**Cage2**+2 BF_4^-] $^{2+}$: $m/z = 1018.7453$, found: 1018.2925; calcd for [**Cage2**+ BF_4^-] $^{3+}$: $m/z = 649.8279$, found: 649.8588; calcd for [**Cage2**] $^{4+}$: $m/z = 465.8709$, found: 465.8897.



A mixture of **L3** (23.8 mg, 48.7 μmol) and $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (10.8 mg, 24.3 μmol) in dimethyl sulfoxide (1.0 mL) was stirred at 70 °C overnight. After cooling to room temperature, diethyl ether (10.0 mL) was added into it to obtain the crude product, and the precipitate was washed by toluene (4.0 mL) and diethyl ether (4.0 mL) and dried under reduced pressure to obtain a brown solid in 90%. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ (ppm) 9.83 (s, 12H), 9.46–9.45 (m, 12H), 8.51 (d, $J = 8.0$ Hz, 12H), 7.96–7.56 (m, 60H), 6.15 (br, 24H), 5.54 (br, 24H). ESI-MS: calcd for [**Cage3**+3 BF_4^-] $^{3+}$: $m/z = 1169.9745$, found: 1169.9906; calcd for [**Cage3**+2 BF_4^-] $^{4+}$: $m/z = 855.9808$, found: 855.9849.

3 Additional figures and table

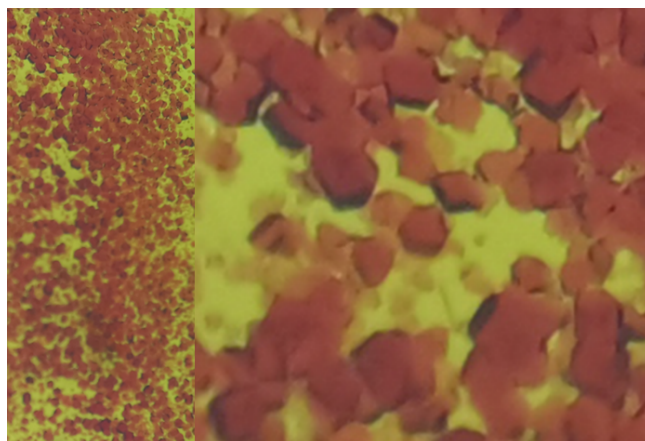


Figure S1. Schematic representation of the **Cage2** single crystal.

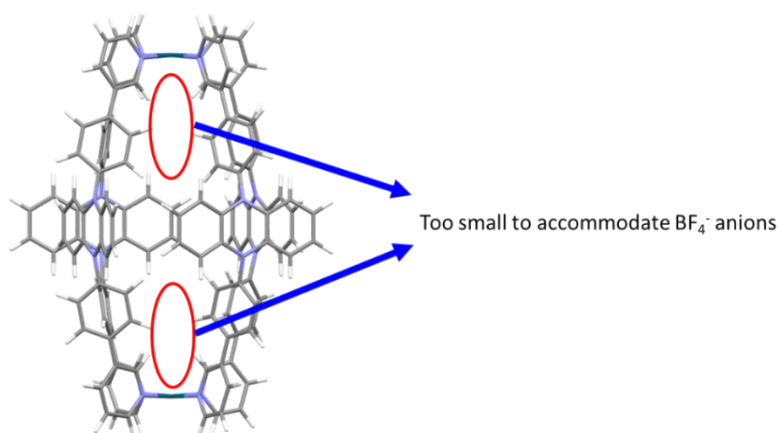


Figure S2. Optimized structure of assuming Pd_2L_4 -typed **Cage3**. The size and the shape of the cavity may make it unsuitable for guest BF_4^- anions encapsulation.

Table S1 Summary of the H–F and Pd–F bond length.

	Cage1	Cage2	Cage3
Average F–H bond length (\AA) ^a	2.33	2.34	2.51
F–H van der Waals radius (\AA) ^b	2.55	2.55	2.55
F–Pd bond length (\AA) ^a	2.72 (F–Pd ₁) 3.01 (F–Pd ₂)	3.45	3.18 (F–Pd ₁) 3.19 (F–Pd ₂) 2.97 (F–Pd ₃)
Average X–Pd bond length (\AA) ^a	2.86	3.45	3.11
F–Pd van der Waals radius (\AA) ^b	3.50	3.50	3.50

^a The bond length and cage volume data were determined from single crystals.

^b The data were obtained based on the standard van der Waals radii.⁴

4. NMR and mass spectra

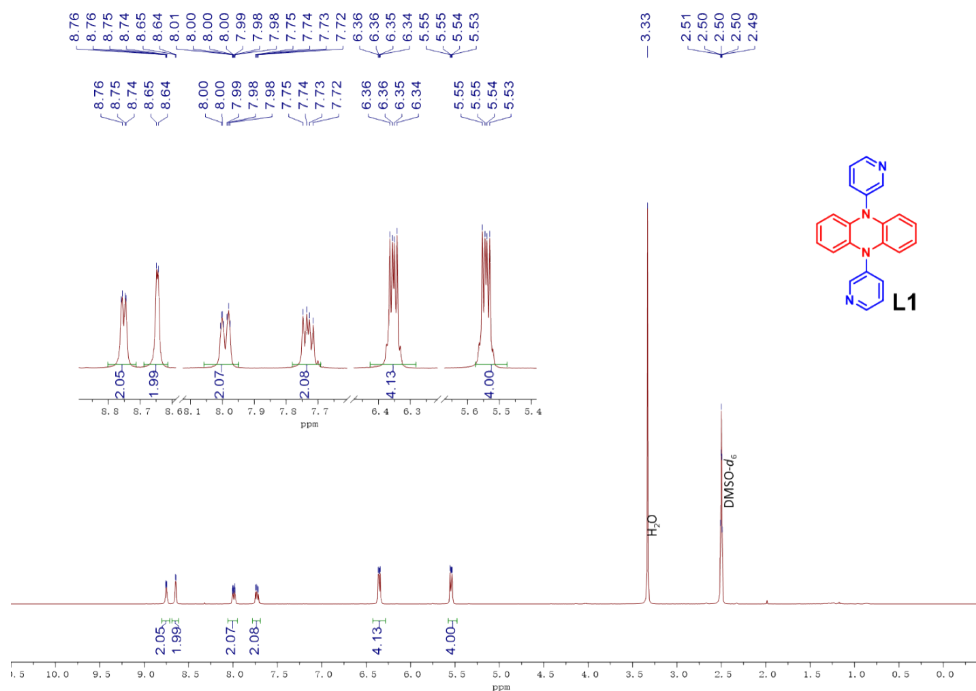


Figure S3. The ^1H NMR (400 MHz, 298 K) spectrum of **L1** in $\text{DMSO-}d_6$.

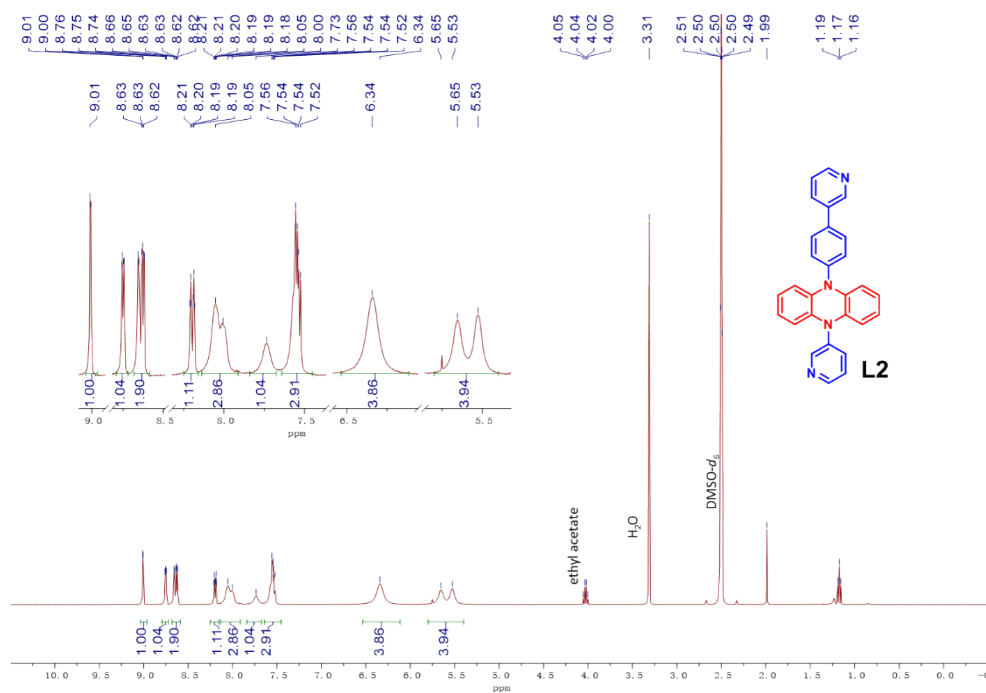


Figure S4. The ^1H NMR (400 MHz, 298 K) spectrum of **L2** in $\text{DMSO-}d_6$.

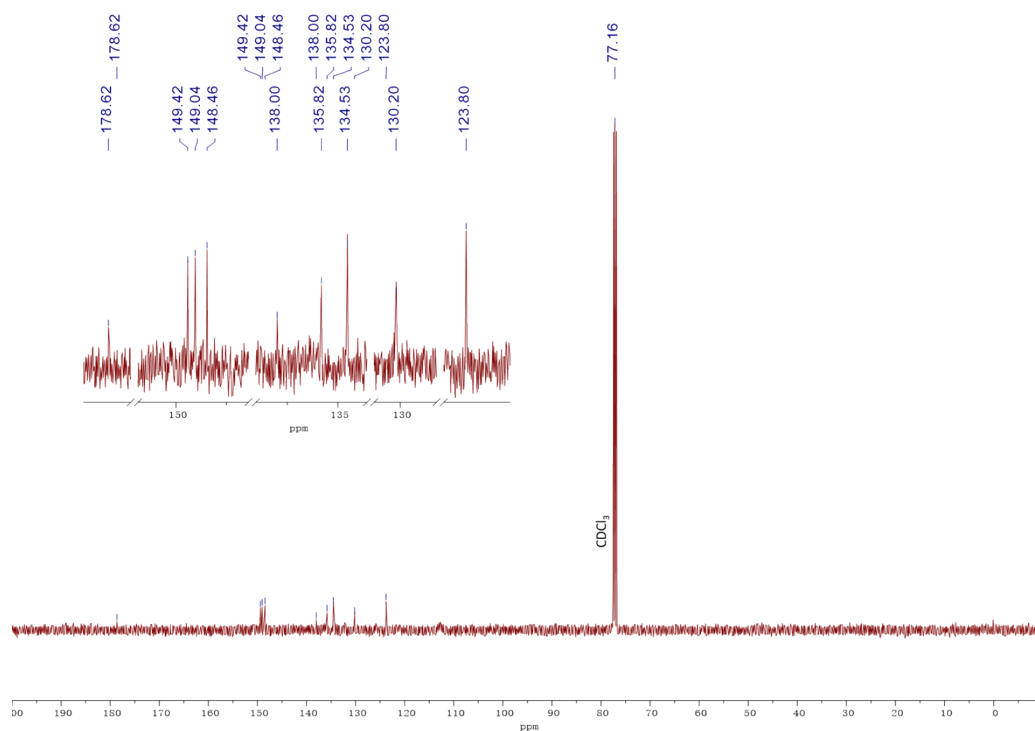


Figure S5. ^{13}C NMR (101 MHz, CDCl_3 , 298 K) spectrum of L2.

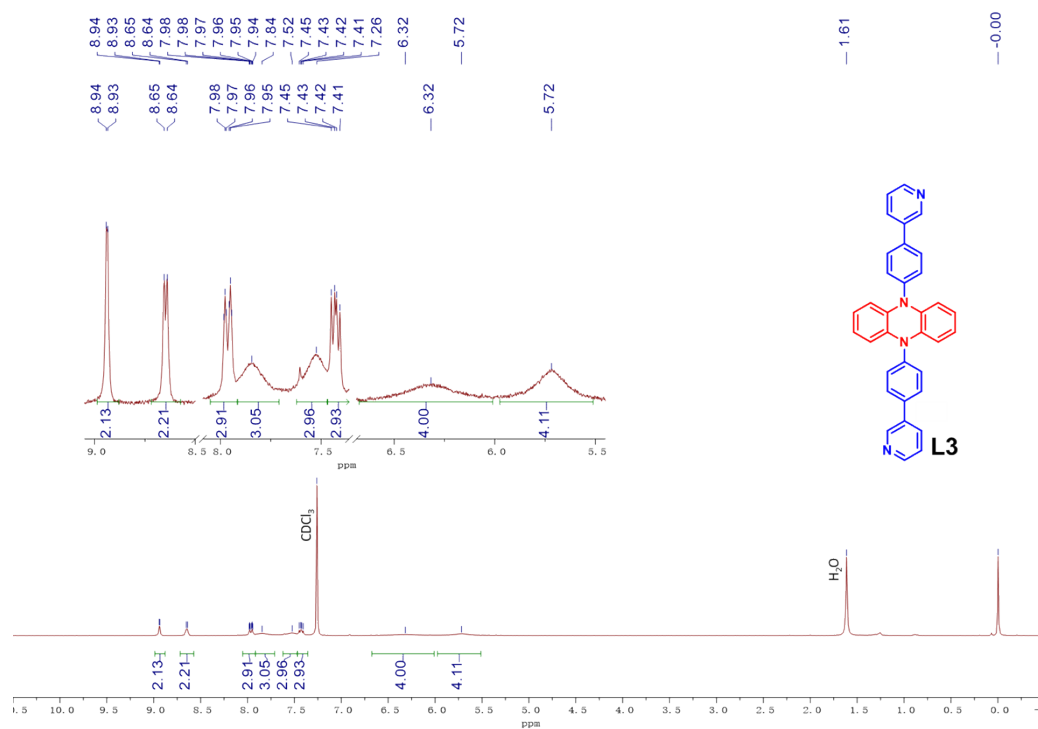


Figure S6. The ^1H NMR (300 MHz, 298 K) spectrum of L3 in CDCl_3 .

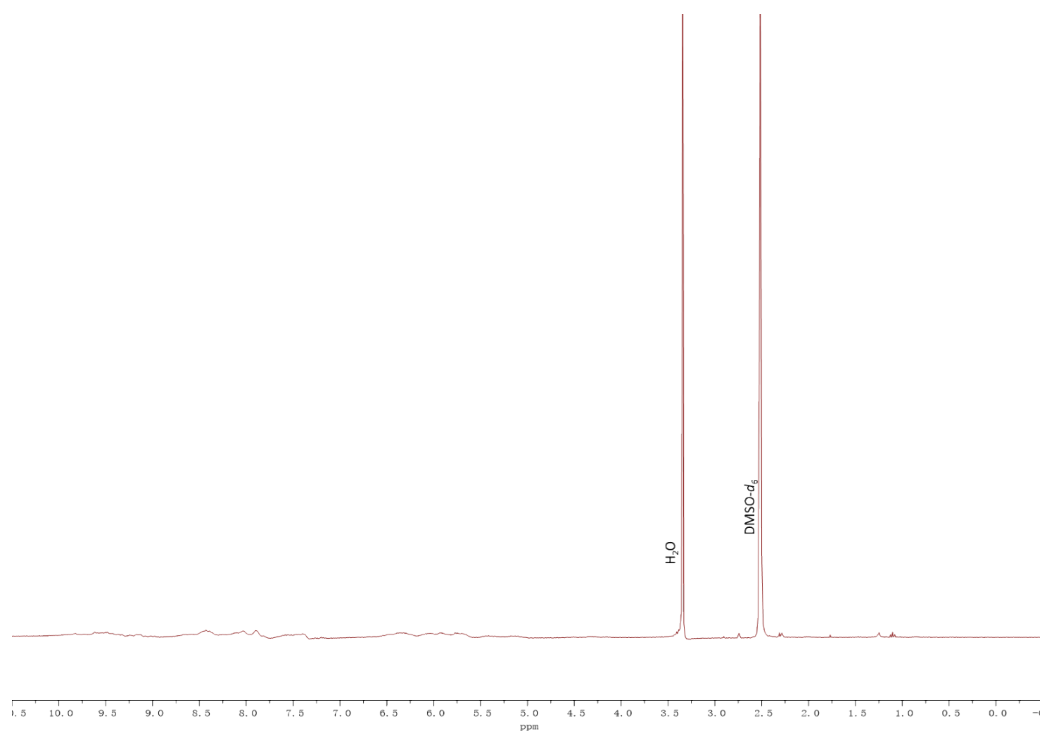


Figure S9. The ^1H NMR (400 MHz, 298 K) spectrum of the prepared pristine **Cage2** in $\text{DMSO-}d_6$.

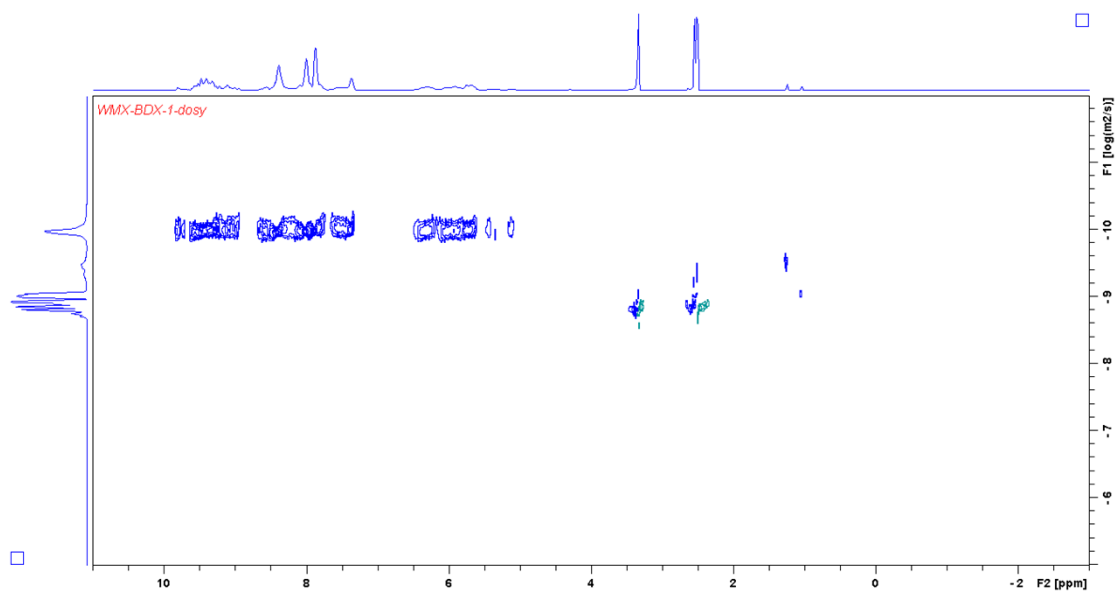


Figure S10. The DOSY-NMR (500 MHz, 298 K) spectrum of **Cage2** in $\text{DMSO-}d_6$.

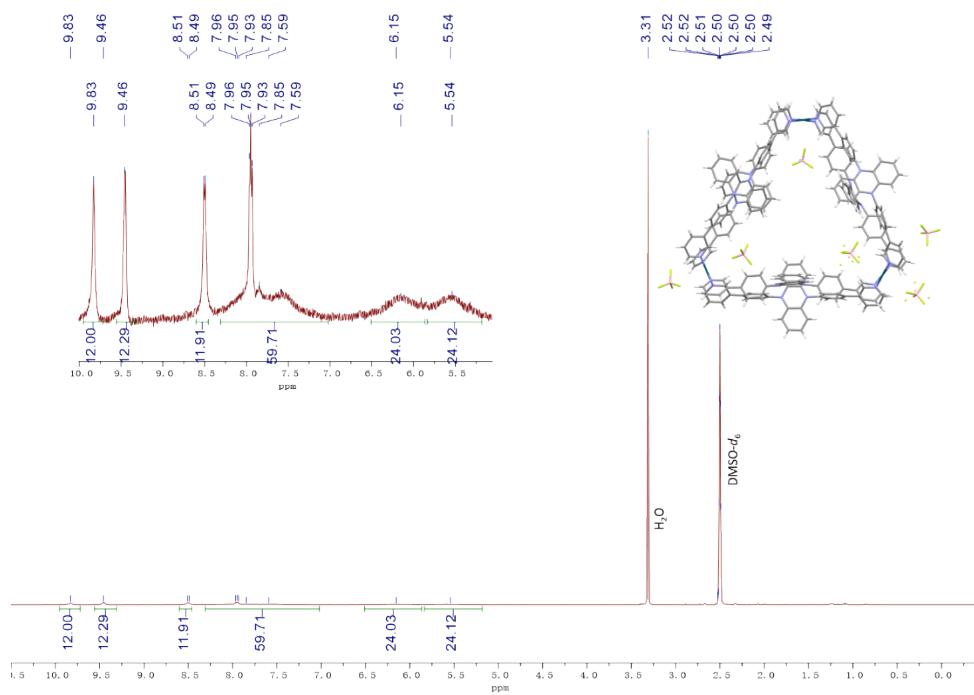


Figure S11. The ^1H NMR (400 MHz, 298 K) spectrum of **Cage3** in $\text{DMSO-}d_6$.

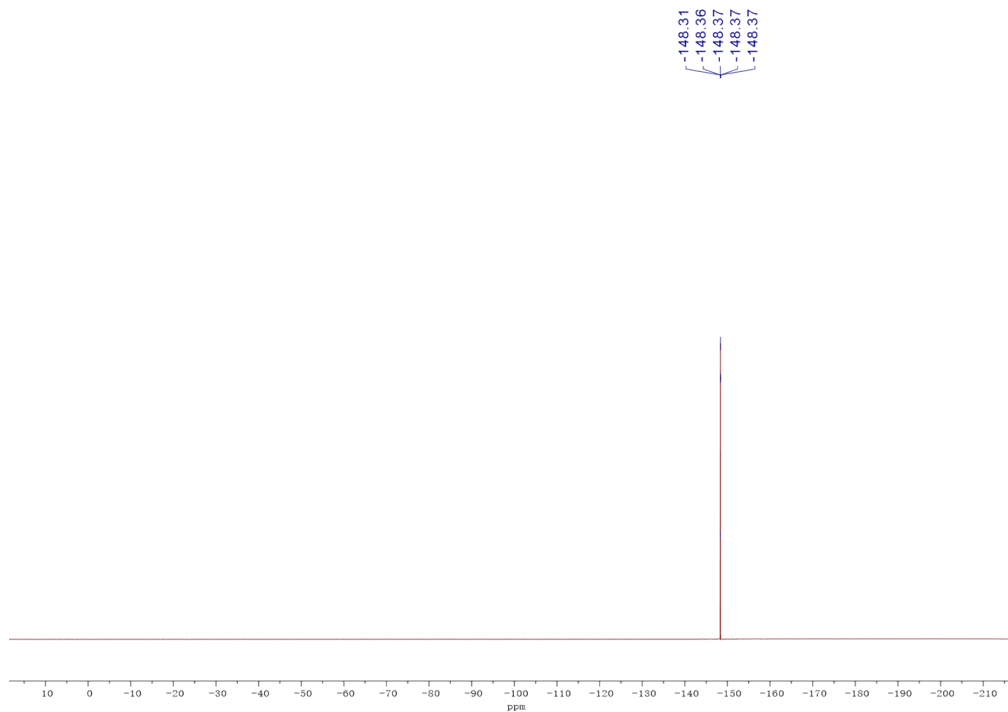


Figure S12. ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$, 298 K) spectrum of NaBF_4 .

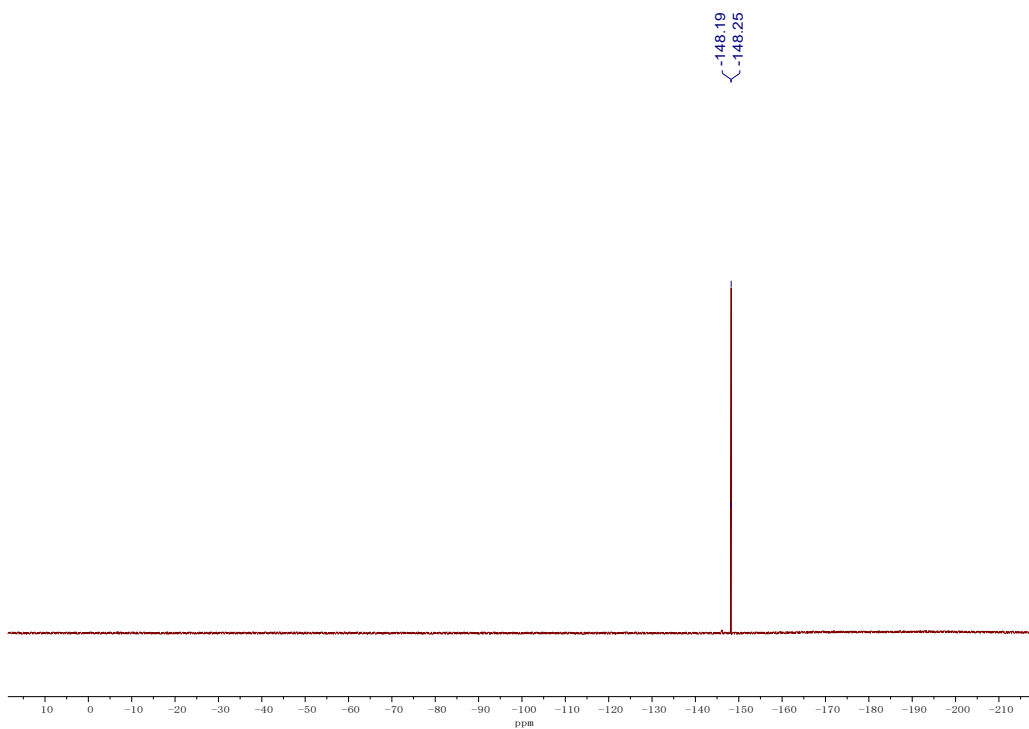


Figure S13. ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$, 298 K) spectrum of $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$.

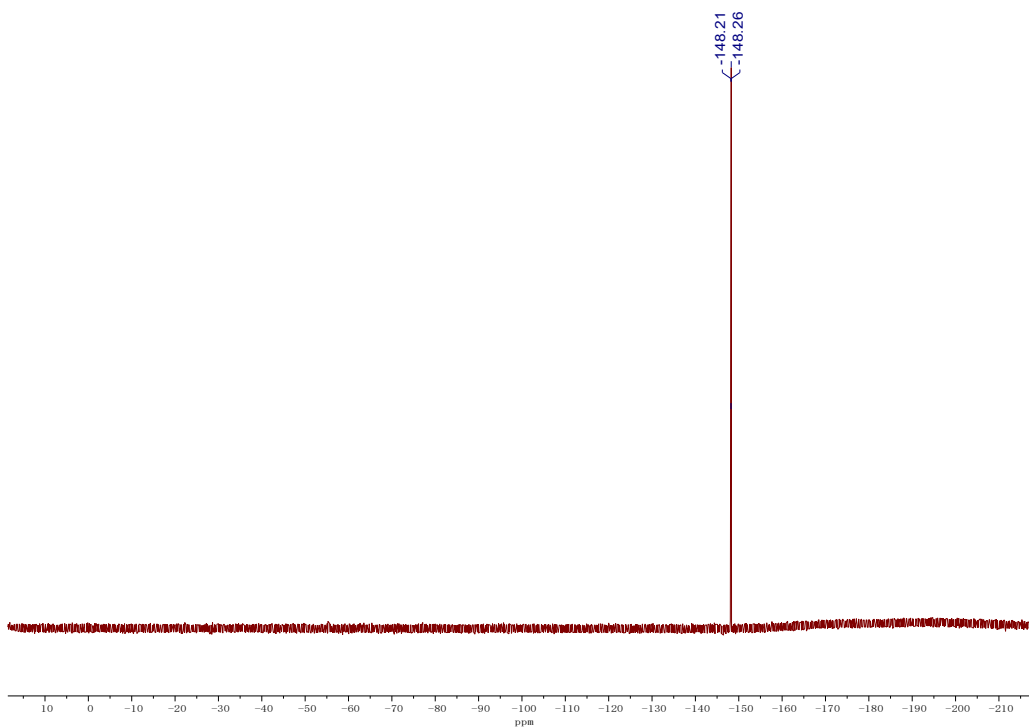


Figure S14. The ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$, 298 K) spectrum of **Cage1**.

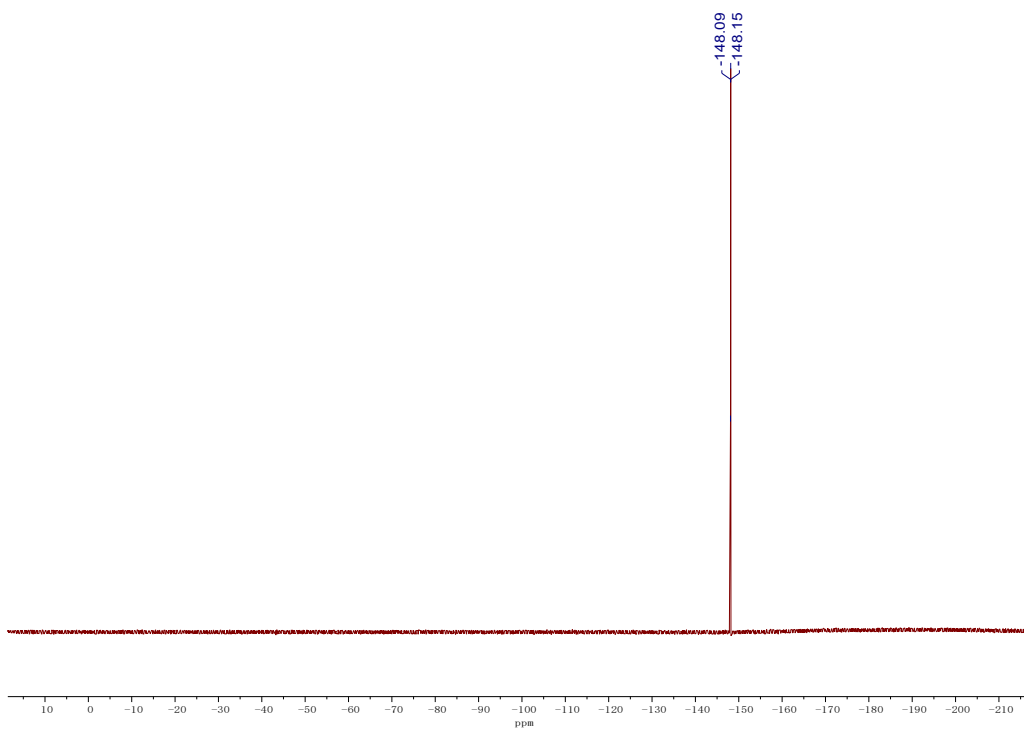


Figure S15. The ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$, 298 K) spectrum of **Cage2**.

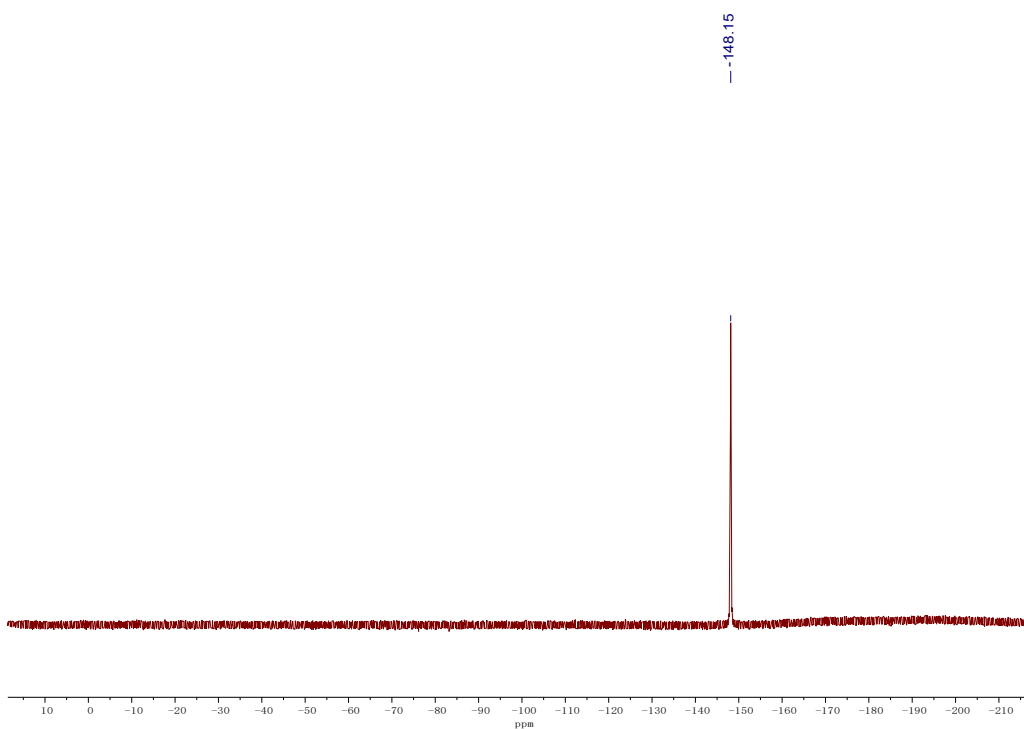


Figure S16. The ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$, 298 K) spectrum of **Cage3**.

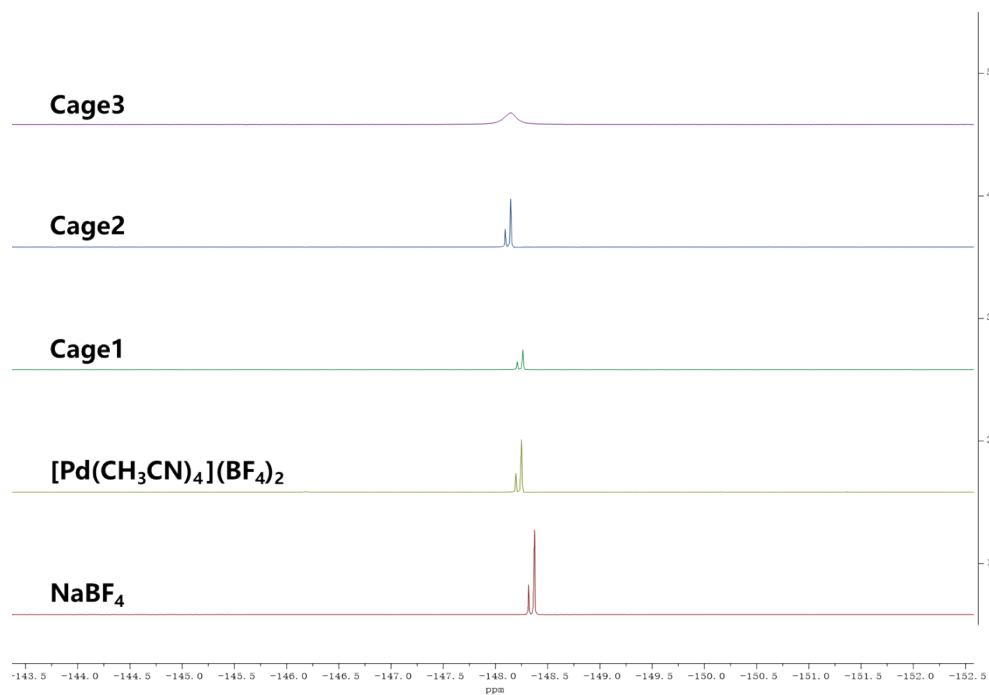


Figure S17. Partial ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$, 298 K) of **Cages**, $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ and NaBF_4 .

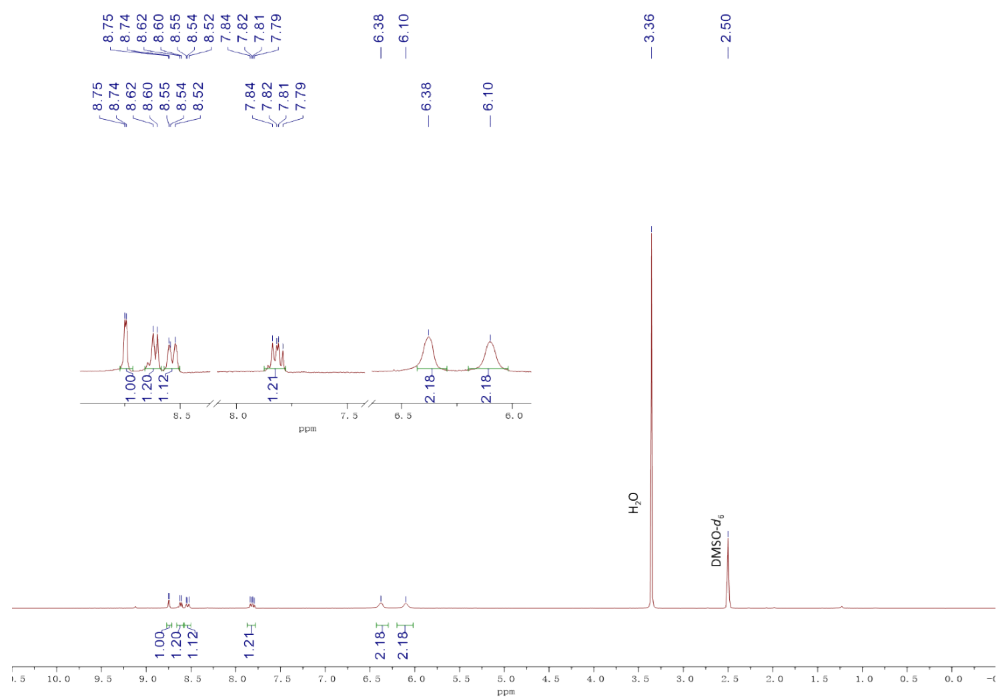


Figure S18. The ^1H NMR (400 MHz, 298 K) spectrum of **Cage1** (NO_3^-) in $\text{DMSO-}d_6$.

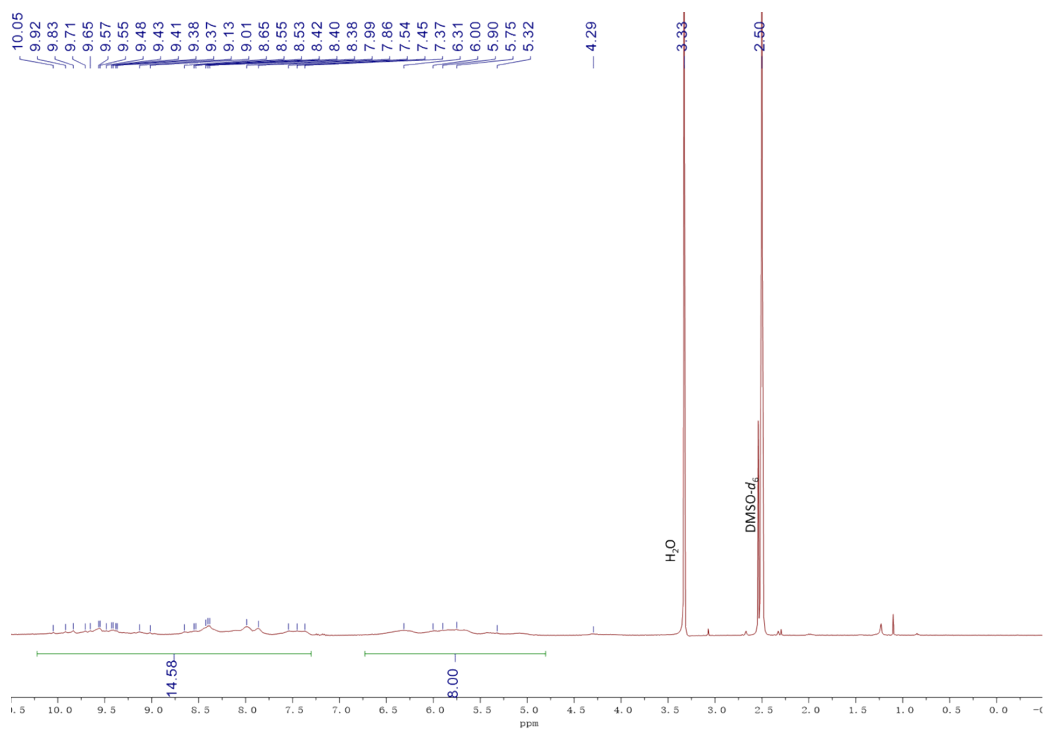


Figure S19. The ¹H NMR (400 MHz, 298 K) spectrum of **Cage2** (NO₃⁻) in DMSO-*d*₆.

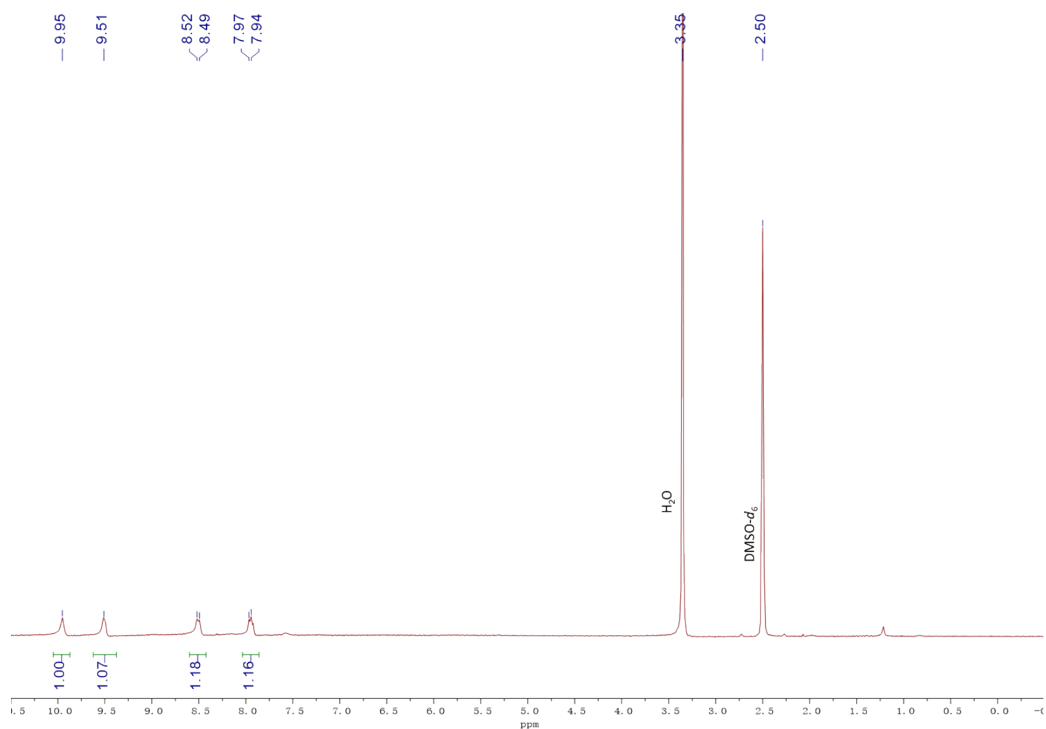


Figure S20. The ¹H NMR (400 MHz, 298 K) spectrum of **Cage3** (NO₃⁻) in DMSO-*d*₆.

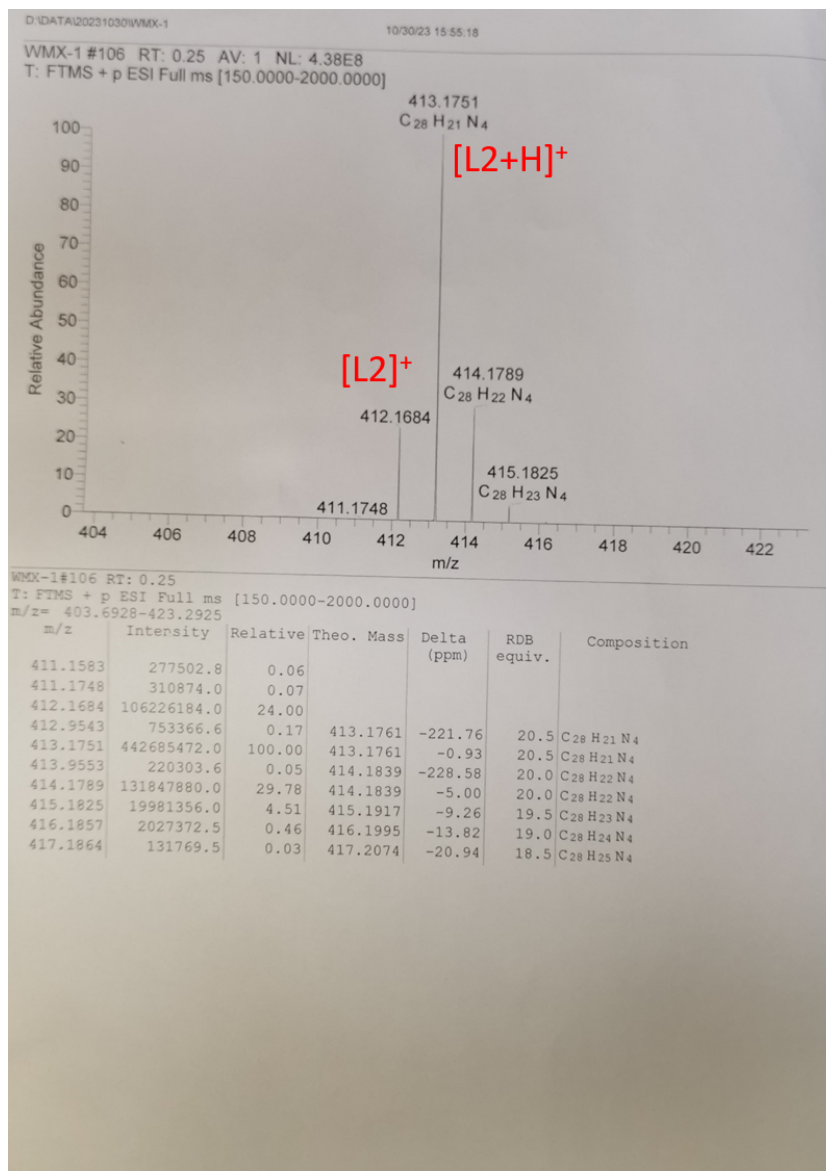


Figure S21. HRMS spectrum (ESI) of L2 (M)⁺.

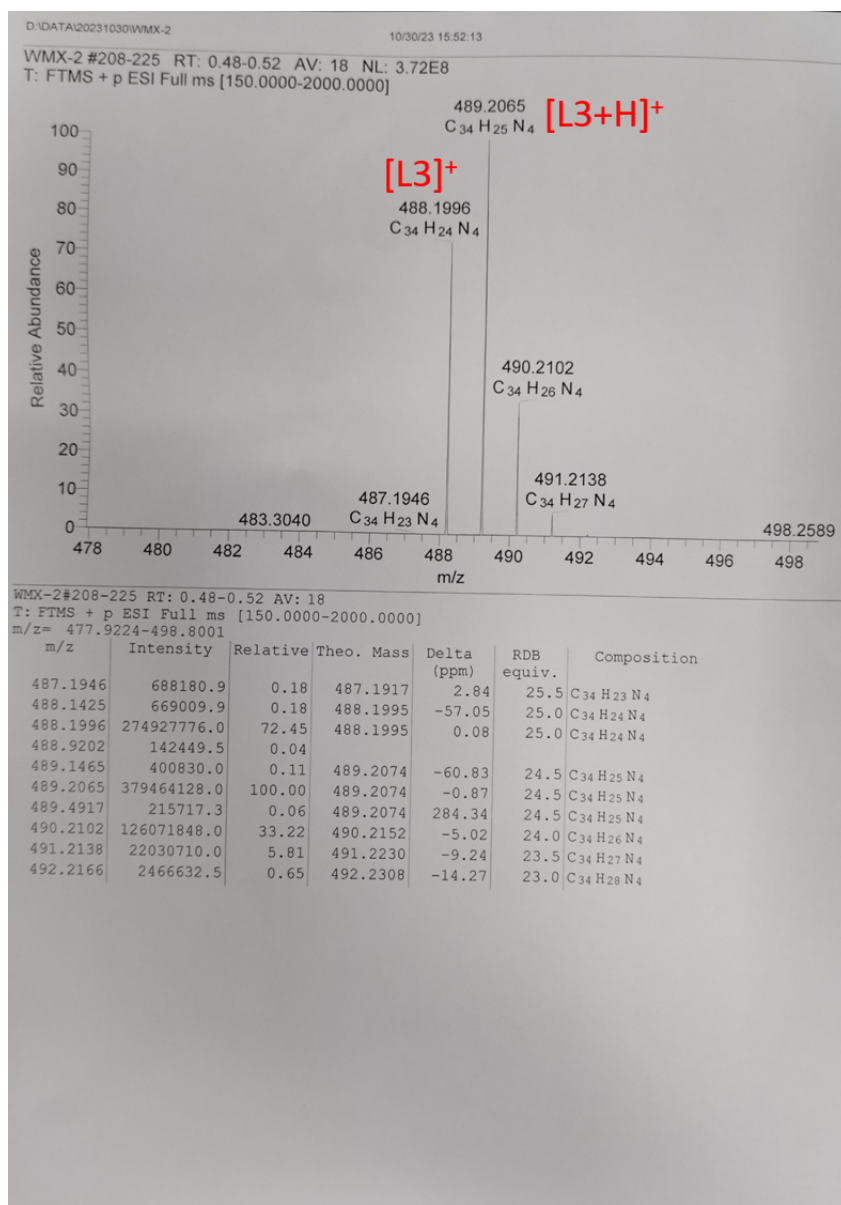


Figure S22. HRMS spectrum (ESI) of L3 (M)⁺.

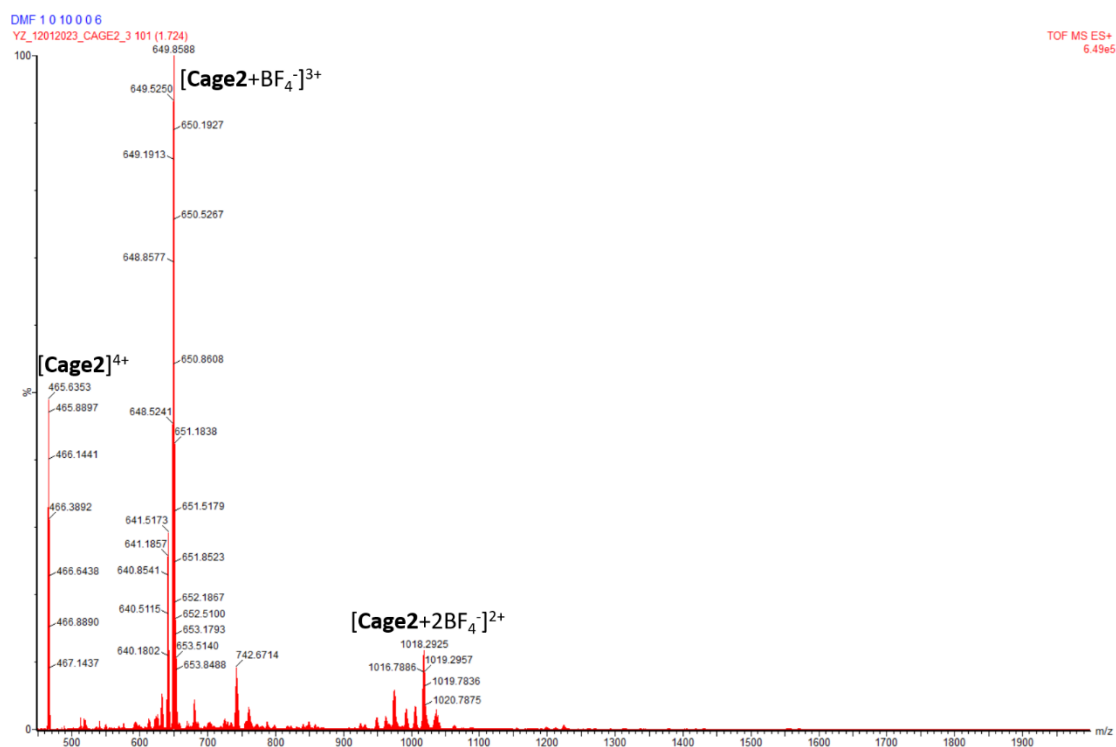


Figure S23. ESI-MS spectrum of [Cage2](BF₄)₀₋₂.

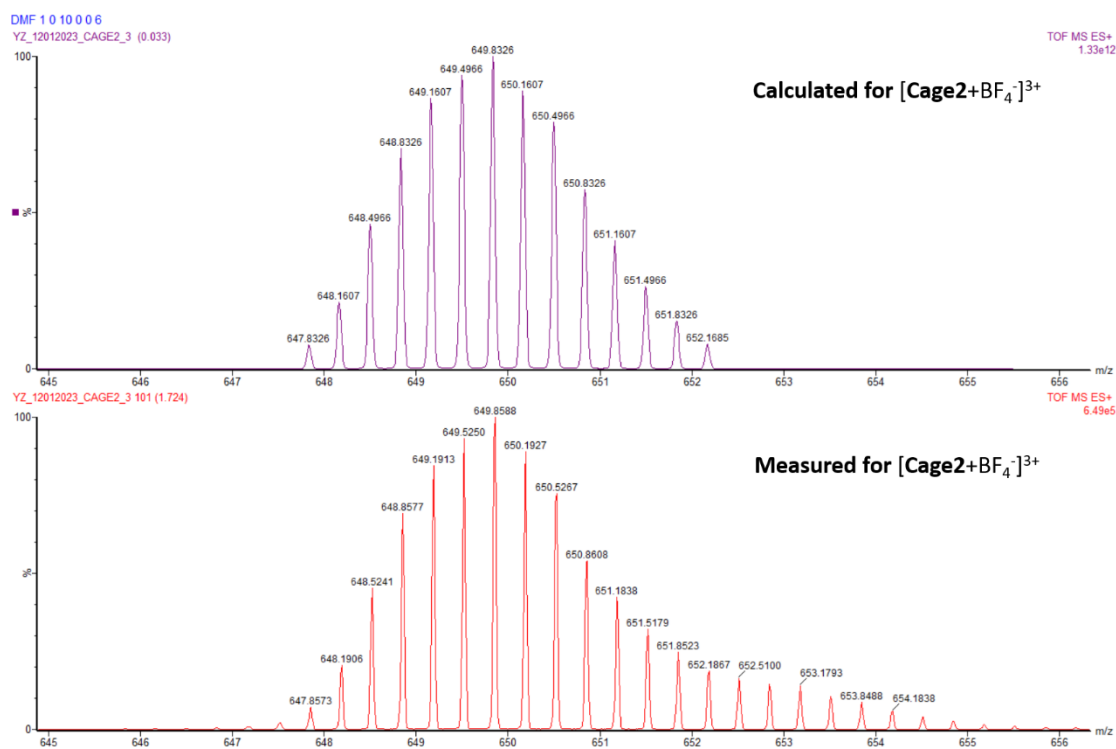


Figure S24. The calculated and measured isotopic pattern of species [Cage2+BF₄]³⁺.

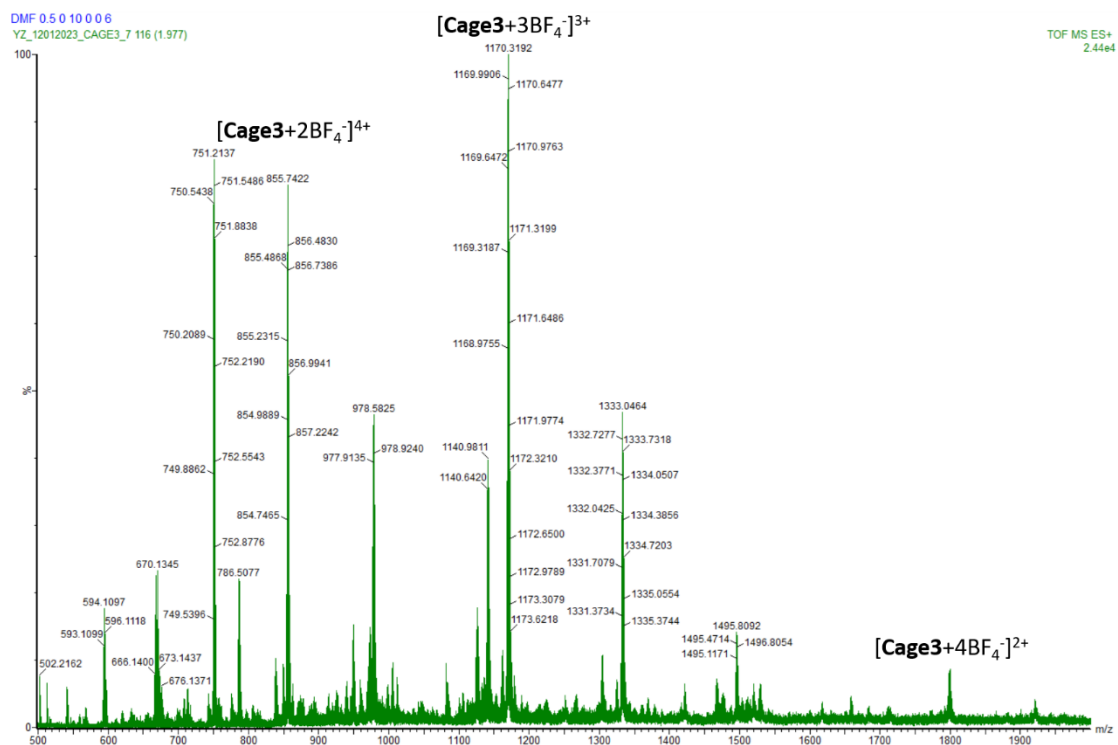


Figure S25. ESI-MS spectrum of [Cage3](BF₄)_{2.4}.

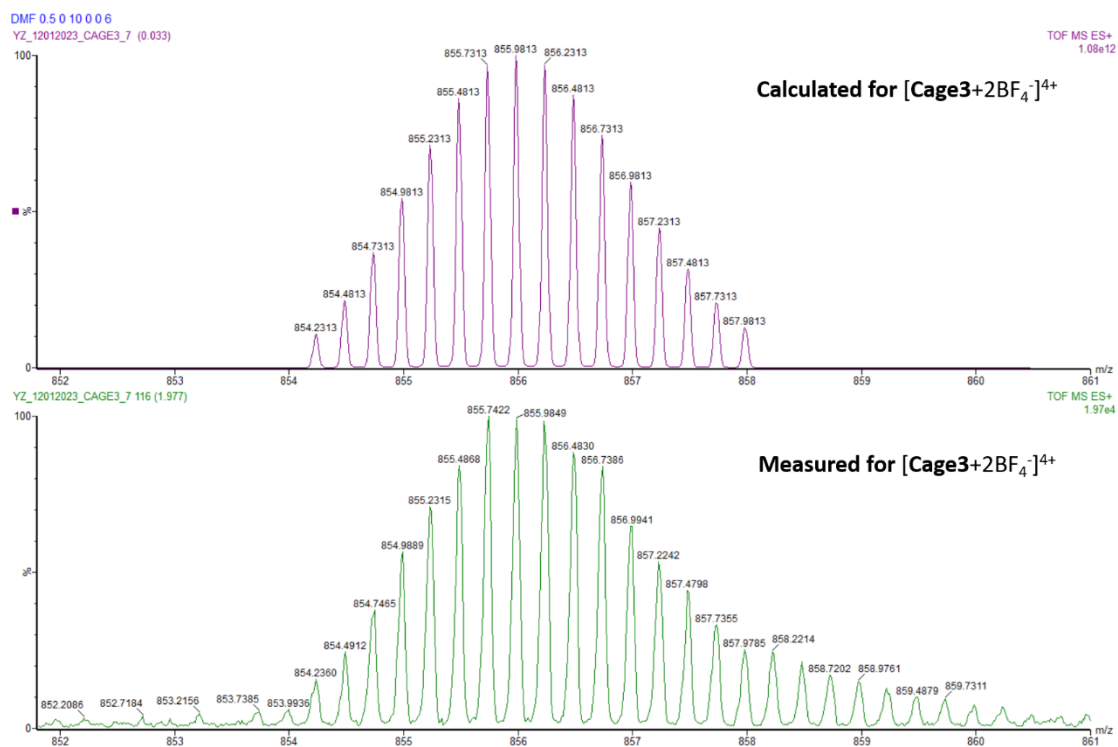


Figure S26. The calculated and measured isotopic pattern of species [Cage3+2BF₄⁻]⁴⁺.

5 Single crystal data

Table S2. X-ray single crystal data of **L2** and **L3**

Compound	L2	L3
Empirical formula	C _{29.5} H ₂₄ Cl ₃ N ₄	C ₃₆ H ₂₈ Cl ₄ N ₄
Formula weight	540.88	658.42
Temperature/K	173.00(10)	173.00(10)
Crystal system	monoclinic	monoclinic
Space group	C2	P2 ₁ /n
a / Å	26.380(4)	13.1218(6)
b / Å	7.7267(9)	7.9693(4)
c / Å	12.8140(17)	15.0239(9)
α / °	90	90
β / °	98.307(13)	98.834(5)
γ / °	90	90
Volume / Å ³	2584.5(6)	1552.44(14)
Z	4	2
ρ _{calc} / cm ³	1.390	1.409
μ / mm ⁻¹	3.417	3.724
F (000)	1120.0	680.0
Crystal size / mm ³	0.32 × 0.26 × 0.02	0.32 × 0.26 × 0.18
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection / °	8.994 to 134.132	8.336 to 134.098
Reflections collected	12548	14584
Data/restraints/parameters	3675/18/343	2768/0/199
Goodness-of-fit on F ²	1.153	1.081
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0958, wR ₂ = 0.2678	R ₁ = 0.0763, wR ₂ = 0.1969
Final R indexes [all data]	R ₁ = 0.1625, wR ₂ = 0.3543	R ₁ = 0.0947, wR ₂ = 0.2107
Largest diff. peak/hole / e Å ⁻³	0.37/-0.49	0.66/-0.86
CCDC	2298306	2298307

Table S3 X-ray single crystal data of **Cage2** and **Cage3**.

Compound	Cage2	Cage3
Empirical formula	C ₁₁₈ H ₈₉ B ₂ F ₈ N ₁₉ Pd ₂	C ₂₀₄ H ₁₄₄ B ₆ F ₂₄ N ₂₄ Pd ₃
Formula weight	2159.50	3771.48
Temperature/K	173(2)	307.0
Crystal system	monoclinic	triclinic
Space group	P2 ₁	P-1
a/Å	14.567(3)	16.7748(3)
b/Å	22.094(4)	28.6322(5)
c/Å	18.901(4)	29.6738(5)
α /°	90	110.4510(10)
β /°	105.02(3)	94.9270(10)
γ /°	90	100.3290(10)
Volume/Å ³	5875(2)	12965.9(4)
Z	2	2
$\rho_{\text{calc}}/\text{cm}^3$	1.221	0.966
μ/mm^{-1}	0.372	1.451
F(000)	2208.0	3840.0
Crystal size/mm ³	0.32 × 0.26 × 0.22	0.07 × 0.05 × 0.05
Radiation	MoK α (λ = 0.71073)	GaK α (λ = 1.34139)
2 θ range for data collection/°	5.79 to 55.842	4.72 to 110.03
Reflections collected	25580	157808
Data/restraints/parameters	25580/79/1344	48916/2107/2433
Goodness-of-fit on F ²	1.012	0.961
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0931, wR ₂ = 0.2469	R ₁ = 0.1022, wR ₂ = 0.2379
Final R indexes [all data]	R ₁ = 0.0981, wR ₂ = 0.2499	R ₁ = 0.2494, wR ₂ = 0.3090
Largest diff. peak/hole / e Å ⁻³	1.43/-0.72	0.89/-0.67
CCDC	2298304	2298305

6 Reference

1. C. Bannwarth, S. Ehlert and S. Grimme, *J. Chem. Theory Comput.*, 2019, **15**, 1652–1671.
2. Xtb standalone code (version 6.6.0). Please contact xtb@thch.uni-bonn.de for the program.
3. W.-L. Jiang, B. Huang, X.-L. Zhao, X. Shi and H.-B. Yang, *Chem*, 2023, **9**, 2655–2668.
4. S. S. Batsanov, *Inorg. Mater.*, 2001, **37**, 871–885.