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1. Materials and methods

General procedure. All reagents and deuterated solvents were used as purchased without further purification. Ligand **1** was purchased in the carboxylic acid form and obtained by the neutralization reaction with NaOH. Ligand **2** was prepared according to the literature procedure^[S1]. Column chromatography was conducted using SiO₂ (200 – 300 mesh). ³¹P{¹H} and ¹H NMR spectra were recorded at 295 K on a 400 MHz or 600 MHz Bruker Avance spectrometer. ¹H NMR chemical shifts were recorded relative to residual solvent signals. ³¹P{¹H} NMR chemical shifts were referenced to an external unlocked sample of 85% H₃PO₄ (δ 0.0). UV/vis absorption spectroscopy was conducted on a Lambda 950 absorption spectrophotometer. The fluorescence spectroscopy was conducted on a Hitachi F-7000 fluorescence spectrophotometer. Electrospray ionization-mass spectrometry (ESI-MS) was collected on a Waters Synapt G2-Si mass spectrometer (Waters Corp., Milford, MA, USA) with traveling wave ion mobility separation capability. The ESI-MS experiments were performed under the following conditions: ESI capillary voltage, 1–5 kV; sample cone voltage, 30–100 V; source temperature, 100 °C; desolvation temperature, 100 °C; cone gas flow, 10 L/h; desolvation gas flow, 800 L/h (N₂); source gas control, 0 mL/min; trap gas control, 2–3 mL/min; helium cell gas control, 180–200 mL/min; ion mobility (IM) cell gas control, 30 mL/min; sample flow rate, 5 μL/min; IM traveling wave height, 25–40 V; and IM traveling wave velocity, 800–1000 m/s. X-ray diffraction analysis was conducted a Bruker D8 VENTURE PHOTON II MetalJet, in which crystals were frozen in paratone oil inside a cryoloop under a cold stream of N₂. An empirical absorption correction using SADABS was applied for all data. The structures were solved and refined to convergence on F2 for all independent reflections by the full-matrix least squares method using the OLEX2 1.2. The anions of metallage **4c** was exchanged into PF₆⁻ and NO₃⁻ according to the published procedure^[S2]. Generally, **4c** (10.00 mg) was first dissolved in 1.0 mL of CH₃CN. The addition of a saturated aqueous solution of KPF₆ or KNO₃ (5 mL) to give a precipitate which was collected, washed with water and then dried to give the corresponding metallage in different anionic forms **4c**-PF₆⁻ and **4c**-

NO₃⁻. The geometry optimization and energy calculations were performed by using the semi-empirical GFN1-xTB method^[S3]. During the optimization, the GEO_OPT method with L-BFGS optimization algorithm^[S4] was employed, and for the electrostatic calculations, periodic boundary conditions were specified with no constraints in the electrostatic boundary conditions direction (NONE). A self-consistent field (SCF) convergence criterion of 1.0E-06 was utilized, and the activated orbital transformation (OT) method^[S5,S6] facilitates the direct minimization of the energy functional by optimizing molecular orbitals.

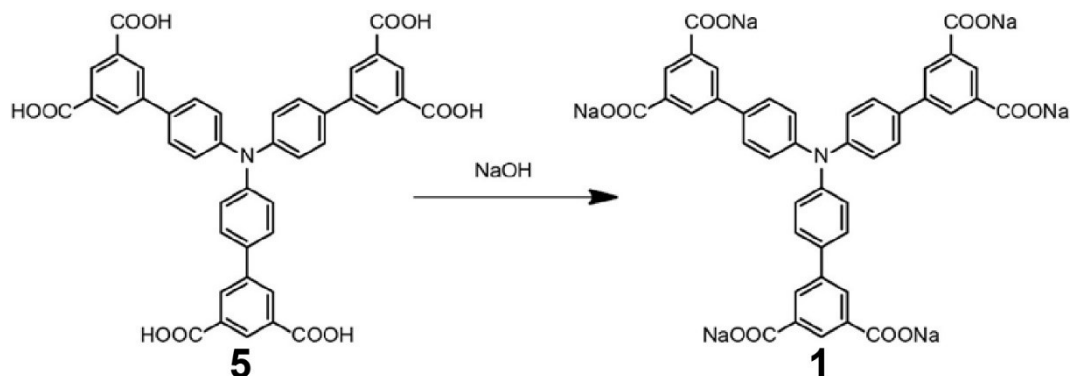
To calculate the hydrodynamic radii, we used the Stokes–Einstein equation^[S7]:

$$r = \frac{kT}{6\pi\eta D}$$

where r is radius, k is Boltzmann constant, T is temperature, η is dynamic viscosity of CD₃CN (3.69×10^{-4} Pa s⁻¹)²³ and D is diffusion value estimated by the DOSY experiment.

2. Synthetic procedures and characterization data

2.1 Synthesis of compound 1



Compound **5** (500.0 mg, 0.68 mmol) and NaOH (170.79 mg, 4.27 mmol) were added in H₂O (50.0 mL) and stirred at room temperature for 6 h. Then the mixture was concentrated and washed by acetone to give **1** (556 mg, 94%) as a white solid. ¹H NMR (400 MHz, CD₃OD, 295 K) δ 8.43 (s, 3H), 8.33 (s, 6H), 7.74 (d, *J* = 8.2 Hz, 6H), 7.26 (d, *J* = 8.2 Hz, 6H).

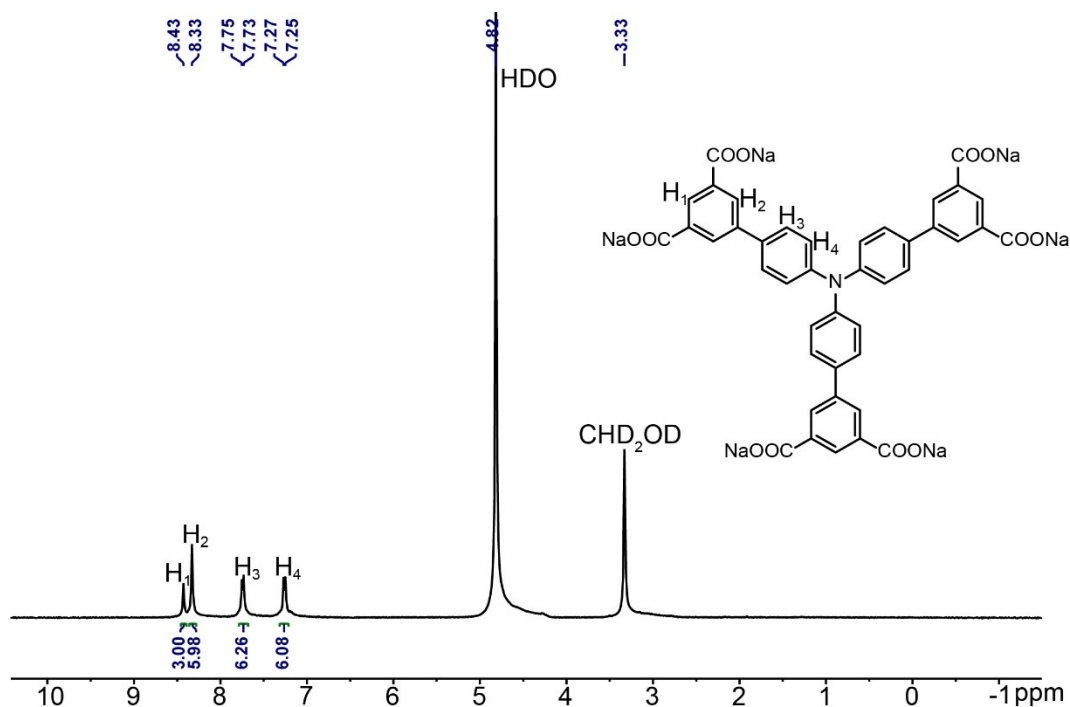
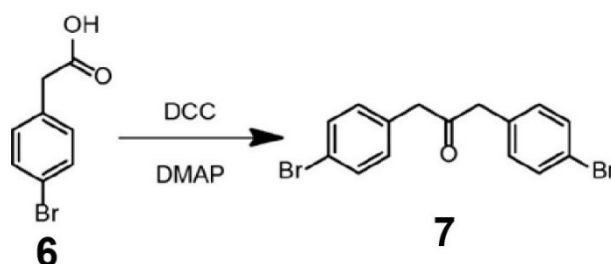


Figure S1. ¹H NMR spectrum (CD₃OD, 400 MHz, 295 K) recorded for **1**.

2.2 Synthesis of compound 7



A solution of *N,N*-dicyclohexylcarbodiimide (4.80 g, 11.16 mmol) and 4-dimethylaminopyridine (0.60 g, 6.05 mmol) in dry DCM (100.0 mL) was stirred at 0 °C under argon, and then a solution of 2-(4-bromophenyl)acetic acid (**6**, 5.20 g, 24.18 mmol) in dry DCM (20.0 mL) was added dropwise. The resulting mixture was stirred at room temperature for another 24 h. The white precipitate was filtered off, and the filtrate was concentrated and purified by flash column chromatography (dichloromethane: petroleum ether = 1: 5) to give the pure product **7** (4.85 g, 65%) as yellow solid. ¹H NMR (400 MHz, CDCl₃, 295K) δ 7.45 (d, *J* = 8.3 Hz, 4H), 7.01 (d, *J* = 8.3 Hz, 4H), 3.68 (s, 4H). The ¹H NMR spectrum of **7** matched well with reported literature.^[S1]

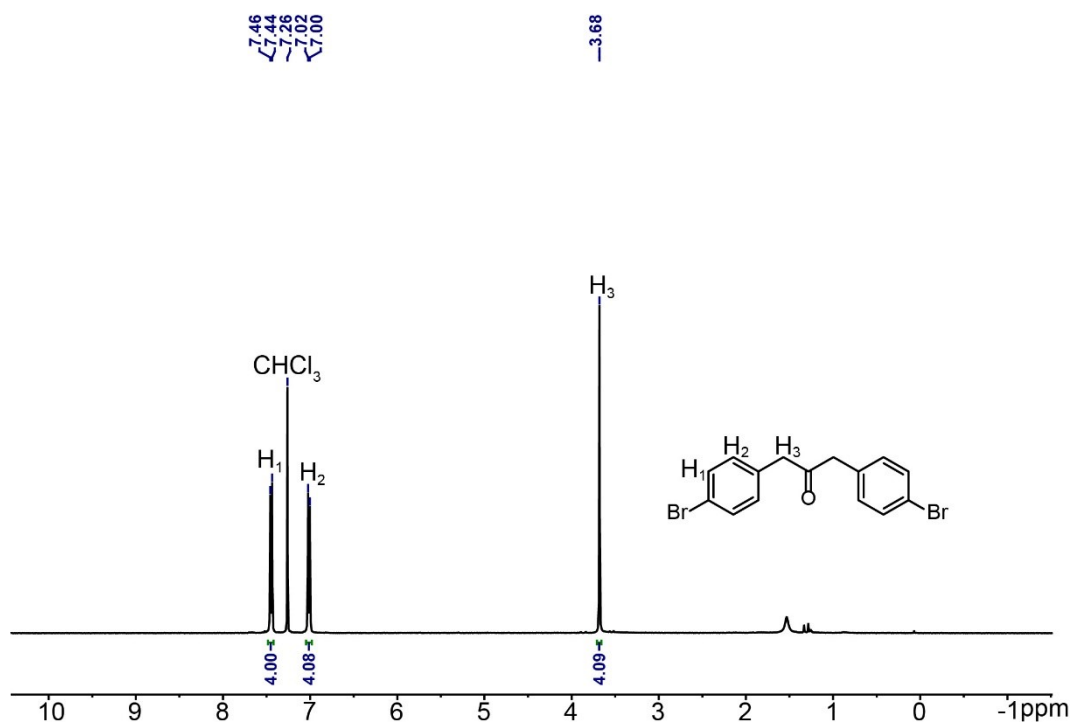
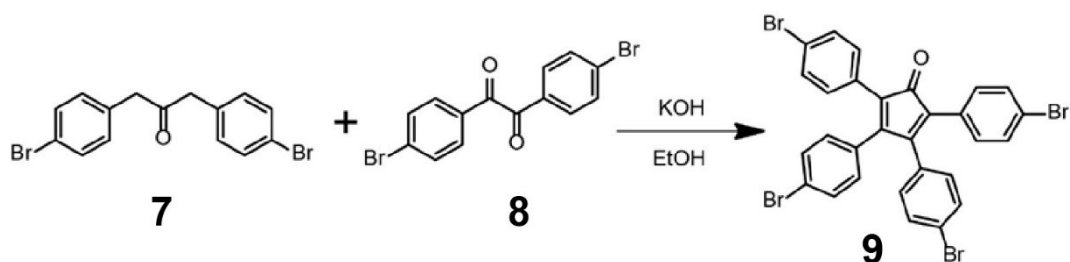


Figure S2. ¹H NMR spectrum (CDCl₃, 400 MHz, 295 K) recorded for **7**.

2.3 Synthesis of compound **9**



A solution of KOH (0.30 g, 5.35 mmol) in ethanol (5.0 mL) was added to a mixture of 1,3-bis(4-bromophenyl)propan-2-one **7** (2.70 g, 7.34 mmol) and 4,4'-dibromobenzil (**8**, 2.70 g, 7.34 mmol) in ethanol (20.0 mL). The resulting mixture was heated at reflux for 3 h. The mixture was then cooled to 0 °C through ice bath, and the resulting precipitate was collected by filtration and dried to give product **9** (4.38 g, 85%) as a dark purple solid. ¹H NMR (400 MHz, CDCl₃, 295K) δ 7.38 (dd, *J* = 12.2, 8.5 Hz, 8H), 7.06 (d, *J* = 8.5 Hz, 4H), 6.77 (d, *J* = 8.5 Hz, 4H). The ¹H NMR spectrum of **9** matched well with reported literature.^[S1]

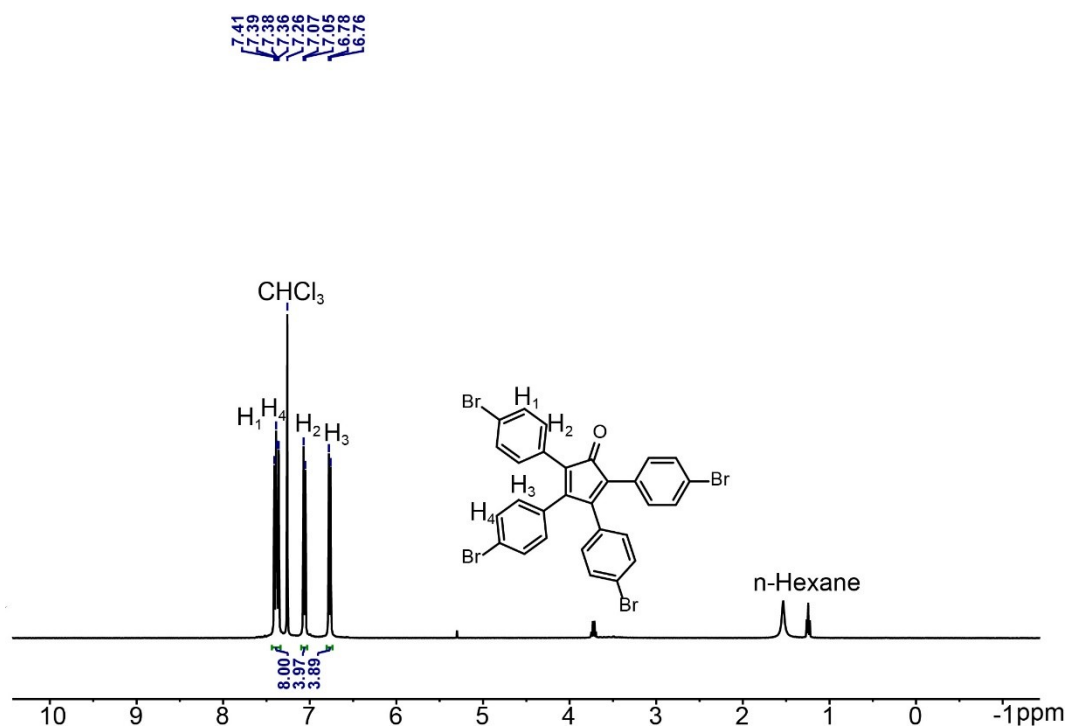
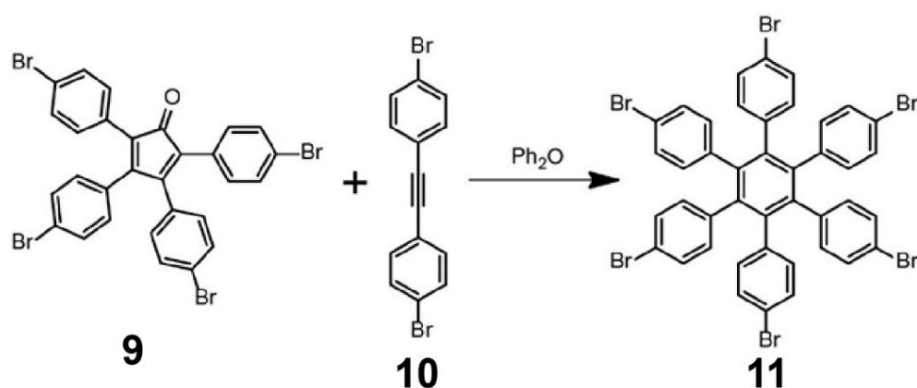


Figure S3. ¹H NMR spectrum (CDCl₃, 400 MHz, 295 K) recorded for **9**.

2.4 Synthesis of compound **11**



A mixture of compound **9** (3.50 g, 5.00 mmol) and bis(4-bromophenyl) acetylene (**10**, 1.68 g, 5.00 mmol) in diphenyl ether (5.0 mL) was heated at 260 °C under N_2 for 48h. The resulting mixture was cooled to 25 °C and then diluted with ethanol. The precipitate was collected by filtration, washed with ethanol and hexane, and dried to give product **11** (4.14 g, 82%) as a light yellow solid. ^1H NMR (400 MHz, CDCl_3 , 295K) δ 7.06 (d, $J = 8.4$ Hz, 12H), 6.61 (d, $J = 8.4$ Hz, 12H). The ^1H NMR spectrum of **11** matched well with reported literature.^[S1]

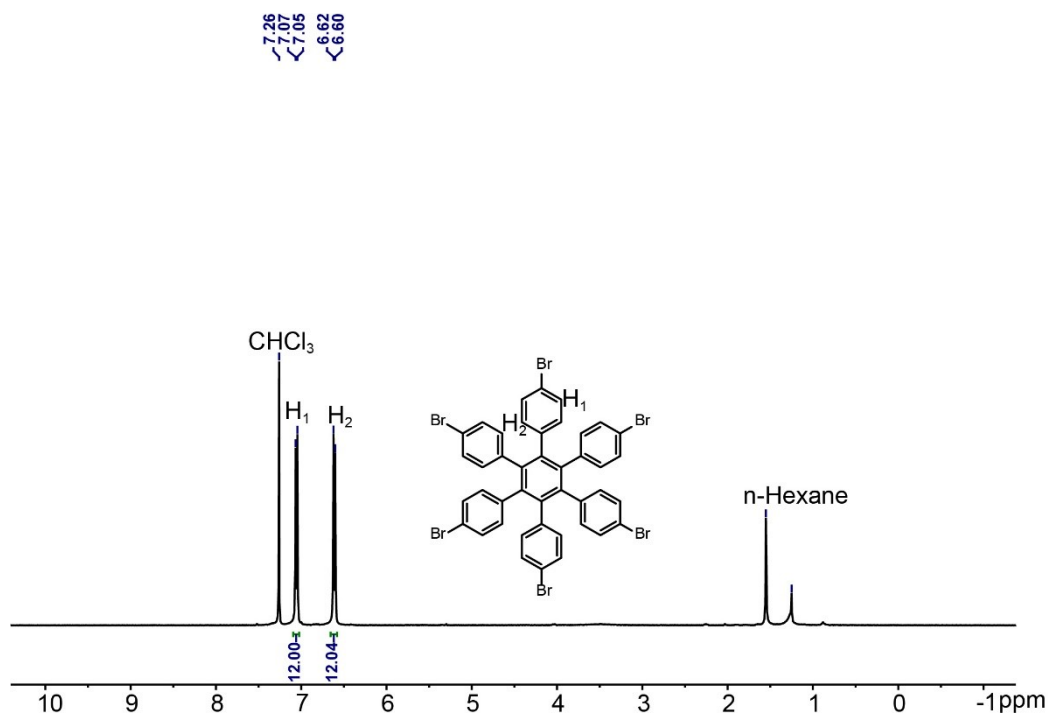
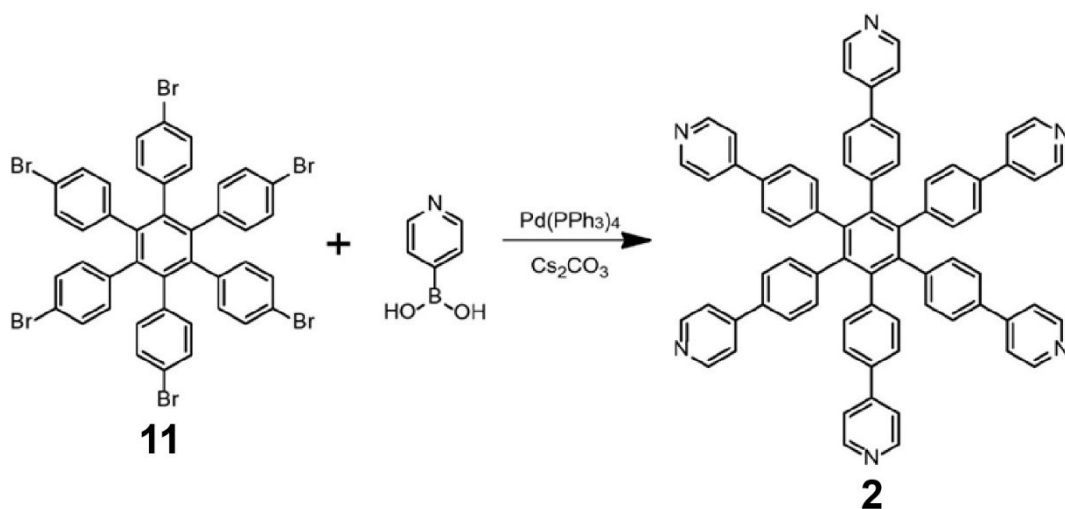


Figure S4. ^1H NMR spectrum (CDCl_3 , 400 MHz, 295 K) recorded for **11**.

2.5 Synthesis of compound 2



4,4''-dibromo-3',4',5',6'-tetrakis(4-bromophenyl)-1,1':2',1''-terphenyl (**11**, 2.00 g, 1.98 mmol), pyridine-4-boronic acid (2.44 g, 19.84 mmol), Pd(PPh₃)₄ (100.0 mg, 158.72 μmol), Cs₂CO₃ (7.76 g, 23.81 mmol) were mixed in a 250.0 mL Schlenk flask. After degassing and backfill with nitrogen for three times. Then toluene/ethanol/water (80.0 mL/20.0 mL/20.0 mL) was added and the whole mixture was heated at 90°C for 6 days under N₂ atmosphere. After being cooled to room temperature, a saturated NaHCO₃ was added the organic components were extracted with CH₂Cl₂. The organic layer was washed with water and brine, dried over MgSO₄, filtrated and evaporated under reduced pressure. The residue was purified by flash column chromatography (dichloromethane: methanol = 20:1) to give ligand **2** (0.63 g, 32%) as a white solid. ¹H NMR (600 MHz, CDCl₃, 295K) δ 8.54 (d, *J* = 3.6 Hz, 8H), 7.33 (d, *J* = 3.6 Hz, 8H), 7.25 (d, *J* = 7.6 Hz, 8H), 7.02 (d, *J* = 7.6 Hz, 8H). ESI-HR-MS: *m/z* 997.22 [**2** + H⁺], calcd. For [C₇₂H₄₉N₆]⁺, 997.40.

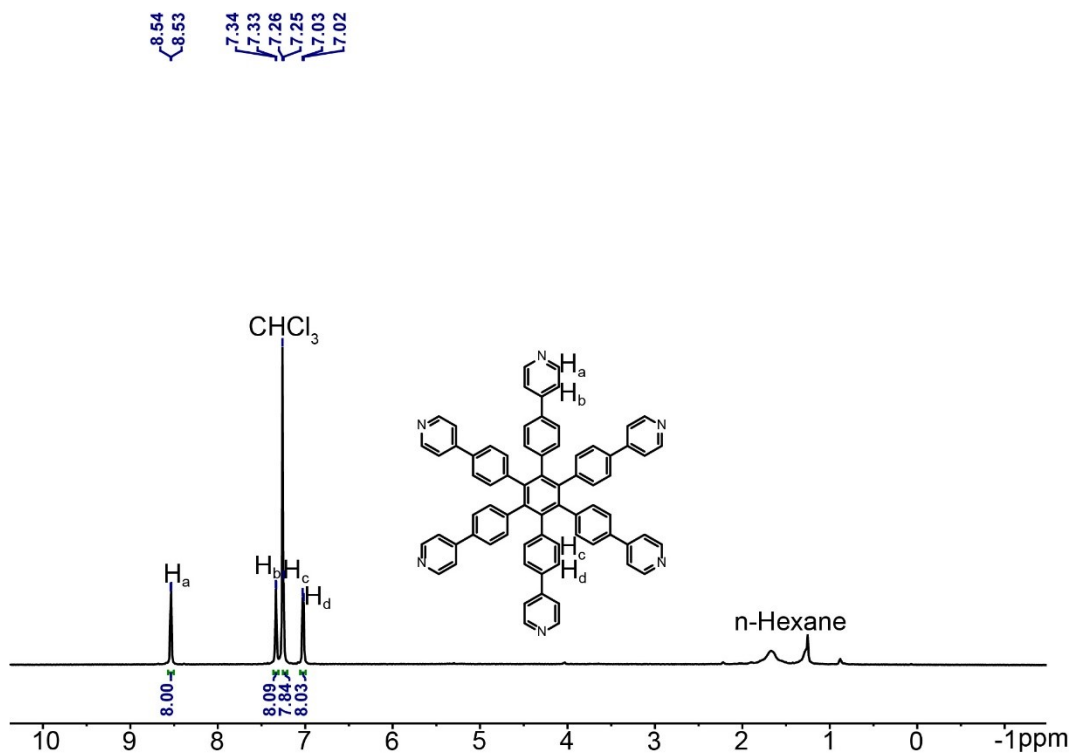


Figure S5. ^1H NMR spectrum (CDCl₃, 600 MHz, 295 K) recorded for **2**.

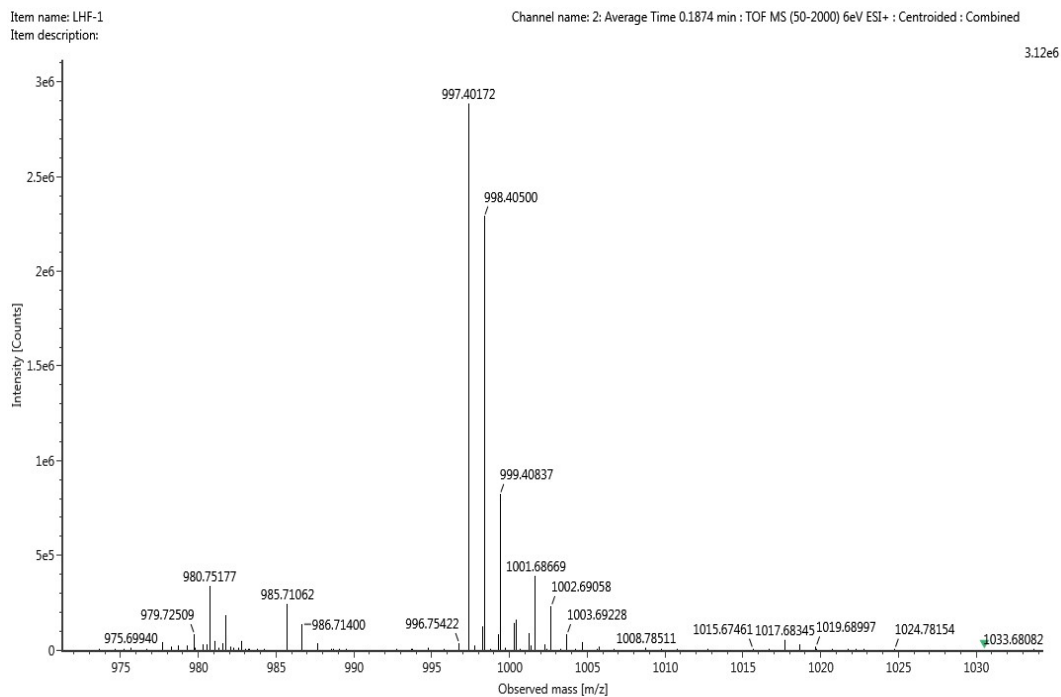
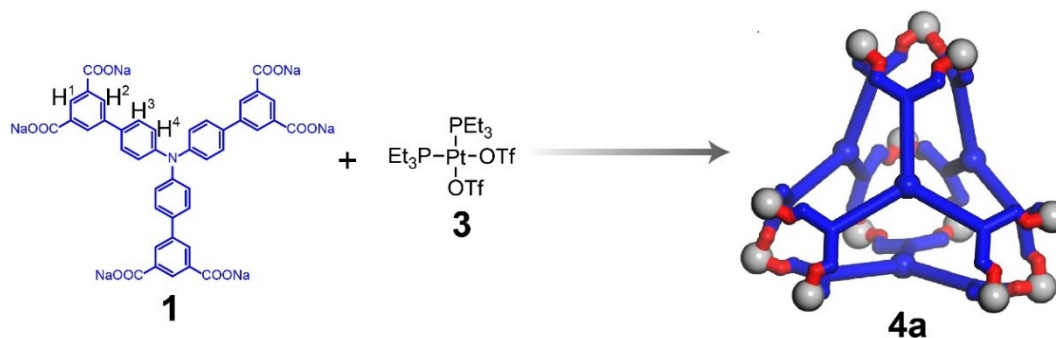


Figure S6. ESI-HR-MS spectrum of **2**.

3. Self-assembly of metallacages and characterization data

3.1 Self-assembly of metallacage **4a**



1 (10.00 mg, 11.50 μmol) and **3** (25.17 mg, 34.50 μmol) were mixed in acetonitrile/water (20.0 mL, 4:1, v/v). The whole reaction mixture was heated at 60 $^{\circ}\text{C}$ for 12 h, and then cooled to room temperature. The solvent was removed by nitrogen flow. The residue was redissolved in CH_3CN (5.0 mL) and filtered, and then ethyl ether (20.0 mL) was added to give a precipitate, which was collected by centrifugation to give metallacage **4a** (5.35 mg, 19%) as a white solid. ^1H NMR (600 MHz, CD_3CN , 295 K) δ 8.32 (s, 12H), 8.12 (s, 24H), 7.45 (d, $J = 8.6$ Hz, 24H), 7.10 (d, $J = 8.6$ Hz, 24H), 1.84–1.93 (m, 288H), 1.25–1.28 (m, 432H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_3CN , 295 K), δ 2.52 (s, ^{195}Pt satellites, $^1J_{\text{Pt-P}} = 3706$ Hz). ESI-TOF-MS: 1035.5970 [**4a** + 8Na] $^{8+}$, 1180.2861 [**4a** + 7Na] $^{7+}$, 1373.1576 [**4a** + 6Na] $^{6+}$, 1643.2198 [**4a** + 5Na] $^{5+}$.

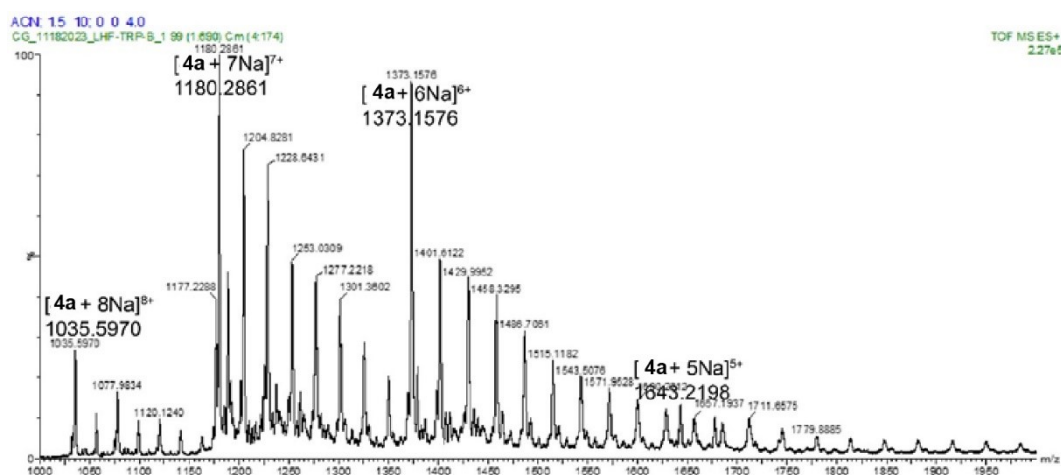


Figure S7. ESI-TOF-MS spectrum of **4a**.

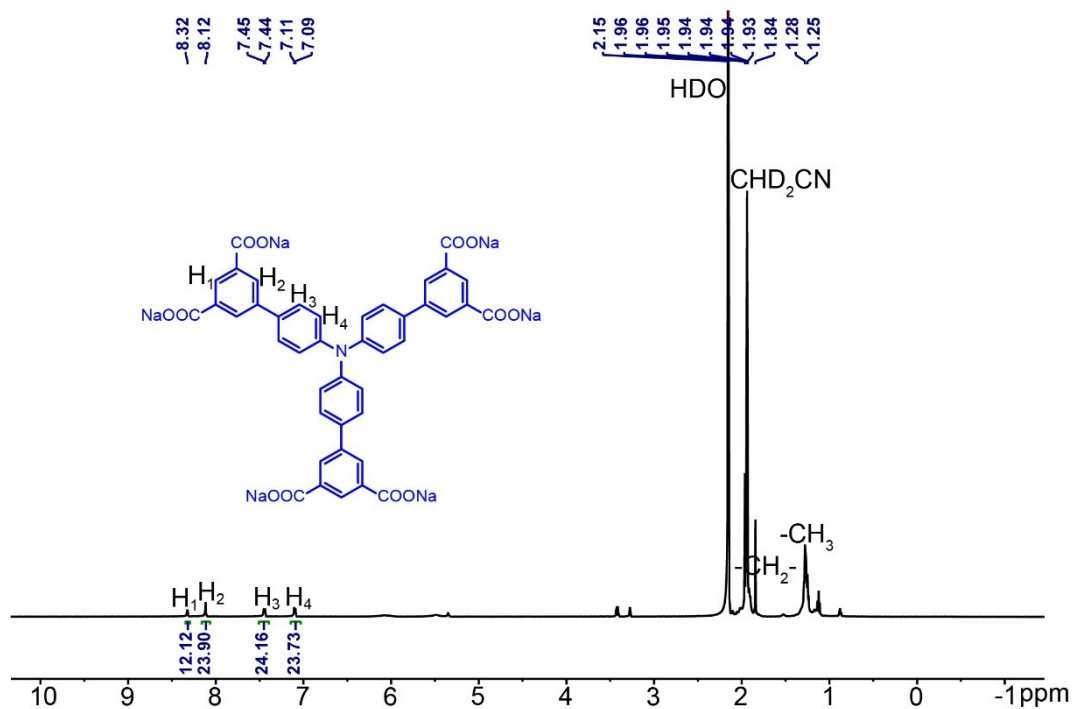


Figure S8. ¹H NMR spectrum (CD₃CN, 600 MHz, 295 K) recorded for **4a**.

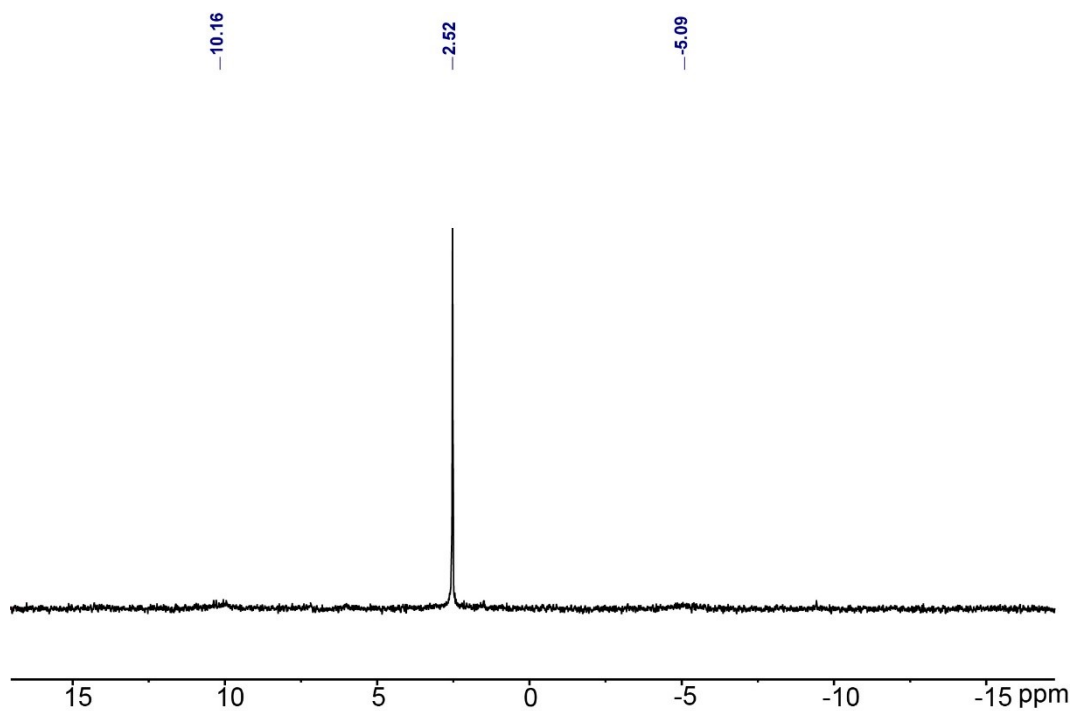
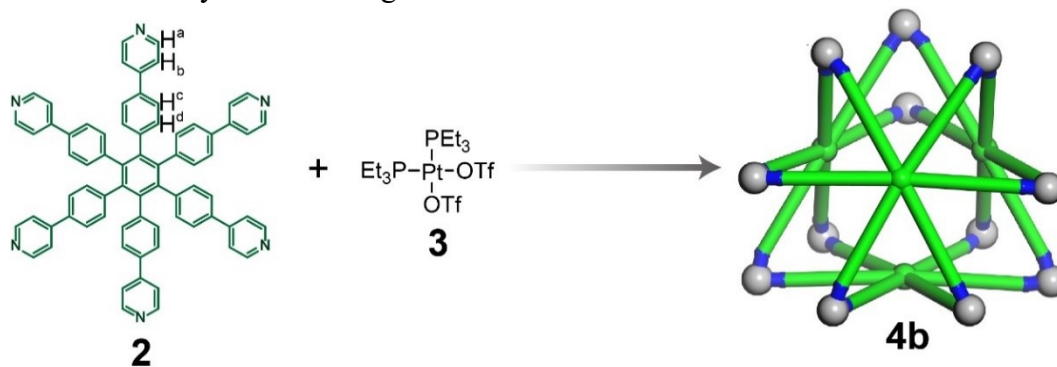


Figure S9. ³¹P{¹H} NMR spectrum (CD₃CN, 243 MHz, 295 K) recorded for **4a**.

3.2 Self-assembly of metallacage **4b**



2 (10.00 mg, 10.03 μmol) and **3** (21.95 mg, 30.08 μmol) were mixed in acetonitrile (16.0 mL). The whole reaction mixture was heated at 60 $^\circ\text{C}$ for 12h, then cooled to room temperature. The solvent was removed by nitrogen flow. The residue was redissolved in CH_3CN (5.0 mL) and filtered, and then ethyl ether (20.0 mL) was added to give a precipitate, which was collected by centrifugation to give metallacage **4b** (27.82 mg, 87%) as a white solid. ^1H NMR (600 MHz, CD_3CN) δ 8.83 (s, 24H), 8.70 (s, 24H), 7.47 (d, $J = 4.9$ Hz, 24H), 7.36 (d, $J = 4.9$ Hz, 24H), 7.12 (dd, $J = 21.7, 8.1$ Hz, 48H), 6.93 (dd, $J = 46.6, 8.1$ Hz, 48H), 1.84–1.94 (m, 288H), 1.20–1.26(m, 432H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_3CN , 295 K), δ 0.47 (s, ^{195}Pt satellites, $^1J_{\text{Pt-P}} = 3081$ Hz). ESI-TOF-MS: 1125.2874 [**4b** – 10OTf] $^{10+}$, 1266.9669 [**4b** – 9OTf] $^{9+}$, 1443.9618 [**4b** – 8OTf] $^{8+}$, 1671.5303 [**4b** – 7OTf] $^{7+}$, 1974.9288 [**4b** – 6OTf] $^{6+}$.

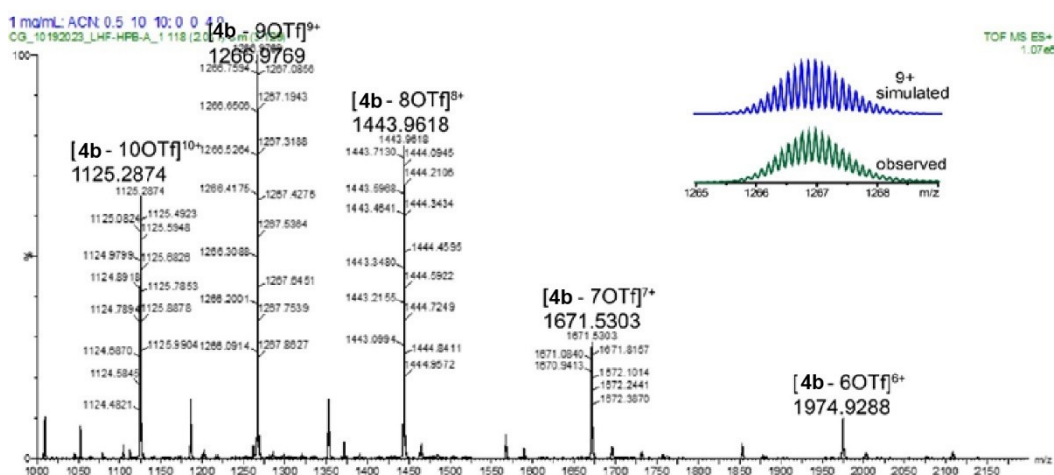


Figure S10. ESI-TOF-MS spectrum of **4b**.

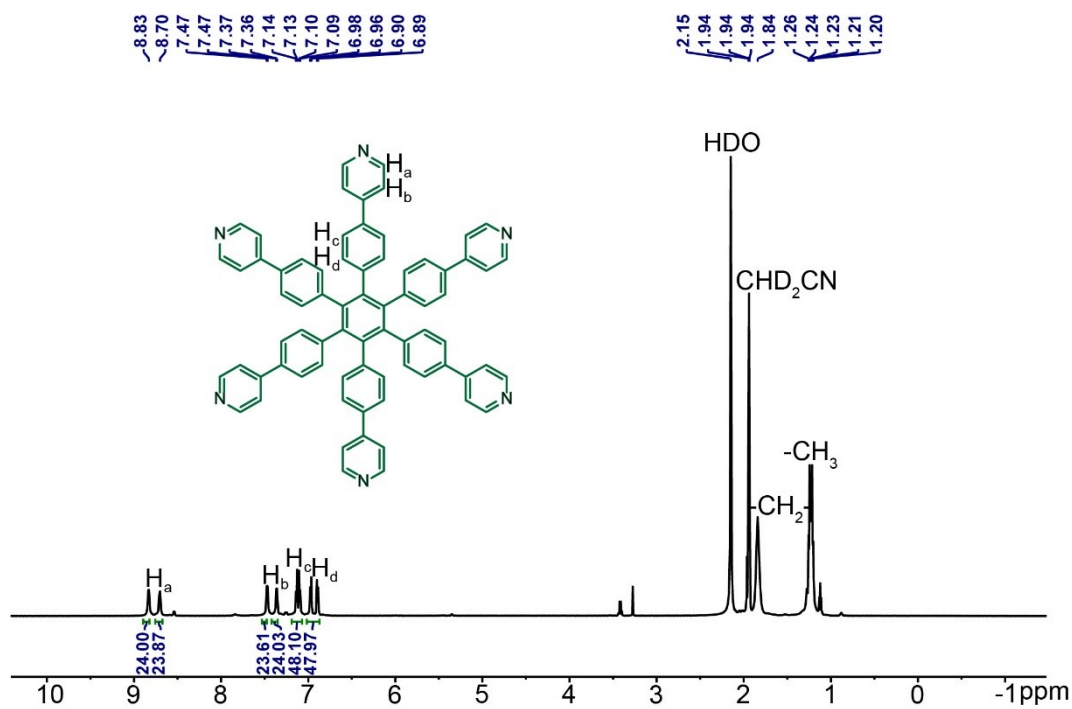


Figure S11. ^1H NMR spectrum (CD_3CN , 600 MHz, 295 K) recorded for **4b**.

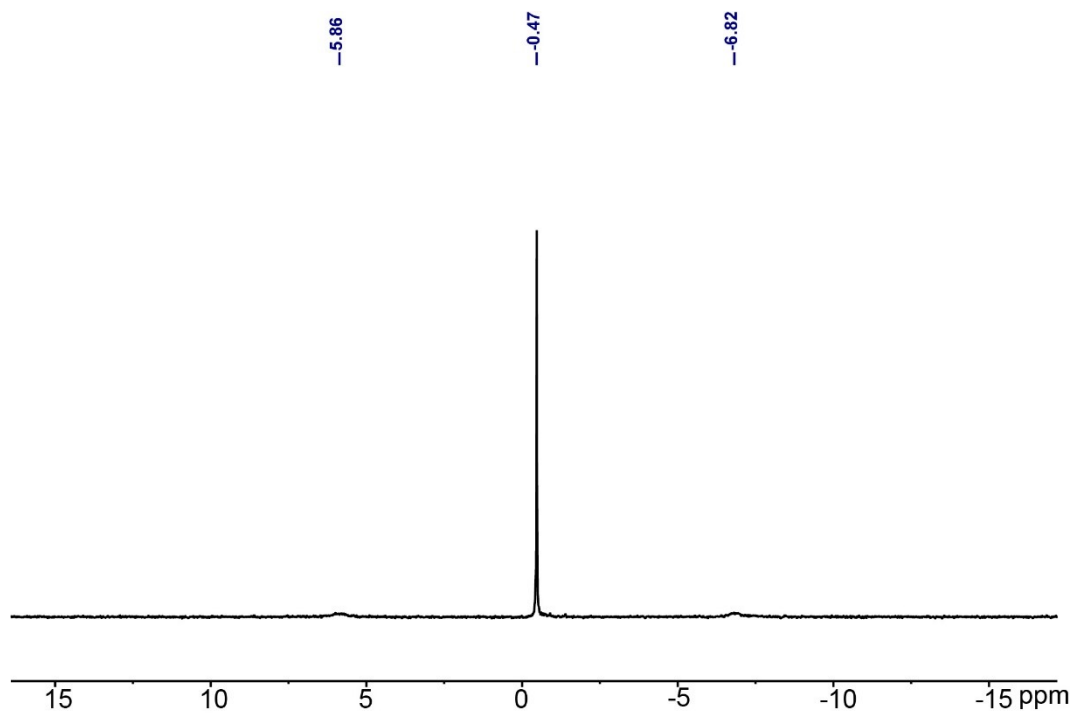


Figure S12. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CD_3CN , 243 MHz, 295 K) recorded for **4b**.

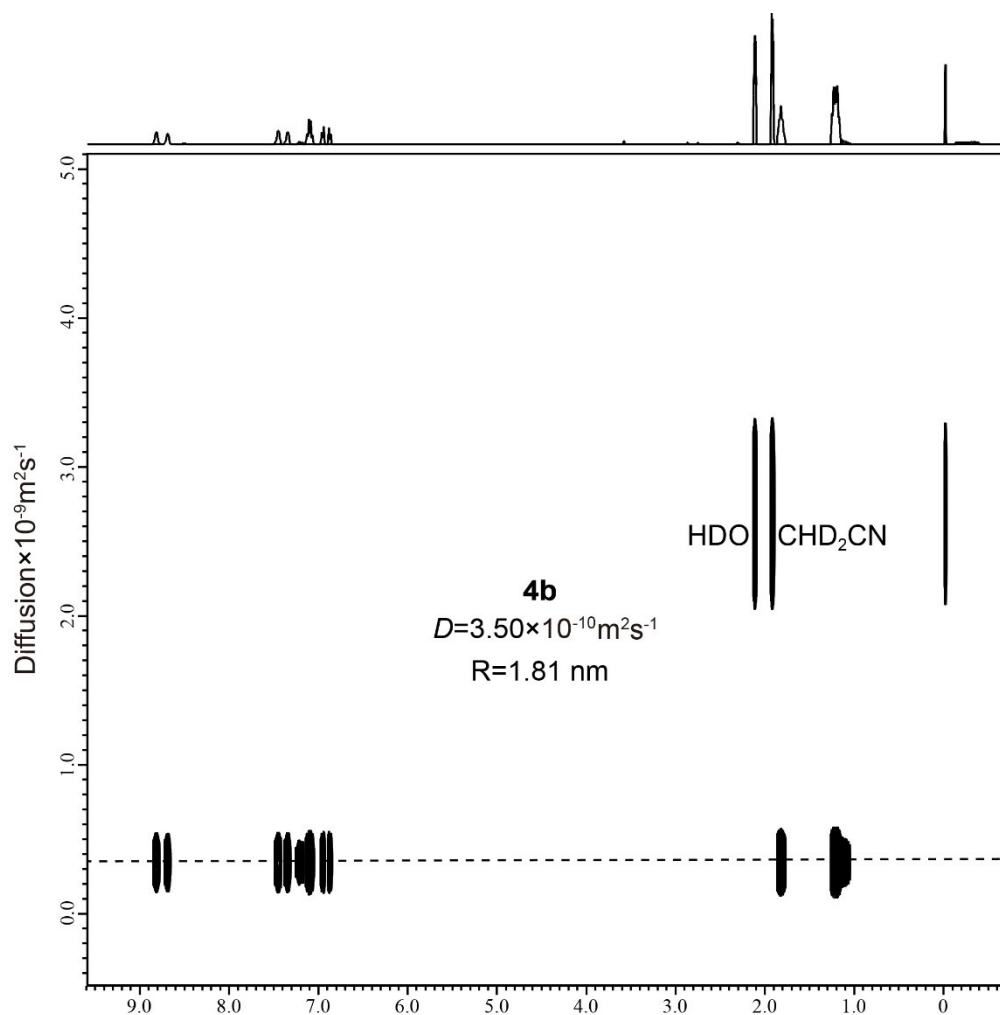
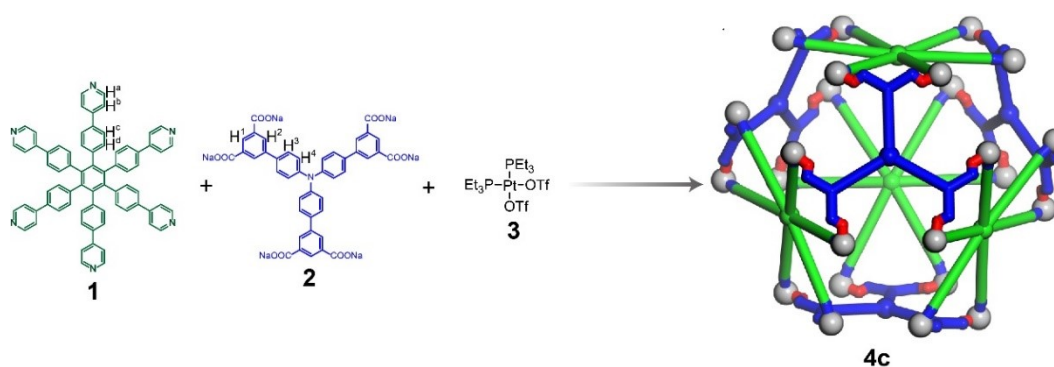


Figure S13. 2D DOSY spectrum (400 MHz, CD₃CN, 295 K) of **4b**

3.3 Self-assembly of metallacage **4c**



1 (8.72 mg, 10.03 μmol), **2** (10.00 mg, 10.03 μmol) and **3** (43.89 mg, 60.17 μmol) were mixed in acetonitrile/water (20.0 mL, 4:1, v/v). The whole reaction mixture was heated at 60 $^{\circ}\text{C}$ for 12h, then cooled to room temperature. The solvent was removed by

nitrogen flow. The residue was redissolved in CH₃CN (5.0 mL) and filtered, and then ethyl ether (20.0 mL) was added to give a precipitate, which was collected by centrifugation to give metallacage **4c** (47.55 mg, 87%) as a white solid. ¹H NMR (600 MHz, CD₃CN) δ 8.77 (s, 24H), 8.51 (s, 24H), 8.07 (s, 6H), 7.93 (s, 12H), 7.66 (d, *J* = 14.8 Hz, 48H), 7.54 – 7.42 (m, 48H), 7.35 (d, *J* = 7.8 Hz, 24H), 7.22 (dd, *J* = 13.2, 8.6 Hz, 48H), 7.17 (d, *J* = 8.1 Hz, 24H), 1.93–1.94 (m, 576H), 1.08–1.27 (m, 864H). ³¹P{¹H} NMR (162 MHz, CD₃CN, 295 K), δ 5.35 (d, ²*J*_{P-P} = 21.6 Hz, ¹⁹⁵Pt satellites, ¹*J*_{Pt-P} = 3346 Hz), 0.10 (d, ²*J*_{P-P} = 21.5 Hz, ¹⁹⁵Pt satellites, ¹*J*_{Pt-P} = 3346 Hz). ESI-TOF-MS: 1153.5021 [**4c** – 16OTf]¹⁶⁺, 1339.8600 [**4c** – 14OTf]¹⁴⁺, 1454.3834 [**4c** – 13OTf]¹³⁺, 1588.0000 [**4c** – 12OTf]¹²⁺, 1745.9076 [**4c** – 11OTf]¹¹⁺, 1935.3961 [**4c** – 10OTf]¹⁰⁺.

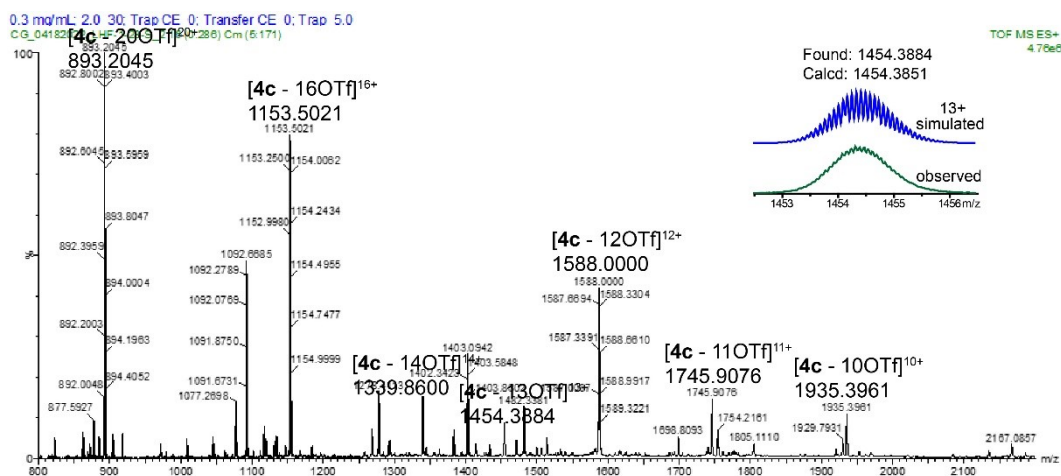


Figure S14. ESI-TOF-MS spectrum of **4c**.

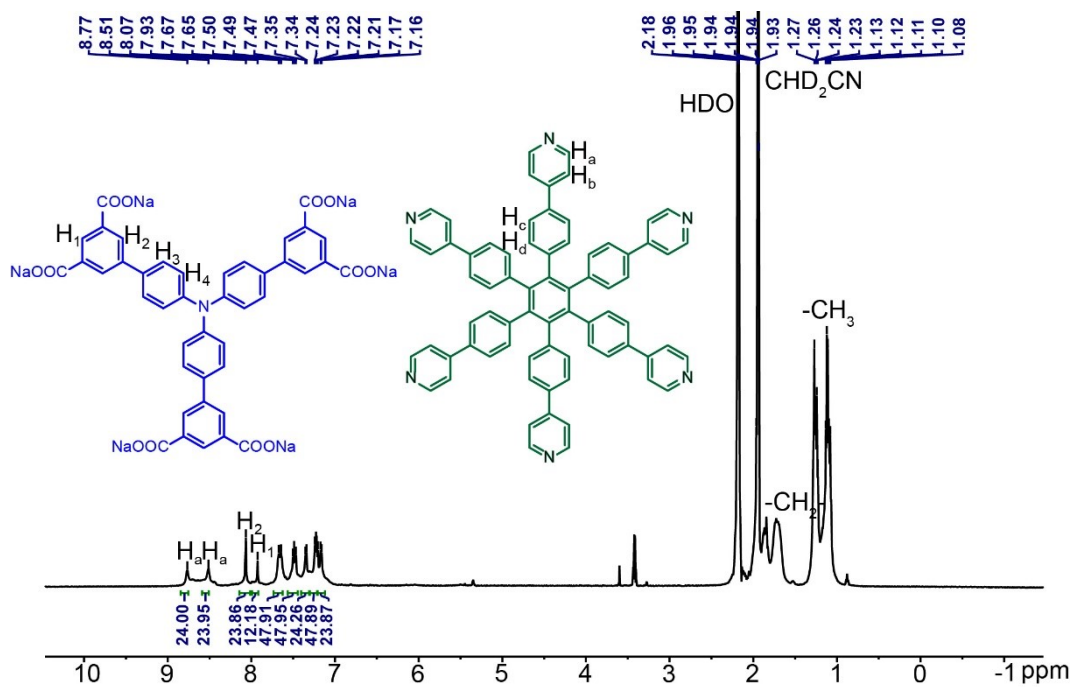


Figure S15. ¹H NMR spectrum (CD₃CN, 600 MHz, 295 K) recorded for **4c**.

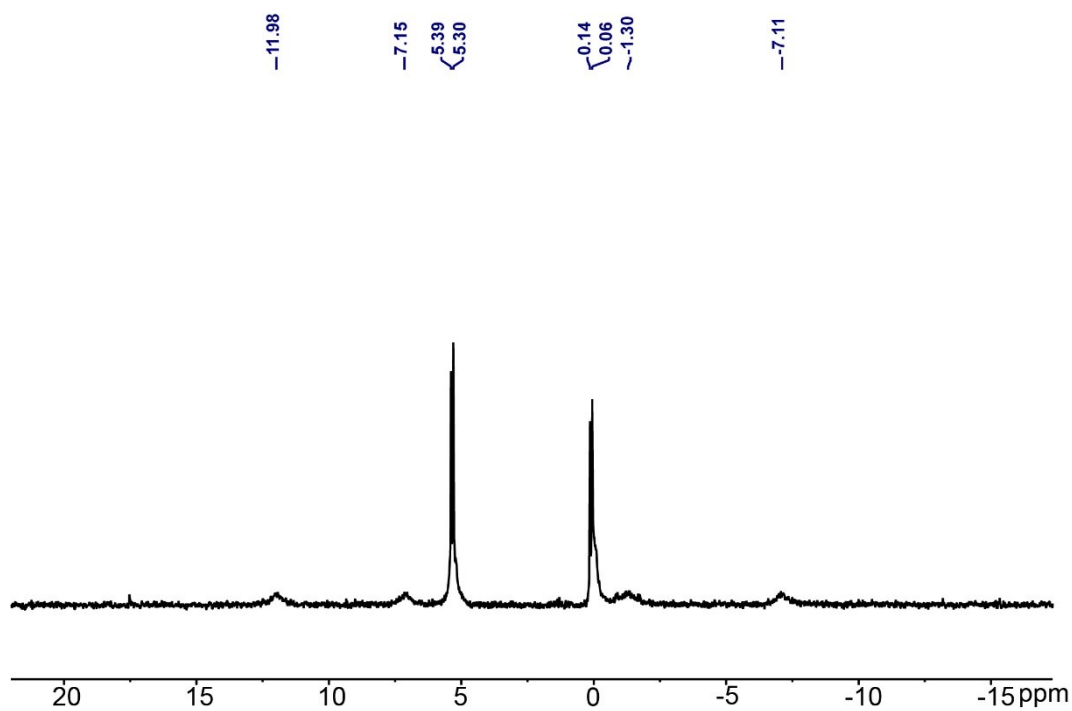


Figure S16. ³¹P {¹H} NMR spectrum (CD₃CN, 243 MHz, 295 K) recorded for **4c**.

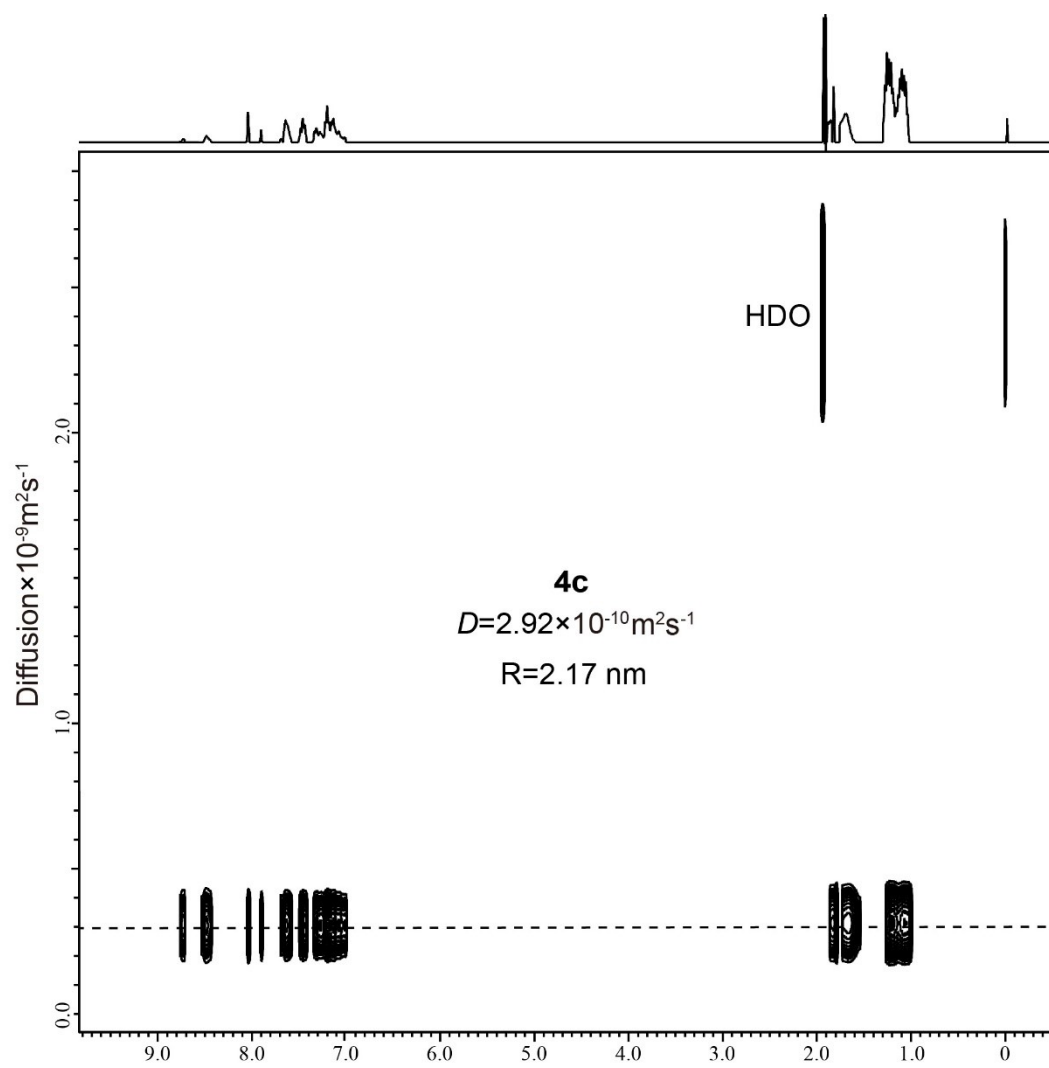


Figure S17. 2D DOSY spectrum (400 MHz, CD_3CN , 295 K) of **4c**

4. X-ray structure determination

Table S1. Crystallographic data and refinement details for metallacage **4a**

Compound	4a
Empirical formula	C ₃₁₂ H ₄₄₄ N ₄ O ₄₈ P ₂₄ Pt ₁₂
F_w	8102.96
Crystal system	cubic
Space group	<i>P</i> -43n
$a / \text{\AA}$	29.1614(16)
$b / \text{\AA}$	29.1614(16)
$c / \text{\AA}$	29.1614(16)
$\alpha / ^\circ$	90
$\beta / ^\circ$	90
$\gamma / ^\circ$	90
$V / \text{\AA}^3$	24798(4)
Z	8
$D_{\text{calc}} / \text{g cm}^{-3}$	1.085
$F(000)$	8048.0
μ / mm^{-1}	4.950
θ max	114.486
Independent reflns	8540
Reflns [$I > 2\sigma(I)$]	170473
$R_1; wR_2$ [$I > 2\sigma(I)$]	0.0417; 0.1154

Table S2. Crystallographic data and refinement details for metallage **4c**

Compound	4c
Empirical formula	C ₇₄₄ H ₉₉₆ N ₂₈ O ₄₈ P ₄₈ Pt ₂₄
F_w	17260.44
Crystal system	trigonal
Space group	R -3
$a / \text{\AA}$	59.444(6)
$b / \text{\AA}$	59.444(6)
$c / \text{\AA}$	167.23(3)
$\alpha / ^\circ$	90
$\beta / ^\circ$	90
$\gamma / ^\circ$	120
$V / \text{\AA}^3$	511754(140)
Z	12
$D_{\text{calc}} / \text{g cm}^{-3}$	0.633
$F(000)$	91632.0
μ / mm^{-1}	4.207
θ max	50.667
Independent reflns	114995
Reflns [$I > 2\sigma(I)$]	312328
$R_1; wR_2$ [$I > 2\sigma(I)$]	0.1570; 0.3446

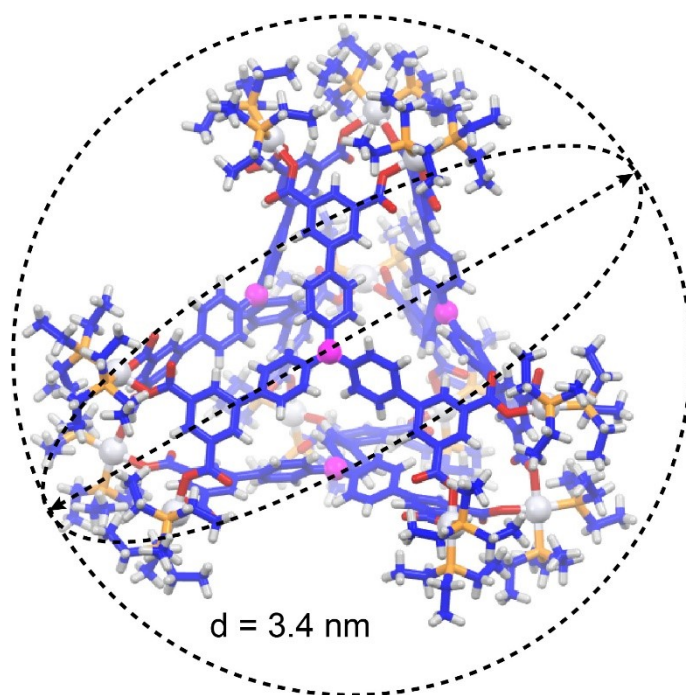


Figure S18. Crystal structures of metallacage **4a**, Hydrogen atoms, counterions, solvent molecules units are omitted for clarity.

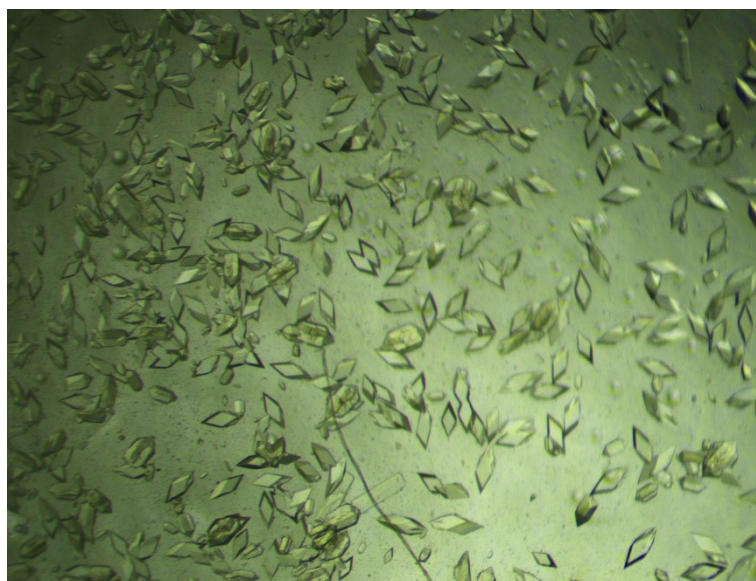


Figure S19. Optical image of crystals of metallacage **4c**.

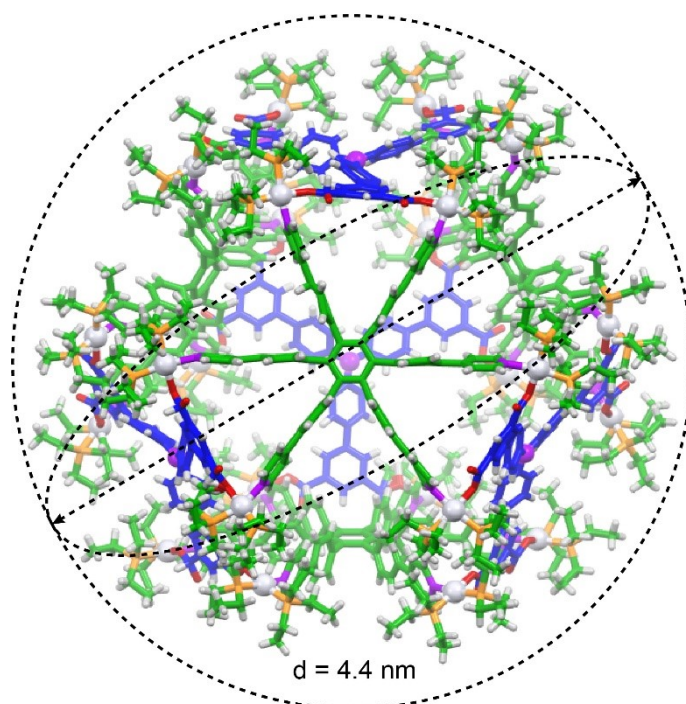


Figure S20. Crystal structures of metallacage **4a**, Hydrogen atoms, counterions, solvent molecules units are omitted for clarity.

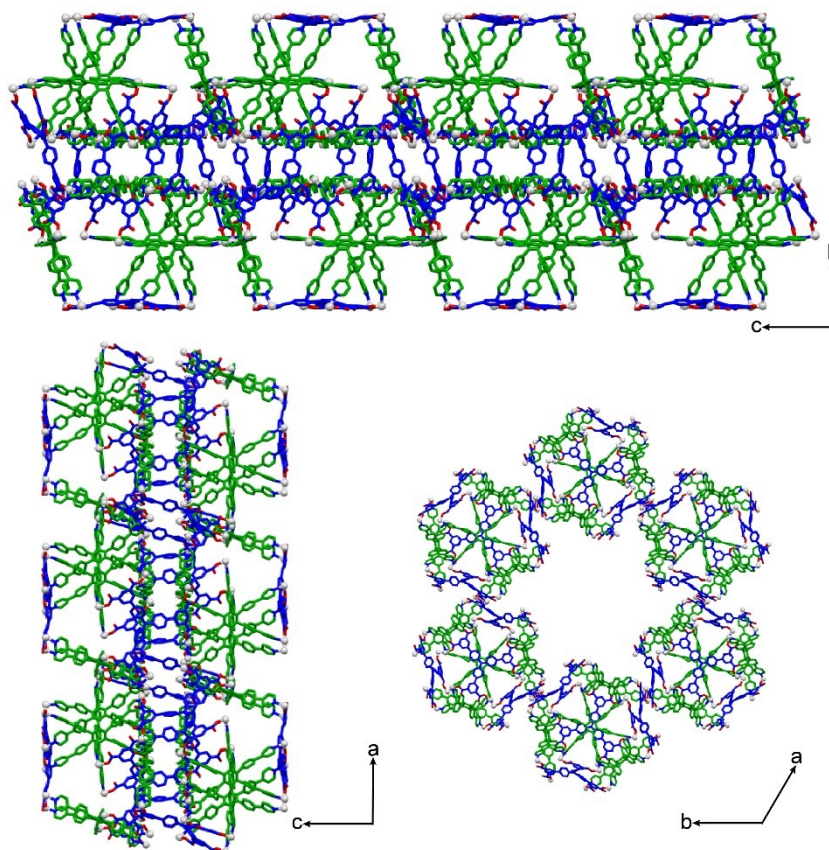


Figure S21. Crystal packing model of metallacage **4c** viewed from (a) a axis, (b) b axis, and (c) c axis. Hydrogen atoms, counterions, triethylphosphine units and solvent molecules are omitted for clarity.

5. Photophysical properties of compounds

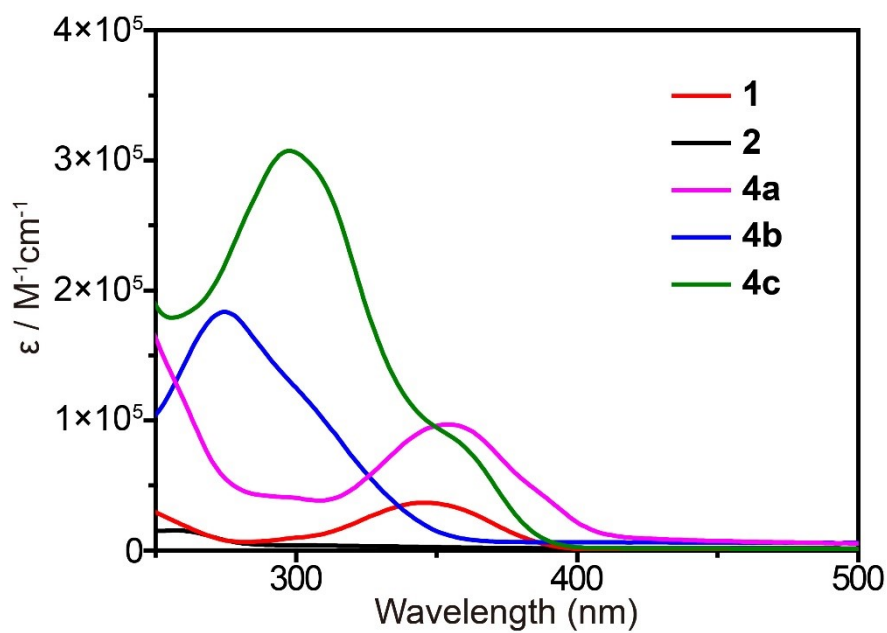


Figure S22. UV/Vis absorption spectrum of ligand **1** in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ ($v:v = 9:1$), ligand **2** and metallacages **4a–4c** in CH_3CN .

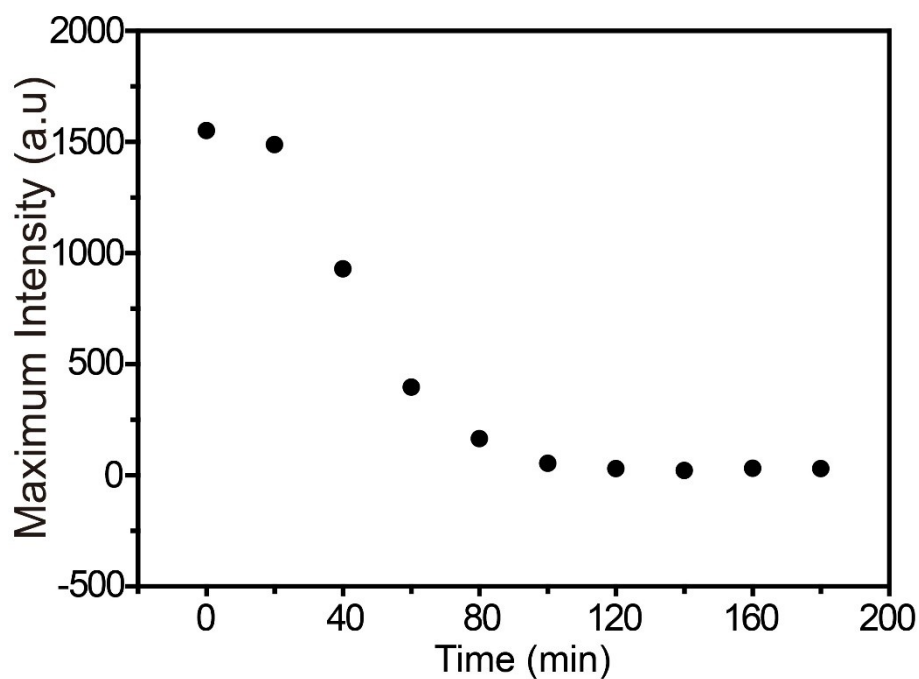


Figure S23. Plot of the emission at 450 nm of the equimolar mixture of **4a** and **4b** in CH_3CN ($\lambda_{\text{ex}} = 265 \text{ nm}$, $c = 10.0 \text{ } \mu\text{M}$).

7. The effect of solvent and counterion in the formation of the metallage 4c

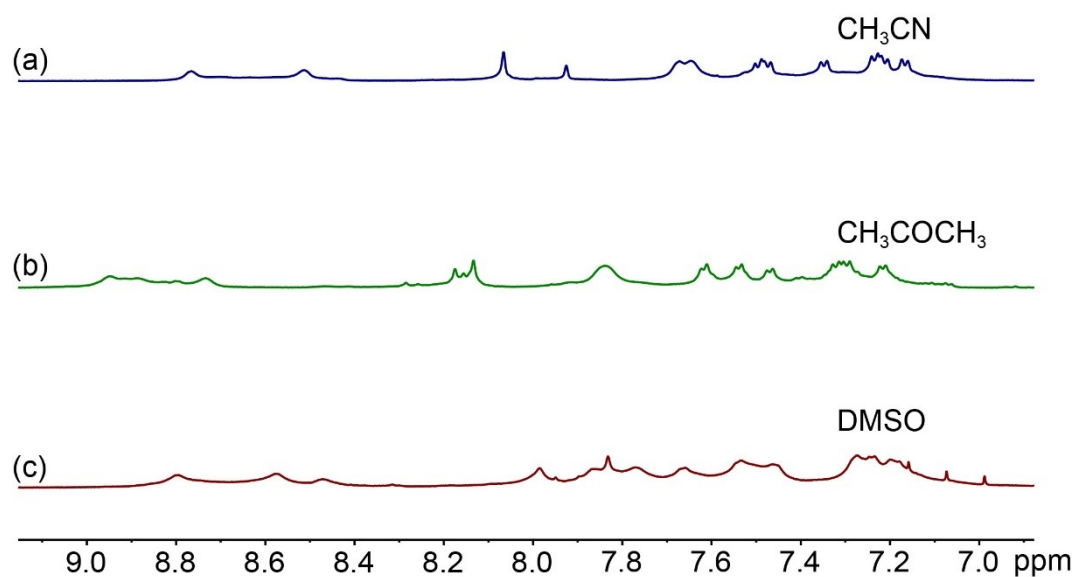


Figure S26. Partial ^1H NMR (600 MHz, CD_3CN , 295 K) spectra of (a) **4c** (CD_3CN), (b) **4c** (Acetone- d_6) and (c) **4c** (DMSO- d_6).

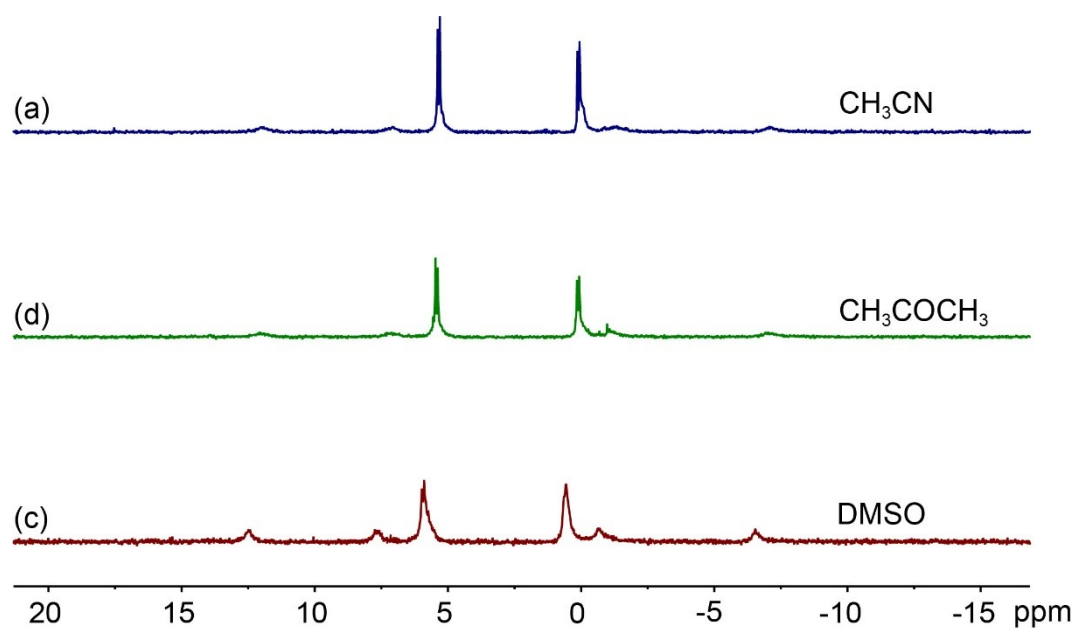


Figure S27. Partial $^{31}\text{P}\{^1\text{H}\}$ NMR (600 MHz, CD_3CN , 295 K) spectra of (a) **4c** (CD_3CN), (b) **4c** (Acetone- d_6) and (c) **4c** (DMSO- d_6).

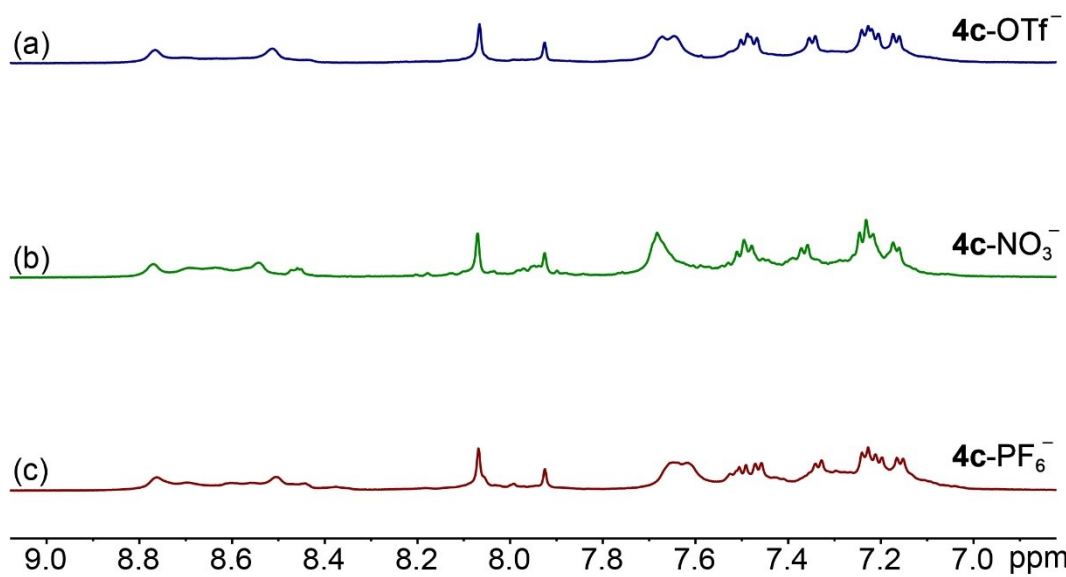


Figure S28. Partial ^1H NMR (600 MHz, CD_3CN , 295 K) spectra of (a) **4c-OTf⁻**, (b) **4c-NO₃⁻** and (c) **4c-PF₆⁻**.

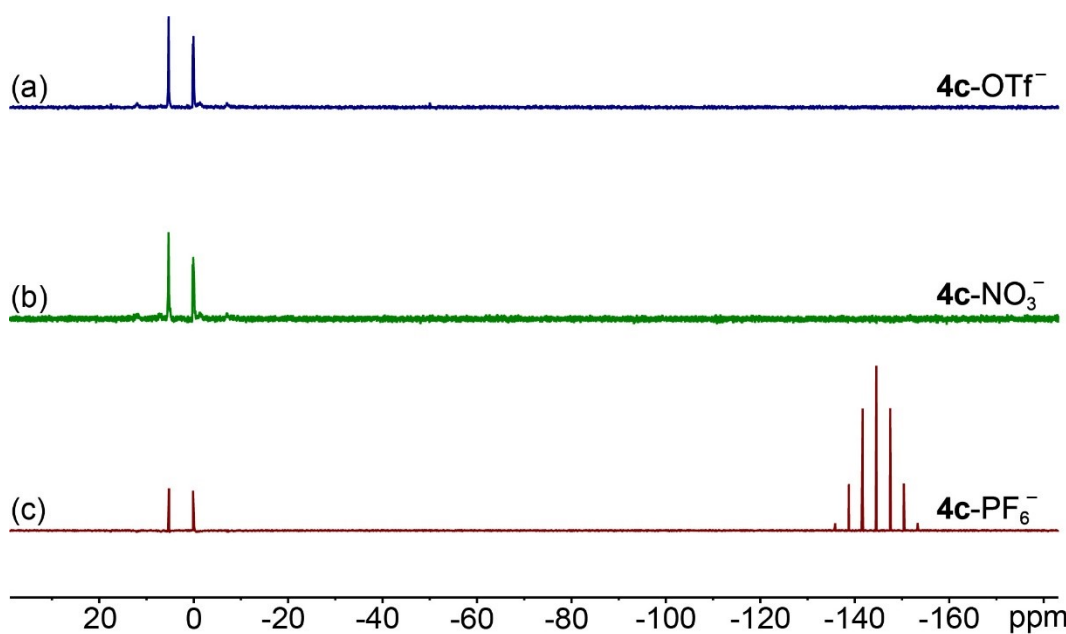


Figure S29. Partial $^{31}\text{P}\{^1\text{H}\}$ NMR (600 MHz, CD_3CN , 295 K) spectra of (a) **4c-OTf⁻**, (b) **4c-NO₃⁻** and (c) **4c-PF₆⁻**.

8. Host-guest complexation study

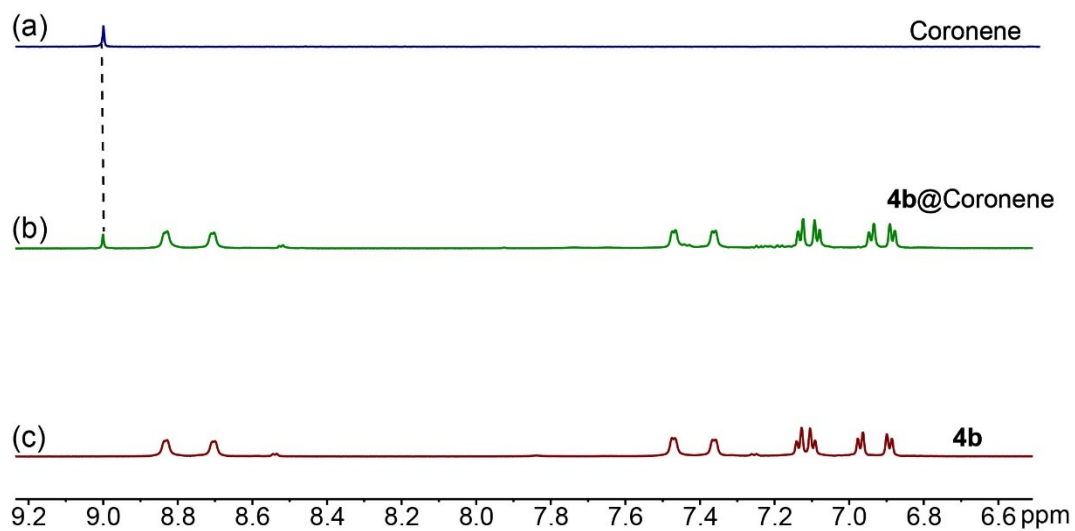


Figure S30. Partial ¹H NMR spectra (600 MHz, CD₃CN, 295 K) recorded for (a) Coronene, (b) **4b@Coronene** and (c) **4b**.

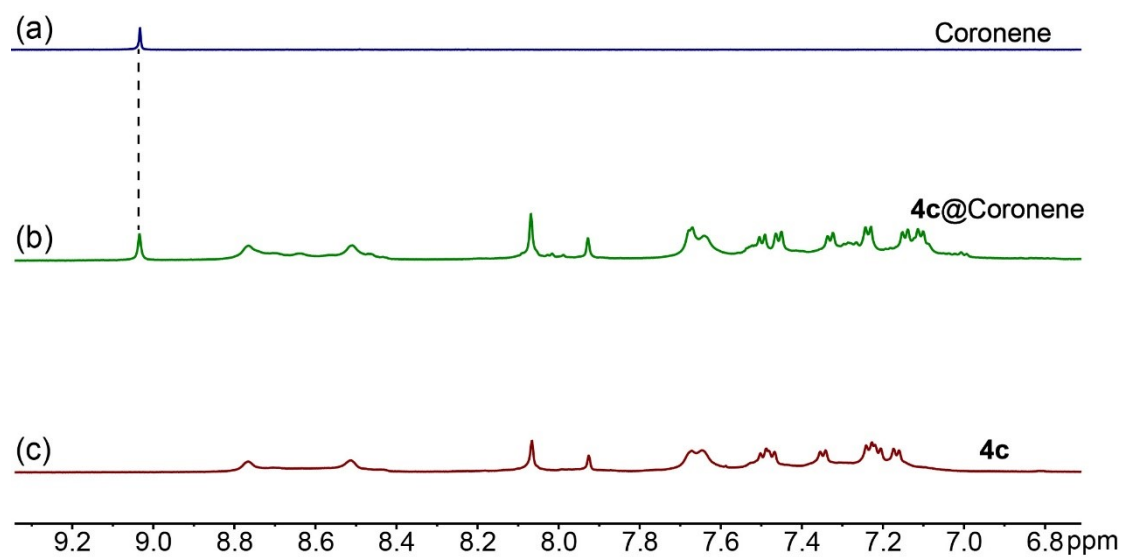


Figure S31. Partial ¹H NMR spectra (600 MHz, CD₃CN, 295 K) recorded for (a) Coronene, (b) **4c@Coronene** and (c) **4c**.

9. Energy Comparisons

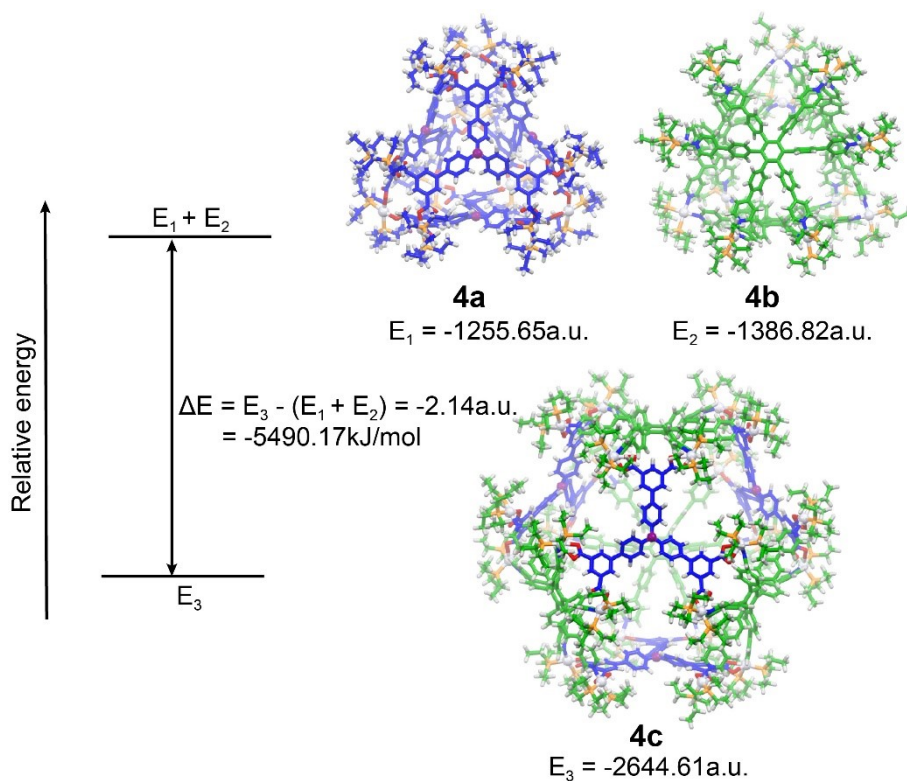


Figure S32. Relative energy of the metallacages in the transformation process.

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