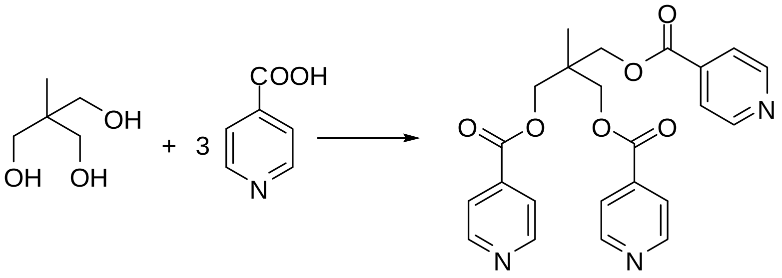
Supporting information

General: All of reagents were commercially available and used as purchased. C, H, and N microanalyses were measured using an elemental Vairo EL analyzer, ^{1}HNMR spectra were recorded at Bruker AM-400 (400 MHZ) spectrometer, IR spectra were recorded on a Shimadzu IR-440 spectrometer.

Synthesis of L (L= tris(isonicotinoxymethyl)ethane)



A mixture of Isonicotinic acid (3.737g, 30 mmol), 1,1,1-Tris(Hydroxymethyl)ethane (1.213g, 9.8 mmol), DCC (6.612g, 30.5 mmol), DMAP (135mg) were stirred in 200 mL CH_2Cl_2 at ice bath, after 24h stirring, The solution was filtered and washed with $CHCl_3$, and the solvent was evaporated in vacuo. The residue was purified by column chromatography on silica gel with EtOAC/$CHCl_3$ (4:1). The product 2a was obtained as a white powder (2.663g, yield: 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (6H, d, *J*= 6), 7.82 (6H, d, *J*= m), 4.51 (6H, s), 1.34 (3H, 3). ESI-MS (m/z): 436 ($M+H^+$).

Synthesis of compound 1

Layering a $CHCl_3$ solution of ligand L (7mg, 0.0165 mmol) with a MeOH solution of $AgClO_4$ (5mg, 0.025 mmol), about two weeks later, colorless rectangular crystal compound **1** (6mg) were obtained in a 50% yield. Anal. Calcd for

$[Ag_6L_4(ClO_4)_6.CHCl_3]_n$(%): C, 35.77; H, 3.14; N, 5.31; Found (%): C, 35.97; H, 2.76; N, 5.41. IR (KBr) ν : 3567, 3014, 2962, 1732, 1614, 1422, 1282, 1211, 760, 701, 621cm^{-1}.

Synthesis of compound 2

Layering a $CHCl_3$ solution of ligand L (7mg, 0.0165 mmol) with a MeOH solution of $AgPF_6$ (6mg, 0.025 mmol), about three weeks later, colorless rectangular crystal compound **1** (5mg) were obtained in a 38% yield. Anal. Calcd for $[Ag_6L_4(PF_6)_6.CHCl_3]_n$ (%): C, 33.19; H, 2.68; N, 5.09; Found (%): C, 33.07; H, 2.54; N, 4.98. IR (KBr) ν:3453, 3112, 2966, 1734, 1615, 1424, 1384, 1283, 1127, 840, 760, 739, 701, 557 cm^{-1}.

X-ray crystallography

Data collections were all performed at 293 K on a Mercury CCD diffractometer with graphite monochromated Mo Ka radiation (λ = 0.71073 Å). The structures were solved by direct methods, and all calculations were performed using the SHELXL package[1]. The structures **1**-**2** were refined by full matrix least-squares with anisotropic displacement parameters for non-hydrogen atoms. All hydrogen atoms were generated geometrically and treated as riding. We employed PLATON/SQUEEZE[2] to calculate the contribution to the diffraction from the solvent region and thereby produced a set of solvent-free diffraction intensities. The final formula was calculated from the SQUEEZE[2] results combined with elemental analysis data. Imposed by the space group symmetry; for compound **1**, the Ag1 and Ag2 atoms are on mirror planes and Ag3 is on a twofold axis; while the Ag1, Ag2, Ag3 and Ag4 atoms in compound **2** are on mirror planes. The crystallographic data are summarized in Table 1 and Table 2. CCDC 888501, 888500 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure determination summary for **1**–**2**.

	1	**2**
CCDC deposit no.	888501	888500
Formula[a-b]	$C_{46.73}H_{42.73}Ag_3Cl_{5.19}N_6O_{24}$	$C_{96}H_{88}Ag_6Cl_{12}F_{36}N_{12}O_{24}P_6$
Formula weight	1579.95	3736.22
Crystal system	Tetragonal	Orthorhombic
Space group	$P4_2/mbc$	*Ibam*
a (Å)	23.153 (4)	32.769 (9)
b (Å)	23.153 (4)	44.126 (12)
c (Å)	23.880 (6)	24.110 (6)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	12801 (4)	34861 (16)
Z	8	8
D_c (g/cm^{-3})	1.640	1.424
μ (mm^{-1})	1.204	0.991
$F(0\ 0\ 0)$	6291	14720
Crystal size (mm^3)	0.20x0.20x0.20	0.20x0.20x0.20
θ range (°)	2.11, 27.66	2.04, 27.36
No. of unique reflections / collected	7644/98593	20126/135648
Goodness-of-fit (GOF)	1.090	1.039
Final R indices ($I > 2\sigma(I)$)	0.0843	0.1053
R indices (all data)	0.0936	0.1449

a) The composition of solvent in compound **1** is determined by Elemental analysis;

b) The Elemental analysis of compound **2** shows that it contains $CHCl_3$ molecules; the exact composition is hard to determine because the solvent is easy removed from compound **2** with large channels.

Table 2. Selected bond lengths [Å] and angles [°] for **1-2**

1

Ag(1)—N(1A)	2.161 (4)	Ag(2)—N(2)	2.124 (5)
Ag(1)—N(1)	2.161 (4)	Ag(3)—N(3B)	2.137 (5)
Ag(2)—N(2A)	2.124 (5)	Ag(3)—N(3)	2.137 (5)
N(1A)—Ag(1)—N(1)	171.2 (2)	N(2A)—Ag(2)—N(2)	162.5 (3)
N(3B)—Ag3—N(3)	173.2 (4)		
Symmetry codes: (A) *x*, *y*,-*z*; (B) -*x*, *1*-*y*, *z*.			
2			
Ag(1)—N(1)	2.153 (7)	Ag(3)—N(3A)	2.158 (6)
Ag(1)—N(1A)	2.153 (7)	Ag(3)—Ag(2B)	3.3714 (15)
Ag(2)—N(2)	2.131 (6)	Ag(4)—N(4A)	2.125 (6)
Ag(2)—N(2A)	2.131 (6)	Ag(4)—N(4)	2.125 (6)
Ag(2)—Ag(3B)	3.3714 (15)	Ag(5)—N(6)	2.143 (7)
Ag(3)—N(3)	2.158 (6)	Ag(5)—N(5)	2.153 (6)
N(1)—Ag(1)—N(1A)	174.0 (4)	N(3)—Ag(3)—Ag(2B)	92.49 (15)
N(2)—Ag(2)—N(2A)	178.0 (3)	N(3A)—Ag(3)—Ag(2B)	92.49 (15)
N(2)—Ag(2)—Ag(3B)	90.64 (16)	N(4A)—Ag(4)—N(4)	175.4 (3)
N(2A)—Ag(2)—Ag(3B)	90.64 (16)	N(6)—Ag(5)—N(5)	172.2 (3)
N(3)—Ag(3)—N(3A)	174.5 (3)		
Symmetry codes: (A) *x*, *y*, -*z*; (B) *1*-*x*, -*y*, *z*.			

Partial structures of compound **1** and **2** are summarized in **Figures 1-11**.

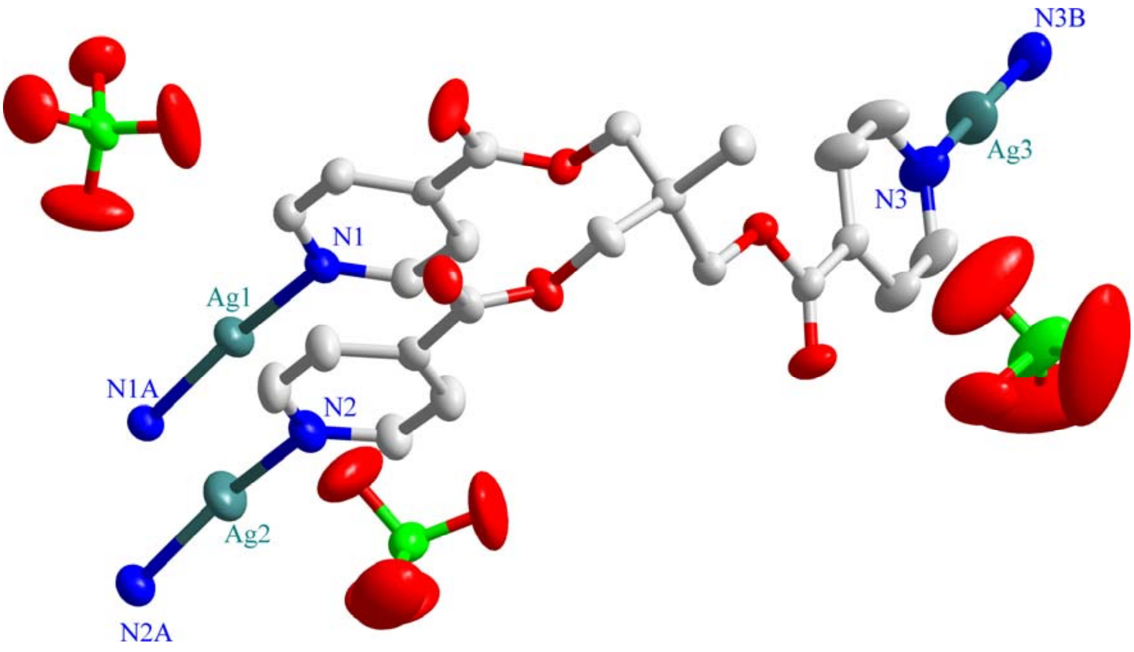


Figure 1 Coordination environment of compound **1**, for clarity, the hydrogen atoms are omitted. Symmetry code: (A) *x*, *y*, -*z*; (B) -*x*, *1*-*y*, *z*.

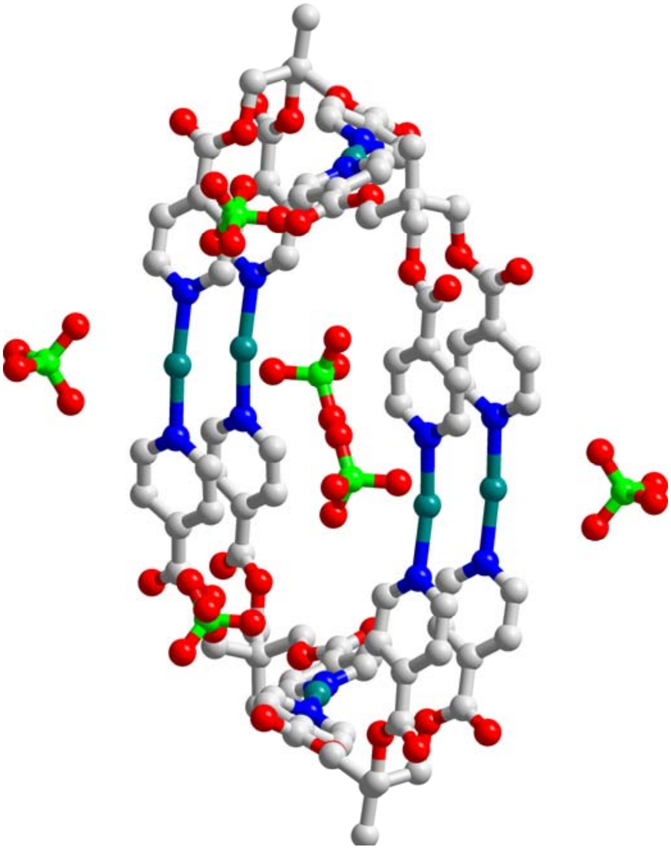


Figure 2 The Ag_6L_4 cage unit in **1** (H atoms have been omitted for clarity).

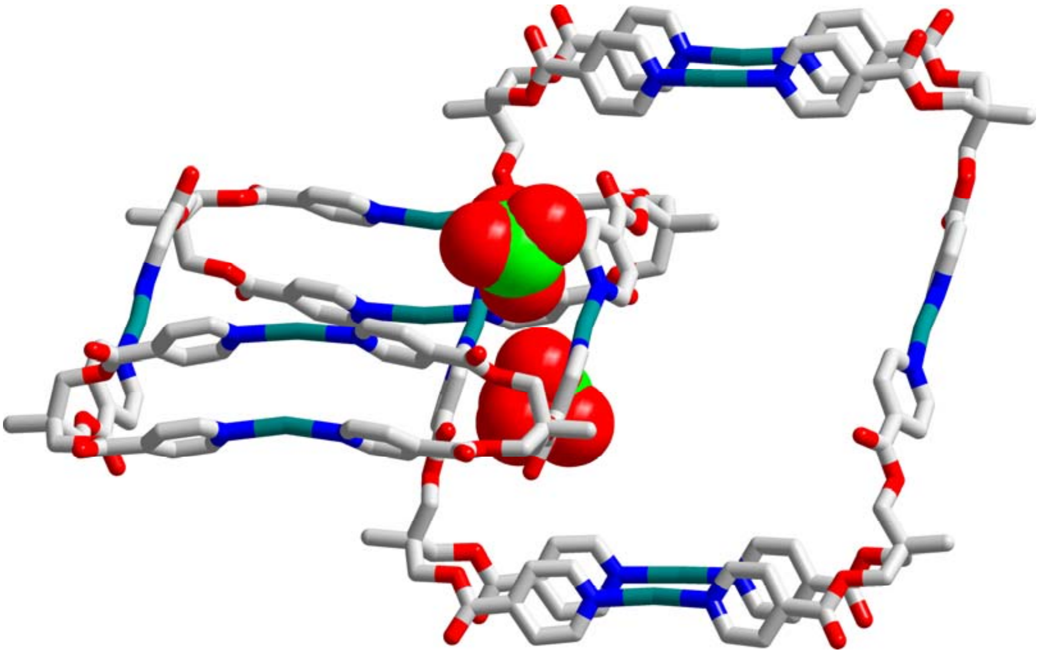


Figure 3 The charge-charge interaction between ClO_4^- and Ag(I), which stabilizes the interlocking.

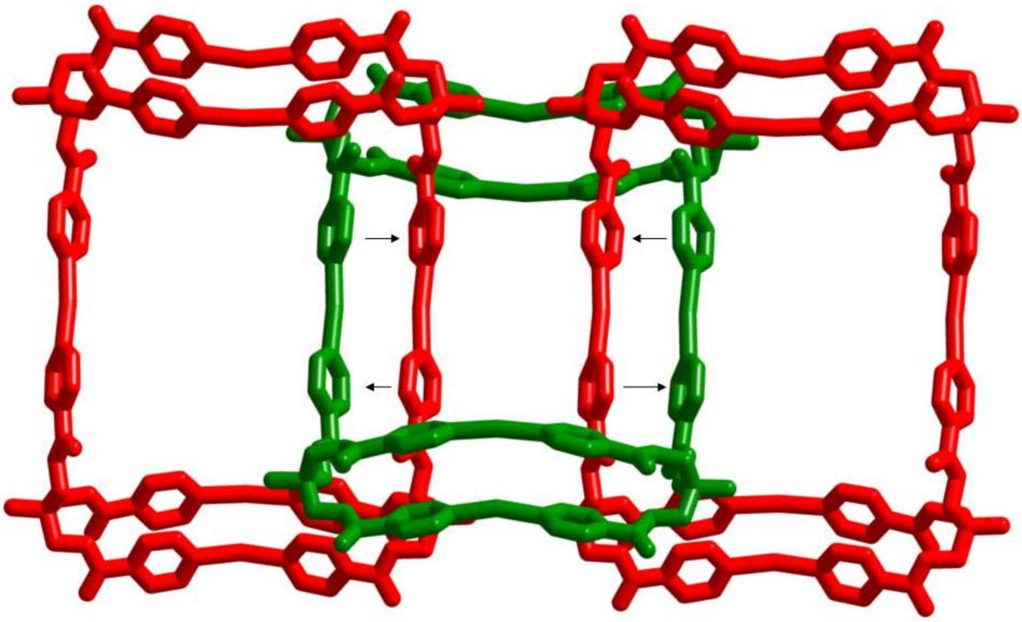


Figure 4 Structural fragment containing three interlaced metallacages in compound **1**.

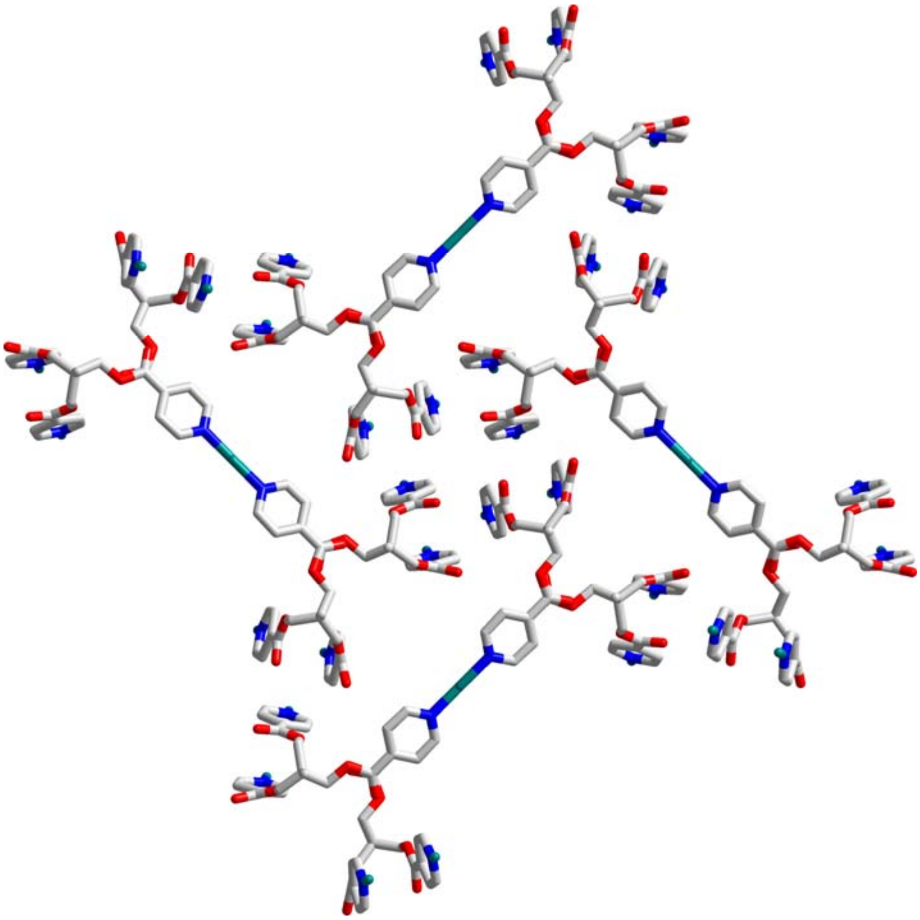


Figure 5 The polycatenane chains stacked closely along the *c* axis.

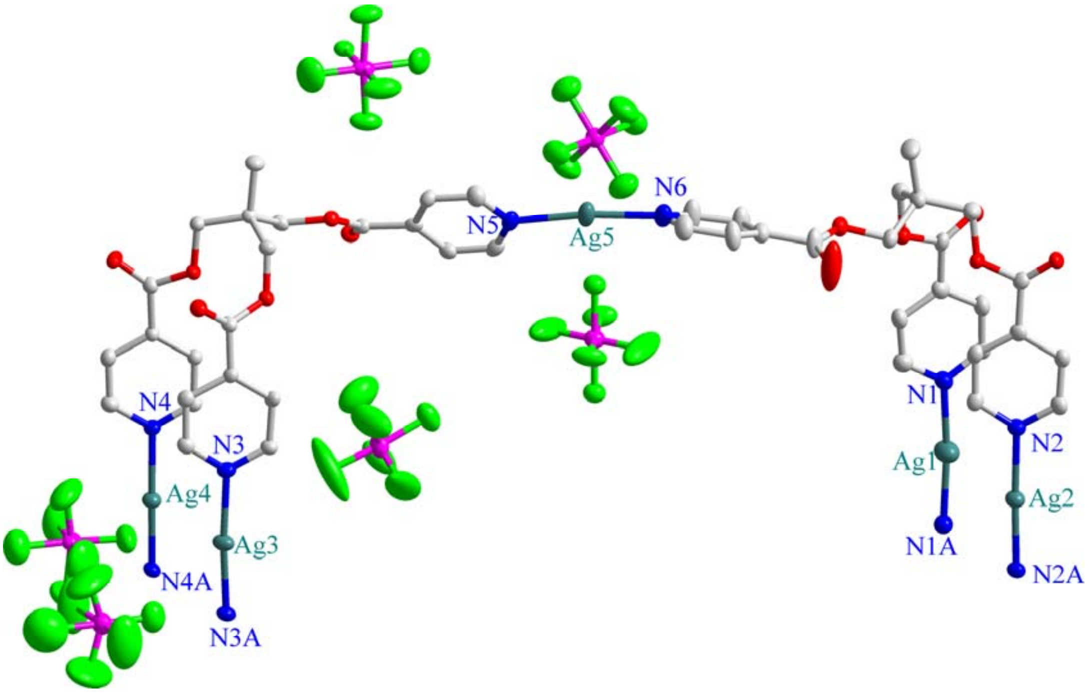


Figure 6 Coordination environment of compound **2**, for clarity, the hydrogen atoms are omitted. Symmetry code: (A) *x*, *y*, -*z*.

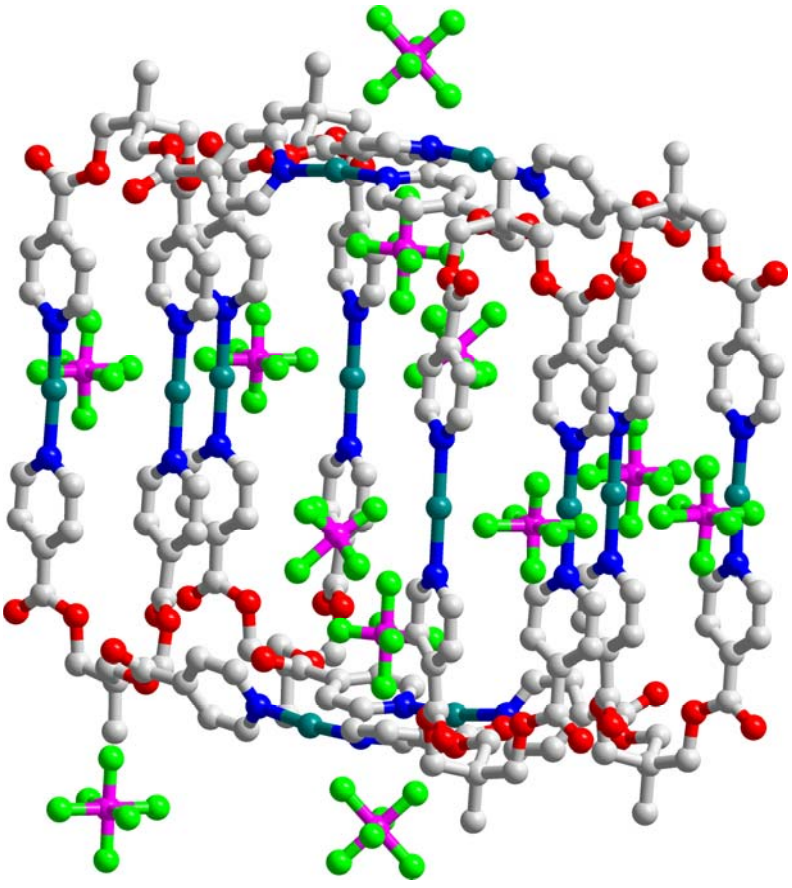


Figure 7 The $Ag_{12}L_8$ cage in **2**. (H atoms have been omitted for clarity).

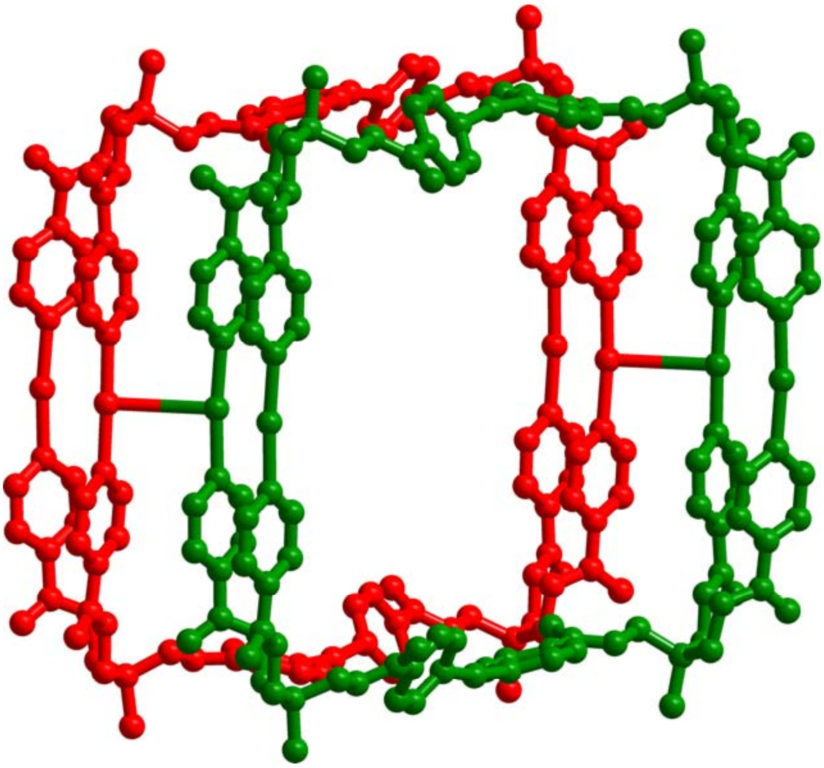


Figure 8 The $Ag_{12}L_8$ cage is the dimmer of Ag_6L_4 unit linking by Ag-Ag interaction.

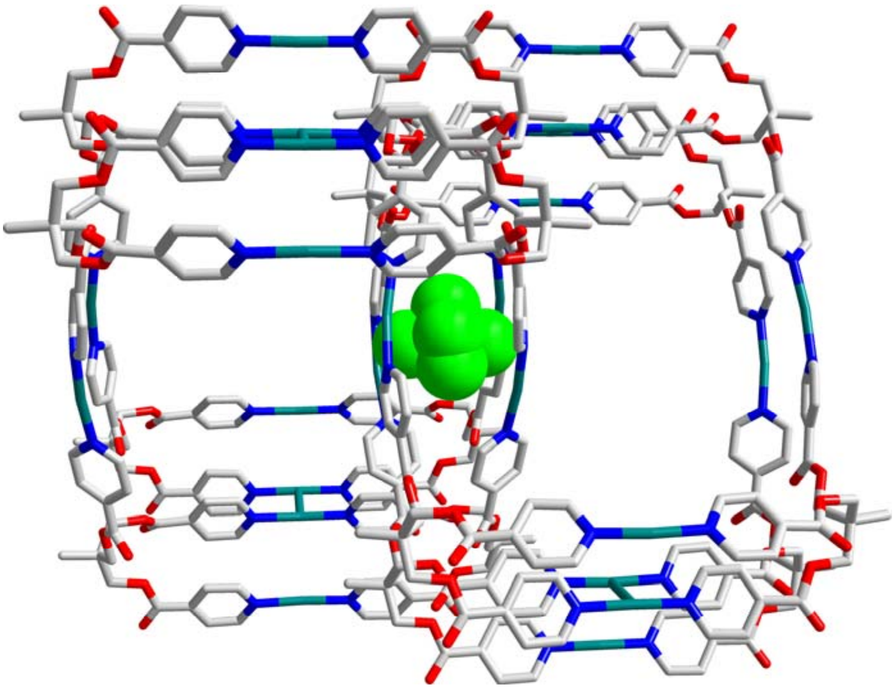


Figure 9 The charge-charge interaction between PF_6^- and Ag(I), which stabilizes the interlocking.

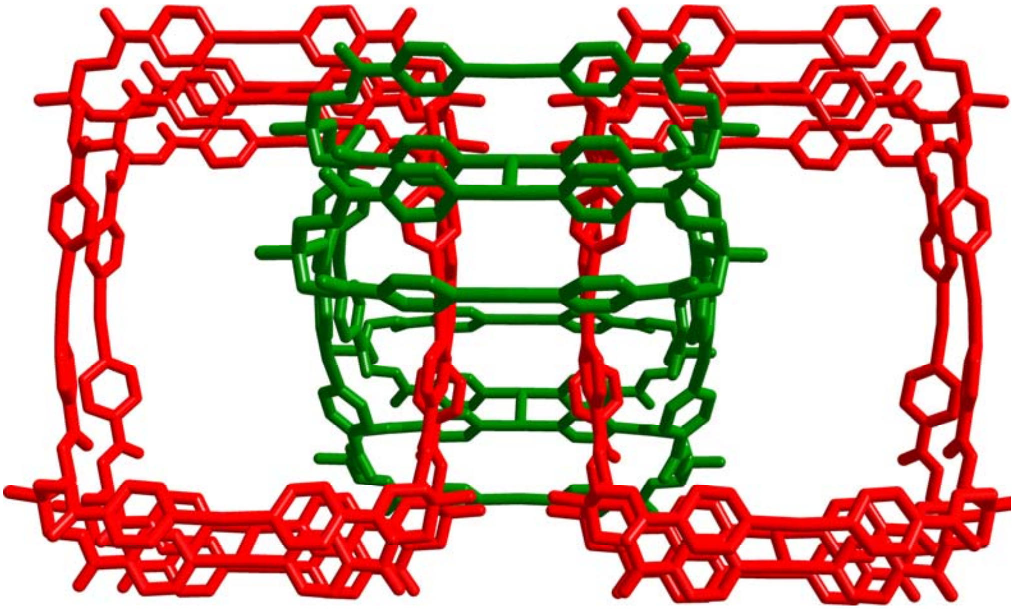


Figure 10 Structural fragment containing three interlaced metallacages in compound **2**.

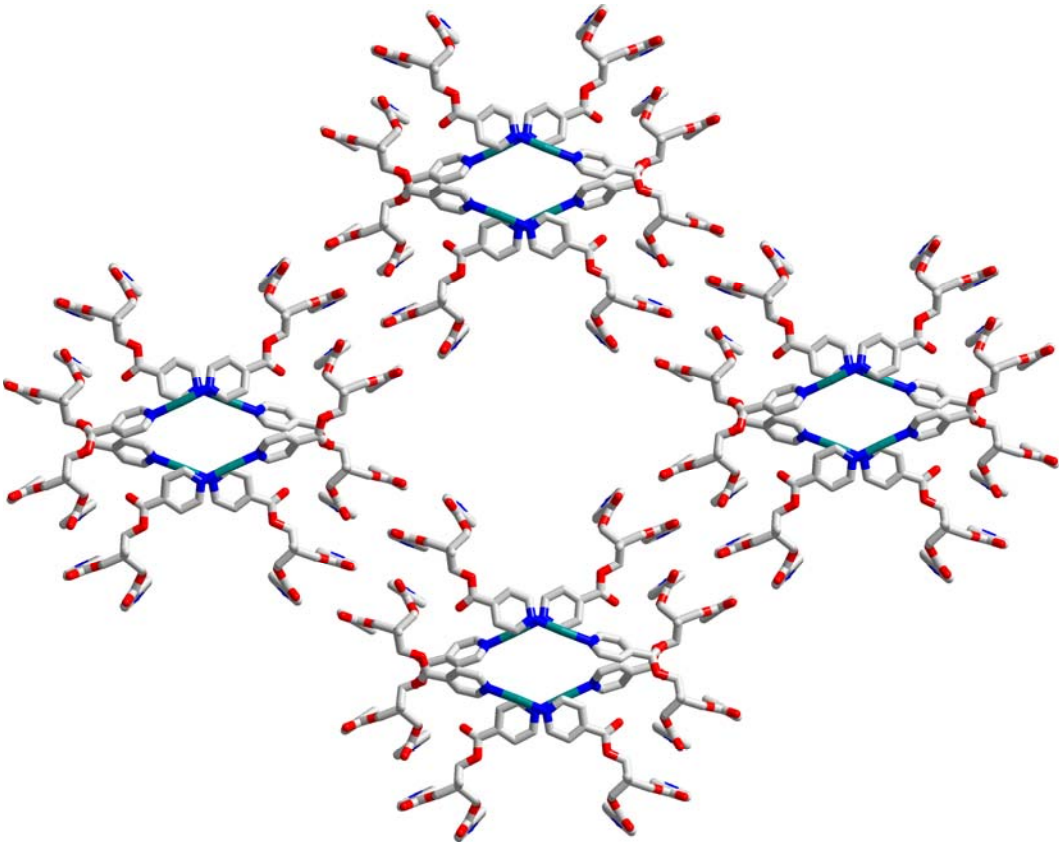


Figure 11 The polycatenane chains stacked along the *c* axis with nano-sized channels.

Capturing of Ag_6L_4 unit induced by ClO_4^-

Mixing of 1 mL $CHCl_3$ solution of ligand L (7mg, 0.0165 mmol) with a 1 mL MeOH solution of $AgClO_4$ (5mg, 0.025 mmol) treating with supersonic 5 minutes gives white powder **1**. Both the ^{1}HNMR and ESI-MS show that the cage Ag_6L_4 has been constructed.

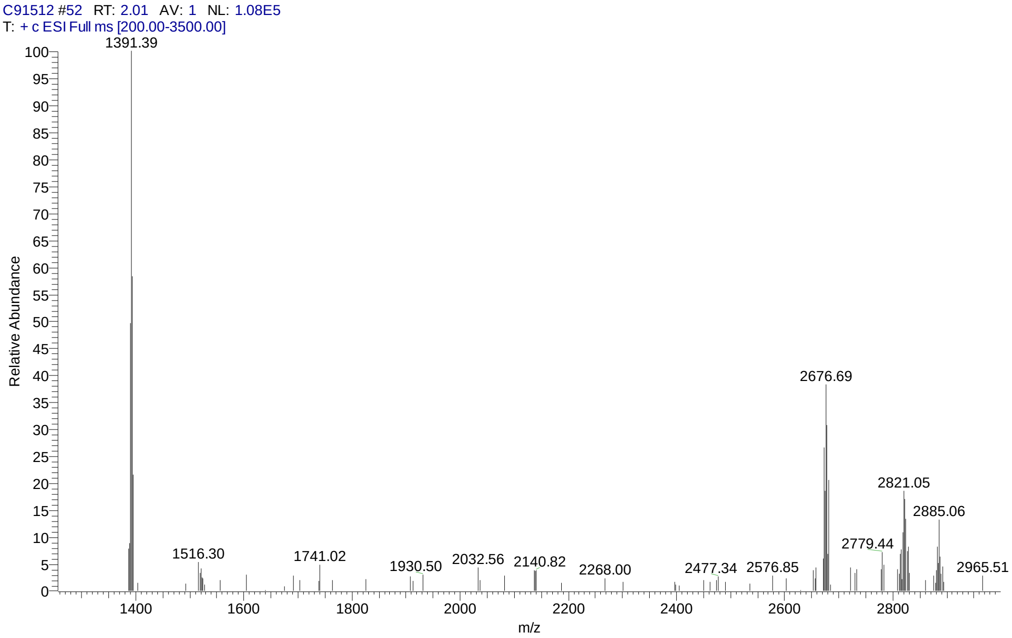


Figure 10 The ESI mass spectra of Ag_6L_4 unit, in which the 1391 peak belongs to $Ag_6L_4(ClO_4)_4^{2+}$, the 2885 peak belongs to $Ag_6L_4(ClO_4)_5^+$, and the 2677 peak belongs to $Ag_5L_4(ClO_4)_4^+$.

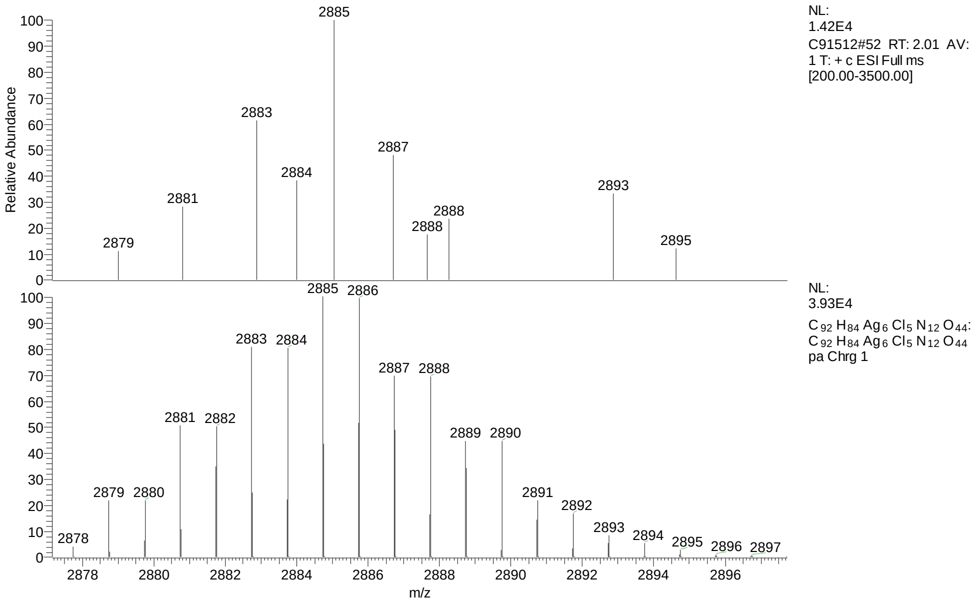


Figure 11 Calculated (down) and experimental (up) ESI-MS mass spectra of $Ag_6L_4(ClO_4)_5^+$.

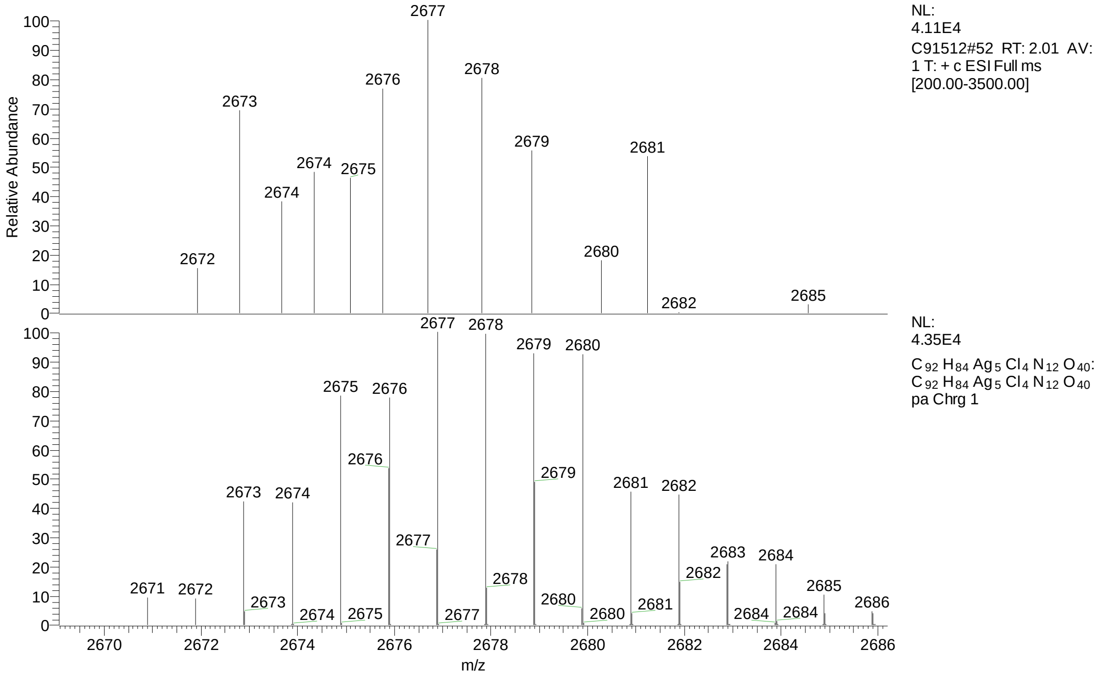
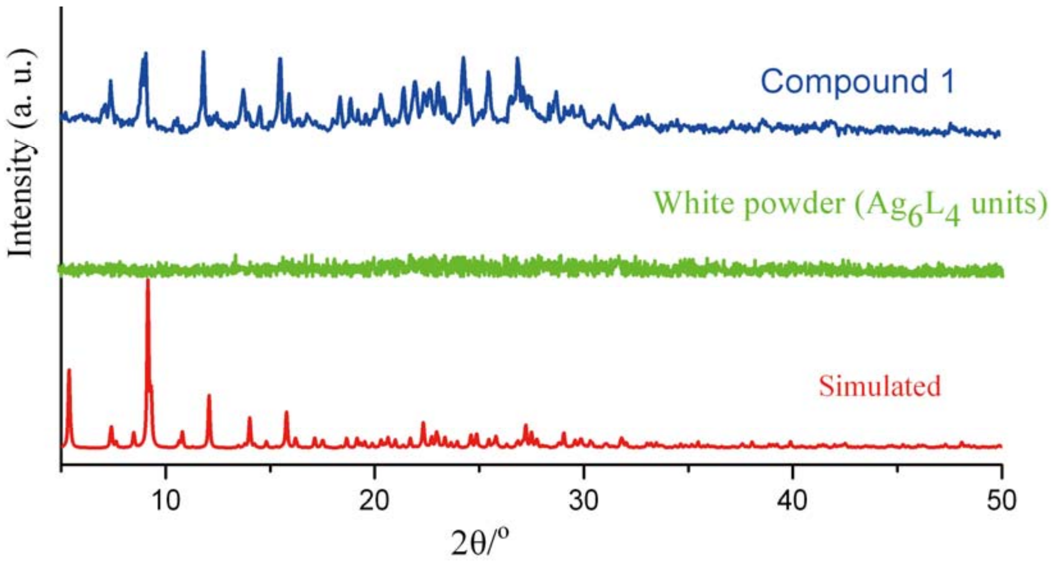


Figure 12 Calculated (down) and experimental (up) ESI-MS mass spectra of $Ag_5L_4(ClO_4)_4^+$.



Scheme 1 The X-ray powder diffractions (XPD) spectra for compound **1** and white powder **1**, which demonstrates that the white powder does not contain the similar polycatenated framework in compound 1.

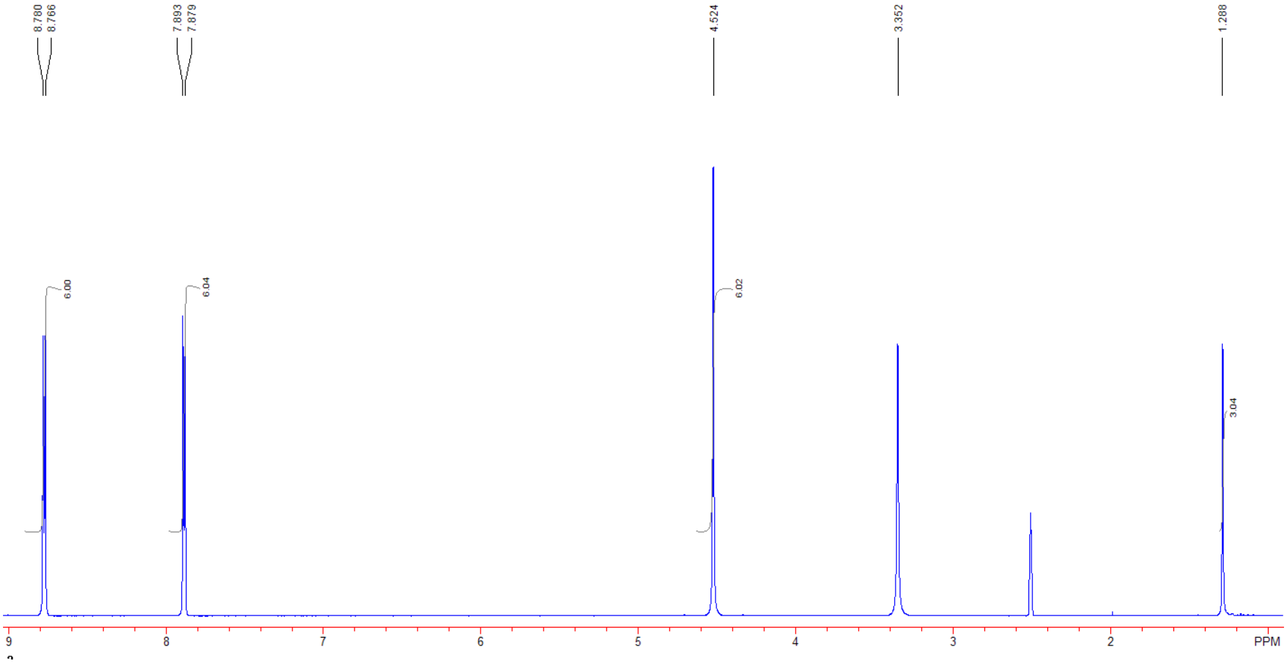


Figure 13 The spectra shows that there are only one type of peaks of coordinated ligand L.

Capturing of Ag_6L_4 unit induced by PF_6^-

Mixing of 1 mL $CHCl_3$ solution of ligand L (7mg, 0.0165 mmol) with a 1 mL MeOH solution of $AgPF_6$ (6mg, 0.025 mmol) treating with supersonic 5 minutes gives white powder. Both the ^{1}HNMR and ESI-MS show that the cage Ag_6L_4 has been constructed.

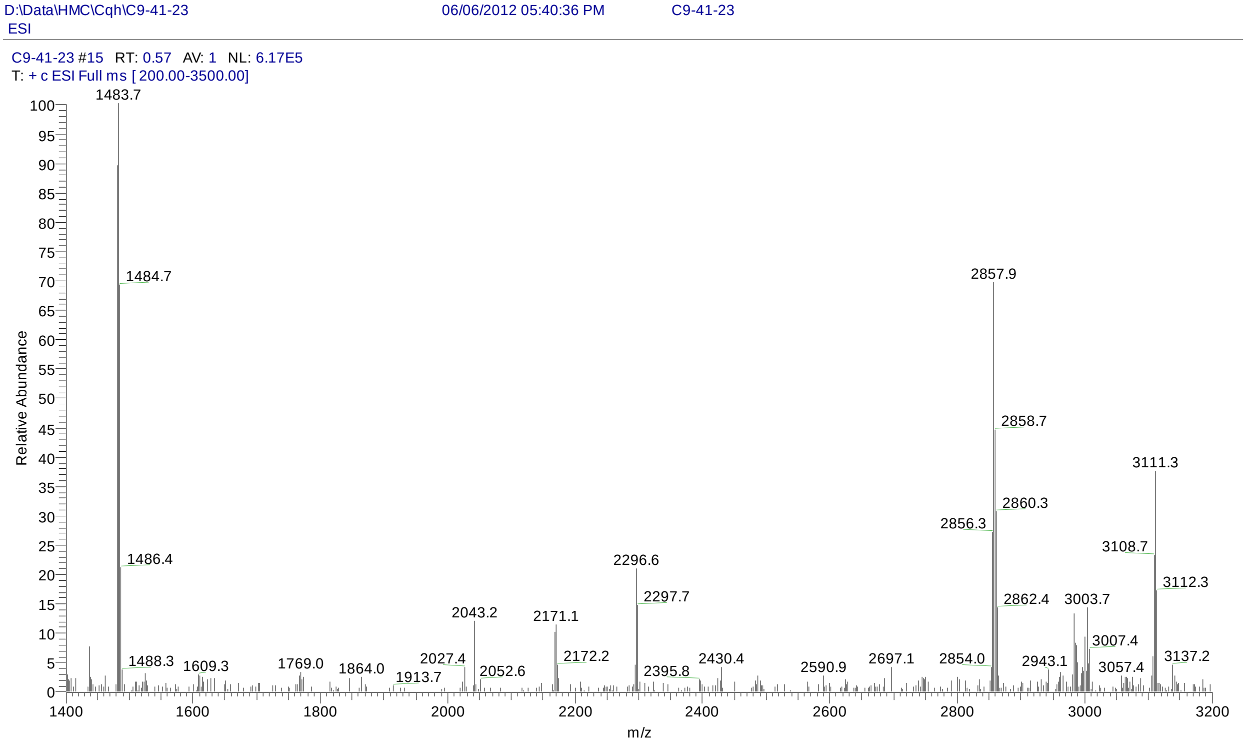


Figure 14 The ESI mass spectra of Ag_6L_4 unit, in which the 1484 peak belongs to $Ag_6L_4(PF_6)_4{}^{2+}$, the 3111 peak belongs to $Ag_6L_4(PF_6)_5{}^{+}$, and the 2858 peak belongs to $Ag_5L_4(PF_6)_4{}^{+}$.

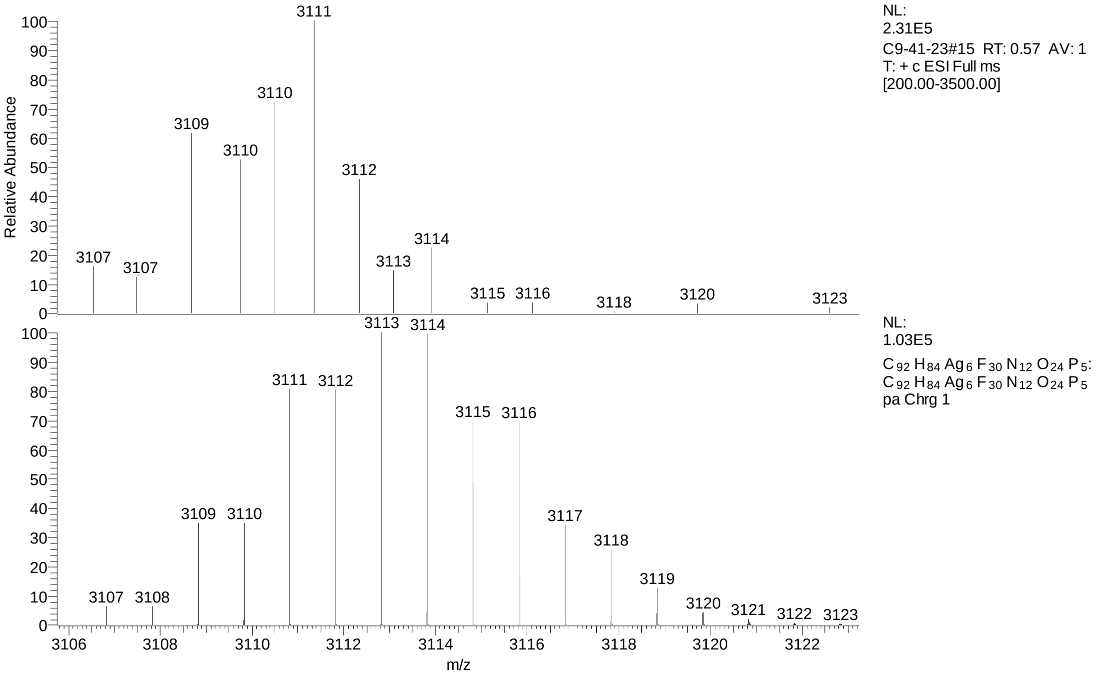


Figure 15 Calculated (down) and experimental (up) ESI-MS mass spectra of $Ag_6L_4(PF_6)_5{}^{+}$.

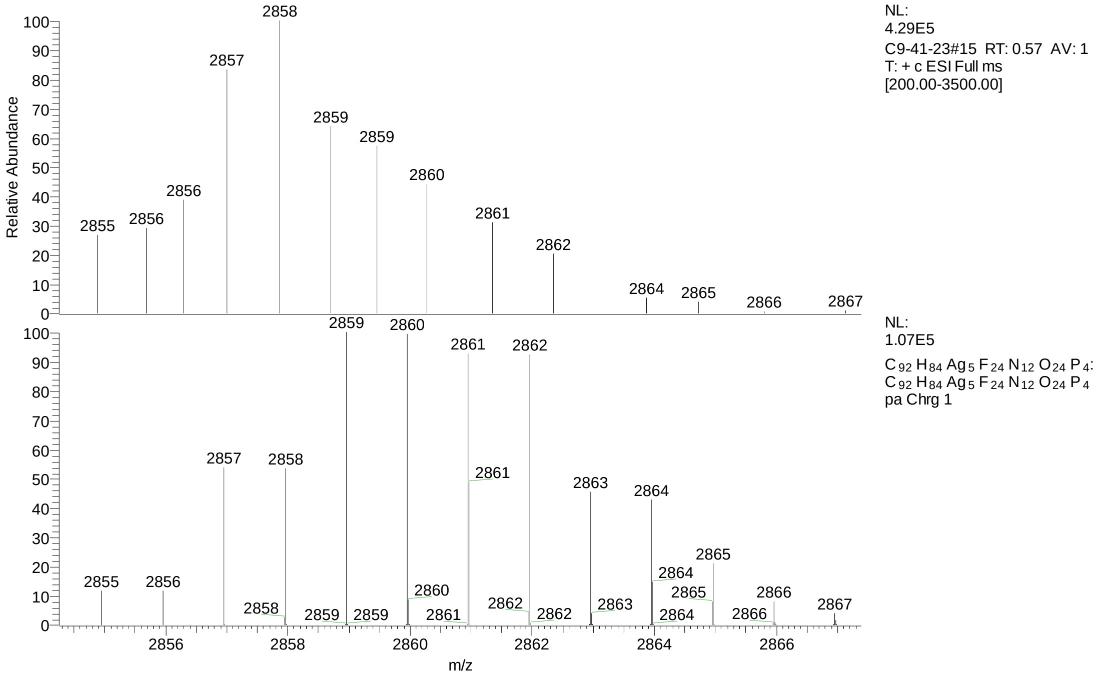


Figure 16 Calculated (down) and experimental (up) ESI-MS mass spectra of $Ag_5L_4(PF_6)_4^+$.

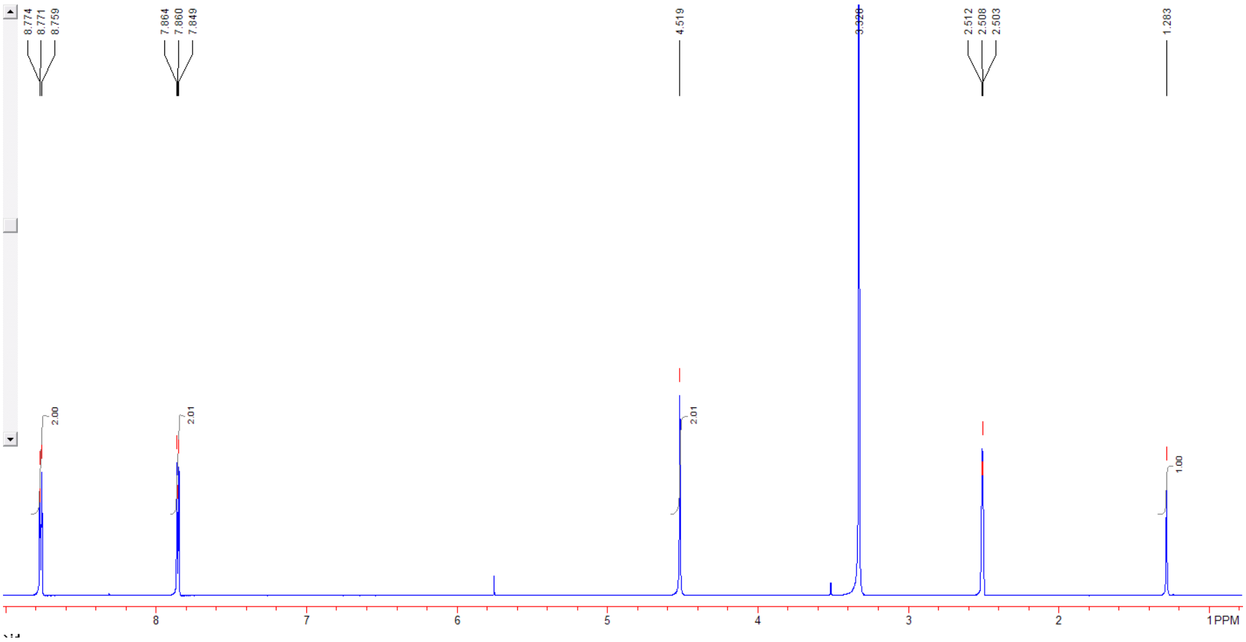


Figure 17 The spectra shows that there are only one type of peaks of coordinated ligand L.

1. G. M. Sheldrick, *SHELXTL-97, Program for the Solution of Crystal Structures,* University of Göttingen, Germany, 1997.
2. (a) A. L. Spek, *J. Appl. Crystallogr.* 2003, **36**, 7; (b) P. v.d. Sluis and A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 194.