Supporting Information for

Self-assembled half-sandwich polyhedral cages *via* flexible Schiff-base ligands: an unusual macrocycle-to-cage conversion

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1. Materials and instrumentations

All reactions and manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques. MeOH was purified by distilling with Mg rod and I_2. CH_2Cl_2 and CH_3CN solvents were purified by distilling with CaH_2. $[Cp^*MCl_2]_2$ (M = Rh and Ir)[1], Schiff-base 4-pyridinecarbaldehyde isonicotinylhydrazone ligand (H**L1**)[2] and 2,3-butanedione bis(isonicotinylhydrazone) ligand (H_2**L2**)[3] were all prepared according to the literature methods. Elemental analyses were performed on an Elementar III Vario EI analyzer. ^{1}H NMR (400/500 MHz) spectra were obtained on a Bruker AVANCE I 400 and VANCE-DMX 500 spectrometers. IR spectra of the solid samples (KBr tablets) in the range 400-4000 cm^{-1} were measured on a Nicolet Avatar-360 spectrophotometer. ESI-MS spectra were recorded on a Micro TOF II

mass spectrometer using electrospray ionization.

2. Syntheses of complexes 1-5

Synthesis of **1.** A mixture of $[Cp^*RhCl_2]_2$ (18.6 mg, 0.03 mmol) and AgOTf (30.8 mg, 0.12 mmol) in methanol was stirred for 5h. After filtration to remove AgCl, H**L1** ligand (13.8 mg, 0.06 mmol) in acetonitrile were added to the filtrate and was continued to stir for 24h. Then, the solution was concentrated to give yellow solid, washed by diethyl ether and dried in vacuum. Crystals suitable of **1** for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a mixture solution of macrocycle **1** in methanol and acetonitrile. Yield: 20.5 mg (43%). Anal. Calcd (%) for $C_{52}H_{56}N_{10}O_{14}S_4F_{12}Rh_2$: C 38.86, H 3.51, N 8.72. Found: C 38.79, H 3.45, N 8.64. IR (KBr disk): 3112(w), 2968(w), 1685(s), 1609(m), 1551(w), 1491(w), 1418(m), 1375(m), 1351(w), 1282(vs), 1251(vs), 1225(m), 1160(vs), 1060(w), 1031(vs), 950(w), 895(w), 847(w), 760(w), 639(s), 575(m), 518(m)cm^{-1}. ESI-MS: *m/z* = 1375.07 (calcd for $[Cp^*_2Rh_2(H\mathbf{L1})_2(OTf)_3]^+$ 1375.07).

Synthesis of **2.** A mixture of $[Cp^*RhCl_2]_2$ (18.6 mg, 0.03 mmol) and AgOTf (30.8 mg, 0.12 mmol) in methanol was stirred for 5h. After filtration to remove AgCl, H**L1** ligand (9.2 mg, 0.04 mmol) in acetonitrile were added to the filtrate and was continued to stir for 24h. Then, the solution was concentrated to give yellow solid, washed by diethyl ether and dried in vacuum. Crystals suitable of **2** for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a mixture solution of cage **2** in methanol and acetonitrile. Yield: 22.8 mg (63%). Anal. Calcd (%) for $C_{120}H_{132}N_{18}O_{28}S_8F_{24}Rh_6$: C 39.99, H 3.69, N 6.99. Found: C 39.90, H 3.60, N 6.91. IR (KBr disk): 2973(w), 2925(w), 1613(m), 1568(m), 1505(s), 1421(w), 1373(s), 1319(w), 1273(vs), 1277(vs), 1259(vs), 1225(m), 1159(vs), 1058(m), 1031(s), 901(w), 854(w), 824(w), 757(w), 709(w), 639(s), 602(w), 574(w), 518(w) cm^{-1}. ^1H NMR (400MHZ, CD_3OD): δ 8.70-8.12 (m, 36H, **L1**), δ 2.03 (s, 6H, CH_3CN), δ 1.81-1.70 (m, 90H, Cp*). ESI-MS: *m/z* = 1652.11 (calcd for $[Cp^*_6Rh_6(\mathbf{L1})_4(CH_3CN)_2(OTf)_6]^{2+}$ 1652.11), 1024.41 (calcd for $[Cp^*_6Rh_6(\mathbf{L1})_4(OTf)_5]^{3+}$ 1024.40).

Synthesis of **3.** A mixture of $[Cp^*RhCl_2]_2$ (18.6 mg, 0.03 mmol) and AgOTf (30.8 mg, 0.12 mmol) in methanol was stirred for 5h. After filtration to remove AgCl, H_2**L2** (9.8 mg, 0.03 mmol) in dichloromethane were added to the filtrate and was continued to stir for 24h. Then, the solution was concentrated to give yellow solid, washed by diethyl ether and dried in vacuum. Crystals suitable of **3** for an X-ray diffraction study were obtained by slow diffusion of hexane into a mixture solution of cage **3** in methanol and dichloromethane. Yield: 19.1 mg (58%). Anal. Calcd (%) for $C_{152}H_{176}N_{24}O_{32}S_8F_{24}Rh_8$: C 41.62, H 4.04, N 7.66. Found: C 41.55, H 3.96, N 7.59. IR (KBr disk): 2964(w), 2921(w), 1610(w), 1571(m), 1529(s), 1480(w), 1458(w), 1418(w), 1370(vs), 1262(vs), 1224(m), 1158(s), 1058(w), 1031(vs), 903(w), 852(w), 755(m), 717(m), 702(w), 638 (vs), 573(w), 517(w)cm^{-1}. ^1H NMR (400MHZ, CD_3OD): δ 8.66 (d, 16H, *J* = 6.4, H_α, **L2**), *δ* 8.04 (d, 16H, *J* = 6.4, H_β, **L2**), *δ* 3.21 (s, 24H, H_γ, **L2**), *δ* 1.69 (s, 120H, Cp*). ESI-MS: *m/z* = 2043.19 (calcd for $[Cp^*_8Rh_8(\mathbf{L2})_4(OTf)_6]^{2+}$ 2043.18), 1312.47 (calcd for $[Cp^*_8Rh_8(\mathbf{L2})_4(OTf)_5]^{3+}$ 1312.47).

Synthesis of **4.** A mixture of $[Cp^*IrCl_2]_2$ (24.0 mg, 0.03 mmol) and H**L1** ligand (4.6 mg, 0.02 mmol) in acetonitrile was stirred for 24h, then the mixture was obtained as solid by filtration, washed with diethyl ether and dried in vacuum. Crystals suitable of **4** for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a mixture solution of complex **4** in methanol and dichloromethane. Yield: 21.5 mg (78%). Anal. Calcd (%) for $C_{42}H_{54}N_4OCl_5Ir_3$: C 36.43, H 3.93, N 4.05. Found: C 36.37, H 3.87, N 3.98. IR (KBr disk): 2965(w), 2918(w), 1617(w), 1565(s), 1507(vs), 1457(m), 1418(w), 1383(s), 1319(w), 1241(w), 1162(w), 1081(w), 1056(m), 1031(s), 1012(m), 897(w), 859(w), 827(w), 756(w), 714(w), 694(w), 606(w) , 583(w) cm^{-1}. ^1H NMR (400MHZ, DMSO): *δ* 8.82 (d, 2H, *J* = 6.4, H_α, **L1**), *δ* 8.75 (d, 2H, *J* = 6.4, $H_{\alpha'}$, **L1**), *δ* 8.36 (d, 2H, *J* = 6.4, H_β, **L1**), *δ* 8.03 (s, 1H, H_γ, **L1**), *δ* 7.98 (d, 2H, *J* = 6.4,$H_{\beta'}$, **L1**), *δ* 1.68 (s, 15H, Cp*), *δ*1.63 (s, 30H, Cp*). ESI-MS: *m/z* = 1349.19 (calcd for $[Cp^*_3Ir_3(\mathbf{L1})Cl_4]^+$ 1349.19).

Synthesis of **5.** A mixture of $[(Cp^*_2Rh_2(C_2O_4)Cl_2]$ (31.8mg, 0.05mmol) and AgOTf

(25.7mg, 0.10mmol) in methanol was stirred at room temperature for 5h. After filtration to remove AgCl, H**L1** ligand (11.5mg, 0.05mmol) in acetonitrile was added to the filtrate, and the mixture was stirred for 24h. Then the solution was concentrated to give yellow solid, which was washed by diethyl ether and dried under vacuum. Crystals suitable of **5** for an X-ray diffraction study were obtained by slow diffusion of diethyl ether into a mixture solution of macrocycle **5** in methanol and acetonitrile. Yield: 49.5 mg (91%). Anal. Calcd (%) for $C_{72}H_{80}N_8O_{22}S_4F_{12}Rh_4$: C 39.72, H 3.70, N 5.15. Found: C 39.69, H 3.61, N 5.10. IR (KBr disk): 2967(w), 2926(w), 1698(w), 1620(vs), 1560(w), 1489(w), 1458(w), 1420(w), 1384(w), 1281(vs), 1258(vs), 1225(m), 1158(s), 1062(w), 1031(vs), 832(w), 796(w), 758(w), 639(s), 574(w), 518(w)cm^{-1}. ^{1}H NMR (400MHZ, DMSO): δ 12.74 (s, 2H, -NH, H**L1**, *trans*), δ 12.49 (s, 2H, -NH, H**L1**, *cis*), δ 8.37 (s, 2H, H_γ, H**L1**, *cis*), δ 8.29-8.30 (m, 6H, H_γ+H_α, H**L1**, *trans*; 4H, H_α, H**L1**, *cis*), δ 8.04-8.05 (m, 4H, $H_{\alpha'}$, H**L1**, *trans*; 4H, $H_{\alpha'}$, H**L1**, *cis*), δ 7.86 (d, 4H, J = 6.4, H_β, H**L1**, *trans*), δ 7.82 (d, 4H, J = 6.4, H_β, H**L1**, *cis*), δ 7.63 (d, 4H, J = 6.4, $H_{\beta'}$, H**L1**, *cis*), δ 7.60 (d, 4H, J = 6.4, $H_{\beta'}$, H**L1**, *trans*), δ 1.55 (s, 60H, Cp*, *cis*), δ 1.54 (s, 60H, Cp*, *trans*).

3. The ^{1}H NMR and ESI-MS spectra of complexes 1-5

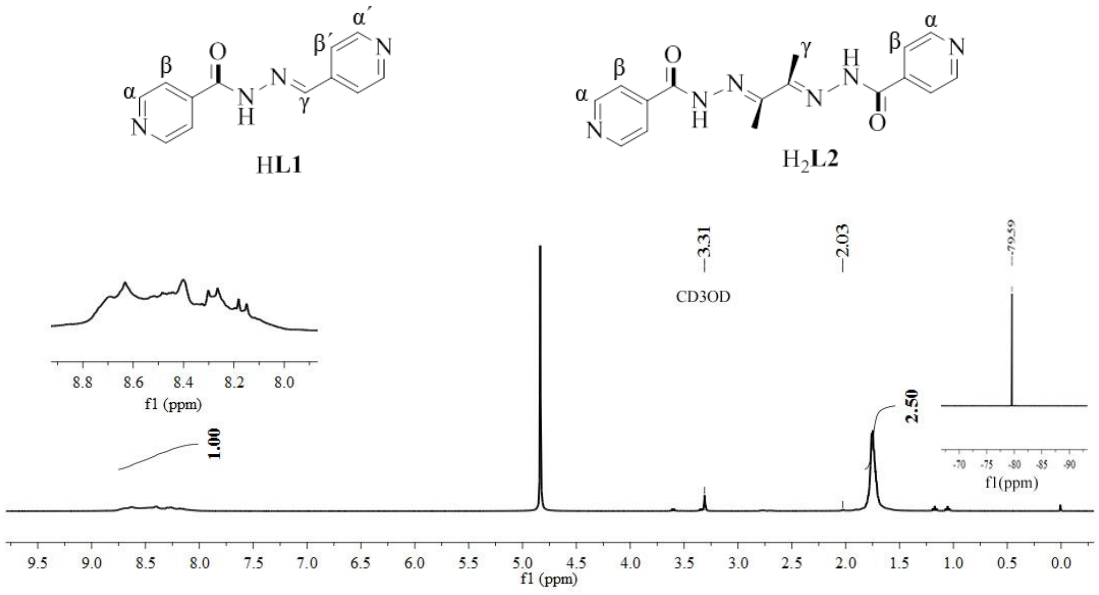

Figure S1. The ^{1}H NMR spectrum of cage **2** in methanol.

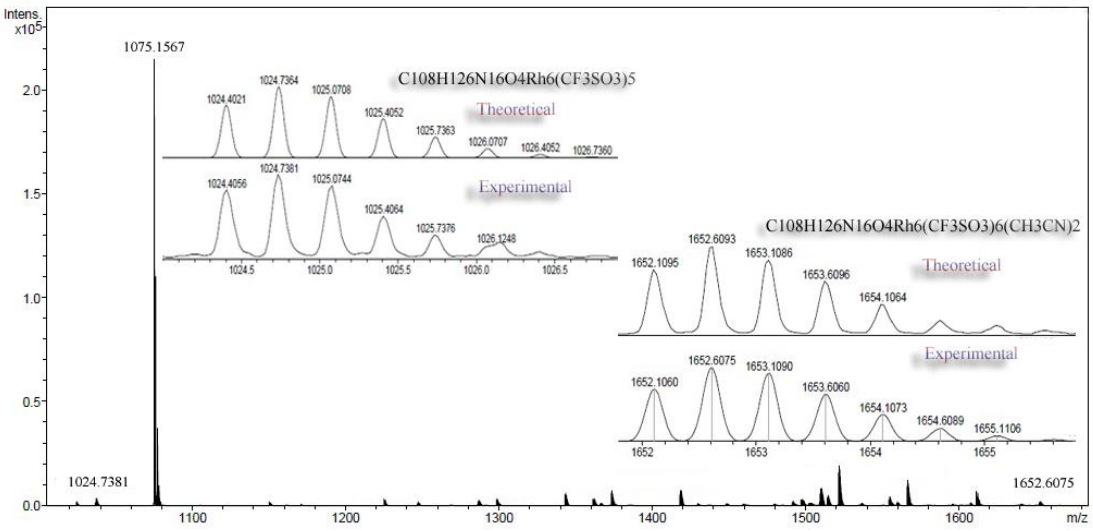

Figure S2. The ESI-MS spectrum ($\mathbf{2}^{2+}$) and ($\mathbf{2}^{3+}$) of cage **2**.

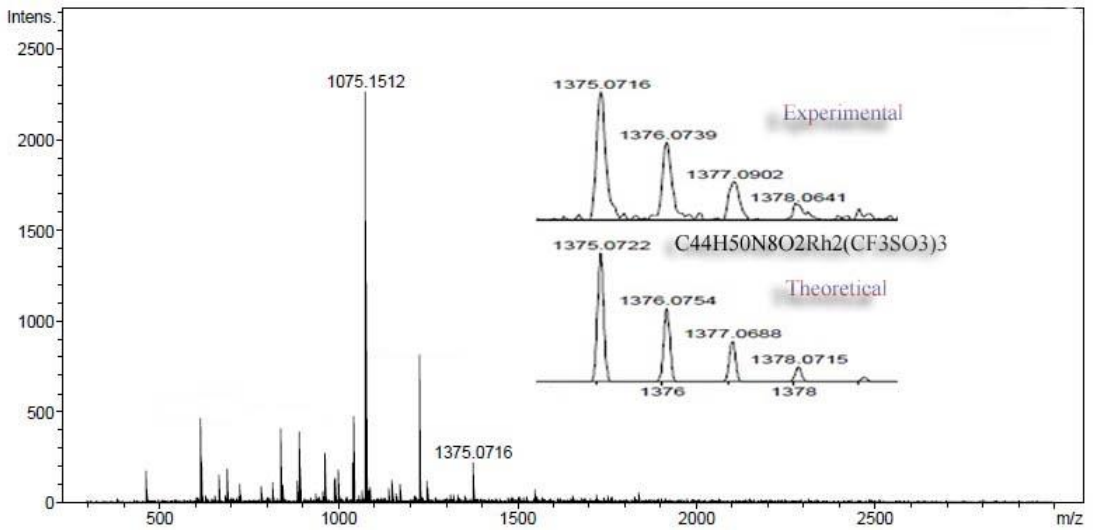

Figure S3. The ESI-MS spectrum ($\mathbf{1}^{+}$) of macrocycle **1**.

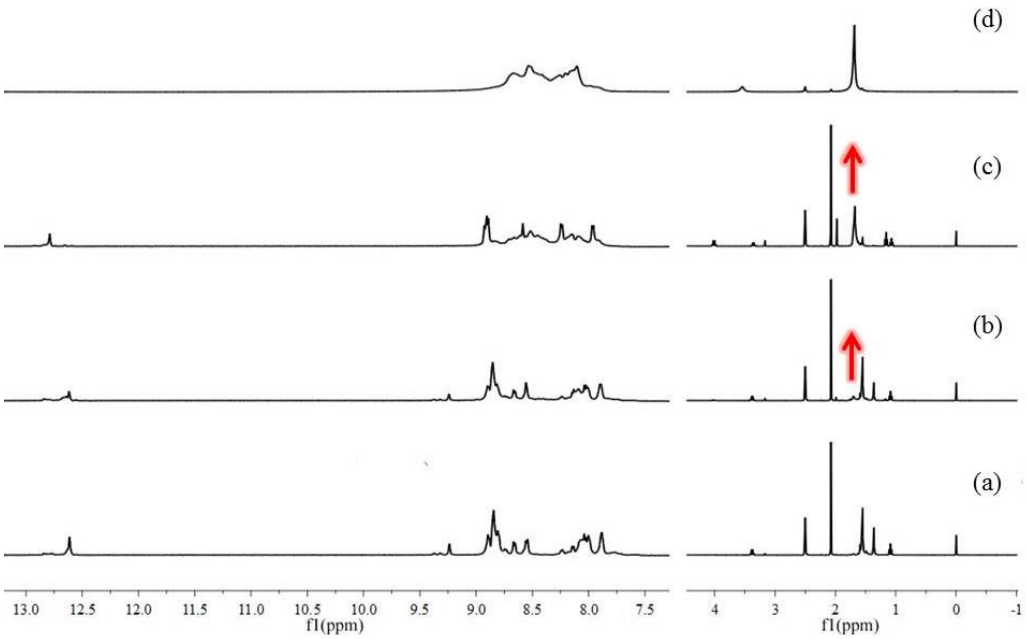

Figure S4. Time course ^{1}H NMR experiment of the crystalline macrocycle **1** displaying degradation and rearrangement to M_6(**L1**)$_4$ cage in DMSO-d_6 solvent. (a) Spectrum immediately after dissolution of macrocycle **1**; (b)(c) Spectrum after dissolution of macrocycle **1**, but measured 1 day and two weeks later, respectively; (d) Spectrum after redissolved cage **2** in DMSO-d_6 solvent.

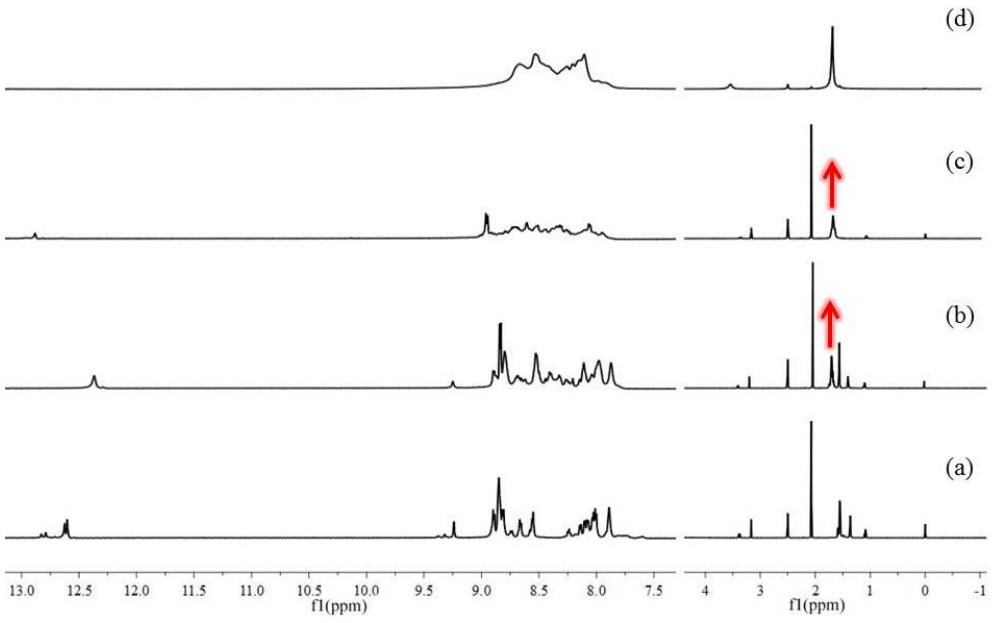

Figure S5. The ^{1}H NMR experiment of the crystalline macrocycle **1** displaying degradation and rearrangement to M_6(**L1**)$_4$ cage in DMSO-d_6 solvent. (a) Spectrum immediately after dissolution of macrocycle **1** (25℃); (b) Spectrum after dissolution of macrocycle **1** (80℃); (c) Spectrum after redissolvedmacrocycle **1** kept at 80℃ for

1d; (d) Spectrum after redissolved cage **2** in DMSO-d_6 solvent.

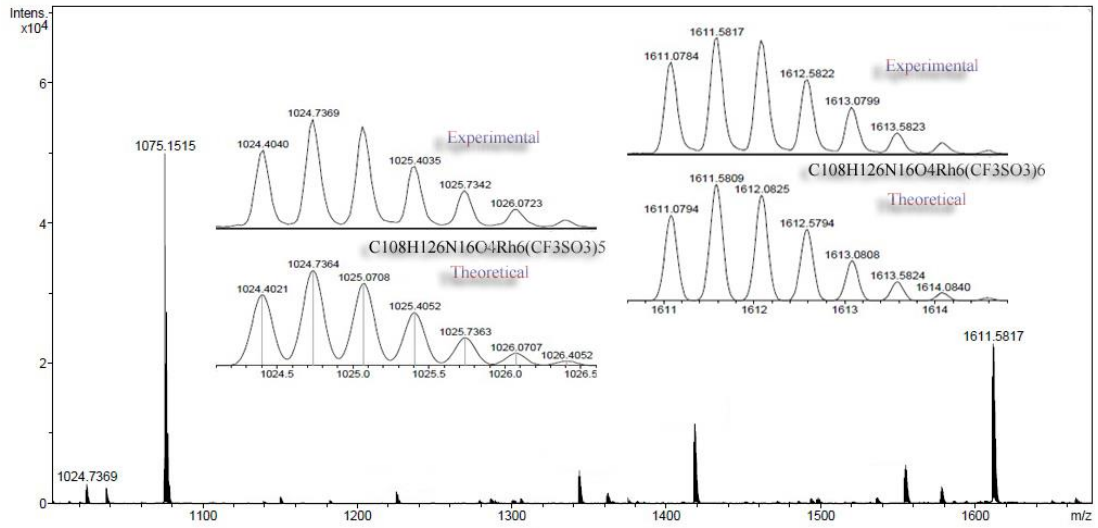

Figure S6. The ESI-MS spectrum after redissolved macrocycle **1** heated to 80℃ in DMSO-d_6 solvent, indicating that the formation of M_6(**L1**)$_4$ cage.

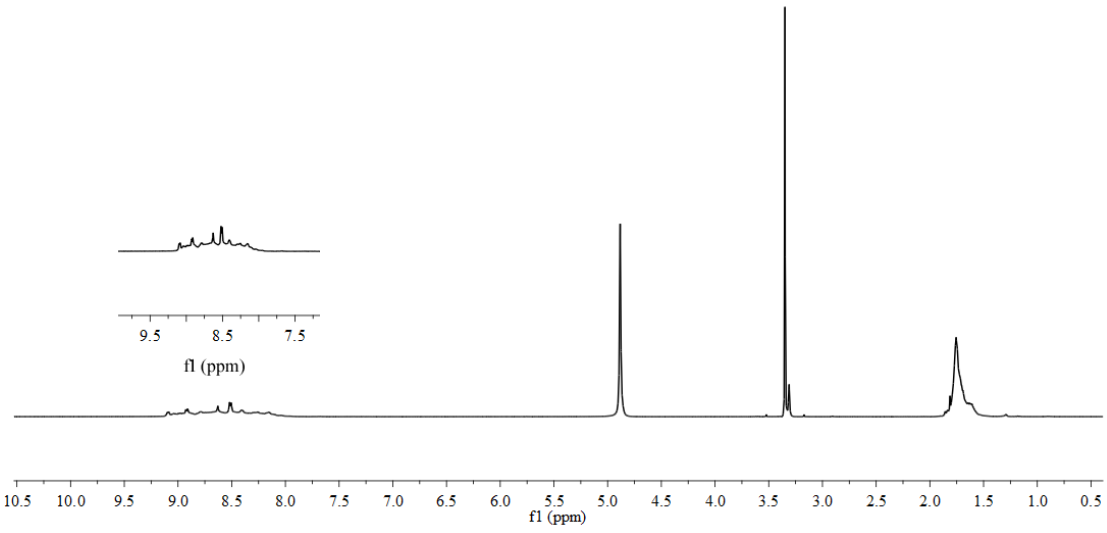

Figure S7. The ^{1}H NMR spectrum after mixing {Cp*Rh} fragments with H**L1** ligands in a 1:1 ratio in MeOH solvent, then heated to 50℃, indicating that the formation of M_6(**L1**)$_4$ cage.

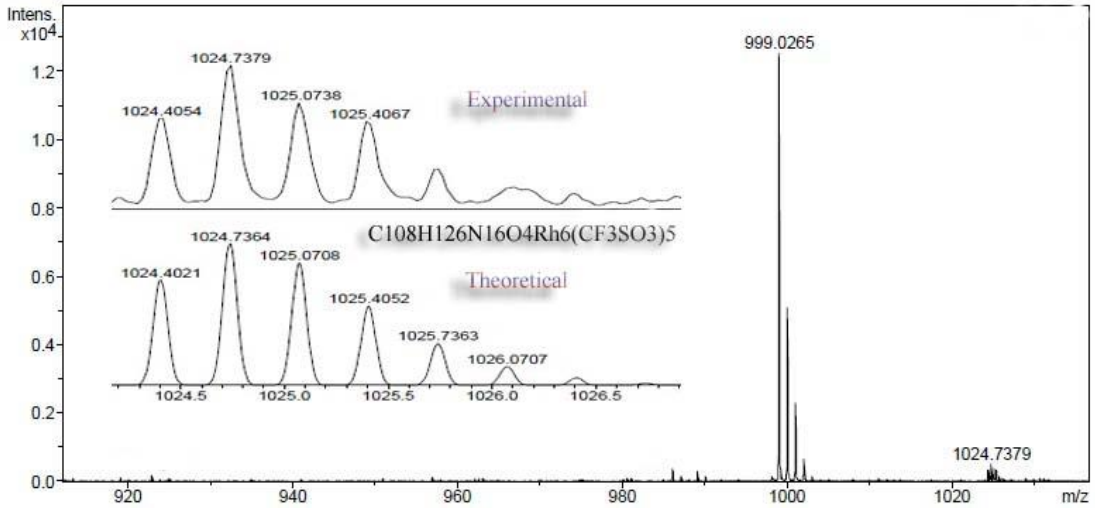

Figure S8. The ESI-MS spectrum after mixing {Cp*Rh} fragments with H**L1** ligands in a 1:1 ratio in MeOH solvent, then heated to 50℃, indicating that the formation of M_6(**L1**)$_4$ cage.

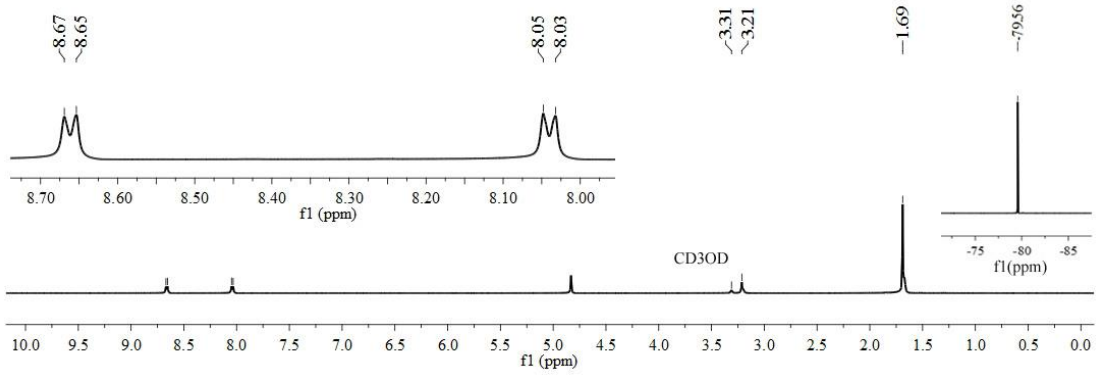

Figure S9. The ^{1}H NMR spectrum of cage **3**.

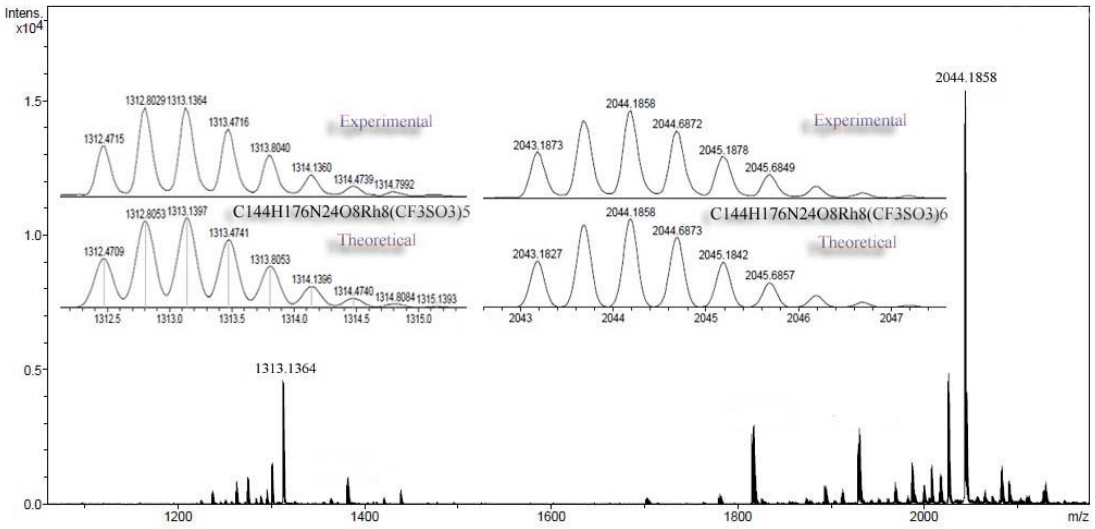

Figure S10. The ESI-MS spectrum ($\mathbf{3}^{2+}$) and ($\mathbf{3}^{3+}$) of cage **3**.

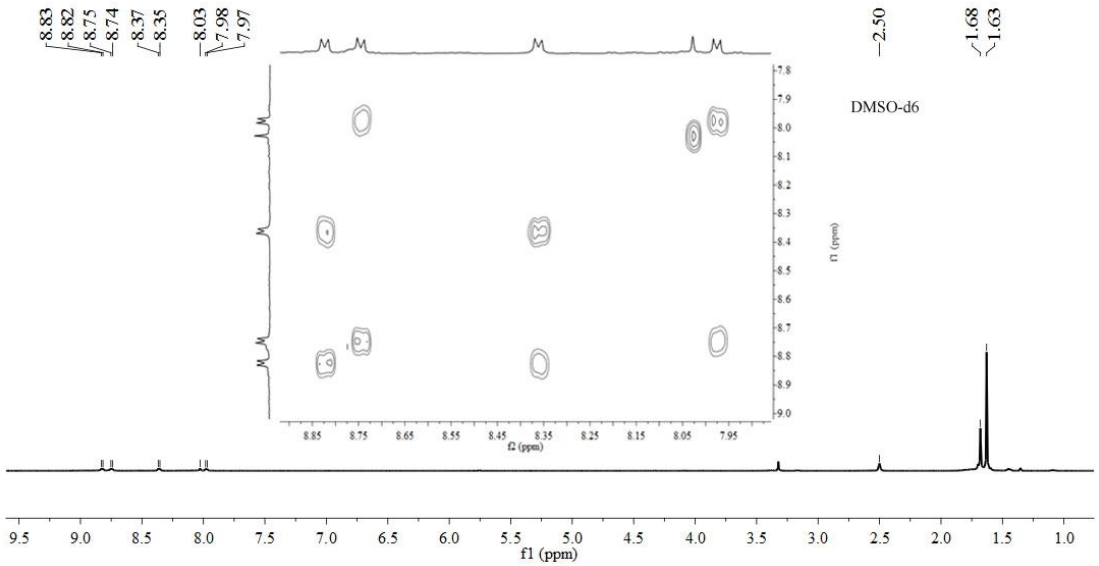

Figure S11. The ^{1}H NMR and partial ^{1}H *COSY* spectra of complex **4**.

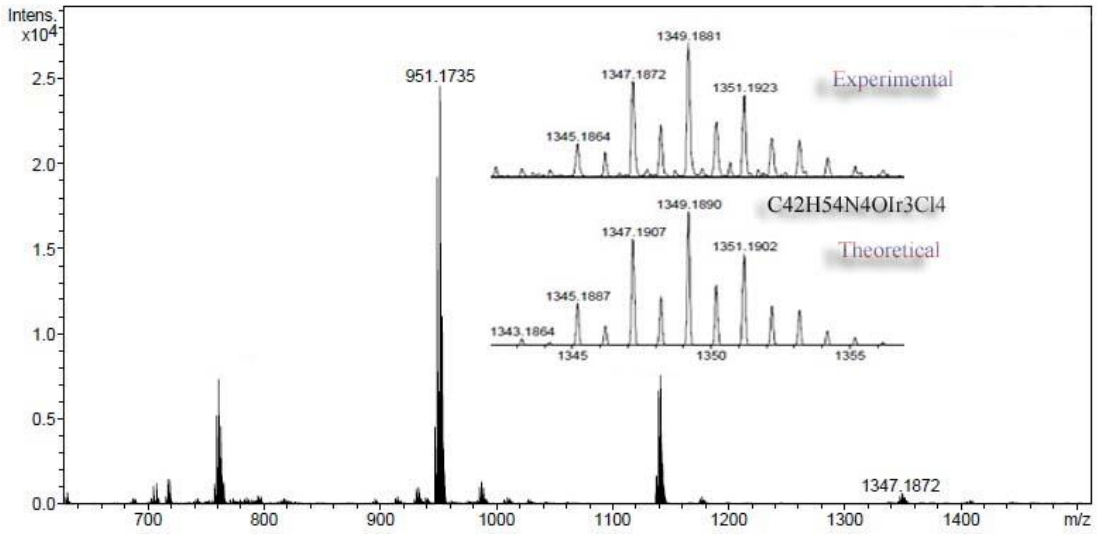

Figure S12. The ESI-MS spectrum ($\mathbf{4}^{+}$) of complex **4**.

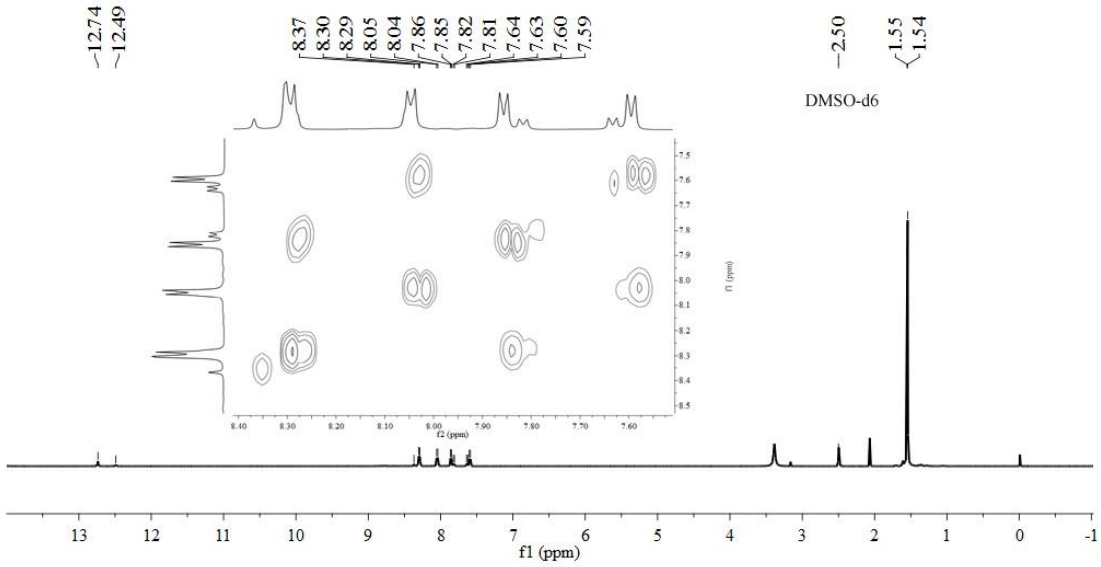

Figure S13. The ^{1}H NMR and partial ^{1}H *COSY* spectra of macrocycle **5**.

4. DFT computational details

All the calculations were performed with the B97-D3 density functional method[4] **Error! Reference source not found.**using the Gaussian 09 software package.[5] The empirical long-range correction of Grimme et al was used for the B97-D3 functional.[6] The basis sets used were: the 3-21G* basis set[7] for C and H, the 6-31+G(d) basis set[8] for N and O, and the SDD pseudo potential basis set[9] for Rh. The solvent effect was

taken into consideration using the SMD solvation model of Truhlar et al.[10] All geometries ware fully optimized and harmonic vibrational frequencies were calculated to guarantee that the optimized structures are genuine minima.

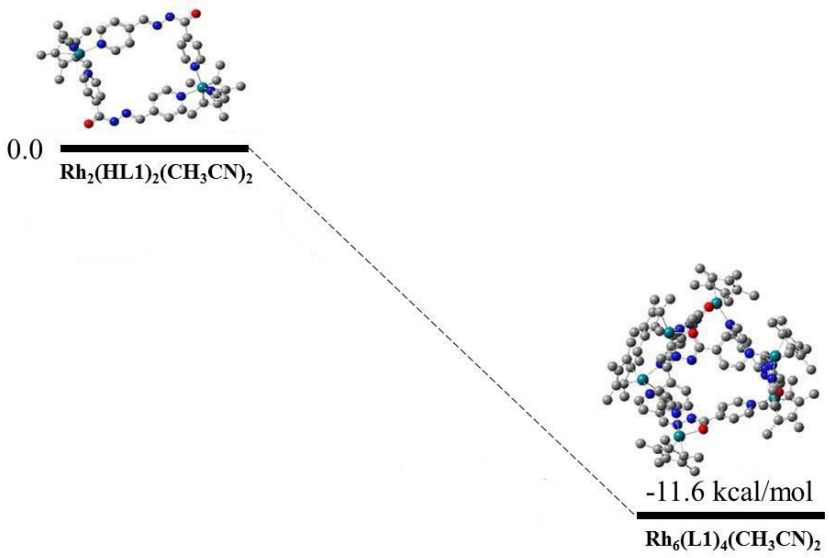

Figure S14. Free-energy change at 298.15 K for the formation of M_6(**L1**)$_4$ cage from M_2(H**L1**)$_2$ macrocycle.

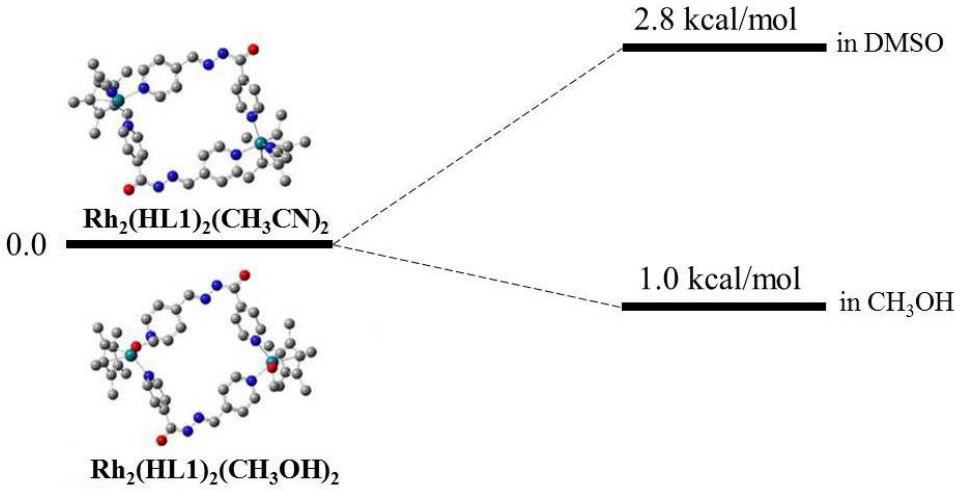

Figure S15. Free-energy change at 298.15 K for removing a CH_3CN or CH_3OH ligand from M_2(H**L1**)$_2$ macrocycle in DMSO or CH_3OH solution, respectively.

5. Single-crystal structure determination of complexes 1-5

All the determinations of unit cell and intersity data were performed with

graphite-monochromated Mo K_α radiation (λ = 0.71073 Å) on the CCD-Bruker APEX DUO for complexes **1**, **2**, **4**, **5** and expecially Cu radiation (λ = 1.54184 Å) on the Bruker D8 ADVANCE for complex **3**. All the data were collected at 173(2) or 150 K using the ω scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on *F2* by a full-matrix least-squares method. All the calculations were carried out with the SHELXTL program.[11] Crystallographic data for complexes **1**-**5** are summarized in Table S1.

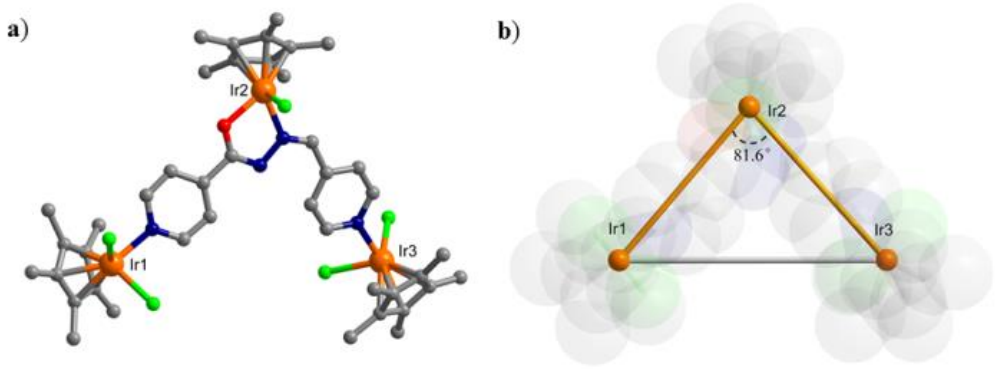

Figure S16. (a) X-ray crystal structure of complex **4**; (b) Perspective image showing the triangle in **4**. Hydrogen atom and solvent molecules are omitted for clarity.

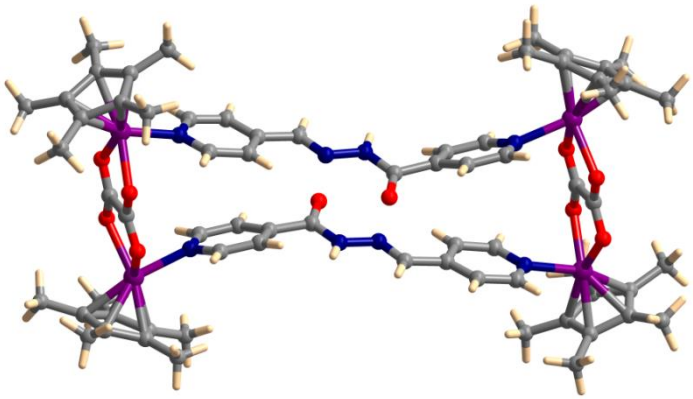

Figure S17. X-ray crystal structure of macrocycle **5**. Triflate anions and solvent molecules are omitted for clarity.

Table S1. Crystallographic data and structure refinement parameters for complexes **1-5**

	1	**2**	**3**	**4**	**5**
formula	$C_{52}H_{56}N_{10}O_{14}S_4F_{12}Rh_2\cdot 2CH_3CN$	$C_{120}H_{132}N_{18}O_{28}S_8F_{24}Rh_6\cdot 2CH_3CN$	$C_{152}H_{176}N_{24}O_{32}S_8F_{24}Rh_8\cdot 8CH_2Cl_2\cdot C_6H_{14}\cdot 11H_2O$	$C_{42}H_{54}N_4OCl_5Ir_3$	$C_{72}H_{80}N_8O_{22}S_4F_{12}Rh_4\cdot 3CH_3CN\cdot Et_2O\cdot H_2O$
Mr	1687.22	3686.48	5350.67	1384.74	2356.58
crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
space group	*P ccn*	*P* $2_1/n$	*C2/c*	*P* $2_1/c$	*P* $2_12_12_1$
a [Å]	31.650(4)	19.658(17)	17.9390(7)	14.562(4)	14.4394(11)
b [Å]	13.2146(15)	25.83(2)	33.1198(13)	23.143(6)	24.9880(19)
c [Å]	16.8363(19)	34.51(3)	36.5625(16)	14.823(4)	27.232(2)
α [º]	90	90	90	90	90
β [º]	90	97.740(13)	103.848(2)	114.904(4)	90
γ [º]	90	90	90	90	90
V [$Å^3$]	7041.6(14)	17365(27)	21091.7(15)	4530.8(19)	9825.7(13)
T [K]	173(2)	173(2)	150(2)	173(2)	173(2)
Z	4	4	4	4	4
ρ_{calcd} [g cm^{-3}]	1.592	1.410	1.685	2.030	1.593
μ [mm^{-1}]	0.687	0.743	8.387	9.121	0.842
F(000)	3416	7440	10848	2632	4784
[*R*(int)]	0.0585	0.0620	0.0714	0.0634	0.0722
data/restraints/ parameters	8041/20/462	37739/117/1799	18856/315/1245	10154/196/568	21374/49/1203
R_1/wR_2 [I＞2σ(I)]	0.0555/0.1448	0.0839/0.2370	0.1470/0.3532	0.0445/0.1011	0.0513/0.1173
R_1/wR_2 (all data)	0.0831/0.1615	0.1292/0.2634	0.1590/0.3591	0.1059/0.1269	0.0777/0.1284
goodness-of-fit	1.033	0.993	1.058	0.990	0.984
Largest residuals [e $Å^{-3}$]	1.355/-0.930	2.794/-1.206	3.563/-2.298	1.956/-1.113	1.051/-0.943

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