Supporting Information

Host-Guest Capability of a Three-Dimensional Heterometallic Macrocycle

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1. NMR spectra

Fig. S1 ^{1}H NMR (400 MHz, CD_3OD, ppm) for **1b**

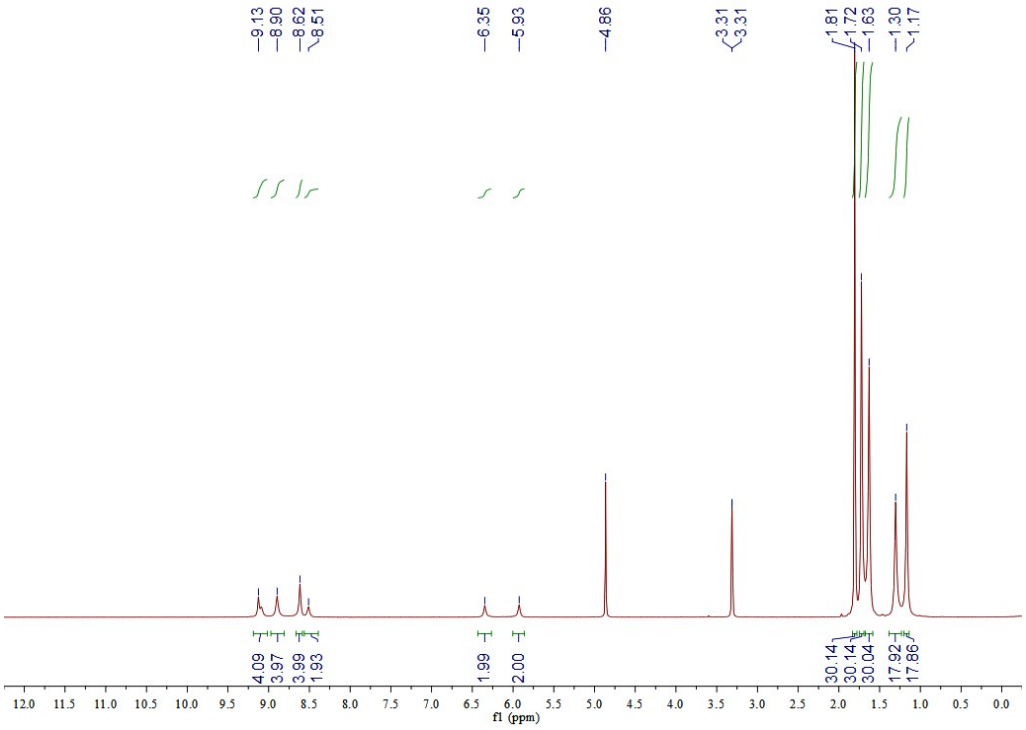
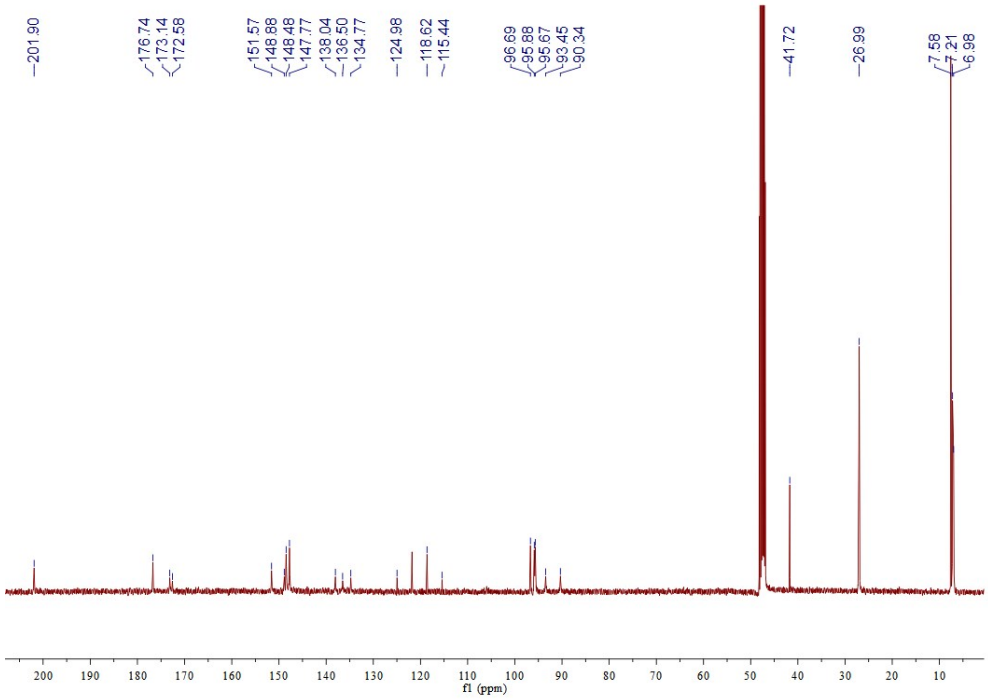
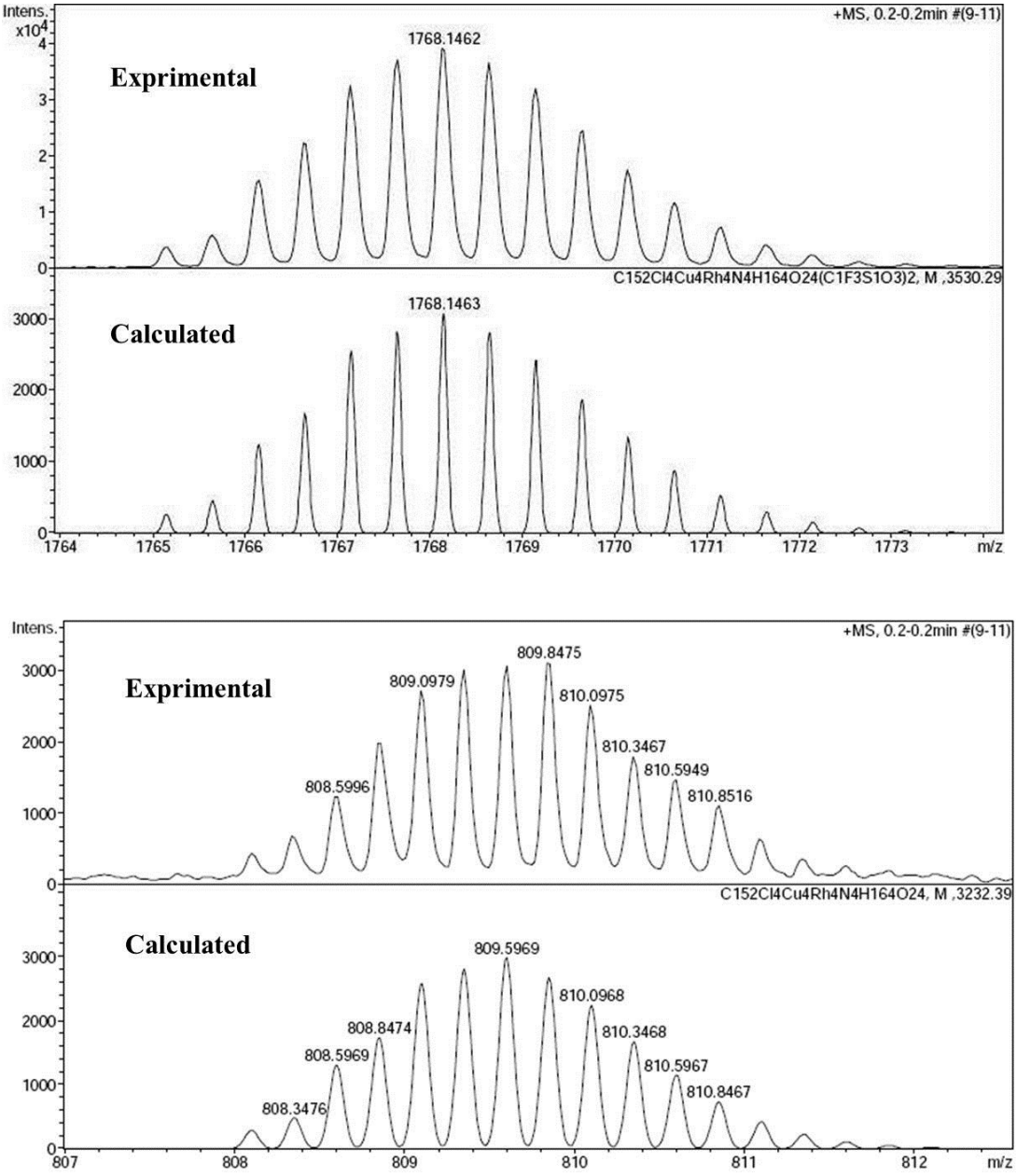


Fig. S2 $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD, ppm) for **1b**



2 ESI-MS spectra

Fig. S3 ESI-MS of $[G_4 \subset 1a - 2OTf]^{2+}$ (top) and $[[G_4 \subset 1a - 4OTf]^{4+}$ (down)



3 UV-Vis titration experiments

Fig. S4 UV-Vis titration of G_4 into 1a in MeOH. The absorbance of G_4 have been subtracted in each spectrum. The black trace is the spectrum of the initial solution (0 eq. G_4) and the blue trace is the final spectrum (2 eq. G_4).

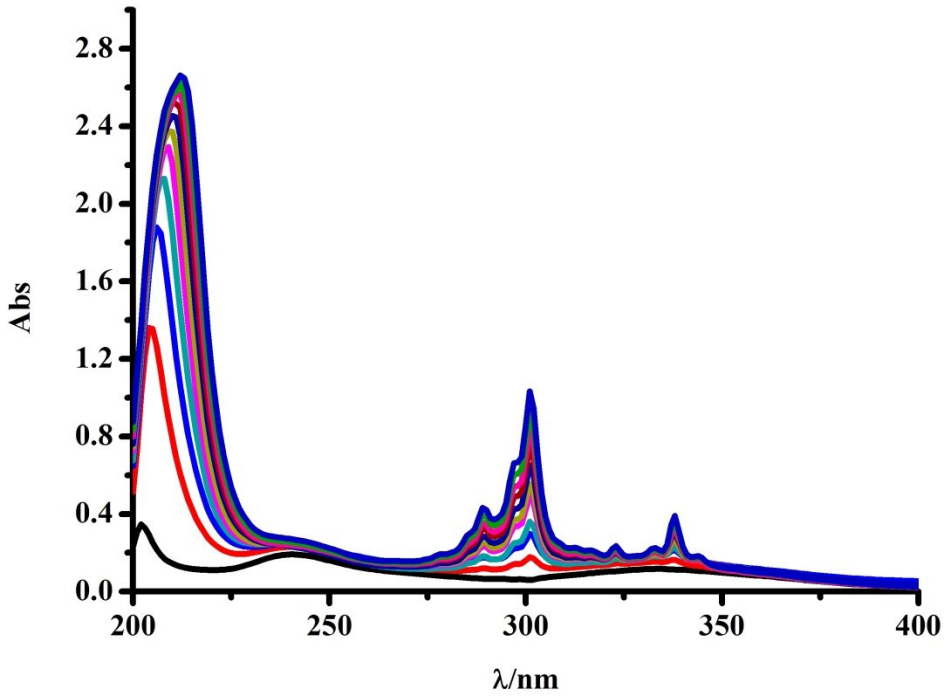
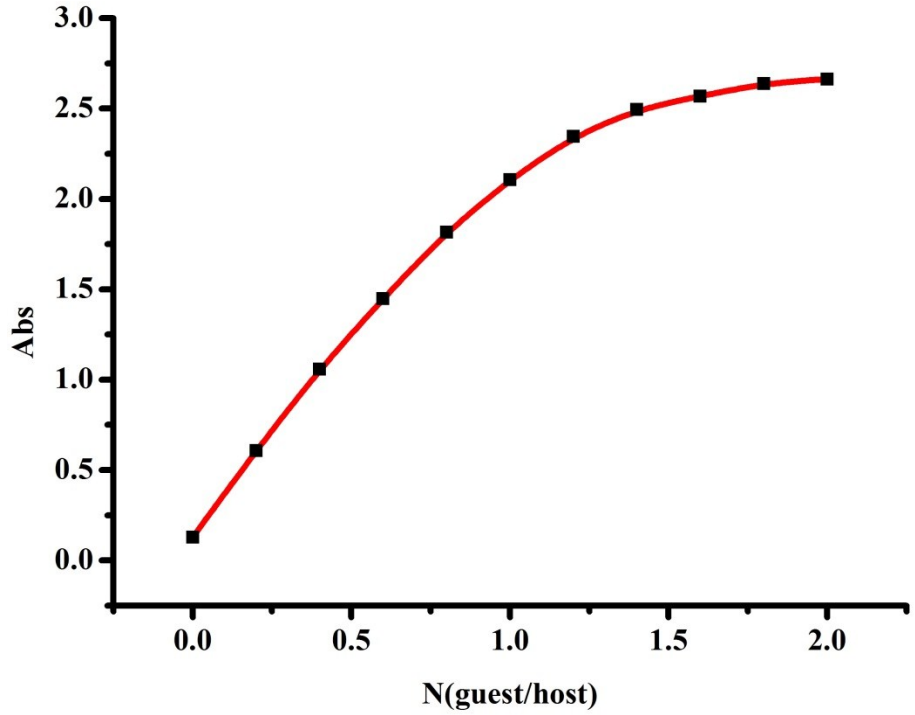


Fig. S5 Non-linear least-squares fit of the titration data in Figure S4 to give *K*a = $1.43*10^6$ M^{-1}.



4. X-ray crystallography details

In asymmetric unit of **G_1⊂1a**, there were disordered anions and solvents (two triflate anions, three methanol and three water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them.

In asymmetric unit of **G_2⊂1a**, there were disordered anions and solvents (three triflate anions, eight methanol and four water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. The metallabipyridine ligands were disordered and they were divided into two parts (52:48 for one ligand, 59:41 for a part of another ligand and 43:57 for the rest). 93 ISOR and 69 DFIX instructions were used to restrain anions, ligands, guest molecules and Cp* fragments so that there were 627 restraints in the data. Hydrogen of methanol, water and corannulene molecules could not be found and others were put in calculated positions.

In asymmetric unit of **G_4⊂1a**, there were disordered solvents (five methanol and one water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. One of four tert-butyl groups was disordered and it was divided into two parts (49:51). 27 ISOR and 5 DFIX instructions were used to restrain anions, tert-butyl groups and Cp* fragments so that there were 167 restraints in the data. Hydrogen of methanol molecules could not be found and others were put in calculated positions.

In asymmetric unit of **1b**, there were disordered anions and solvents (two triflate anions, fifteen methanol and three water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. 13 ISOR, 6 DELU and 24 DFIX instructions were used to restrain anions, tert-butyl groups and Cp* fragments so that there were 108 restraints in the data. Hydrogen of methanol molecules could not be found and others were put in calculated positions.

In asymmetric unit of **2c**, there were disordered anion and solvents (one triflate anion, one diethyl ether two methanol and two water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. One bridging ligand and one coordinated methanol molecule were disordered and they were divided into two parts (65:35 for ligand and 62:38 for methanol). 20 ISOR and 6 DFIX instructions were used to restrain ligands and Cp* fragments so that there were 126 restraints in the data. Hydrogen of methanol and water molecules could not be found and others were put in calculated positions.

In asymmetric unit of **2b**, there were disordered anions and solvents (two triflate anions, one diethyl ether, two methanol and two water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. Two tert-butyl fragments and two triflate anions were disordered and they were divided into two parts (58:42, 56:44 for t-Bu group and 61:39, 40:60 for anions). 77 ISOR, 5 SIMU and 53 DFIX instructions were used to restrain anions, ligands and Cp* fragments so that there were 683 restraints in the data. Hydrogen of methanol and water molecules could not be found and others were put in calculated position.

Table S1. X-Ray crystal structure parameters of compounds **1b, 2b, 2c.**

Parametres	1b	2c	2b
Formula	$C_{135}H_{222}Cl_2F_{18}N_6O_{52}Rh_6S_6$	$C_{170}H_{226}Cu_6F_{12}N_{10}O_{58}Rh_4S_4$	$C_{145}H_{200}CuF_{18}N_8O_{43}Rh_6S_6$
Mol wt	3983.89	4486.71	3958.48
Cryst syst	Triclinic	Triclinic	Triclinic
Space group	P -1	P-1	P-1
a (Å)	18.4386(14)	16.7301(4)	17.6712(13)
b (Å)	19.8780(16)	17.1520(4)	19.6113(16)
c (Å)	26.209(2)	22.1104(5)	28.815(2)
α (deg)	76.796(4)	96.2437(14)	73.6712(18)
β (deg)	70.094(4)	111.7468(13)	69.8626(17)
γ (deg)	74.016(4)	109.0984(13)	67.9669(14)
V (Å^3)	8586.0(12)	5374.5(2)	8841.0(12)
Z	2	1	2
T/K	200(2)	173(2)	213(2)
λ(Å)	1.54178	1.54178	0.71073
ρ_{calcd} (g/cm^3)	1.423	1.386	1.487
μ (mm^{-1})	6.387	4.143	0.828
F(000)	4104	2306	4054
Θ range (deg)	2.338-67.499	2.229-67.495	0.736- 26.000
limiting indices	-19<=h<=21	-19<=h<=20	-18<=h<=21
	-23<=k<=23	-20<=k<=20	-24<=k<=21
	-31<=l<=31	-26<=l<=26	-35<=l<=35
collected reflns	103779	53564	58302
Unique reflns	30320	18675	34417
absorption correction	Semiempirical	Semiempirical	Semiempirical
max/min transmission	0.006/0.000	0.422/0.321	0.746/0.684
data/restraints/parameters	30320/108 /1626	18675/126/1141	34417 /683 /2044
goodness of fit	1.158	1.048	0.944
$R1/wR2$ [I >2σ(I)][a]	0.1796/0.4159	0.0862/0.2454	0.0814/0.2255
$R1/wR2$ (all data)a	0.1964/0.4294	0.1043/0.2601	0.1480/0.2798

[a] $R_1=\Sigma||F_0|-|F_c||$ (based on reflections with $F_{02}>2\sigma F_2$). $wR_2=[\Sigma[w(F_{02}-F_{c2})_2]/\Sigma[w(F_{02})_2]]_{1/2}$; $w=1/[\sigma_2(F_{02})+(0.095P)_2]$; $P=[\max(F_{02},0)+2F_{c\,2}]/3$ (also with$F_{02}>2\sigma$

Table S2. X-Ray crystal structure parameters of compounds **G_1 ⊂1a, G_2⊂1a, G_4⊂1a.**

Parametres	G_1⊂1a	G_2⊂1a	G_4⊂1a
Formula	$C_{154}H_{192}Cl_4Cu_4F_{12}N_4O_{45}Rh_4S_4$	$C_{161}H_{222}Cl_4Cu_4F_{12}N_4O_{52}Rh_4S_4$	$C_{174}H_{300}Cl_4Cu_4F_{12}N_4O_{56}$ Rh_4S_4
Mol wt	3988.95	4209.25	4508.00
Cryst syst	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
a (Å)	18.9815(9)	18.8853(4)	17.0424(8)
b (Å)	23.9885(11)	23.8735(5)	17.8943(9)
c (Å)	34.8027(8)	24.2980(5)	20.7290(10)
α (deg)	80.7437(17)	76.1101(7)	97.404(2)
β (deg)	85.6454(17)	73.5033(7)	111.887(2)
γ (deg)	70.2326(17)	70.7871(8)	110.504(2)
V ($Å^3$)	14715.0(12)	9788.1(4)	5243.8(5)
Z	3	2	1
T/K	200.0	173(2)	173(2)
λ(Å)	1.54178	1.54178	1.54178
ρ_{calcd} (g/cm^3)	1.350	1.428	1.428
μ (mm^{-1})	4.696	4.761	4.490
F(000)	6130	4336	2.407-67.497
Θ range (deg)	2.198-67.999	2.530- 70.308	2356
limiting indices	-22<=h<=22	-23<=h<=23	-19<=h<=20
	-28<=k<=28	-21<=k<=28	-21<=k<=21
	-41<=l<=39	-29<=l<=29	-24<=l<=24
collected reflns	97360	130906	46876
Unique reflns	50550	36343	17521
absorption correction	Semiempirical	Semiempirical	Semiempirical
max./min. transmission	0.1665/0.0465	0.224/0.102	0.384 /0.222
data/restraints/parameters	50550/683/3208	36343 /627 /2291	17521 / 167 / 1136
goodness of fit	1.440	1.060	1.087
$R1/wR2$ [I >2σ(I)][a]	0.1301/0.3762	0.0598/0.1807	0.1237/ 0.3516
$R1/wR2$ (all data)a	0.1626/0.4097	0.0675/0.1890	0.1463/0.3610

[a] $R_1=\Sigma||F_0|-|F_c||$ (based on reflections with $F_{02}>2\sigma F_2$). $wR_2=[\Sigma[w(F_{02}-F_{c2})_2]/\Sigma[w(F_{02})_2]]_{1/2}$; $w=1/[\sigma_2(F_{02})+(0.095P)_2]$; $P=[\max(F_{02},0)+2F_{c2}]/3$ (also with $F_{02}>2\sigma F$