

Supporting information:

Self-Assembly of 1D Mixed-Metal Tubular Network with Coordination Bonds through the Interconnection of Organometallic Metallamacrocycles by Ag(I) Centers

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Experimental details

General Considerations

All reactions were carried out under a nitrogen atmosphere using the standard Schlenk technique. All of the solvents were freshly distilled prior to use. MeOH was distilled over Mg/I₂. (Cp*IrCl₂)₂ was prepared according to reported procedures. Infrared spectra were recorded on a Nicolet AVATAR-360IR spectrometer, whereas ¹H{500MHz}, ¹³C{126MHz} NMR spectra were obtained on a Bruker DMX-500 spectrophotometer in CD₃OD solvent. Elemental analyses were performed on Elementar Analyzer Vario EL III after vacuuming the solvents of the samples. ESI-MS was obtained on a Bruker micrOTOF 11.

**Preparation of 2,4-diacetyl-5-hydroxy-5-methyl-3-(3-pyridinyl)
-cyclohexanone (HL)**

Acetylacetone (0.02mol, 2g) and 3-pyridylaldehyde (0.01mol, 1g) were dissolved in 10ml ethanol. About 10 drops of piperidine were added and the mixture was allowed to stand. After 2-3 days, the product was crystallized from the solution, washed with ethanol, and yielded 2g of white powder (yield: 70%). Anal. Calcd (%) for C₁₆H₁₉NO₄: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.42; H, 6.29; N, 4.76. m. p. 173.9 °C - 174.5 °C. ¹H NMR (500 MHz, CD₃OD): δ 8.47 (s, -pyridyl, 1H), 8.43 (d, *J* = 3.4 Hz, -pyridyl, 1H), 8.39 (d, *J* = 3.4 Hz, -pyridyl, 1H), 8.35 (s, -pyridyl, 1H), 7.88 (d, *J* = 8.0 Hz, -pyridyl, 1H), 7.68 (d, *J* = 8.0 Hz, -pyridyl, 1H), 7.43 – 7.40 (m, -pyridyl, 1H), 7.40 – 7.37 (m, -pyridyl, 1H), 4.57 (s, -CH-, 1H), 4.36 (d, *J* = 10.4 Hz, -CH-, 1H), 4.11 (d, *J* = 12.3 Hz, -CH-, 1H), 3.54 (d, *J* = 12.2 Hz, -CH-, 1H), 3.00 (d, *J* = 10.4 Hz, -CH-, 1H), 2.92 (d, *J* = 14.0 Hz, -CH₂-, 1H), 2.83 (d, *J* = 18.2 Hz, -CH₂-, 1H), 2.47 (d, *J* = 14.0 Hz, -CH₂-, 1H), 2.40 (d, *J* = 18.2 Hz, -CH₂-, 1H), 1.99 (s, -CH₃-, 3H), 1.94 (s, -CH₃-, 3H), 1.93 (s, -CH₃-, 3H), 1.67 (s, -CH₃-, 3H), 1.33 (s, -CH₃-, 3H), 1.28 (s, -CH₃-, 3H). IR (KBr disk): 2995, 1708, 1691, 1592, 1578, 1483, 1429, 1358, 1313, 1284, 1260, 1216, 1246, 1153, 1134, 1104, 1080, 934, 717, 564 and 477 cm⁻¹.

Synthesis of [Cp^{*}Ir(L)]₄·(NO₃)₄·2H₂O (**1**)

A mixture of [Cp^{*}IrCl₂]₂ (0.05mmol, 40mg) and AgNO₃ (0.2mmol, 34mg) in MeOH was stirred at room temperature for 6h. After filtration of AgCl, HL(0.1mmol, 28.8mg) and MeONa(0.1mmol, 5.4mg) were added to the filtrate. The solution kept and stirred for 12h. Then the concentrated solvent was recrystallized by adding Et₂O to get light yellow crystals of **1** (55mg, 80% yield). Elemental analysis calc. For: C,

46.08; H, 4.91; N, 4.13. Found: C, 46.24; H, 4.80; N, 4.14. δ_{H} (500 MHz, CD_3OD) 8.46 (1 H, d, -pyridyl, J 4.9), 8.27 (1 H, s, -pyridyl), 8.00 (1 H, d, -pyridyl, J 8.1), 7.73 – 7.70 (1 H, m, -pyridyl), 4.41 (1 H, d, -CH-, J 11.1), 2.83 (2 H, d, -CH₂-, J 18.3), 2.55 (1 H, d, -CH-, J 18.6), 2.00 (3 H, s, -CH₃), 1.55 (15 H, s, -CH₃), 1.46 (3 H, s, -CH₃), 1.40 (3 H, s, -CH₃). δ_{C} (126 MHz, CD_3OD) 211.15, 190.86, 185.16, 150.19, 145.98, 140.27, 128.58, 120.95, 111.53, 86.79, 70.27, 68.08, 64.46, 42.34, 34.56, 30.70, 28.50, 27.69, 8.62. IR (KBr disk): 2960, 2919, 1655, 1638, 1630, 1617, 1578, 1561, 1566, 1413, 1384, 1122, 1020, 712, and 663 cm^{-1} .

Synthesis of $\{[\text{Cp}^*\text{Ir}(\text{L})]_4\cdot\text{AgNO}_3\cdot\text{H}_2\text{O}\}_n\cdot[\text{Ag}(\text{NO}_3)_3]_{1.5n}\cdot(\text{NO}_3)_n\cdot 6n\text{CH}_3\text{OH}\cdot 5n\text{H}_2\text{O}$

(2)

The compound **1** (0.01 mmol, 27 mg) was treated with AgNO_3 (0.025 mmol, 4.3 mg) in the solvent of MeOH. After slow diffusion of Et_2O , the product **2** was isolated as light yellow crystals [27 mg, yield 77%]. **2** could also be obtained from direct one-pot reaction in which the silver salt was more than 30% (or 40%, 60%) excess. **2** easily decomposed to **1** and dark silver powder when its solution was exposed to the light for several days. Elemental analysis calc. For: C, 39.61; H, 4.28; N, 4.66. Found: C, 39.56; H, 4.24; N, 4.72. IR (KBr disk): 2969, 2919, 1701, 1570, 1384, 1271, 1158, 1102, 1029, 830, 778, 707, and 650 cm^{-1} . $\{\delta_{\text{H}}$ (500 MHz, CD_3OD) (peaks were similar with that of **1**) 8.51 (1 H, d, -pyridyl, J 4.7), 8.32 (1 H, s, -pyridyl), 8.07 (1 H, d, -pyridyl, J 8.1), 7.83 – 7.70 (1 H, m, -pyridyl), 4.46 (1 H, d, -CH-, J 11.1), 2.90 (2 H, d, -CH₂-, J 18.4), 2.60 (1 H, d, -CH-, J 18.5), 2.05 (3 H, s, -CH₃), 1.60 (15 H, s,

-CH₃), 1.51 (3 H, s, -CH₃), 1.45 (3 H, s, -CH₃). δ_c (126 MHz, CD₃OD) 211.13, 190.65, 185.28, 153.50, 150.01, 145.91, 140.23, 128.60, 111.54, 86.65, 70.27, 64.30, 52.33, 42.21, 34.32, 28.36, 27.69, 8.60.}

Analysis of the stereochemistry of the metallamacrocycles:

The three chiral carbon centers of the ligand **HL** and the stereochemistry of the macrocycles are shown in the following pictures.

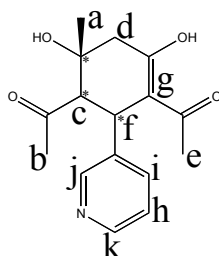


Figure S1. The structure of the ligand HL. The chiral centers are marked.

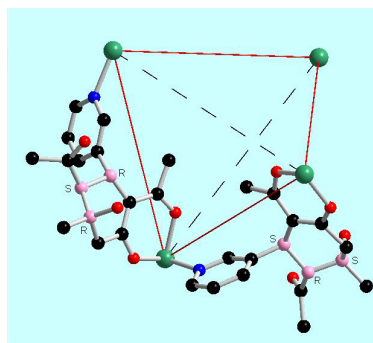


Figure S2. The stereochemistry of the ligand in tetranuclear macrocycles. The chiral carbon centers are represented by pink color.

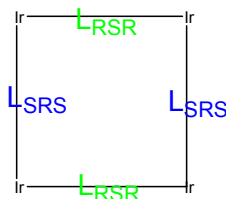


Figure S3. the sketches showing the ligand L_{SRS} & L_{RSR} linked at intervals to form the

whole mesomeric macrocycles

According to the results, we found that there are two kinds of enantiomers of the ligands- L_{SRS} & L_{RSR} in each macrocycle. The two kinds of enantiomers were linked by metal corners one by one to form the whole achiral macrocycles. Also, the space groups of the crystals were achiral. So the tetranuclear macrocycle is actually a kind of mesomer. It provided us the convenience because it was not necessary to further consideration of the stereochemistry in mesomeric macrocycles.

X-Ray Crystallography. Each crystal was mounted on a glass fiber. Crystallographic measurements were made on a Bruker Smart Apex 100 CCD area detector using graphite monochromated $MoK\alpha$ radiation ($\lambda = 0.71073\text{\AA}$). The structures were solved by directed methods (SHELXS-97) and refined on F^2 by full-matrix least squares (SHELX-97) using all unique data. In all compounds, hydrogen atoms that could be found were placed in geometrically calculated positions with fixed isotropic thermal parameters.

In the tetranuclear compound **1**, two nitrate anions outside were strongly disordered and could not be refined properly. New data sets corresponding to omission of the disordered anions were generated with the SQUEEZE algorithm before the structures were refined to convergence.

In the compound **2**, there were disordered solvent molecules which could not be refined properly so that the SQUEEZE algorithm was used to omit them. The

hydrogen atoms in the solvents MeOH and water could not be found.

Table S1 The selected bond distances and angles for **1** and **2**

1			
Bond Distances (Å)			
Ir(1)-O(2)	2.076(5)	Ir(1)-O(1)	2.082(5)
Ir(1)-N(1)#1	2.108(6)	N(1)-Ir(1)#2	2.108(6)
N(2)-O(5)#3	1.201(11)		
Bond Angles (deg)			
O(2)-Ir(1)-O(1)	84.7(2)	O(2)-Ir(1)-N(1)#1	83.1(2)
O(1)-Ir(1)-N(1)#1	81.8(2)	C(13)-N(1)-Ir(1)#2	121.7(5)
C(9)-N(1)-Ir(1)#2	119.1(5)	O(6)-N(2)-O(5)#3	122.4(9)
O(5)-N(2)-O(5)#3	115.1(18)		
#1 $y-1/4, -x+5/4, -z+1/4$	#2 $-y+5/4, x+1/4, -z+1/4$	#3 $-x+1, -y+1/2, z+0$	
2			
Bond Distances (Å)			
Ir(1)-O(2)	2.046(11)	Ir(1)-N(4)	2.083(11)
Ir(1)-O(1)	2.084(8)	Ir(2)-O(6)	2.033(13)
Ir(2)-O(5)	2.082(10)	Ir(2)-N(1)	2.104(11)

Ir(3)-O(10)	2.050(12)	Ir(3)-O(9)	2.081(10)
Ir(3)-N(2)	2.124(12)	Ir(4)-N(3)	2.056(11)
Ir(4)-O(13)	2.058(9)	Ir(4)-O(14)	2.059(12)
Ag(1)-O(37)	2.27(4)	Ag(1)-O(17)	2.38(3)
Ag(1)-O(12)	2.431(17)	Ag(1)-O(8)#1	2.49(2)
Bond Angles (deg)			
O(2)-Ir(1)-N(4)	84.5(5)	O(2)-Ir(1)-O(1)	83.0(4)
N(4)-Ir(1)-O(1)	79.7(5)	O(6)-Ir(2)-O(5)	83.3(4)
O(6)-Ir(2)-N(1)	85.1(5)	O(5)-Ir(2)-N(1)	82.0(5)
O(10)-Ir(3)-O(9)	84.5(4)	O(10)-Ir(3)-N(2)	83.1(5)
O(9)-Ir(3)-N(2)	82.1(5)	N(3)-Ir(4)-O(13)	82.1(5)
N(3)-Ir(4)-O(14)	83.6(5)	O(13)-Ir(4)-O(14)	84.8(4)
O(37)-Ag(1)-O(17)	110.8(14)	O(37)-Ag(1)-O(12)	101.8(9)
O(17)-Ag(1)-O(12)	103.5(9)	O(37)-Ag(1)-O(8)#1	91.2(8)
O(17)-Ag(1)-O(8)#1	85.8(9)	O(12)-Ag(1)-O(8)#1	159.9(6)

#1 $x, -y+1, z+1/2$

#2 $-x+1, y, -z+1/2$

#3 $x, -y+1, z-1/2$

ESI-MS spectra

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	150 °C
Scan Begin	50 m/z	Set Capillary	4000 V	Set Dry Gas	8.0 l/min
Scan End	1500 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

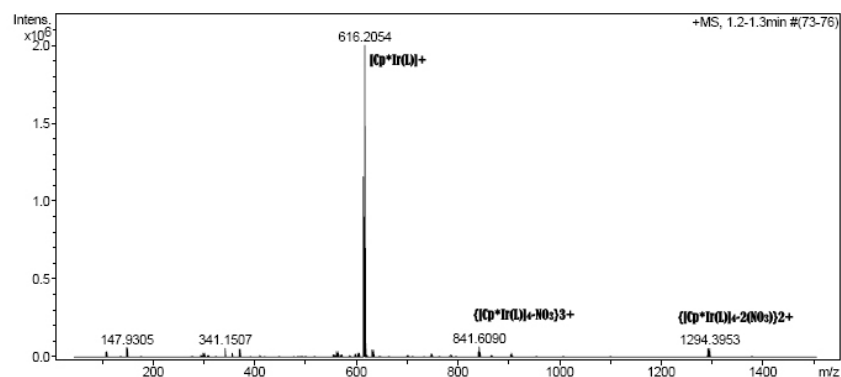


Figure S4 ESI-mass spectrum of polymer 2 in methanol.

Simulated (bottom) and experimental (top) peaks

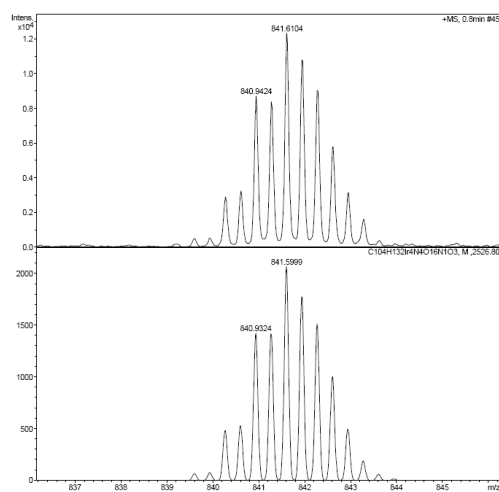


Figure S5 isotopic peaks of $\{[\text{Cp}^* \text{Ir}(\text{L})]_4 \cdot \text{NO}_3\}^{3+}$ $\{m/z = 841.6\}$

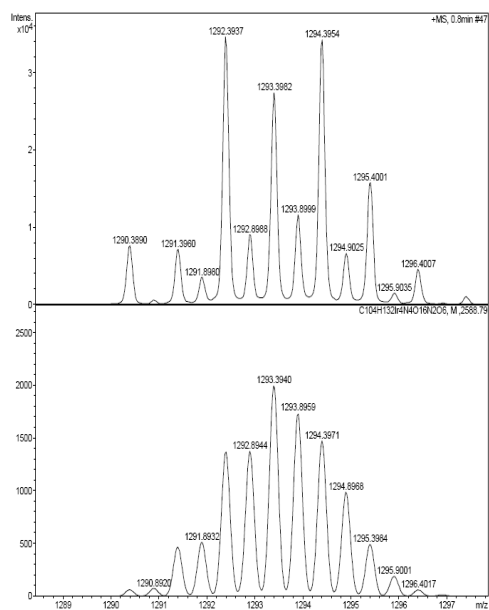


Figure S6 isotopic peaks of $[\text{Cp}^*\text{Ir}(\text{L})_4 \cdot 2(\text{NO}_3)]^{2+}$ $\{m/z = 1294.4\}$

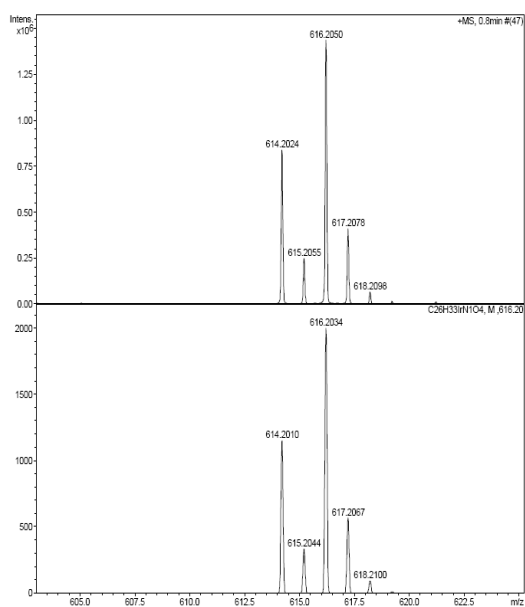
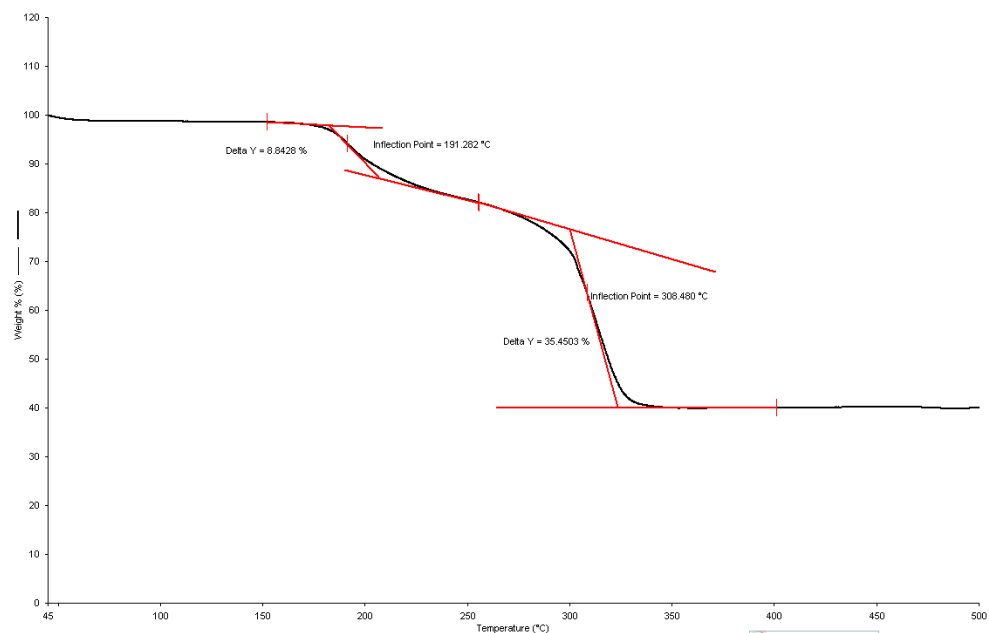


Figure S7 isotopic peaks of the fragment $[\text{Cp}^*\text{Ir}(\text{L})]^+$ $\{m/z = 616.2\}$

Compound 1 is stable in the air. The powder of compound 2 is stable sealed by a black tube, but it easily decomposed to 1 and dark silver powder when its solution was exposed to the light for about two weeks. Thermogravimetric analysis (TGA) of 1 and 2 measurements gave the similar thermal decomposition temperature (Td) 180-190 °C. The TGA of 2 is very complicated, because there are several groups in the molecule, such as Cp*Ir, the ligand L, AgNO₃, Ag(NO₃)₃²⁻, NO₃⁻. It is not clear which group decomposed in the first step, but the last more than 30% residue could be considered as the metal of Ir, Ag (sum: more than 33%) or their oxide. For compound 1, the last residue (about 30%) is considered as the iridium (28%) and its oxide.

TGA of 2



TGA of 1

