Electronic Supplementary Material (ESI) for ChemComm.

Electronic supplementary information

Metallosupramolecules of pillar[5]-*bis*-trithiacrown including a mercury(II) iodide ion-triplet complex

Mingyeong Shin,[a] Sujin Seo, [a] In-Hyeok Park, [a] Eunji Lee, [a,b] Yoichi Habata[b] and Shim Sung Lee*[a]

Experimental section

General. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. NMR spectra were recorded on a Bruker DRX 300. The IR were recorded on a Thermo Fisher Scientific Nicolet iS 10 FT-IR spectrometer using KBr pellets. ESI-Mass spectra were obtained on a Thermo Scientific LCQ Fleet spectrometer. The absorption spectra were recorded on a Scinco S-3150 UV-visible spectrophotometer. The elemental analysis was performed on a Thermo-Fisher Scientific Flash 2000 elemental analyser.

X-ray crystallographic analysis. Crystal data were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection, data reduction and semi-empirical absorption correction were carried out using the software package of APEX2.[S1] All of the calculations for the structure determination were carried out using the SHELXTL package[S2] All nonhydrogen atoms were refined anisotropically and all H atoms were placed in idealized positions and refined isotropically in a riding manner along with their respective parent atoms. In the refinement procedure of **L**, the S1-C24-C25-S2-C26 and O3-C19 segments are disordered over two sites occupied in a 70 : 30 ratio (see Fig. S4a). The *n*-hexane in the cavity of **L** is also disordered over two sites occupied in a 50 : 50 ratio (see Fig. S4b). In the refinement procedures for **1** and **3**, the C25-C26 segments are disordered over two sites occupied in a 54 : 46 ratio (see Figs. S5 and S7). Since the lattice solvent molecules in **2** is highly disordered, the contribution of solvent electron density was removed by the SQUEEZE routine in PLATON.[S4] Relevant crystal data collection and refinement data for the crystal structures are summarized in Table S1. CCDC 2004262 (**L**), 2004263 (**1**), 2004264 (**2**) and 2004265 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of pillar[5]-*bis*-trithiacrown (L). A solution of pillar[5]arene tetrabromide[S3] (1.00 g, 0.89 mmol) and bis(2-mercaptoethyl) sulfide (0.68 g, 4.41 mmol) in CH_3CN (100 mL) was added dropwise to a refluxed solution of K_2CO_3 (0.62 g, 4.48 mmol) in CH_3CN (200 mL) for 1 h under nitrogen and the reaction mixture was refluxed for a further 48 h. After cooling the reaction mixture to room temperature, the solvent was evaporated and the residue was extracted with dichloromethane. The combined organic phases were dried with anhydrous sodium sulfate and then evaporated to dryness. Flash column chromatography (SiO_2; 20 % ethyl acetate: *n*-hexane) afforded the product as a white solid in 25% yield. Mp: 111-112 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.03-6.83 (*m*, 10 H, Ar), 4.20-4.02 (*m*, 8 H, $SCH_2C\mathit{H}_2O$), 3.86-3.70 (*m*, 28 H, $ArC\mathit{H}_2Ar$, $OC\mathit{H}_3$), 3.01-2.96 (*m*, 8 H, $SC\mathit{H}_2CH_2O$), 2.84-2.76 (*m*, 16 H, $SC\mathit{H}_2C\mathit{H}_2S$). ^{13}C NMR (125 MHz, $CDCl_3$): 151.02, 150.52, 149.62, 149.32, 128.36, 128.22, 128.17, 128.01, 127.78, 115.15, 114.45, 113.98, 77.54, 77.12, 76.70, 68.23, 66.87, 56.33, 56.03, 55.89, 33.55, 32.81, 32.59, 32.51, 32.44, 31.59, 29.69, 28.81. IR: 2928, 2483, 2139, 2030, 1724, 1610, 1496, 1464, 1397, 1308, 1204, 1100, 1041, 929, 877, 851, 772, 725, 702 cm^{-1}. Anal. calcd. for [$C_{57}H_{70}O_{10}S_6$]·CH_2Cl_2: C, 58.42; H, 6.09%. Found: C, 58.27; H, 6.34%. MS (ESI) *m/z* = 1129.50 [**L**+Na]$^+$.

Preparation of 1, [$HgCl_2(CH_2Cl_2$@L)]. Toluene (0.2 mL) was added to a dichloromethane (1.0 mL) solution of **L** (20.3 mg, 0.018 mmol) in a capillary tube (i.d. 5 mm); then $HgCl_2$ (14.7 mg, 0.054 mmol) in acetonitrile (1.0 mL) was layered on the toluene phase. Slow evaporation of the solution in the capillary tube afforded block-shaped colorless crystals of **1** (30% yield) suitable for the X-ray analysis. Mp: 145-146 °C (decomp.). IR: 2974, 2927, 1722, 1610, 1498, 1464, 1399, 1209, 1094, 1046, 930, 880, 854, 772, 726, 702 cm^{-1}. Anal. Calcd for [$C_{57}H_{70}Cl_2HgO_{10}S_6$]·2$CH_2Cl_2$: C, 45.75; H, 4.82%. Found: C, 45.54; H, 4.81%. MS (ESI) *m/z* = 1342.92 [Hg**L**Cl]$^+$

Preparation of 2, [$Hg_6Br_{12}(CH_3CN$@L$)_2]_n$. A solution of $HgBr_2$ (19.7 mg, 0.055 mmol) in acetonitrile (1.0 mL) was layered onto a solution of **L** (20.0 mg, 0.018 mmol) in chloroform (1.0 mL). Slow evaporation of the solution in a capillary tube afforded a lump of the block-shaped colorless of **2** (10% yield) suitable for the X-ray analysis. Mp: 154-155 °C (decomp.). IR: 2973, 2929, 2872, 2488, 2044, 1748, 1611, 1499, 1464, 1400, 1308, 1211, 1094, 1048, 930, 879, 854, 773, 726 cm^{-1}. Anal. Calcd for [$C_{57}H_{70}Br_6Hg_3O_{10}S_6$]·3$CHCl_3$: C, 28.30; H, 2.89%. Found: C, 28.17; H, 3.00%.

Preparation of 3, [I·Hg·I@L]. Toluene (0.2 mL) was added to a dichloromethane (0.7 mL) solution of **L** (20.3 mg, 0.018 mmol); then HgI_2 (24.6 mg, 0.054 mmol) in methanol (1.0 mL) was layered on the toluene phase. Slow evaporation of the solution in a capillary tube afforded a lump of the needle-shaped yellow of **3** (10% yield) suitable for the X-ray analysis. Mp: 165-166 °C (decomp.). IR: 2971, 2926, 2825, 2483, 1611, 1498, 1464, 1399, 1263, 1095, 1047, 934, 877, 852, 772, 702 cm^{-1}. Anal. Calcd for [$C_{57}H_{70}HgI_2O_{10}S_6$]: C, 43.83; H, 4.52%. Found: C, 44.03; H, 4.54%. MS (ESI) *m/z*: 1484.83 [(Hg·I)@**L**]$^+$ or [**3**-I]$^+$.

Table S1 Crystal and experimental data

	L	**1**	**2**	**3**
Formula	$C_{63}H_{84}O_{10}S_6$	$C_{59}H_{74}Cl_6HgO_{10}S_{62}$	$C_{118}H_{147}Br_{12}ClHg_6N_2O_{20}S_{12}$	$C_{57}H_{70}HgI_2O_{10}S_6$
Formula weight	1193.66	1548.83	4496.00	1561.88
Temperature	223(2)	223(2)	173(2)	193(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*Cc*	*Pc*	$P2_1/c$
Z	4	4	2	4
a (Å)	20.2460(9)	11.9926(6)	15.5878(2)	20.1865(4)
b (Å)	15.2630(7)	27.5154(12)	20.0801(3)	15.1666(3)
c (Å)	21.6226(10)	20.3121(11)	24.7383(4)	22.7025(4)
α (deg)	90	90	90	90
β (deg)	114.172(2)	93.071(3)	94.6820(10)	120.1480(10)
γ (deg)	90	90	90	90
V (Å^3)	6095.9(5)	6620.0(6)	7717.4(2)	6010.4(2)
Flack parameter		0.029(9)		
D_{calc} (g/cm^3)	1.301	1.554	1.935	1.726
$2\theta_{max}$ (deg)	52.00	52.00	52.00	52.00
R_1, wR_2 [$I > 2\sigma(I)$]	0.1043, 0.3368	0.0583, 0.1282	0.0438, 0.0718	0.0557, 0.1518
R_1, wR_2 [all data]	0.1489, 0.3753	0.0941, 0.1453	0.0673, 0.0763	0.1095, 0.1827
Goodness-of-fit on F^2	1.354	1.025	1.014	1.065
No. of reflection used [>2σ(*I*)]	5986 [R_{int} = 0.0613]	12237 [R_{int} = 0.0557]	25567 [R_{int} = 0.0565]	11802 [R_{int} = 0.0629]
CCDC No.	2004262	2004263	2004264	2004265

Table S2 Selected bond lengths (Å) and bond angles (°) for **1**

Hg1-S2	2.611(4)	Hg1-S3	2.714(3)
Hg1-Cl1	2.363(4)	Hg1-Cl2	2.378(4)
Cl1-Hg1-Cl2	126.39(14)	Cl1-Hg1-S2	111.71(16)
Cl2-Hg1-S2	113.10(14)	Cl1-Hg1-S3	110.31(11)
Cl2-Hg1-S3	103.34(12)	S2-Hg1-S3	82.41(12)

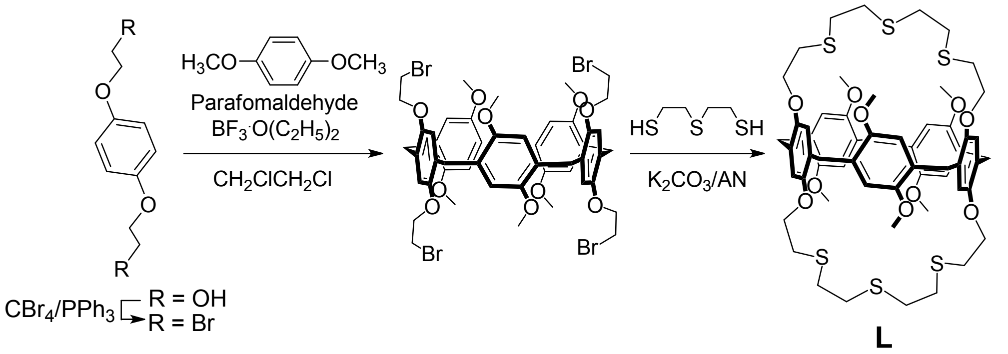
Table S3 Selected bond lengths (Å) and bond angles (°) for **2**

Hg1-Br1	2.4428(15)	Hg1-Br2	2.4448(16)
Hg1-S1	2.851(4)	Hg2-Br3	2.4764(17)
Hg2-Br4	2.5528(17)	Hg2-S2	2.674(4)
Hg2-S3	2.670(4)	Hg3-Br5	2.5393(2)
Hg3-Br6	2.5103(17)	Hg3-S4	2.584(4)
Hg3-S5	2.677(4)	Hg4-Br6	3.3172(1)
Hg4-Br7	2.4607(15)	Hg4-Br8	2.4537(16)
Hg4-Br11A	3.3711(1)	Hg4-S9	2.738(3)
Hg5-Br9	2.4661(18)	Hg5-Br10	2.5003(17)
Hg5-S7	2.732(4)	Hg5-S8	2.735(4)
Hg6-Br11	2.5537(15)	Hg6-Br12	2.4587(16)
Hg6-S11	2.766(4)	Hg6-S12	2.616(4)
Br1-Hg1-Br2	166.20(6)	Br1-Hg1-S1	98.88(8)
Br2-Hg1-S1	93.70(8)	Br3-Hg2-Br4	123.23(6)
Br3-Hg2-S3	120.50(9)	Br4-Hg2-S3	102.62(8)
Br3-Hg2-S2	118.04(9)	Br4-Hg2-S2	101.34(9)
S2-Hg2-S3	82.74(11)	Br5-Hg3-Br6	123.05(6)
Br6-Hg3-S4	117.97(10)	Br5-Hg3-S4	109.65(10)
Br6-Hg3-S5	111.16(11)	Br5-Hg3-S5	101.55(11)
S4-Hg3-S5	85.52(13)	Br6-Hg4-Br7	99.909(1)
Br6-Hg4-Br8	88.857(1)	Br6-Hg4-Br11A	170.665(1)
Br6-Hg4-S9	89.086(1)	Br7-Hg4-Br8	147.14(6)
Br7-Hg4-Br11A	85.327(1)	Br7-Hg4-S9	103.36(8)
Br8-Hg4-S9	108.43(8)	Br8-Hg4-Br11A	90.801(1)
Br11A-Hg4-S9	108.089(1)	Br9-Hg5-Br10	139.95(6)
Br9-Hg5-S7	106.09(9)	Br9-Hg5-S8	111.19(9)
Br10-Hg5-S7	102.28(9)	Br10-Hg5-S8	100.72(9)
S7-Hg5-S8	80.76(11)	Br11-Hg6-Br12	126.99(6)
Br11-Hg6-S11	97.65(9)	Br11-Hg6-S12	104.17(9)
Br12-Hg6-S11	110.90(9)	Br12-Hg6-S12	122.77(9)
S12-Hg6-S11	82.10(11)		

Symmetry code: A) -1+x, -y, -1/2+z

Table S4 Selected bond lengths (Å) and bond angles (°) for **3**

I1-H21A	3.2335(1)	I1-H28A	3.3335(0)
I1-H36B	3.3874(1)	I1-H47B	3.2132(0)
I1-H55B	3.5277(0)	I2-H7A	3.2447(1)
I2-H14A	3.444(0)	I2-H37B	3.2286(1)
I2-H46B	3.4232(0)	I2-H54B	3.2496(0)
I1-H21A-C21	135.084(2)	I1-H28A-C28	133.193(2)
I1-H36B-C36	141.176(1)	I1-H47C-C47	155.295(1)
I1-H55B-C55	157.987(2)	I2-H7A-C7	141.596(2)
I2-H14A-C14	143.707(2)	I2-H37B-C37	139.66(1)
I2-H46B-C46	150.819(2)	I2-H54B-C54	148.957(1))



Scheme S1 Synthesis of pillar[5]-*bis*-trithiacrown **L**.

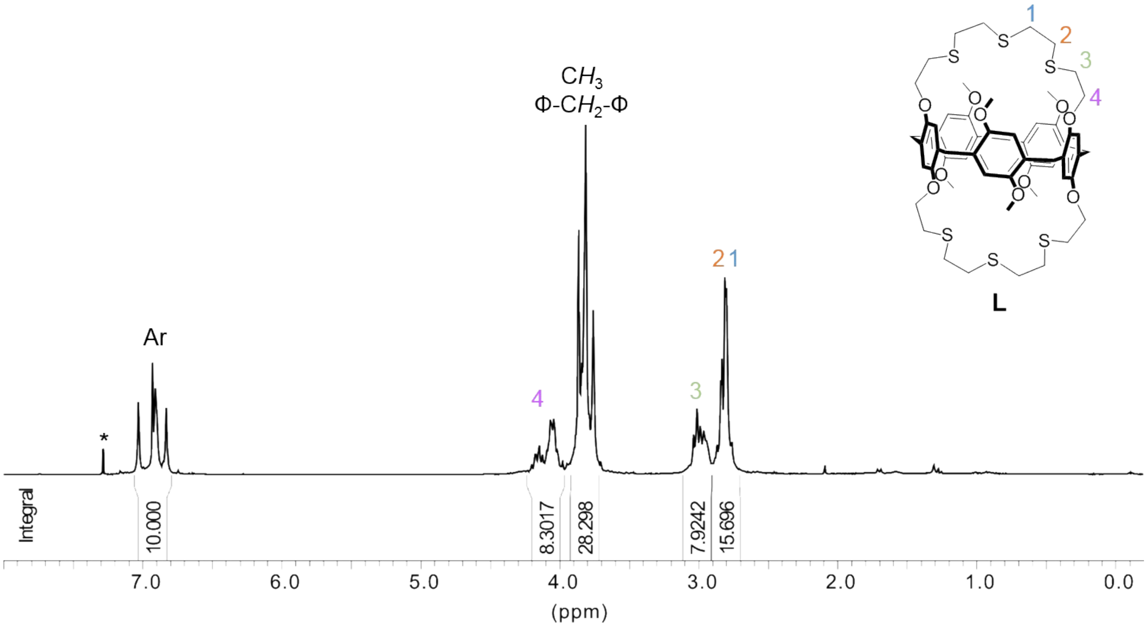


Fig. S1 ^{1}H NMR spectrum of **L** in $CDCl_3$.

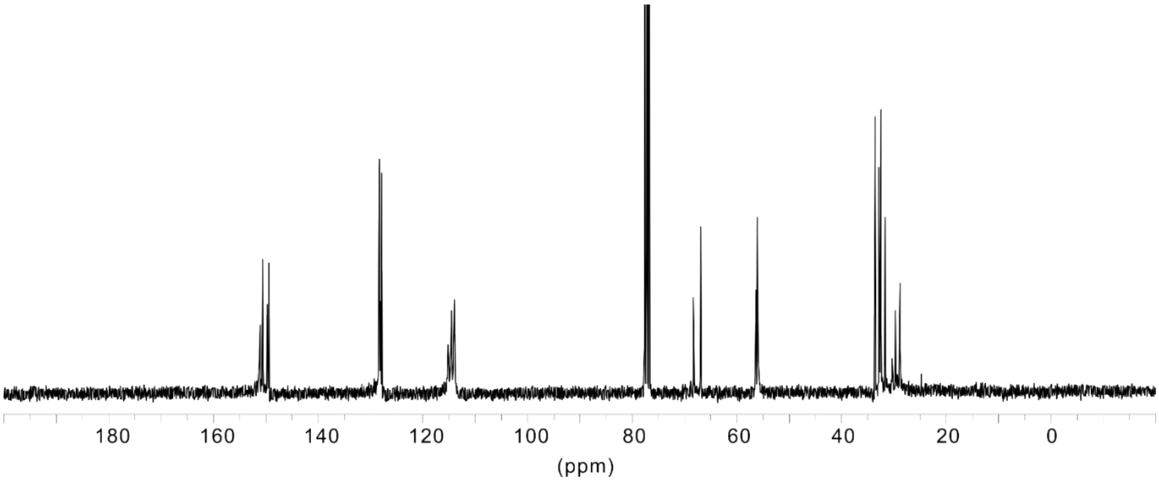


Fig. S2 ^{13}C NMR spectrum of **L** in $CDCl_3$.

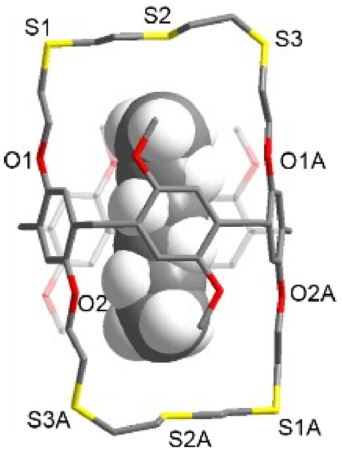
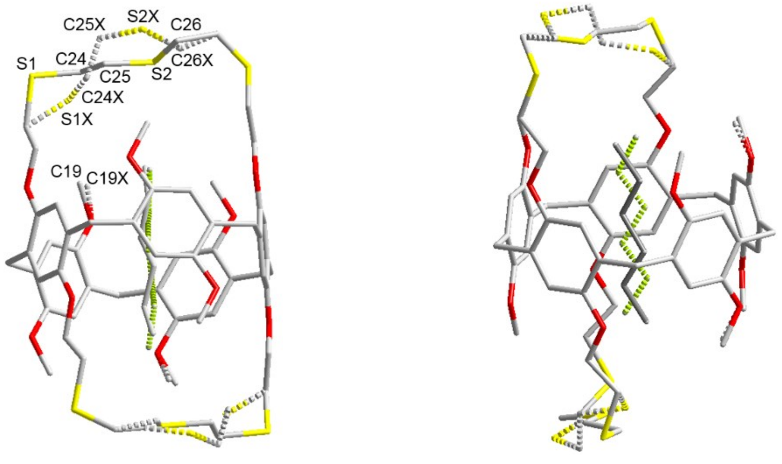


Fig. S3 Crystal structure of *n*-hexane@**L**. Symmetry operation for A: 1-x, y, 0.5-z.



(a) (b)

Fig. S4 Crystal structure of *n*-hexane@**L**: (a) front view showing the atomic labelling for disorders of S1-C24-C25-S2-C26 segment, methoxy C19 atom and *n*-hexane molecule and (b) side view.

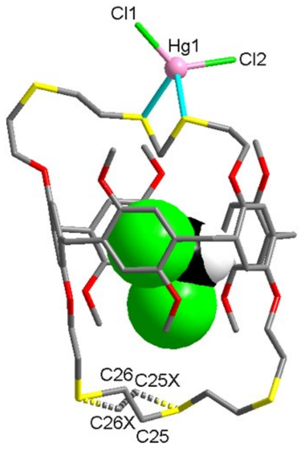
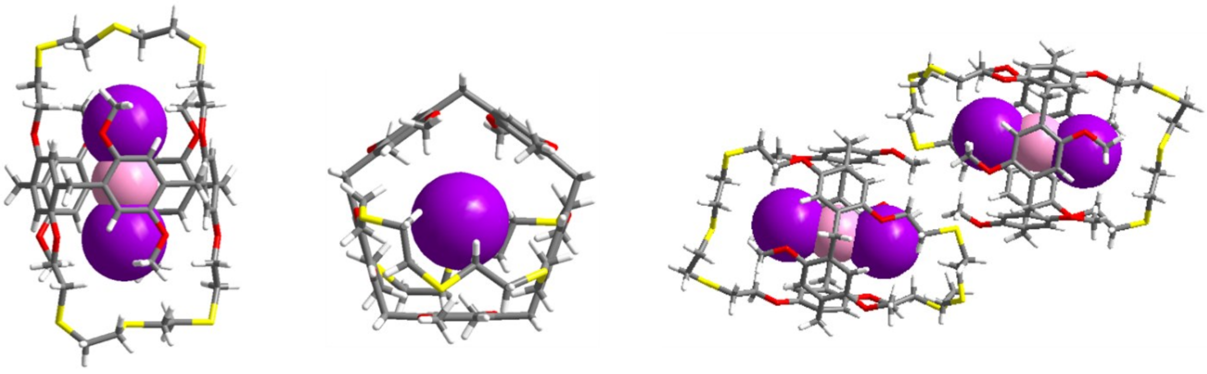


Fig. S5 Crystal structure of **1** showing the thiacrown part disordered (C25-C26, 54:46).



(a) (b) (c)

Fig. S6 Crystal structure of **3**: (a) front view, (b) top view and (c) packing mode.

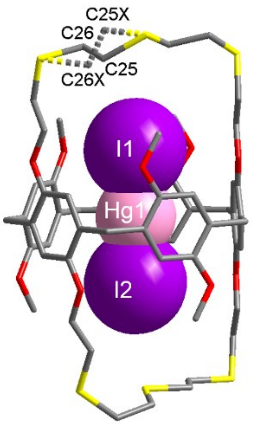
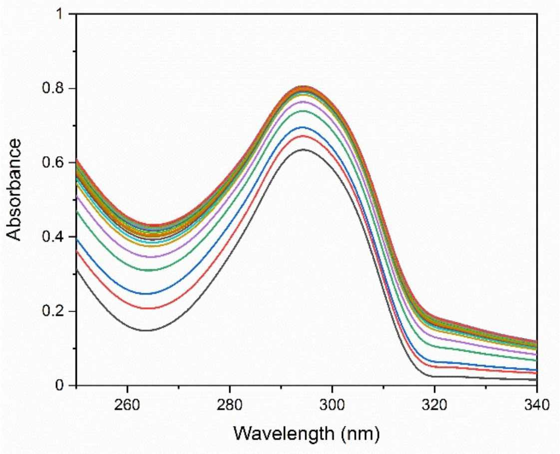
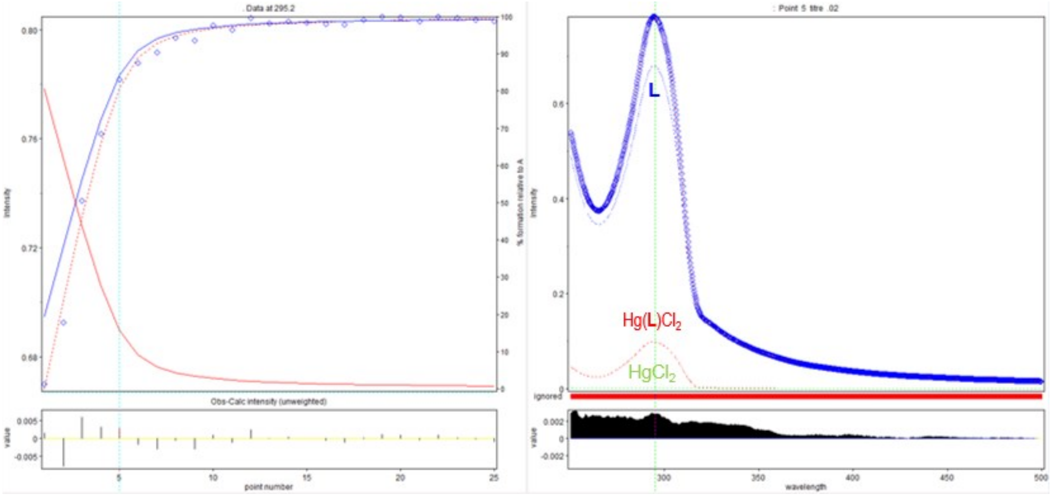


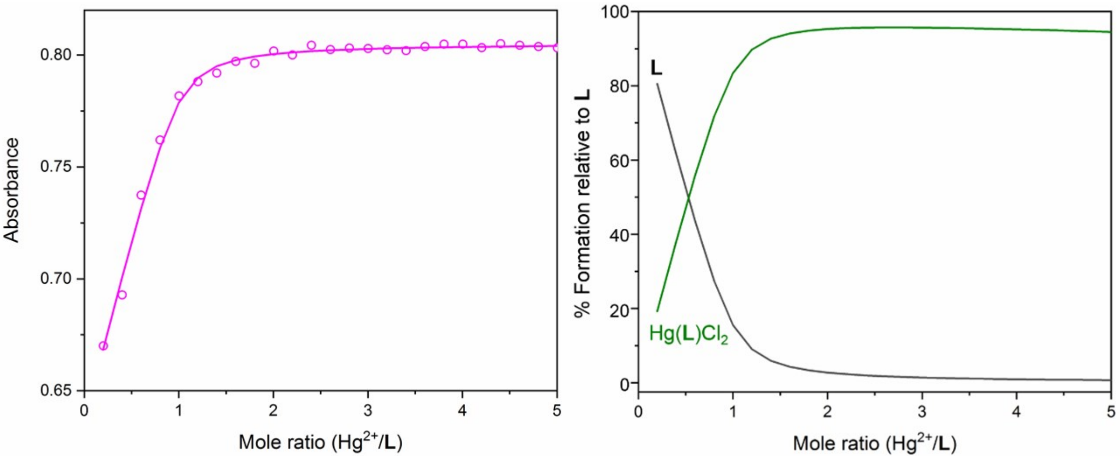
Fig. S7 Crystal structure of **3** showing the thiacrown part disordered (C25-C26, 54:46).



(a)

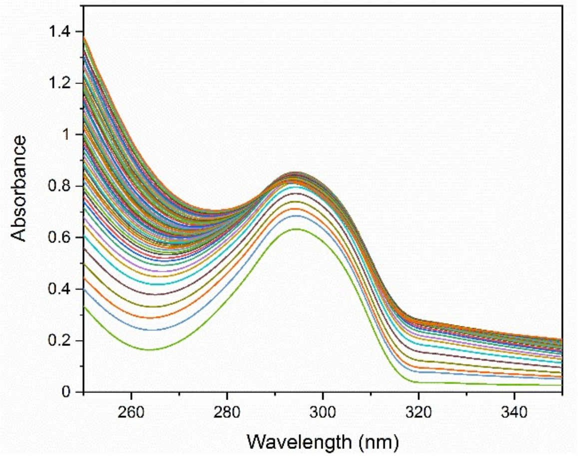


(b)

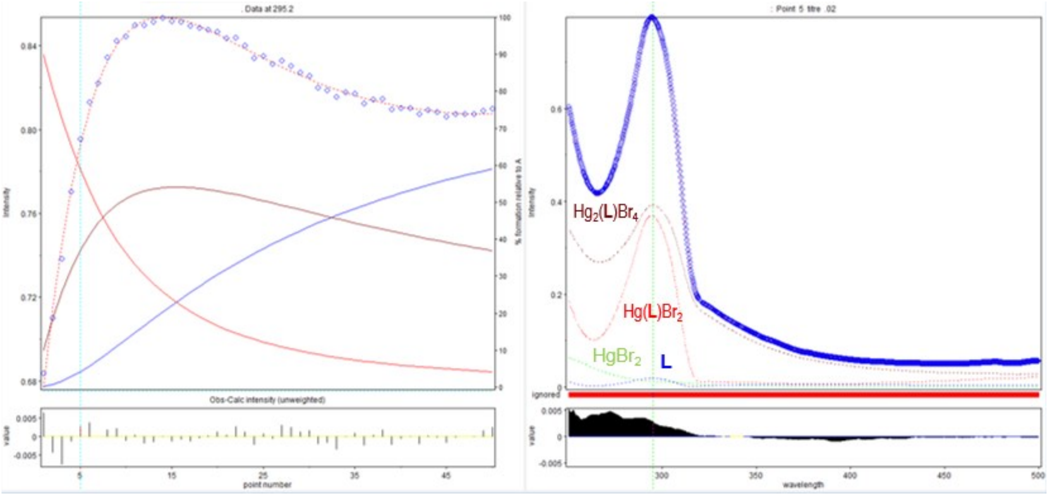


(c) (d)

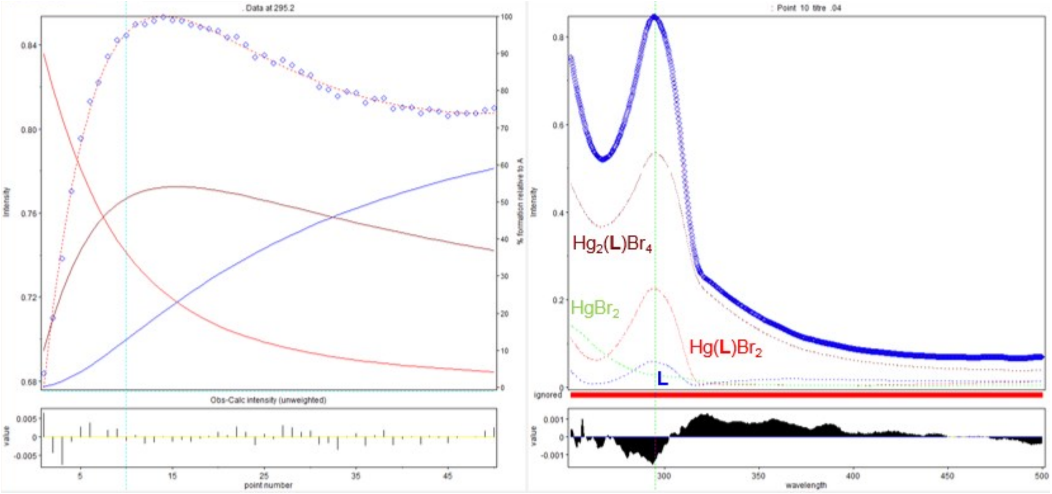
Fig. S8 (a) UV-vis titration of **L** (0.04 mM) with $HgCl_2$ (0-5.0 equiv.) in $CHCl_3/CH_3OH$ (1:2.5 *v*/*v*), (b) HypSpec[S5] output for the fitting of UV-vis titration data (input data: 250-500 nm) to determine the formation constant by employing the 1:1 (M-to-**L**) binding model [variables: 1.0 equiv. (left), 295.2 nm (right)], (c) modified plot (mole ratio vs Abs. at 295.2 nm) for the fitting data (circle: experimental points, solid line: theoretical fit) and (d) modified plot (mole ratio vs fraction%) for the species distribution showing free **L** (black), 1:1 complex (Hg(**L**)Cl_2, green).


Absorbance
Wavelength (nm)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
260
280
300
320
340

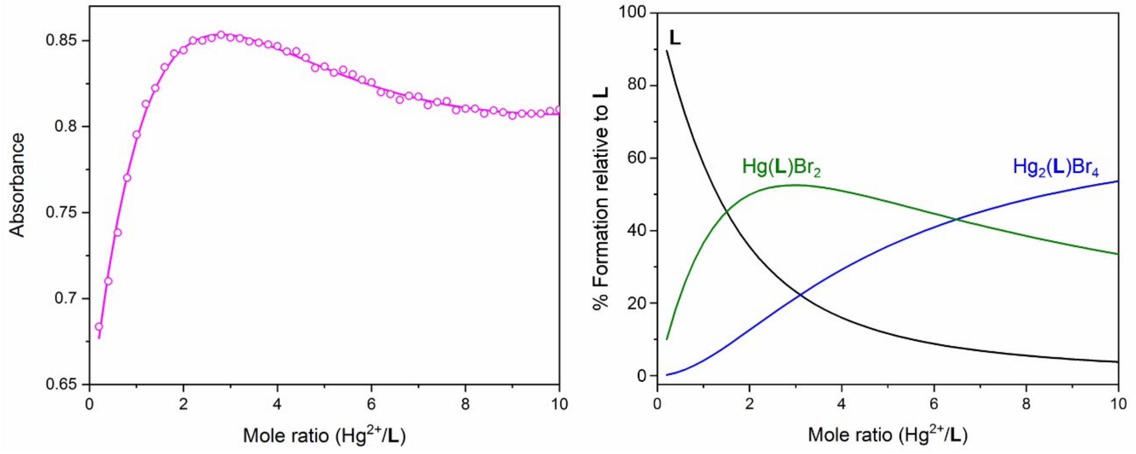
(a)


Data at 295.2
Point 5 titre .02
Intensity
% formation relative to A
$Hg_2(L)Br_4$
$Hg(L)Br_2$
$HgBr_2$
L
Obs-Calc intensity (unweighted)
point number
wavelength
ignored
value

(b)

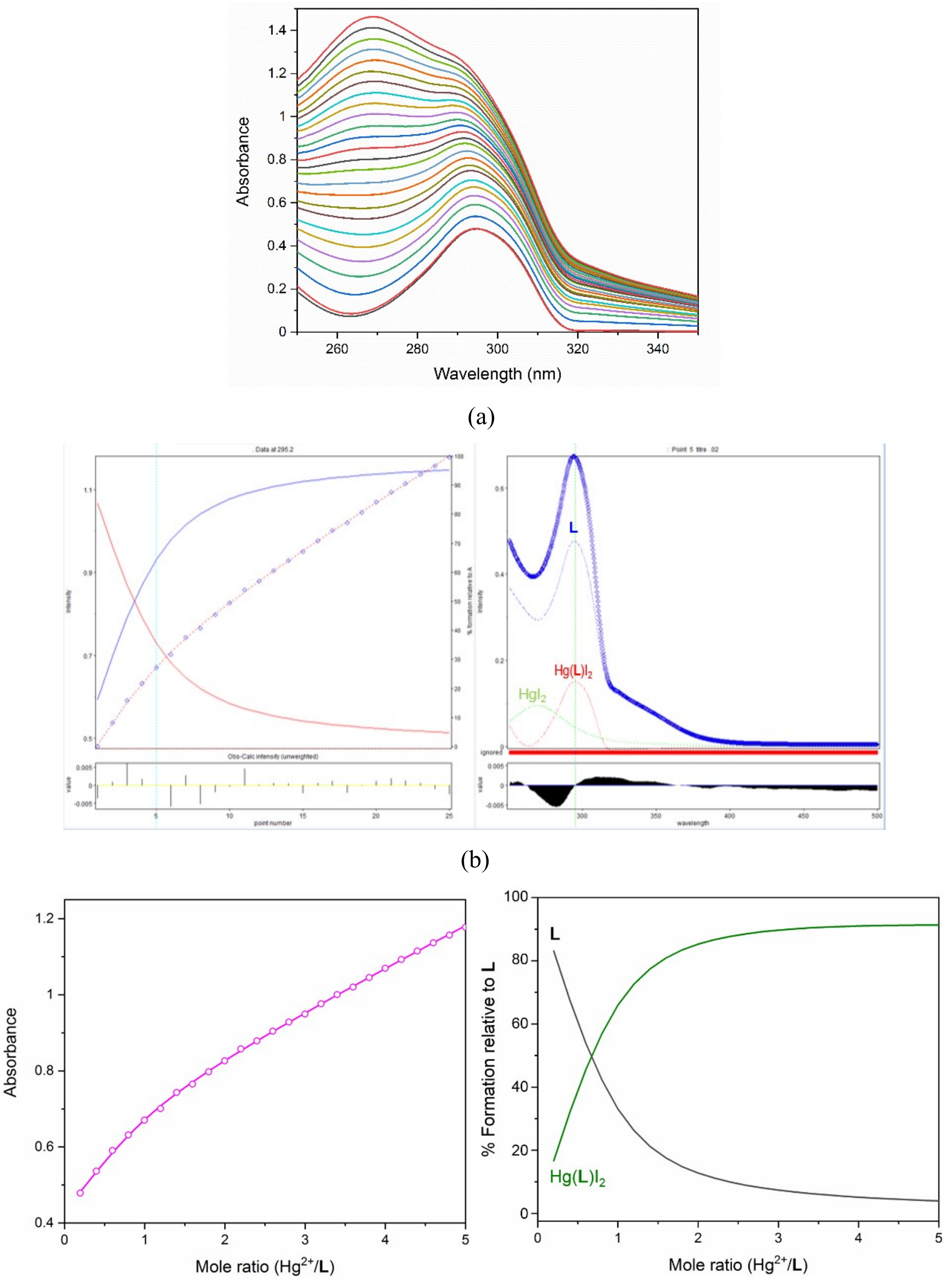

Data at 295.2
Point 10 titre .04
Intensity
% formation relative to A
$Hg_2(L)Br_4$
$HgBr_2$
$Hg(L)Br_2$
L
Obs-Calc intensity (unweighted)
point number
wavelength
ignored
value

(c)



(d) (e)

Fig. S9 (a) UV−vis titration of **L** (0.04 mM) with $HgBr_2$ (0-10.0 equiv.) in $CHCl_3/CH_3OH$ (1:2.5 *v*/*v*), (b) HypSpec^{S5} output for the fitting of UV-vis titration data (input data: 250-500 nm) to determine the formation constants by employing the 1:1 and 2:1 (M-to-**L**) binding models [variables: 1.0 equiv. (left), 295.2 nm (right)], (c) [variables: 2.0 equiv. (left), 295.2 nm (right)], (d) modified plot (mole ratio vs Abs. at 295.2 nm) for the fitting data (circle: experimental points, solid line: theoretical fit) and (e) modified plot (mole ratio vs fraction%) for the species distribution showing free **L** (black), 1:1 complex (Hg(**L**)Br_2, green), and 2:1 complex (Hg_2(**L**)Br_4, blue).



(a)

(b)

(c) (d)

Fig. S10 (a) UV-vis titration of **L** (0.04 mM) with HgI_2 (0-5.0 equiv.) in $CHCl_3/CH_3OH$ (1:2.5 *v*/*v*), (b) HypSpec[S5] output for the fitting of UV-vis titration data (input data: 250-500 nm) to determine the formation constants by employing the 1:1 (M-to-**L**) binding model [variables: 1.0 equiv. (left), 295.2 nm (right)], (c) modified plot (mole ratio vs Abs. at 295.2 nm) for the fitting data (circle: experimental points, solid line: theoretical fit) and (d) modified plot (mole ratio vs fraction%) for the species distribution showing free **L** (black), 1:1 complex (Hg(**L**)I_2, green).

References

[S1] *Bruker, APEX2 Version 2009.1-0 Data collection and Processing Software,* Bruker AXS Inc., Madison, Wisconsin, U.S.A., 2008.

[S2] *Bruker, SHELXTL-PC Version 6.22 Program for Solution and Refinement of Crystal Structures,* Bruker AXS Inc., Madison, Wisconsin, U.S.A., 2008.

[S3] E. Lee, H. Ryu, H. Ju, S. Kim, J.-E. Lee, J. H. Jung, S. Kuwahara, M. Ikeda, Y. Habata and S. S Lee, *Chem. Eur. J.*, 2019, **25**, 949-953.

[S4] A. L. Spek, PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Cryst.* 2015, **C71**, 9-18.

[S5] (a) Online at http://www.hyperquad.co.uk/HypSpec2014.htm. (b) P. Gans, A. Sabatini, A. Vacca, *Talanta* 1996, **43**, 1739-1753.