Electronic Supplementary Material

Self-Assembly of Coordination Molecular baskets as inorganic analogues of cyclotriveratrylenes (CTV)

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Experimental Section

Self-assembly of **1a**, **2a**: Compound [Pd$(NO_3)_2$(phen-crown-6)] or [Pd $(NO_3)_2$(phen-crown-5)] (0.03 mmol) was added to a suspended aqueous solution (2 ml) of L (0.03 mmol), and the mixture was stirred for twenty minutes under ambient temperature. The resulting yellow clear solution was evaporated to dry, and dried under vacuo, yield 97 %(for **1a**), 96 %(for **2a**).

Self-assembly of **1b**, **2b**: [Pt$(NO_3)_2$(phen-crown-6)] or [Pt$(NO_3)_2$(phen-crown-5)] (0.03 mmol) was added to a suspended aqueous solution (2 ml) of L (0.03 mmol), and the mixture was stirred for 3 days under 100^{o}C. The resulting yellow clear solution was evaporated to dry, and dried under vacuo, yield 91 %(for **1b**), 89 %(for **2b**).

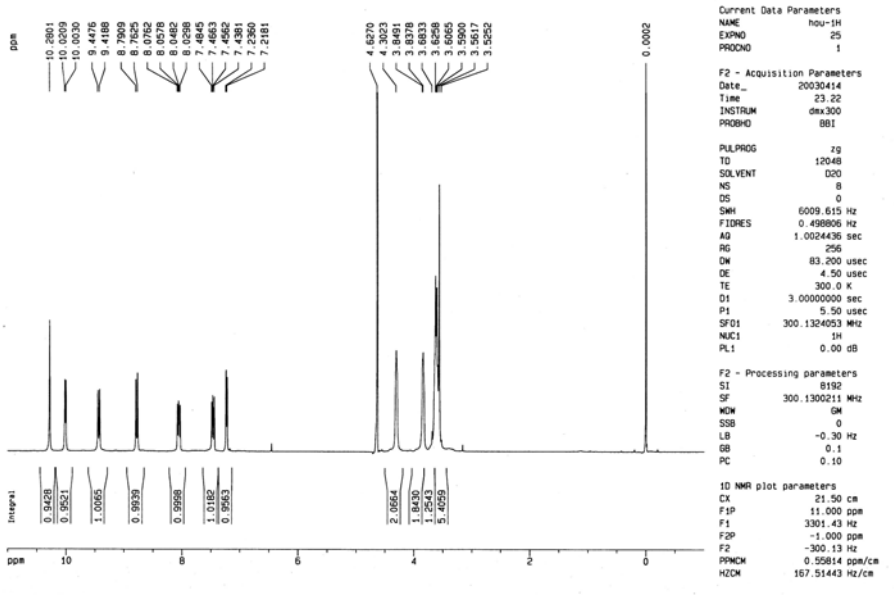
1a: ^{1}H NMR(300MHz, D_2O, 25^{o}C, TMS as an external standard) δ = 10.28 (s, 6 H), 10.01 (d, 6 H, ^3J (H,H) = 5.4 Hz), 9.43 (d, 6 H, ^3J (H,H) = 8.6 Hz), 8.78 (d, 6 H, ^3J (H,H) = 8.5 Hz), 8.03-8.08 (m, 6 H), 7.44-7.45 (m, 6 H), 7.23 (d, 6 H, ^3J (H,H) = 5.4 Hz), 4.30 (bs,12 H, 6CH_2), 3.84-3.85(bm, 12 H, 6CH_2), 3.59-3.62(bm, 24 H, 12CH_2), 3.52 (s, 12 H, 6CH_2); ^{13}C NMR(75MHz, D_2O, 25^{o}C, TMS as an external standard)δ=154.7, 149.1, 144.9, 144.7, 143.0, 137.6, 136.0, 132.0, 127.9, 127.7, 125.4, 125.3, 95.9, 73.8, 69.5, 69.3, 69.0 ppm. CSI-MS (CH_3OH, NO_3^- as counter anions): m/z 1175.6[**1a**-2 NO_3^-]$^{2+}$, 763.1[**1a**-3NO_3^-]$^{3+}$, Elemental analysis Calcd. For $C_{102}H_{102}N_{18}O_{36}Pd_3 \cdot 3H_2O$(%):C 48.44, H 4.30, N 9.97; found: C 48.32, H 4.34, N 9.97.

1b: ^{1}H NMR(300MHz, D_2O, 25^{o}C, TMS as an external standard) δ = 10.11 (s, 6 H), 9.98 (d, 6 H, ^{3}J (H,H) = 5.4 Hz), 9.47 (d, 6 H, ^{3}J (H,H) = 8.7 Hz), 8.90 (dd, 6 H, ^{3}J (H,H) = 8.4 Hz, ^{5}J (H,H) = 1.9 Hz), 8.01-8.06 (m, 6 H), 7.48-7.53 (m, 12 H), 3.84-3.85 (bs,12 H, $6CH_2$), 3.61-3.70(bm, 24 H, $6CH_2$), 3.56(s, 12 H, $6CH_2$); CSI-MS(CH_3OH, NO_3^- as counter anions): m/z 1308.4[**1b**-$2NO_3^-$]$^{2+}$, 623.2[**1b**-$4NO_3^-$]$^{4+}$, Elemental analysis Calcd. For $C_{102}H_{102}N_{18}O_{36}Pt_3 \cdot 7H_2O$(%):C 42.37, H 3.59, N 8.79; found: C 42.57, H 3.80, N 8.67.

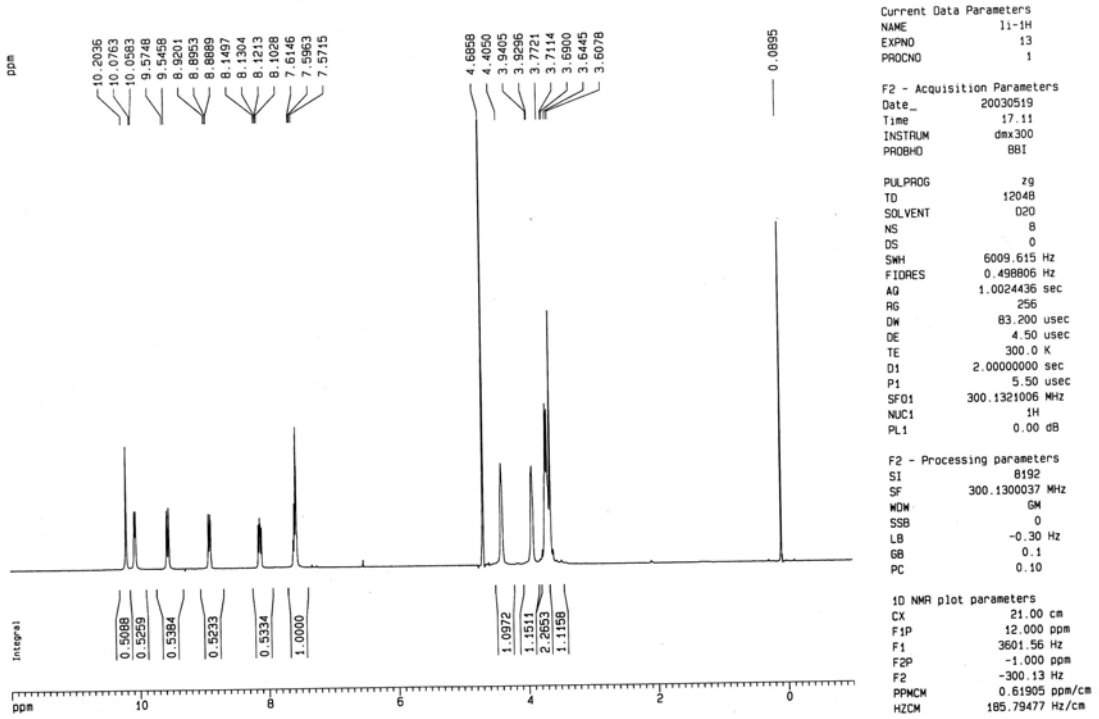
2a: ^{1}H NMR(300MHz, D_2O, 25^{o}C, TMS as an external standard) δ = 10.31 (s, 6 H), 10.03 (d, 6 H, ^{3}J (H,H) = 5.4 Hz), 9.45 (d, 6 H, ^{3}J (H,H) = 8.7 Hz), 8.77 (d, 6 H, ^{3}J (H,H) = 8.5 Hz), 8.04-8.09 (m, 6 H), 7.45-7.49 (m, 6 H), 7.24 (d, 6 H, ^{3}J (H,H) = 5.4 Hz), 4.27-4.28 (bs,12 H, $6CH_2$), 3.86(bm, 12 H, $6CH_2$), 3.63-3.64(bm, 24 H, $12CH_2$); CSI-MS(CH_3OH, NO_3^- as counter anions): m/z 1109.5[**2a**-2 NO_3^-]$^{2+}$, 719.1[**2a**-$3NO_3^-$]$^{3+}$, Elemental analysis Calcd. For $C_{96}H_{90}N_{18}O_{33}Pd_3 \cdot 3H_2O$(%):C 48.10, H 4.04, N 10.52; found: C 47.95, H 4.09, N 10.30.

2b: ^{1}H NMR(300MHz, D_2O, 25^{o}C, TMS as an external standard) δ = 10.10 (s, 6 H), 9.93 (d, 6 H, ^{3}J (H,H) = 6.1 Hz), 9.41 (d, 6 H, ^{3}J (H,H) = 8.7 Hz), 8.56 (d, 6 H, ^{3}J (H,H) = 8.3 Hz), 7.98-8.02 (m, 6 H), 7.47 (d, ^{3}J (H,H) = 5.3 Hz, 6 H), 7.35-7.40 (m, 6 H), 4.01 (bs,12 H, $6CH_2$), 3.66(bs, 12 H, $6CH_2$), 3.44(bs, 24 H, $12CH_2$); CSI-MS(CH_3OH, NO_3^- as counter anions): m/z 1242.4[**2b**-$2NO_3^-$]$^{2+}$, 807.6[**2b**-$3NO_3^-$]$^{3+}$, 590.2[**2b**-$4NO_3^-$]$^{4+}$, 459.8[**2b**-$5NO_3^-$]$^{5+}$. Elemental analysis Calcd. For $C_{96}H_{90}N_{18}O_{33}Pt_3 \cdot 3H_2O$(%):C 43.29, H 3.63, N 9.46; found: C 43.06, H 3.68, N 9.19.

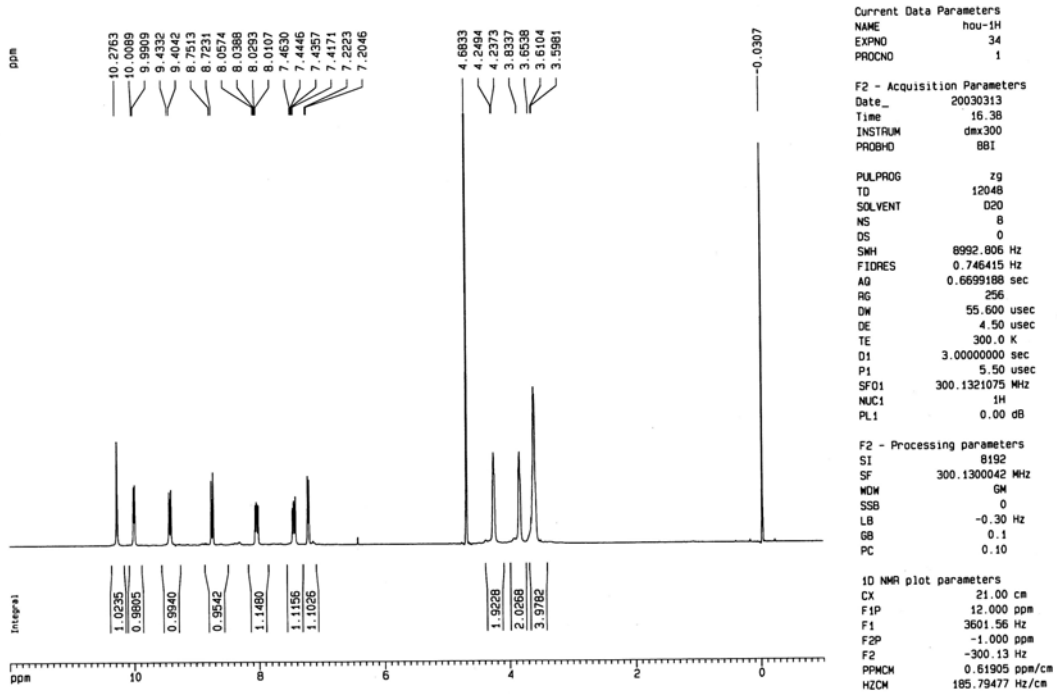
^{1}H NMR spectra of **1a** in D_2O(TMS as an external standard)



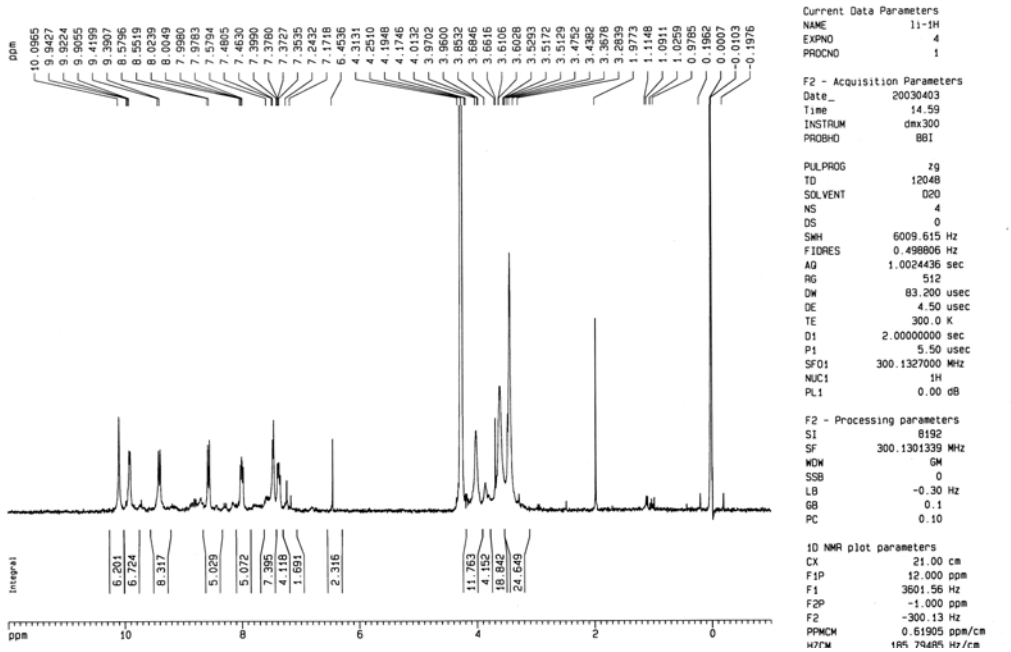
^{1}H NMR spectra of **1b** in D_2O(TMS as an external standard)



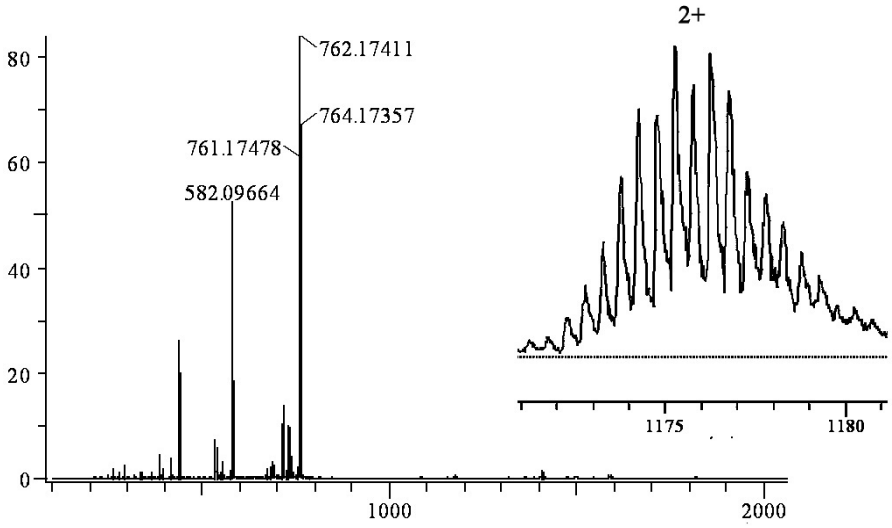
^{1}H NMR spectra of **2a** in D_2O(TMS as an external standard)



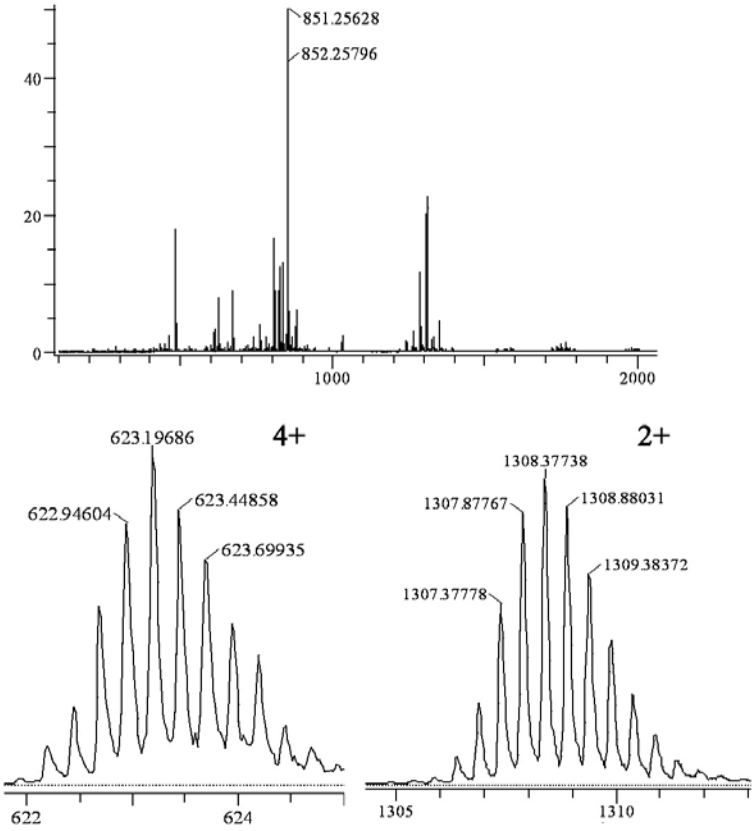
^{1}H NMR spectra of **2b** in D_2O(TMS as an external standard)



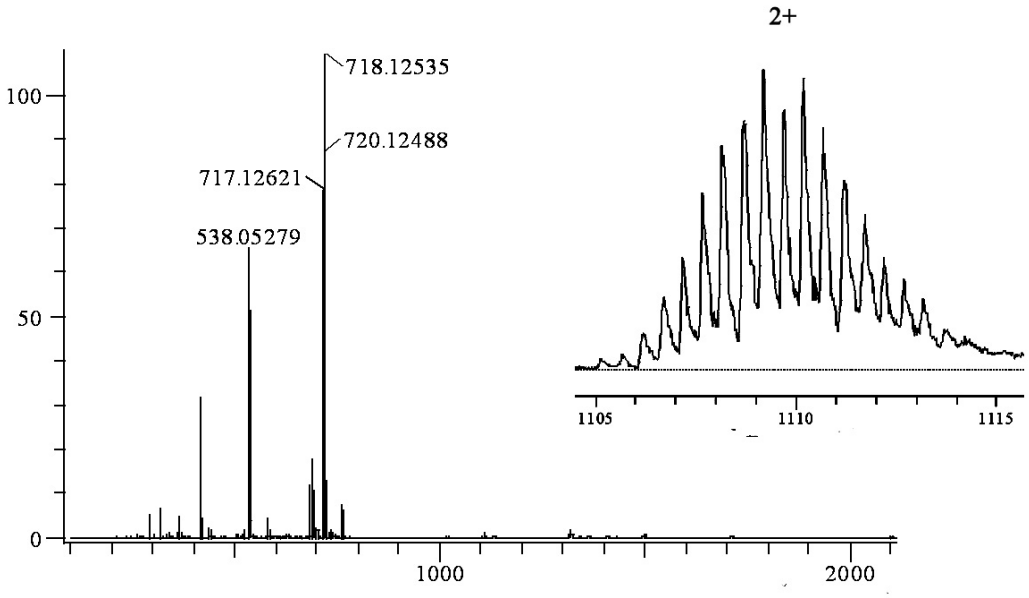
CSI-MS spectra of **1a** in methanol



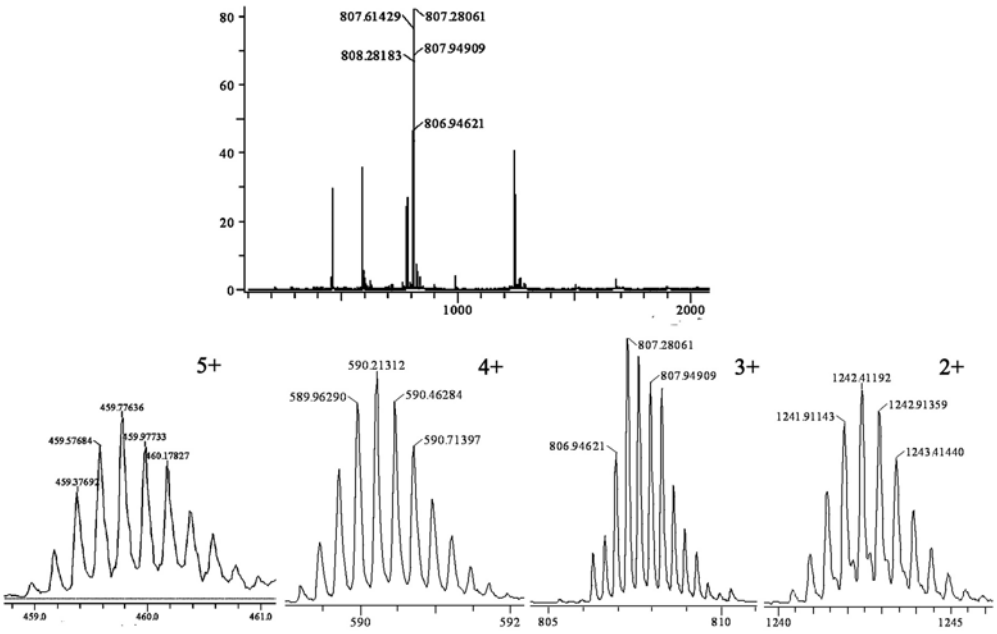
CSI-MS spectra of **1b** in methanol



CSI-MS spectra of **2a** in methanol



CSI-MS spectra of **2b** in methanol



Crystallography: Experimental and Refinement

X-ray diffraction measurement for **1a** was carried out at 293(2)K on a Bruker Smart Apex CCD area detector equipped with a graphite monochromated MoKα radiation (λ = 0.71073 Å). The empirical absorption correction was performed using SADABS. The data frames were integrated using SAINT (Bruker, 2000). The structure was solved by direct methods by using SHELXTL (Bruker, 2000) program and refined by full-matrix least-squares on F^2 by using SHELXTL and expanded using Fourier techniques. All non-H atoms of the complex were refined with anisotropic thermal parameters and all hydrogen atoms were placed in the idealized positions.

Further refinement on the crystal structure of 1a has made and all of the six counter anions-NO_3^- were located. The final values of R_1 = 0.0558; wR_2 =0.1159; GOF =1.03

There are also some partially occupied solvent molecules-water molecules in the cif file. The occupancies of water molecules were determined through setting free variables and refining. The hydrogen of water were found in the difference map and then refined by riding mode and given isotropic thermal parameters 1.2 to 1.5 times the Ueq for the parent atom.

The molecular structure of **1a** was given as follow: