Supplementary Information

Fusion of Two Homoleptic Truncated Tetrahedra into a Heteroleptic Truncated Octahedron

Haifei Liu,[‡,1] Chenxing Guo,[‡,2] Yujuan Huang,[‡,1] Zilin Zhou,[1] Chaoqun Mu,[3] Zeyuan Zhang,[1] Yali Hou,[1] and Mingming Zhang[1*]

[1] State Key Laboratory for Mechanical Behavior of Materials, Shaanxi International Research Center for Soft Matter, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, P. R. China

[2] College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518055, P. R. China

[3] School of Chemistry and Chemical Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, Shaanxi, P. R. China

[‡]These authors contributed equally to this work.

[*]Corresponding authors. E-mails: mingming.zhang@xjtu.edu.cn

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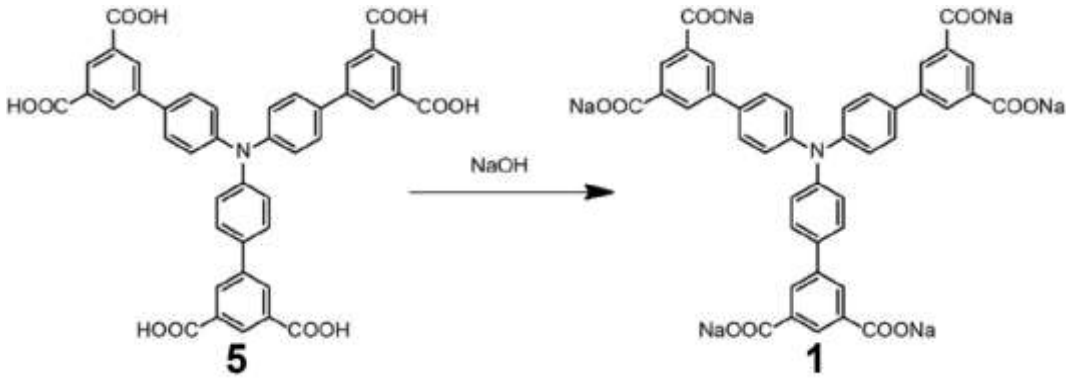
1. Materials and methods

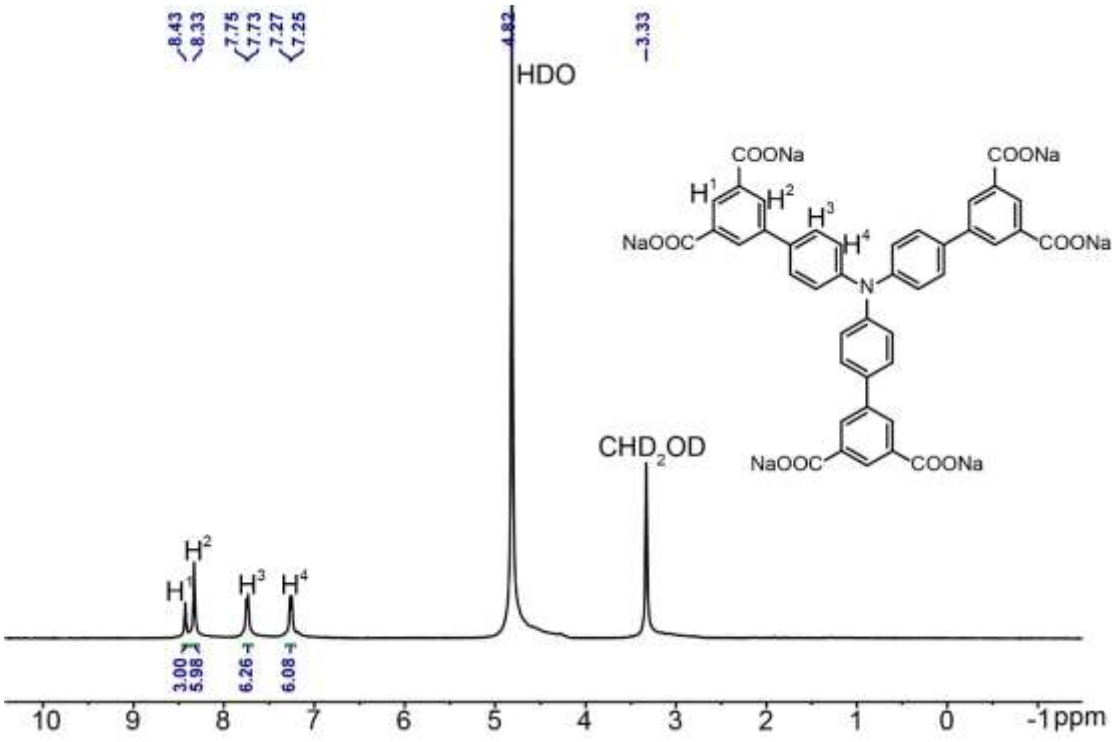
General procedure. All reagents and deuterated solvents were used as purchased without further purification. Ligand **1** was purchased in the carboxylic acid form and obtained by the neutralization reaction with NaOH. Ligand **2** was prepared according to the literature procedure[1]. Column chromatography was conducted using SiO_2 (200 − 300 mesh). $^{31}P\{^1H\}$ 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. $^{31}P\{^1H\}$ NMR chemical shifts were referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). UV/vis absorption spectroscopy was conducted on a Lambd 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 ºC; desolvation temperature, 100 ºC; cone gas flow, 10 L/h; desolvation gas flow, 800 L/h (N_2); 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 N_2. 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.

2. Synthetic procedures and characterization data

2.1 Synthesis of compound **1**

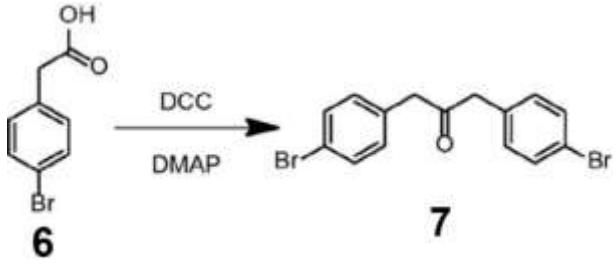


Compound **5** (500.0 mg, 0.68 mmol) and NaOH (170.79 mg, 4.27 mmol) were added in H_2O (50.0 mL) and stirred at room temperature for 6 h. Then the mixture was concentrated and washed by acetone to give **1** (556 mg, 94%) as a white solid.^{1}H NMR (400 MHz, CD_3OD, 295 K) δ 8.43 (s, 3H), 8.33 (s, 6H), 7.74 (d, J = 8.2 Hz, 6H), 7.26 (d, J = 8.2 Hz, 6H).

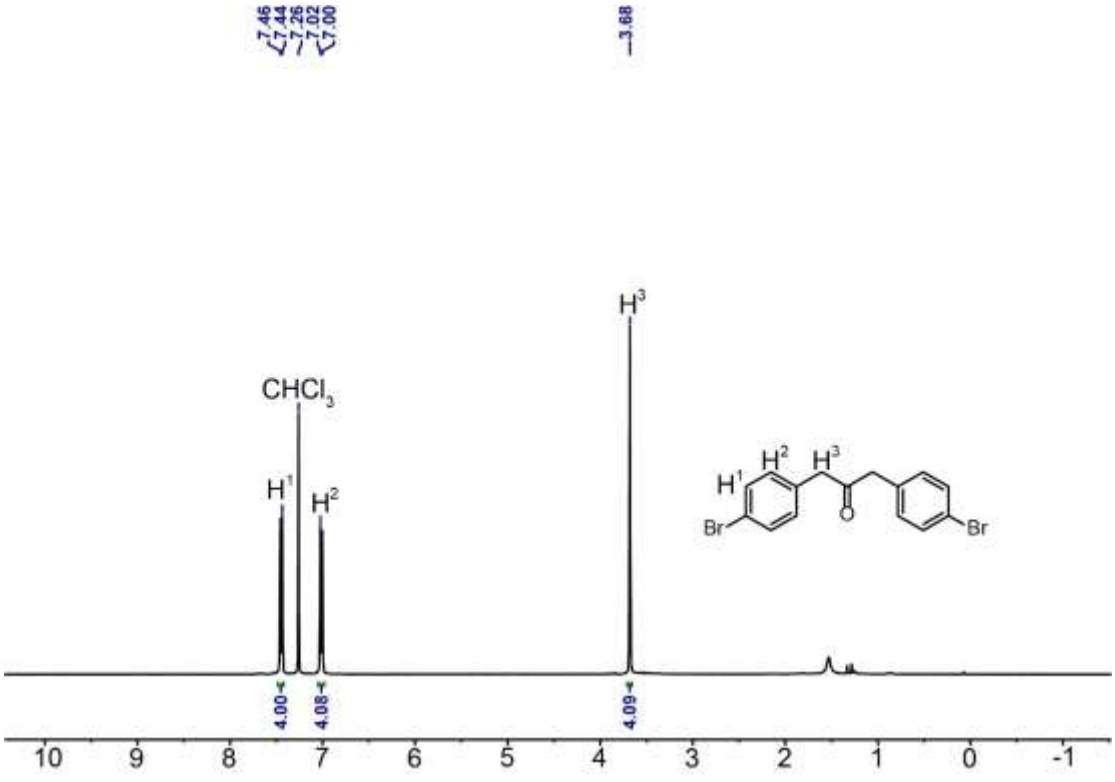


Supplementary Fig. 1 ^{1}H NMR spectrum (CD_3OD, 400 MHz, 295 K) recorded for **1**.

2.1 Synthesis of compound **7**

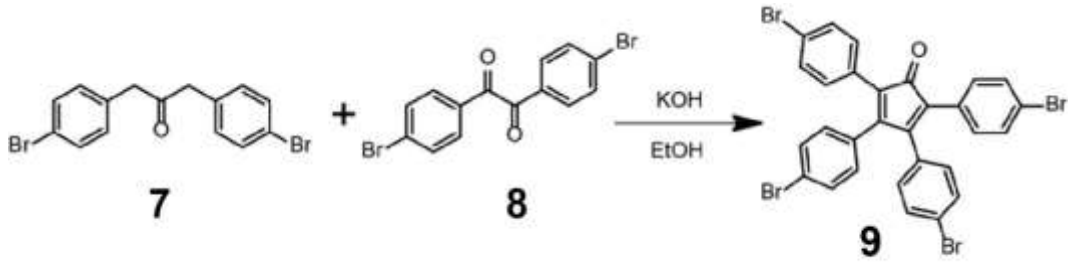


A solution of *N*,*N*'-dicyclohexylcarbodiimide (4.80 g, 11.16 mmol) and 4-dimethylaminopyridine (0.60 g, 6.05 mmol) in dry DCM (100.0 mL) was stirred at 0 °C under argon, and then a solution of 2-(4-bromophenyl)acetic acid (**6**, 5.20 g, 24.18 mmol) in dry DCM (20.0 mL) was added dropwise. The resulting 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. ^{1}H NMR (400 MHz, $CDCl_3$, 295K) δ 7.45 (d, J = 8.3 Hz, 4H), 7.01 (d, J = 8.3 Hz, 4H), 3.68 (s, 4H). The ^{1}H NMR spectrum of **7** matched well with reported literature[1].

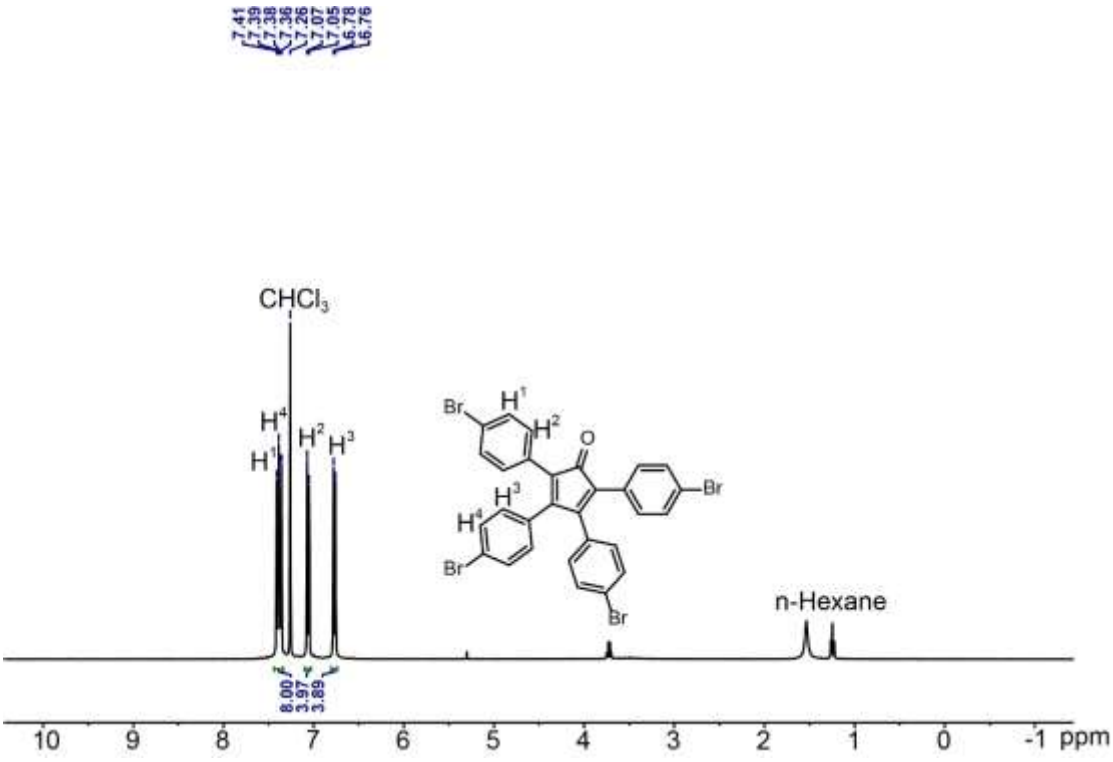


Supplementary Fig. 2 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 295 K) recorded for **7**.

2.3 Synthesis of compound **9**

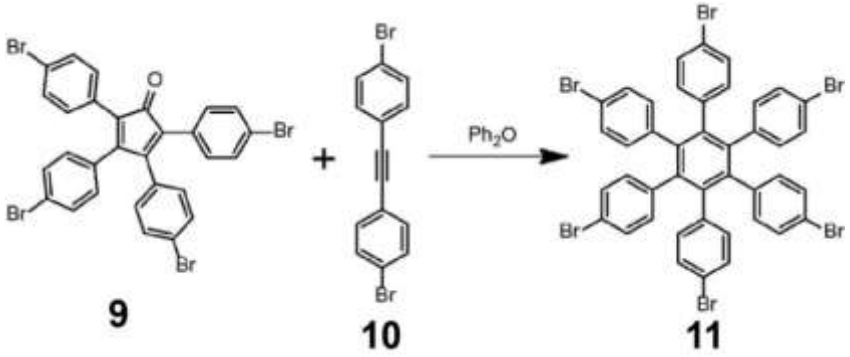


A solution of KOH (0.30 g, 5.35 mmol) in ethanol (5.0 mL) was added to a mixture of 1,3-bis(4-bromophenyl)propan-2-one **7** (2.70 g, 7.34 mmol) and 4,4'-dibromobenzil (**8**, 2.70 g, 7.34 mmol) in ethanol (20.0 mL). The resulting mixture was heated at reflux for 3 h. The mixture was then cooled to 0 °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. ^{1}H NMR (400 MHz, $CDCl_3$, 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 ^{1}H NMR spectrum of **9** matched well with reported literature[1].

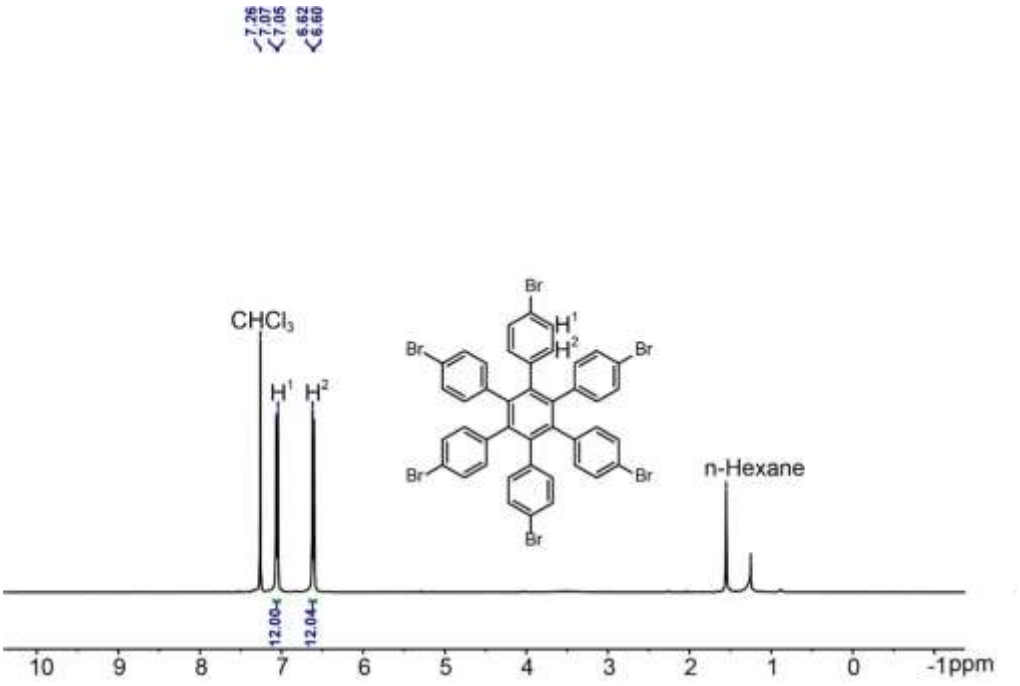


Supplementary Fig. 3 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 295 K) recorded for **9**.

2.4 Synthesis of compound **11**

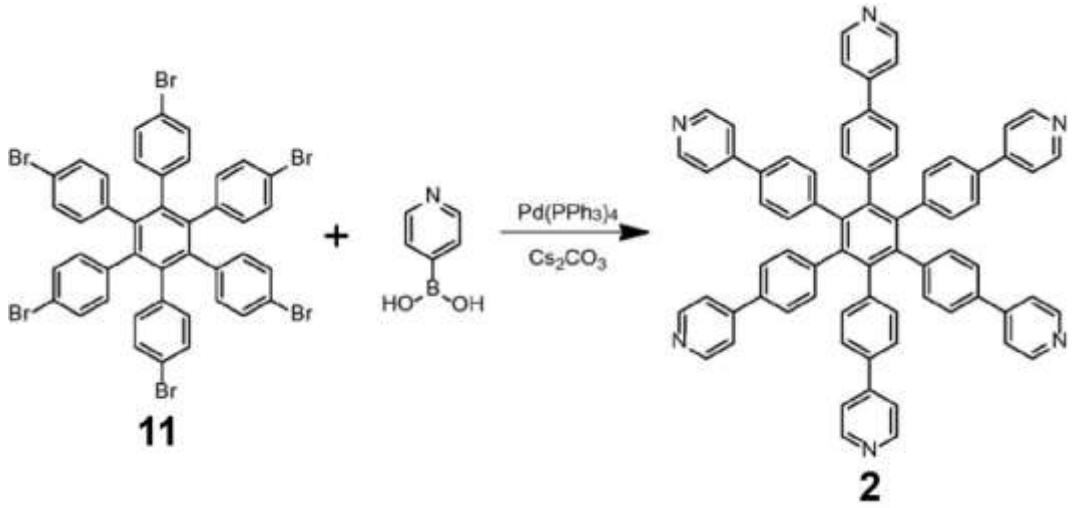


A mixture of compound **9** (3.50 g, 5.00 mmol) and bis(4-bromophenyl) acetylene (**10**, 1.68 g, 5.00 mmol) in diphenyl ether (5.0 mL) was heated at 260 °C under N_2 for 48h. The resulting mixture was cooled to 25 °C and then diluted with ethanol. The precipitate was collected by filtration, washed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

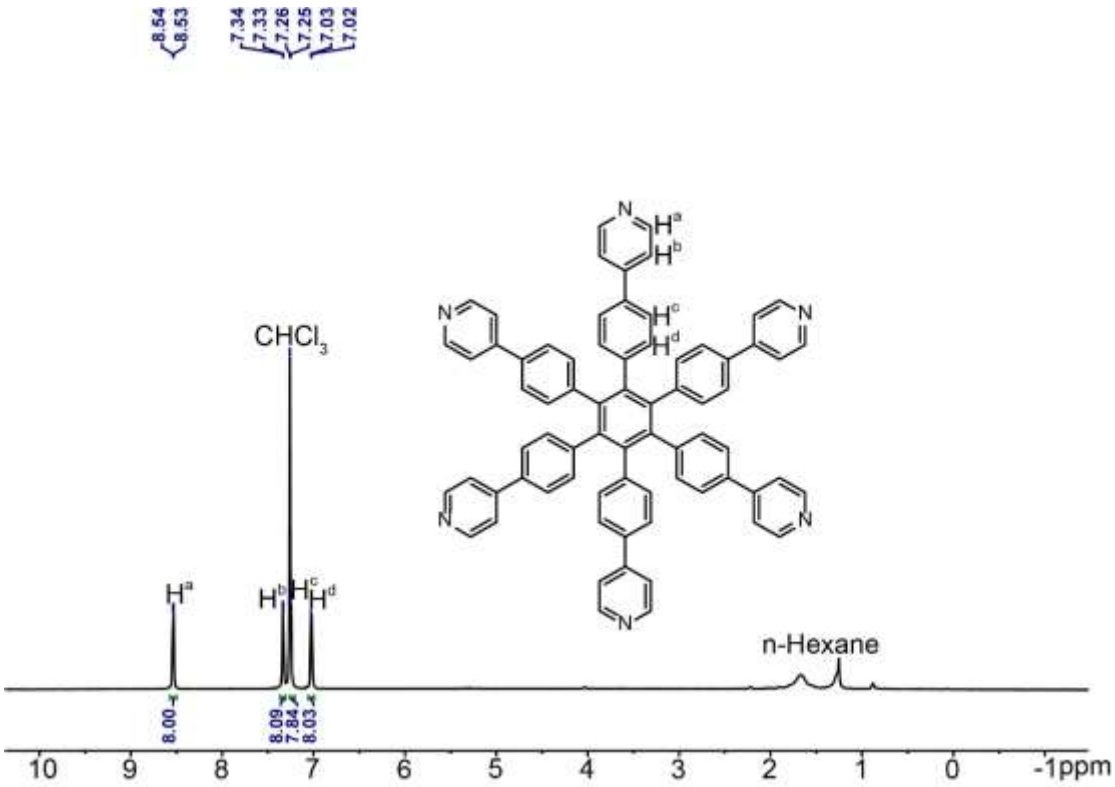


Supplementary Fig. 4 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 295 K) recorded for **11**.

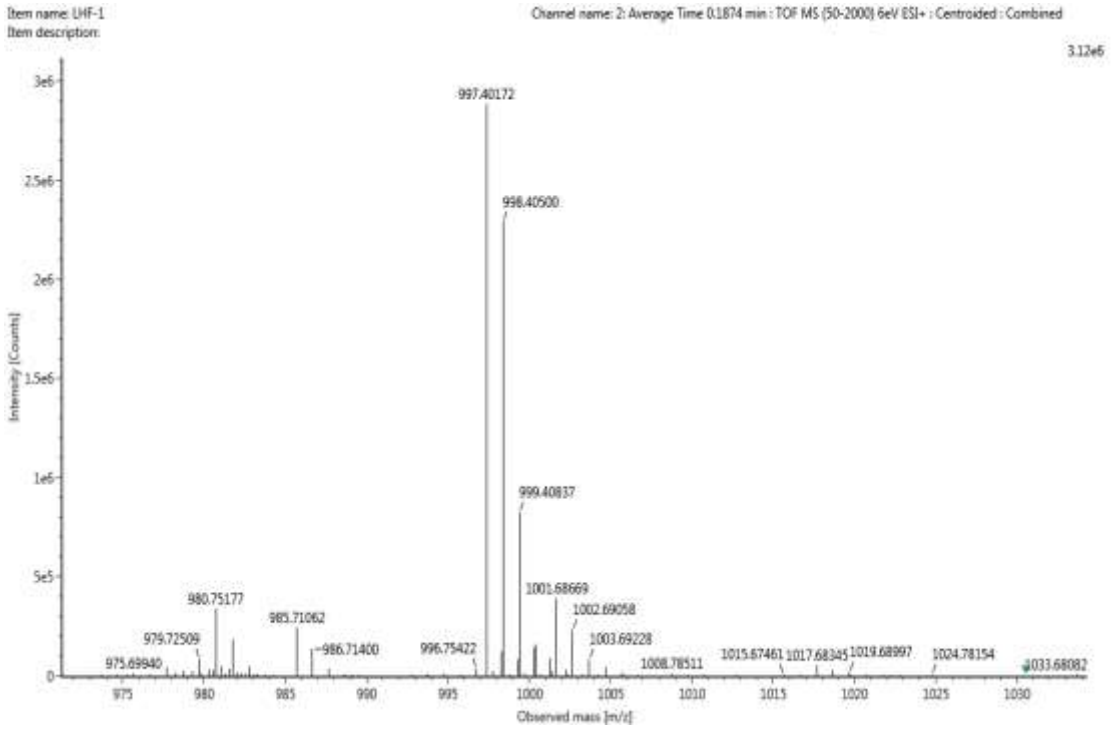
2.5 Synthesis of compound **2**



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), $Pd(PPh_3)_4$ (100.0 mg, 158.72 μmol), Cs_2CO_3 (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℃ for 6 days under N_2 atmosphere. After being cooled to room temperature, a saturated $NaHCO_3$ was added the organic components were extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over $MgSO_4$, 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, $CDCl_3$, 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 $[C_{72}H_{49}N_6]^+$, 997.40.



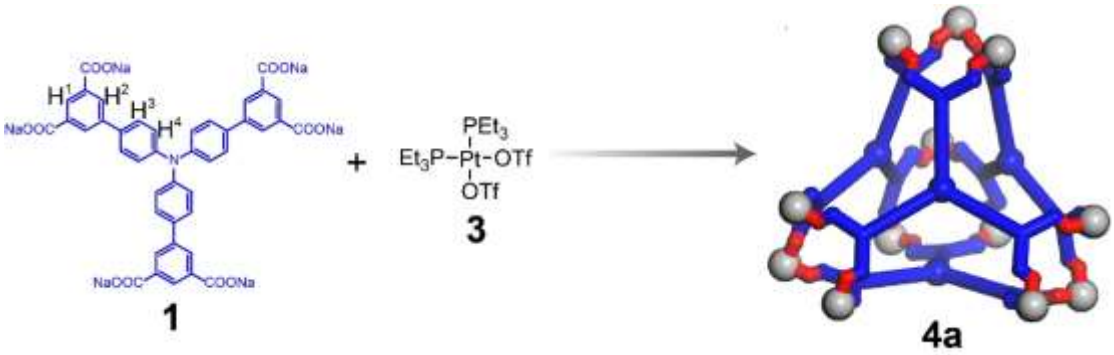
Supplementary Fig. 5 ^{1}H NMR spectrum ($CDCl_3$, 600 MHz, 295 K) recorded for **2**.



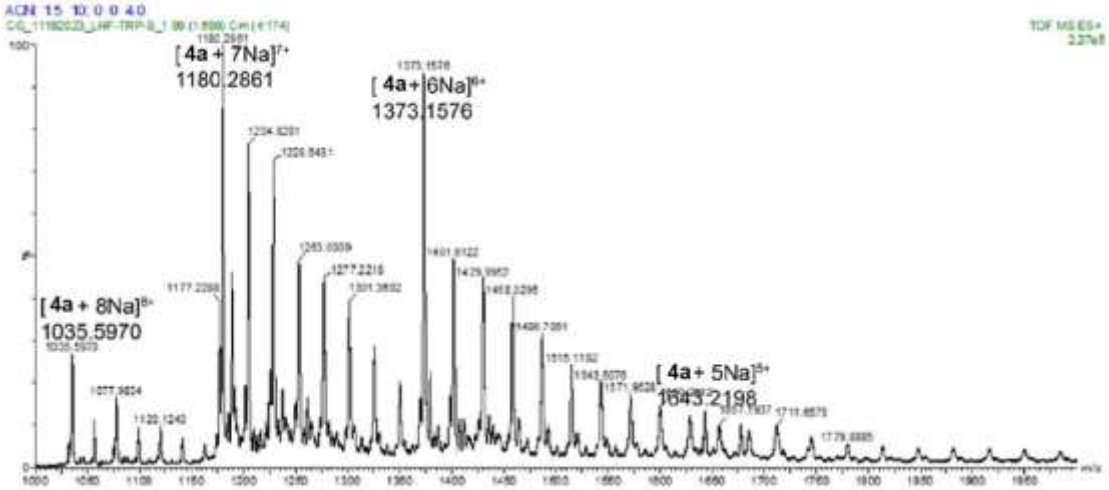
Supplementary Fig. 6 ESI-HR-MS spectrum of **2**.

3. Self-assembly of metallacages and characterization data

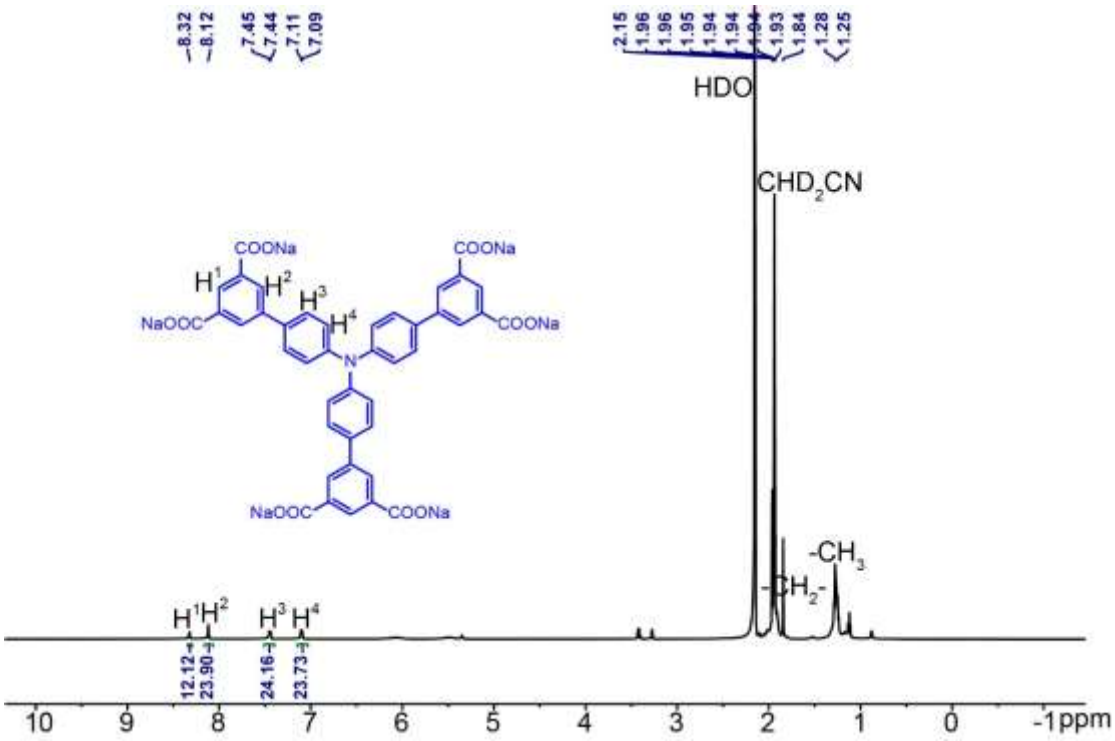
3.1 Self-assembly of metallacage **4a**



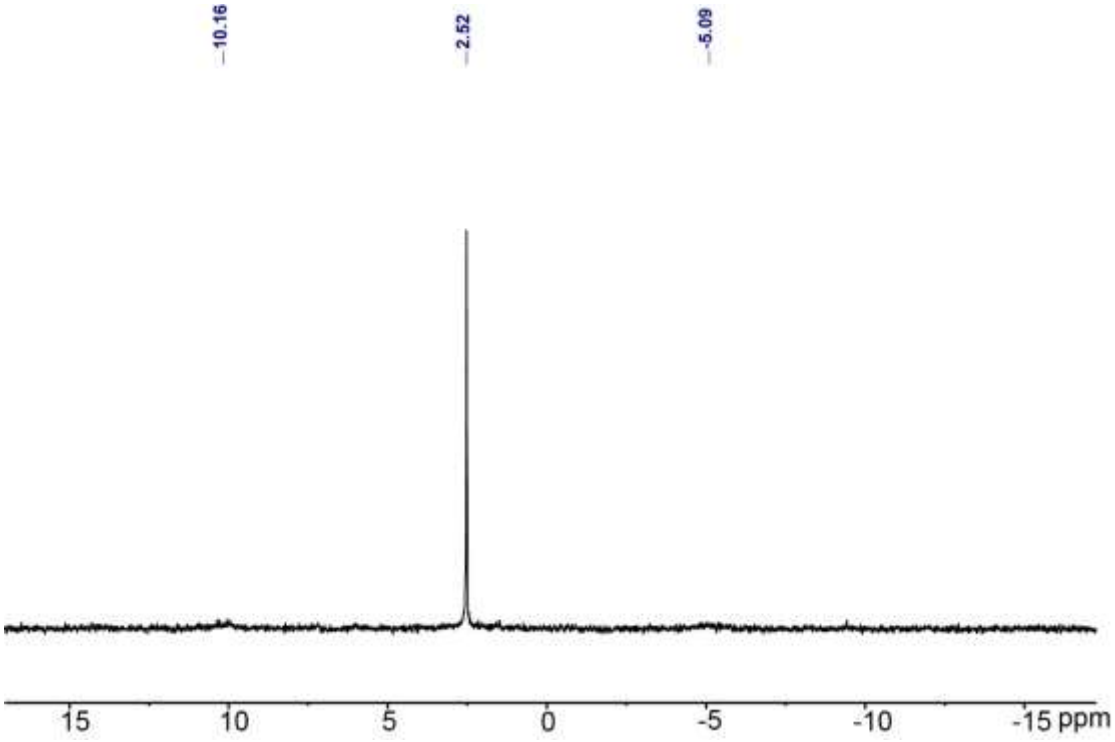
1 (10.00 mg, 11.50 μmol) and **3** (25.17 mg, 34.50 μmol) were mixed in acetonitrile/water (20.0 mL, 4:1, *v*/*v*). The whole reaction mixture was heated at 60 ℃ for 12 h, and then cooled to room temperature. The solvent was removed by nitrogen flow. The residue was redissolved in CH_3CN (5.0 mL) and 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. ^{1}H 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}P{^{1}H} NMR (162 MHz, CD_3CN, 295 K), δ 2.52 (s, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 3706 Hz). ESI-TOF-MS: 1035.5970 [**4a** + 8Na]$^{8+}$, 1180.2861 [**4a** + 7Na]$^{7+}$, 1373.1576 [**4a** + 6Na]$^{6+}$, 1643.2198 [**4a** + 5Na]$^{5+}$.



Supplementary Fig. 7 ESI-TOF-MS spectrum of **4a**.

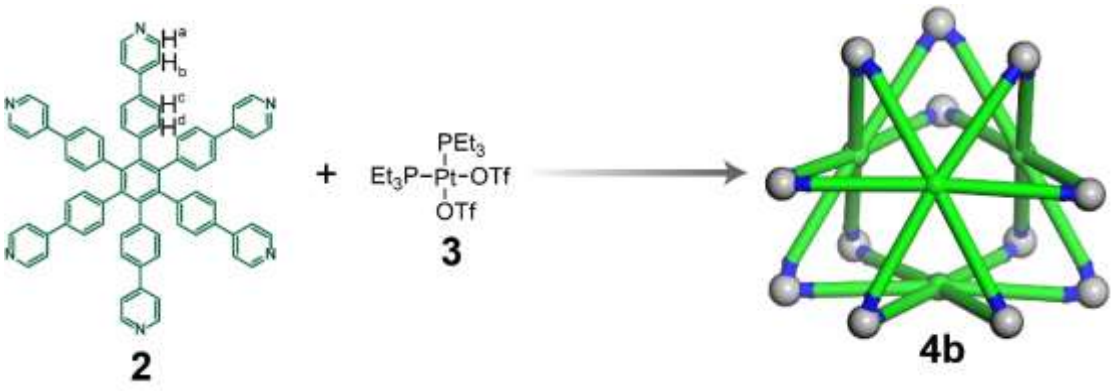


Supplementary Fig. 8 ^{1}H NMR spectrum (CD_3CN, 600 MHz, 295 K) recorded for **4a**.

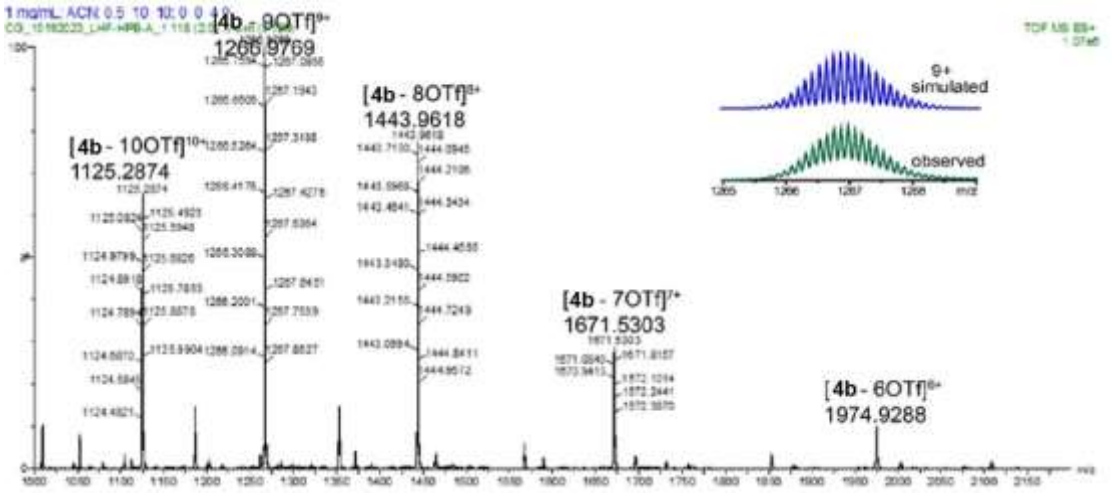


Supplementary Fig. 9 $^{31}P\{^{1}H\}$ NMR spectrum (CD_3CN, 243 MHz, 295 K) recorded for **4a**.

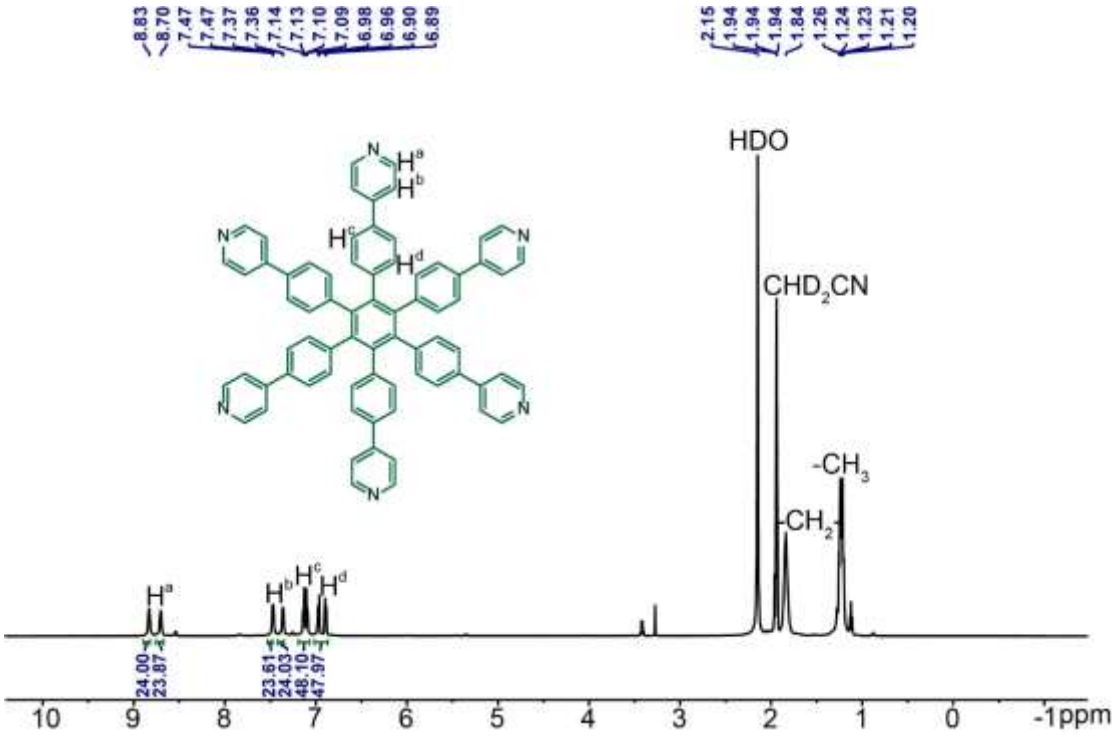
3.2 Self-assembly of metallacage **4b**



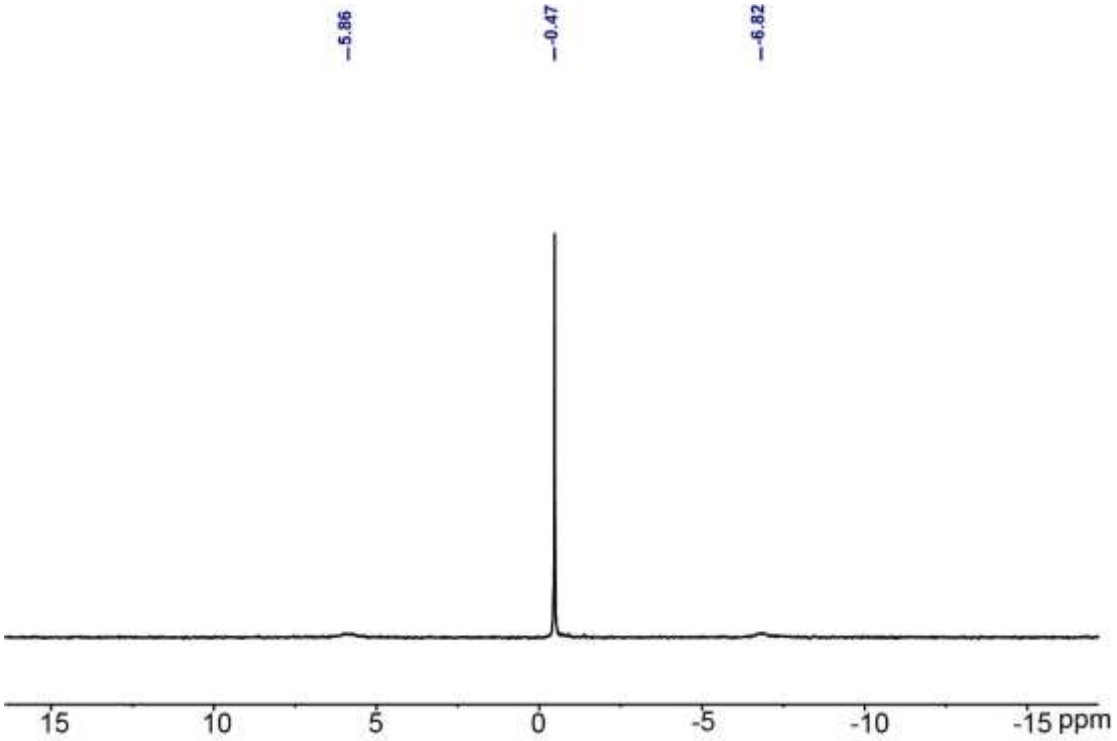
2 (10.00 mg, 10.03 μmol) and **3** (21.95 mg, 30.08 μmol) were mixed in acetonitrile (16.0 mL). The whole reaction mixture was heated at 60 ℃ for 12h, then cooled to room temperature. The solvent was removed by nitrogen flow. The residue was redissolved in CH_3CN (5.0 mL) and filtered, and then ethyl 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. ^{1}H 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}P{^{1}H} NMR (162 MHz, CD_3CN, 295 K), δ 0.47 (s, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 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]$^{6+}$.



Supplementary Fig. 10 ESI-TOF-MS spectrum of **4b**.

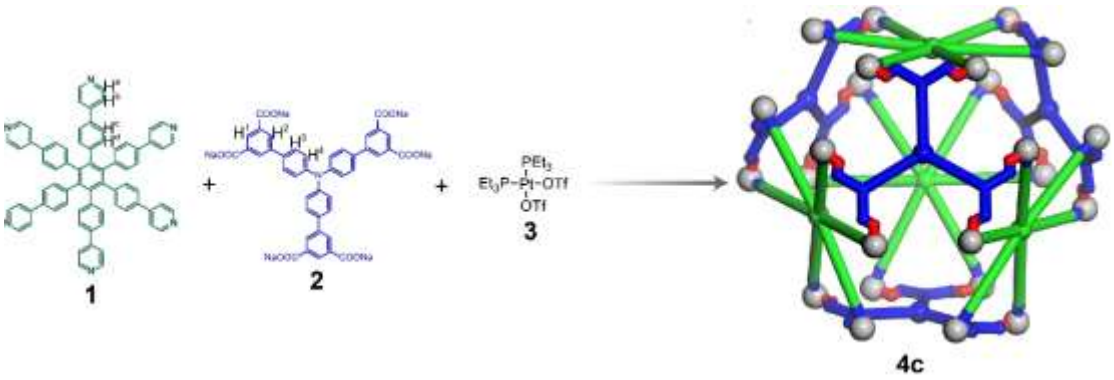


Supplementary Fig. 11 ^{1}H NMR spectrum (CD_3CN, 600 MHz, 295 K) recorded for **4b**.

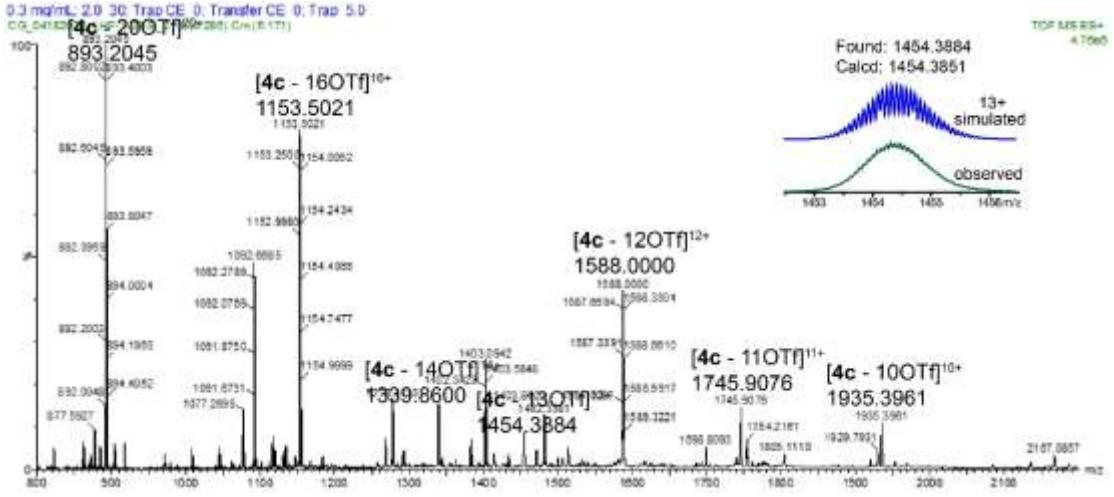


Supplementary Fig. 12 ^{31}P{^{1}H} NMR spectrum (CD_3CN,243 MHz, 295 K) recorded for **4b**.

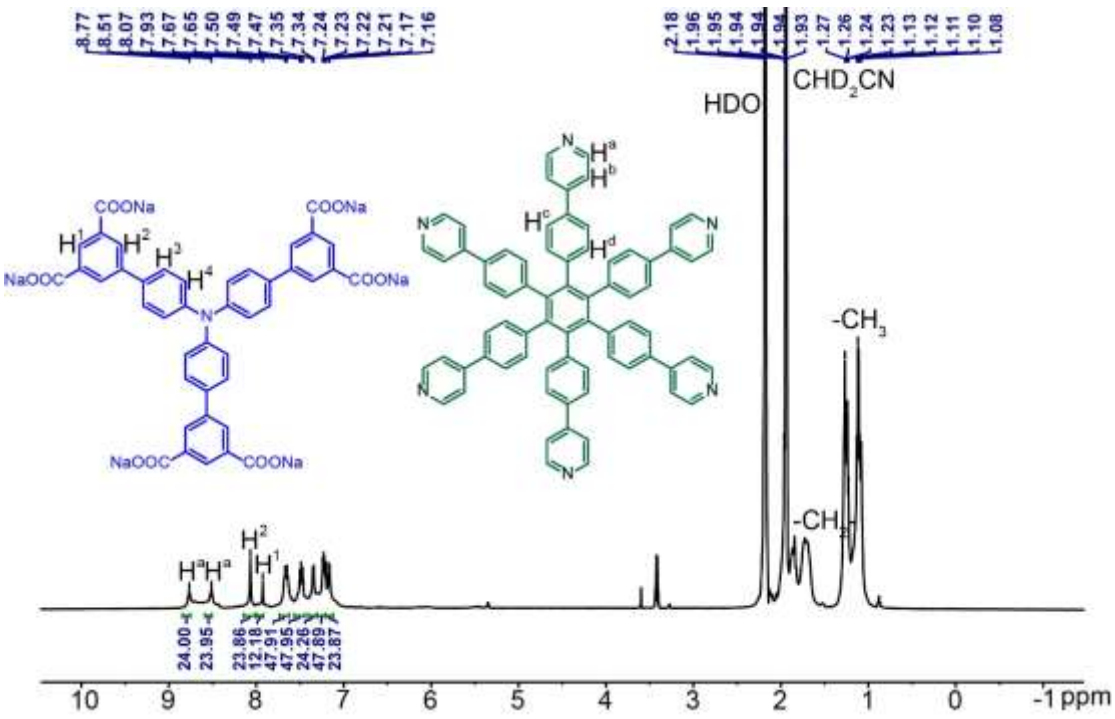
3.3 Self-assembly of metallacage **4c**



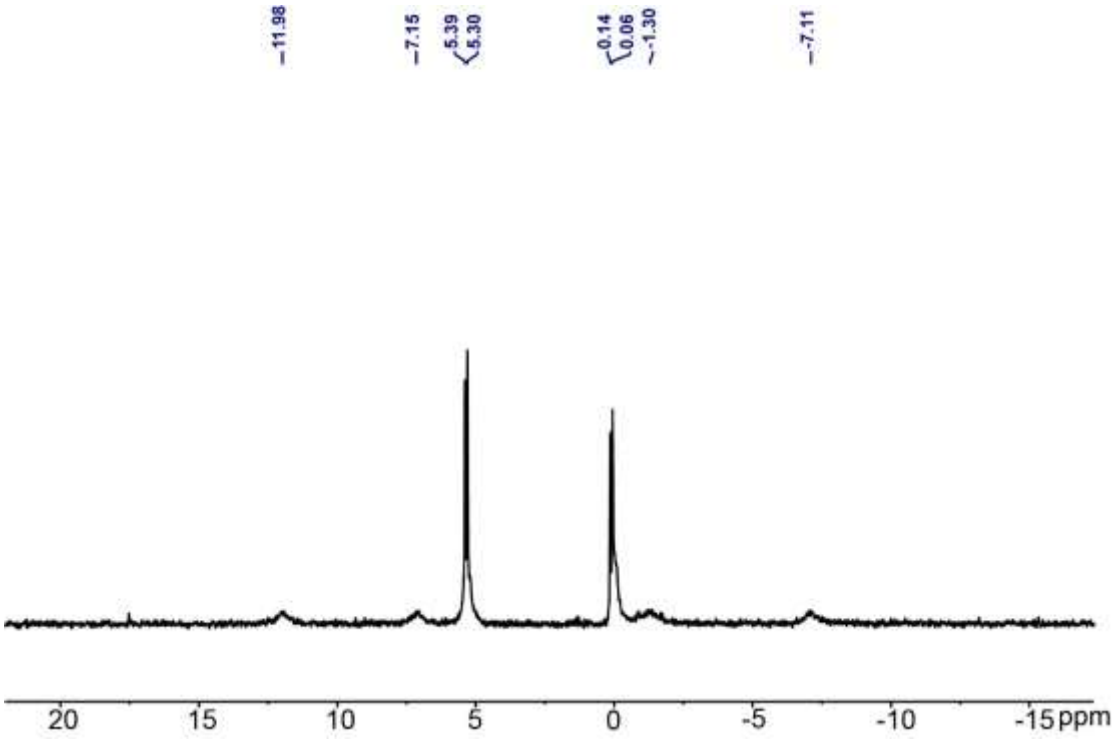
1 (8.72 mg, 10.03 μmol), **2** (10.00 mg, 10.03 μmol) and **3** (43.89 mg, 60.17 μmol) were mixed in acetonitrile/water (20.0 mL, 4:1, *v*/*v*). The whole reaction mixture was heated at 60 ℃ for 12h, then cooled to room temperature. The solvent was removed by nitrogen flow. The residue was redissolved 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 **4c** (47.55 mg, 87%) as a white solid. ^{1}H NMR (600 MHz, CD_3CN) 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). ^{31}P{^{1}H} NMR (162 MHz, CD_3CN, 295 K), δ 5.35 (d, $^2J_{P\text{-}P}$ = 21.6 Hz, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 3346 Hz), 0.10 (d, $^2J_{P\text{-}P}$ = 21.5 Hz, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 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]$^{10+}$.



Supplementary Fig. 13 ESI-TOF-MS spectrum of **4c**.



Supplementary Fig. 14 ^{1}H NMR spectrum (CD_3CN, 600 MHz, 295 K) recorded for **4c**.



Supplementary Fig. 15 ^{31}P{^{1}H} NMR spectrum (CD_3CN,243 MHz, 295 K) recorded for **4c**.

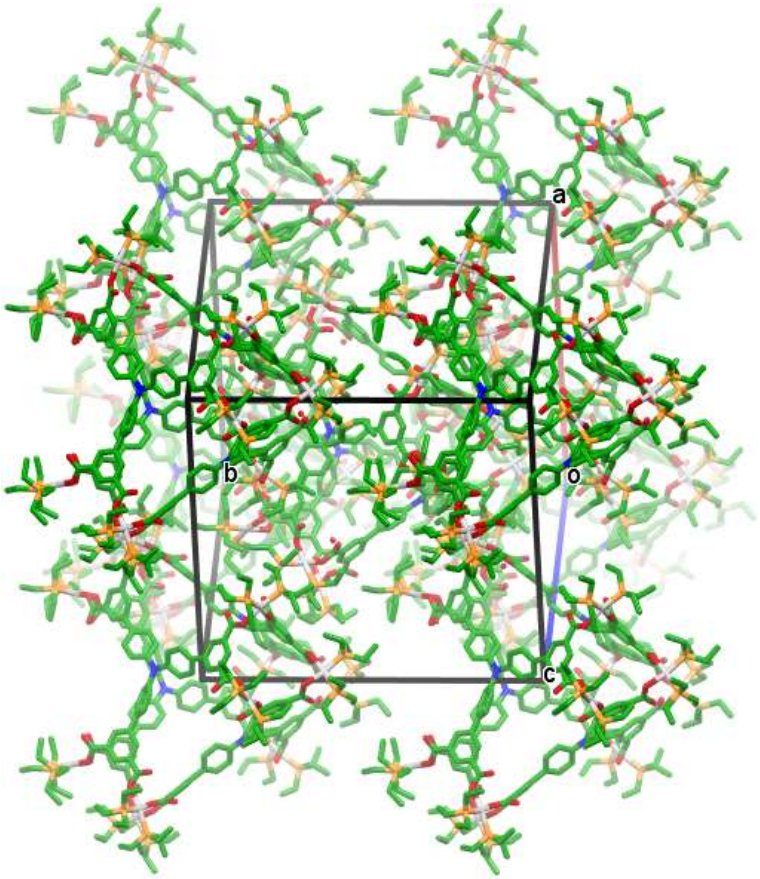
4. X-ray structure determination

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

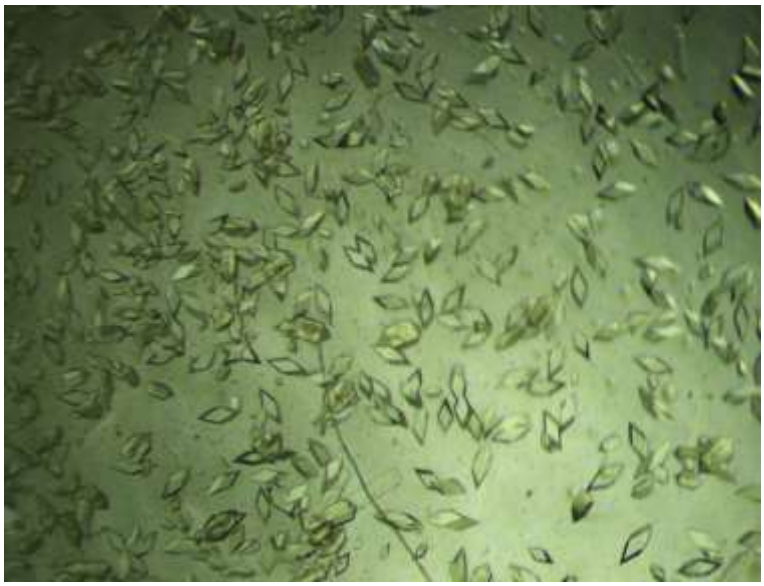
Compound	**4a**
Empirical formula	C_{312} H_{444} N_4 O_{48} $P_{24}Pt_{12}$
F_w	8102.96
Crystal system	cubic
Space group	*P*-43n
a /Å	29.1614(16)
b /Å	29.1614(16)
c /Å	29.1614(16)
α /°	90
β /°	90
γ /°	90
V /Å^3	24798(4)
Z	8
D_{calc}/g cm^{-3}	1.085
F (000)	8048.0
μ /mm^{-1}	4.950
θ max	114.486
Independent 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 metallacage **4c**

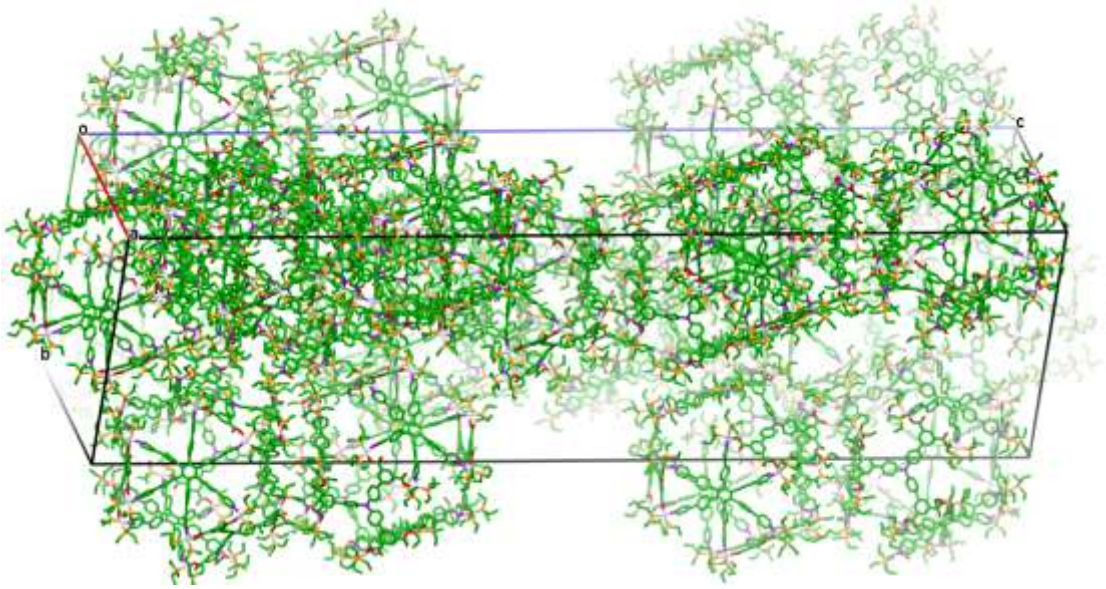
Compound	**4c**
Empirical formula	C_{744} $H_{996}N_{28}$ O_{48} P_{48} Pt_{24}
F_w	17260.44
Crystal system	trigonal
Space group	R -3
a /Å	59.444(6)
b /Å	59.444(6)
c /Å	167.23(3)
α /°	90
β /°	90
γ /°	120
V /Å^3	511754(140)
Z	12
D_{calc}/g cm^{-3}	0.633
F (000)	91632.0
μ /mm^{-1}	4.207
θ max	50.667
Independent reflns	114995
Reflns [$I > 2\sigma(I)$]	312328
R_1; wR_2 [$I > 2\sigma(I)$]	0.1570; 0.3446



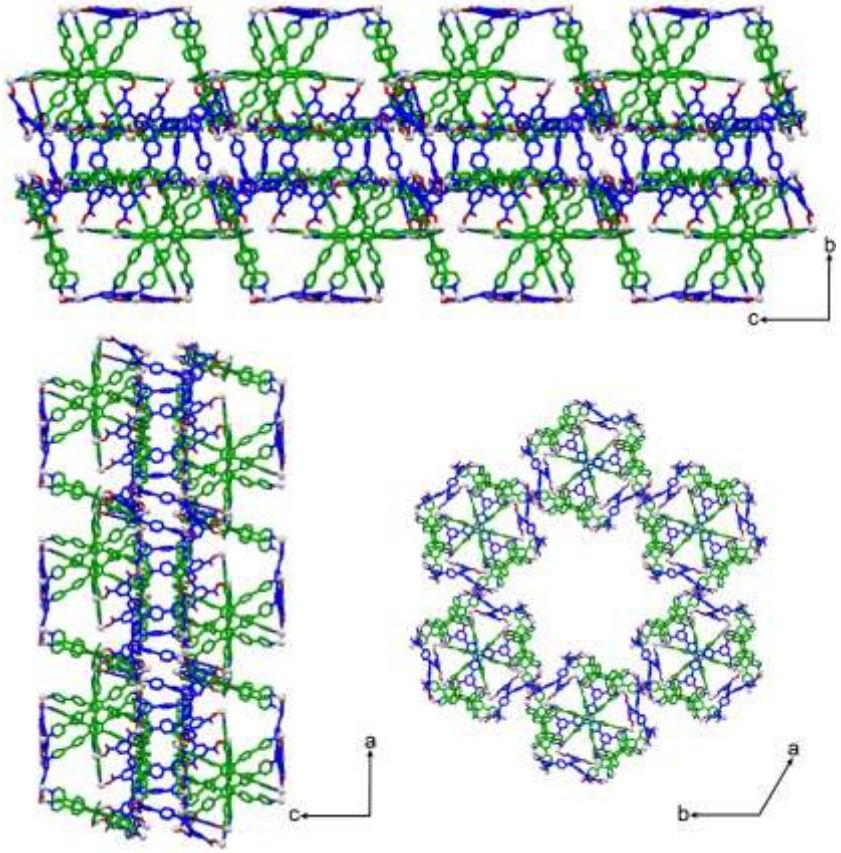
Supplementary Fig. 16 Stacking of metallacage **4a** in a unit cell. Hydrogen atoms are omitted for clarity.



Supplementary Fig. 17 Optical image of crystals of metallacage **4c**.

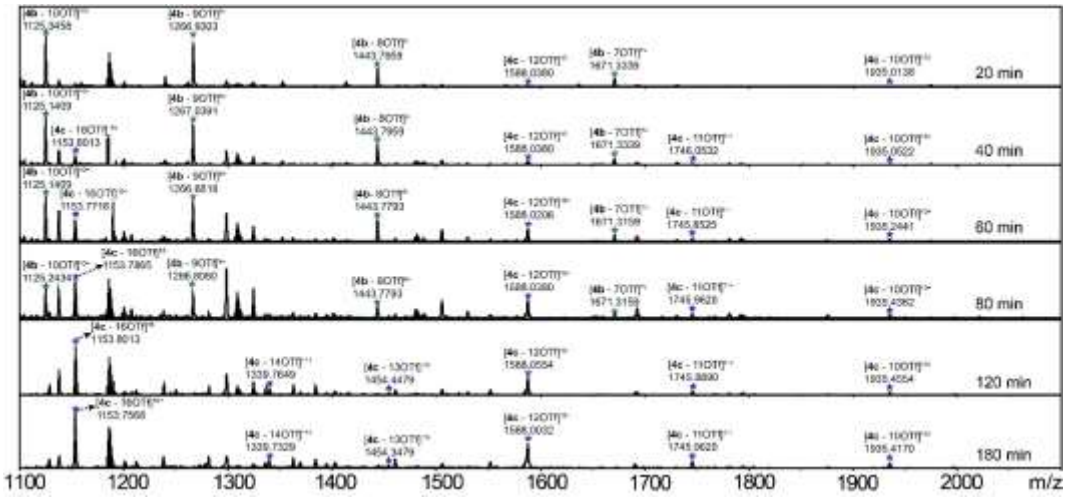


Supplementary Fig. 18 Stacking of metallacage **4c** in a unit cell. Hydrogen atoms are omitted for clarity.

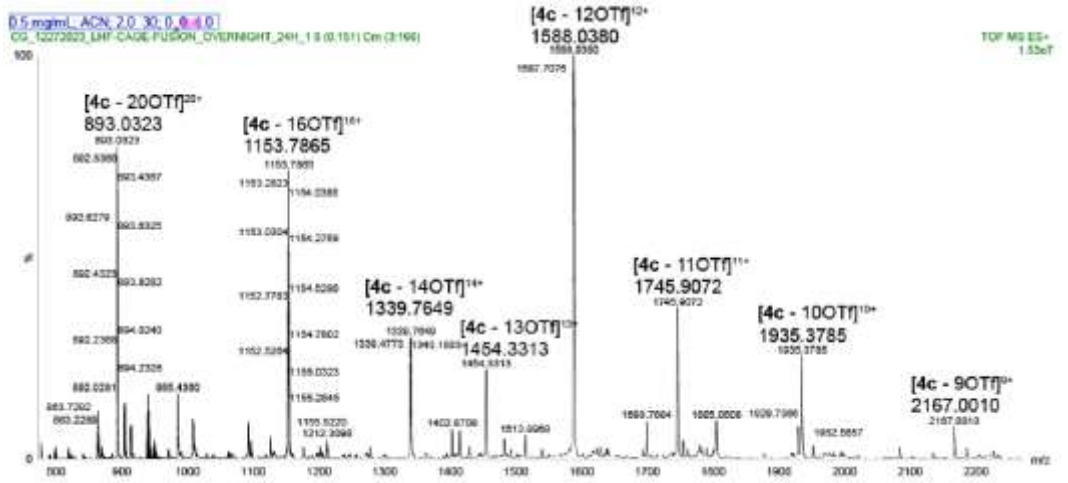


Supplementary Fig. 19 Crystal packing model of metallacage **4c** viewed from (a) a axis, (b) b axis, and (c) c axis. Hydrogen atoms, counterions, triethylphosphine units and solvent molecules are omitted for clarity.

5. Monitoring the supramolecular self-assembly and fusion process



Supplementary Fig. 20. Time-dependent ESI-TOF-MS spectra of equimolar mixture of **4a** and **4b**.



Supplementary Fig. 21 ESI-TOF-MS spectrum of equimolar mixture of **4a** and **4b** after being stirring overnight.

6. Supplementary References

1. Liu, H. et al. Hexaphenylbenzene-based deep blue-emissive metallacages as donors for light-harvesting systems. *Angew. Chem. Int. Ed.* **61**, e202207289 (2022).