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Electronic Supplementary Information

for

Molecular botanical garden: assembly of supramolecular silver(I) and mercury(II) complexes of NS_2-donor macrocycles with flower-, leaf- and tree-shaped structures

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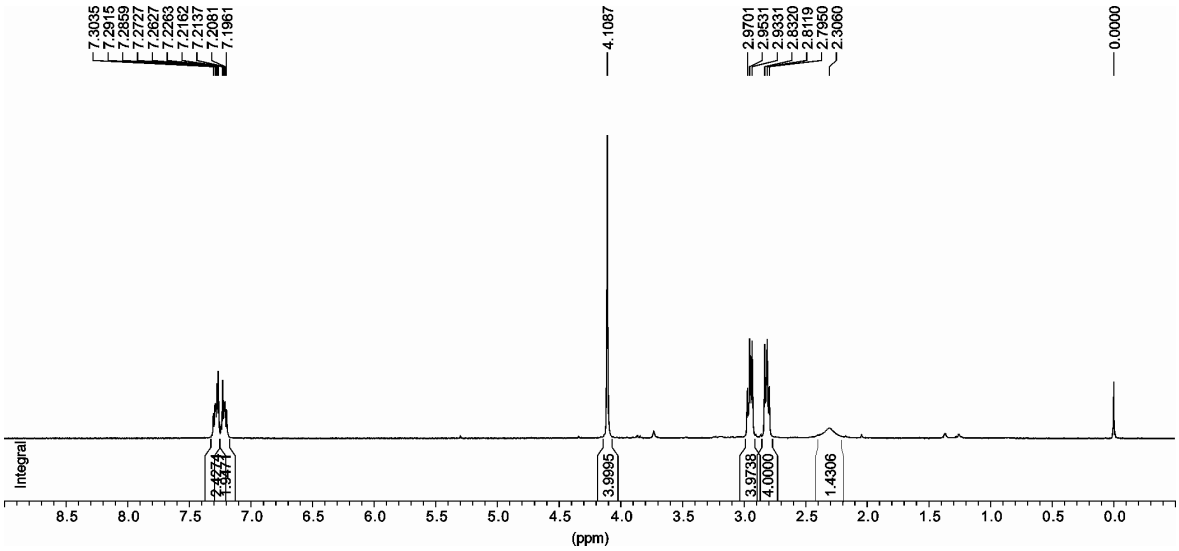


Fig. S1 ^{1}H NMR spectrum of $\mathbf{L^1}$ in $CDCl_3$.

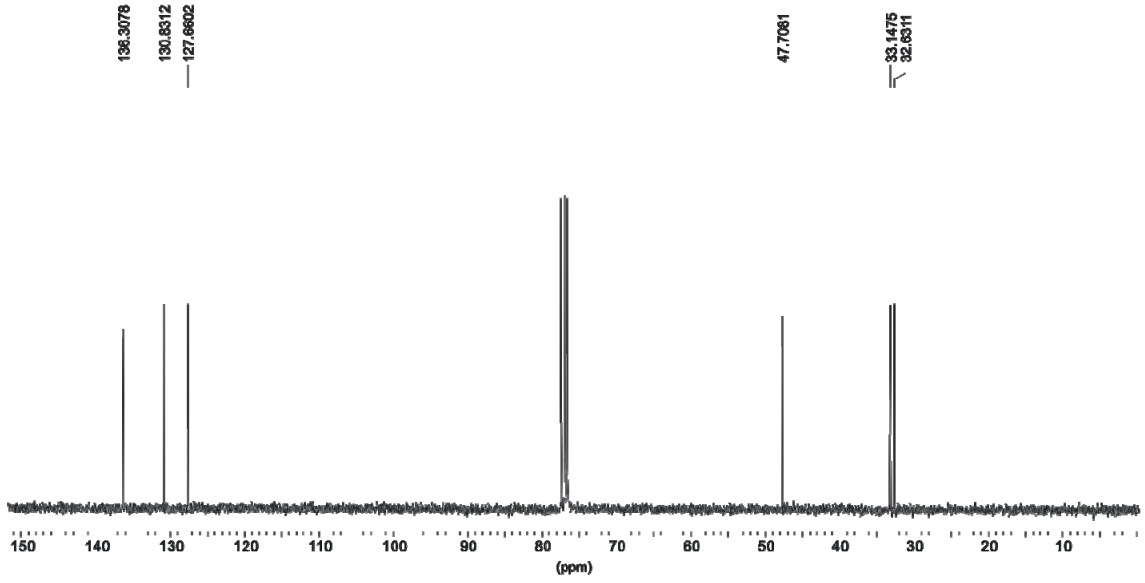


Fig. S2 ^{13}C NMR spectrum of $\mathbf{L^1}$ in $CDCl_3$.

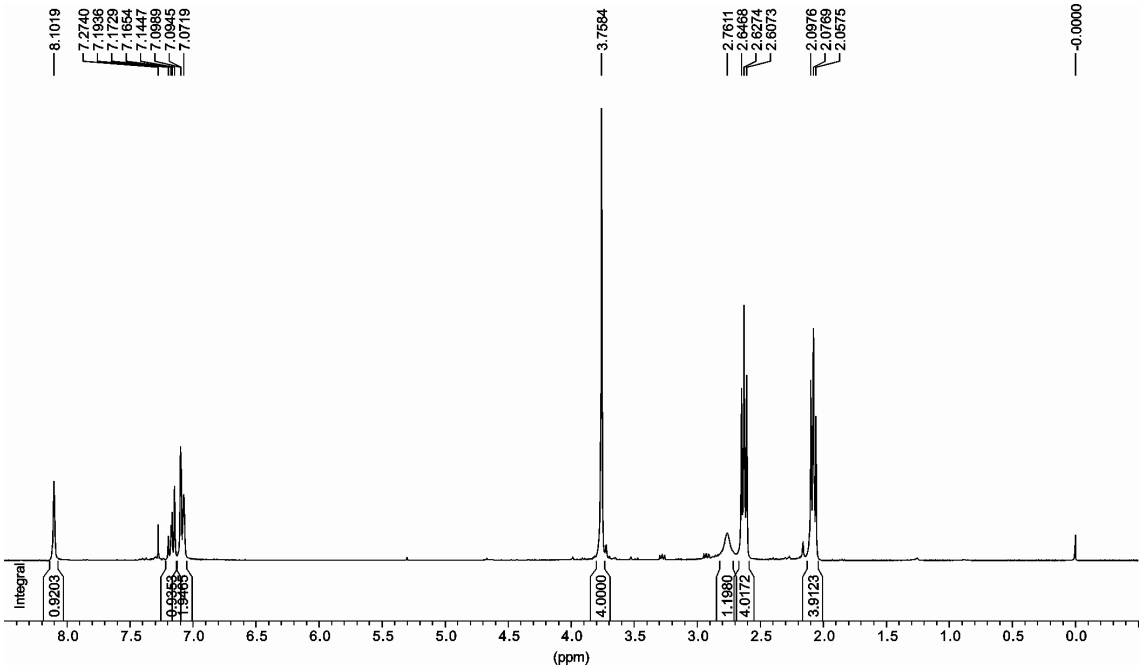


Fig. S3 ^{1}H NMR spectrum of $\mathbf{L^2}$ in $CDCl_3$.

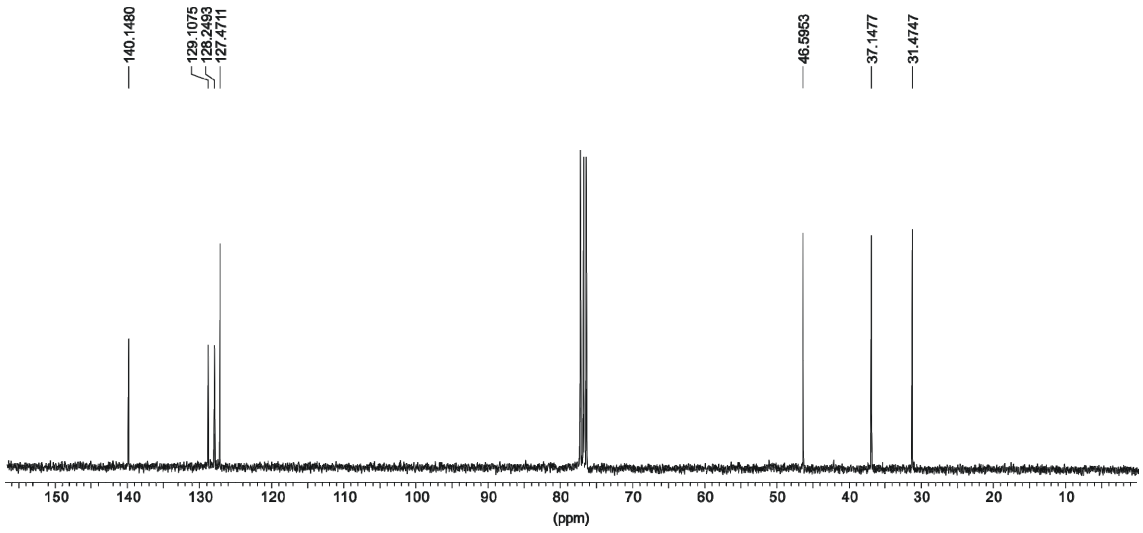


Fig. S4 ^{13}C NMR spectrum of $\mathbf{L^2}$ in $CDCl_3$.

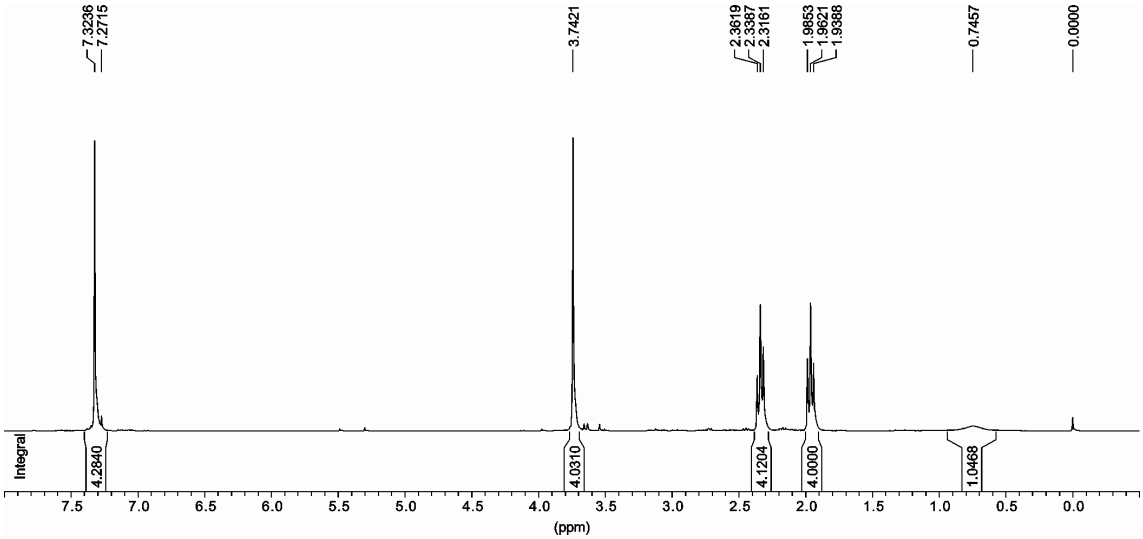


Fig. S5 ^{1}H NMR spectrum of $\mathbf{L^3}$ in $CDCl_3$.

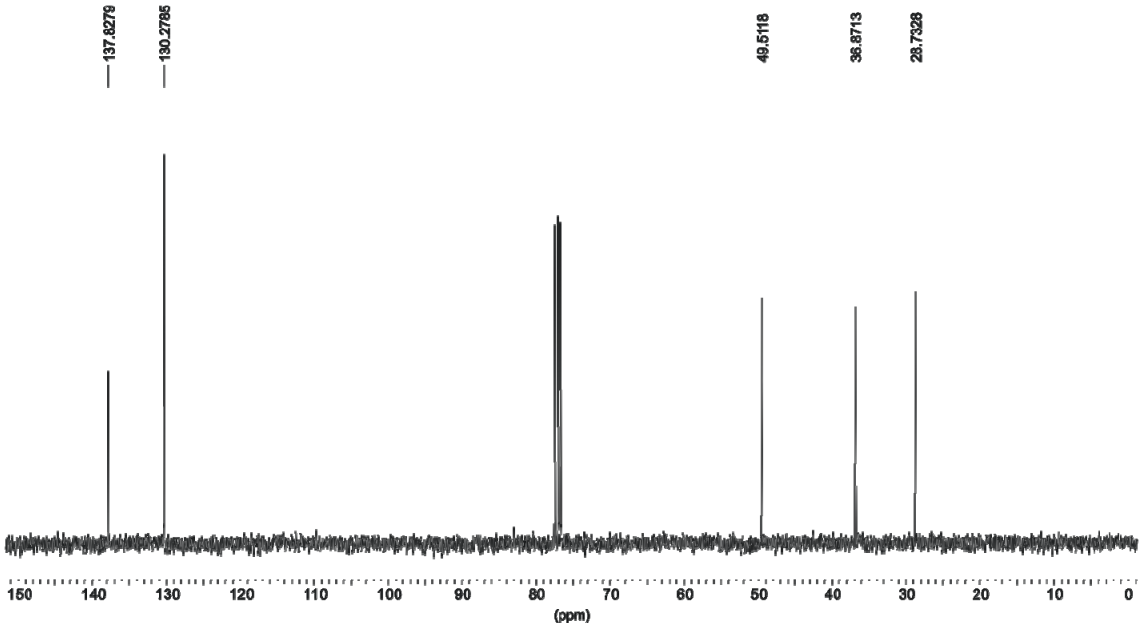


Fig. S6 ^{13}C NMR spectrum of $\mathbf{L^3}$ in $CDCl_3$.

$[Ag_6(\mathbf{L^1})_6(PF_6)](PF_6)_5$ (**1**). Layering a methanol (3 mL) of $AgPF_6$ (15.9 mg, 0.06 mmol) onto a dichloromethane solution (2 mL) of $\mathbf{L^1}$ (15.2 mg, 0.06 mmol) afforded colourless crystalline **1** suitable for X-ray analysis. M.p. 169.5 ºC (decomp.). IR (KBr, cm^{-1}): 3336, 2933, 1662, 1456, 1105, 841 (PF_6^-), 775, 557. Anal. Calc. for $C_{72}H_{102}Ag_6F_{36}N_6P_6S_{12}$: C, 29.28; H, 3.48; N, 2.85. Found: C, 28.93; H, 3.26; N, 3.19%.

$[Ag_3(\mathbf{L^2})_4](PF_6)_3 \cdot C_6H_5CH_3$ (**2**). Complex **2** was obtained after adding a small amount of toluene to the top layer of dichloromethane solution of $\mathbf{L^2}$ (15.2 mg, 0.06 mmol) then layering this with a methanol (3 mL) of $AgPF_6$ (15.9 mg, 0.06 mmol), allowing the three phase system to stand. M.p 198.6 ºC (decomp.). IR (KBr, cm^{-1}): 3305, 1552, 1425, 1380, 1108, 837 (PF_6^-), 713. ESI-MS: *m*/*z* 426.1 $[Ag_3(\mathbf{L^2})_4]^{3+}$.

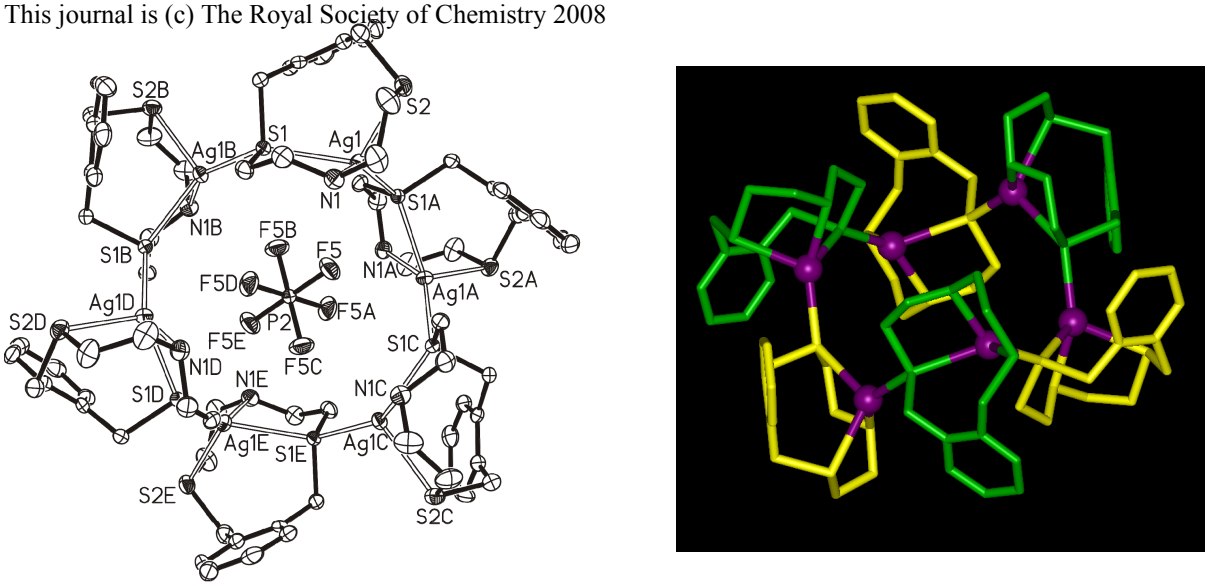
$[Hg_2(\mathbf{L^2})Br_4]_n$ (**3a**). To the stirring solution of $\mathbf{L^2}$ (20.2 mg, 0.08 mmol) in dichloromethane was added to $HgBr_2$ (29.2 mg, 0.08 mmol) in methanol afforded colourless precipitate. After the filtration, the vapor diffusion of diethyl ether to DMSO solution gave rise to crystalline product, affording colourless single crystals. M.p. 185.1 ºC (decomp.), IR (KBr, cm^{-1}): 3191, 2358, 1686, 1518, 1410, 1301, 1218, 1047, 952, 712, 455. Anal. Calc. for $C_{12}H_{17}Br_4Hg_2NS_2$: C, 15.01; H, 1.78; N, 1.46. Found: C, 15.38; H, 2.08; N, 1.83%.

$[Hg_2(\mathbf{L^2})I_4]_n$ (**3b**). To the stirring solution of $\mathbf{L^2}$ (20.2 mg, 0.08 mmol) in dichloromethane was added to HgI_2 (36.3 mg, 0.08 mmol) in methanol afforded colourless precipitate. After the filtration, the vapor diffusion of diethyl ether to DMSO solution gave rise to crystalline product, affording colourless single crystals. M.p. 203.2 ºC (decomp.). IR (KBr, cm^{-1}): 3177, 2361, 1684, 1520, 1408, 1215, 1136, 1043, 947, 708, 455. Anal. Calc. for $C_{12}H_{17}I_4Hg_2NS_2$: C, 12.55; H, 1.49; N, 1.22; S, 5.59. Found: C, 12.93; H, 1.52; N, 1.49; S, 5.76%.

$[Hg_2(\mathbf{L^3})Br_4]_n$ (**4**). Layering a methanol (3 mL) of HgI_2 (28.6 mg, 0.06 mmol) onto a dichloromethane solution (2 mL) of $\mathbf{L^3}$ (15.2 mg, 0.06 mmol) afforded pale yellow-coloured crystalline **4** suitable for X-ray analysis. M.p. 152.6 ºC (decomp.). IR (KBr, cm^{-1}): 3259, 2912, 1503, 1437, 1408, 1093, 825, 738. Anal. Calc. for $C_{12}H_{17}Br_4Hg_2NS_2$: C, 15.01; H, 1.78; N, 1.46. Found: C, 14.94; H, 2.03; N, 1.66%.

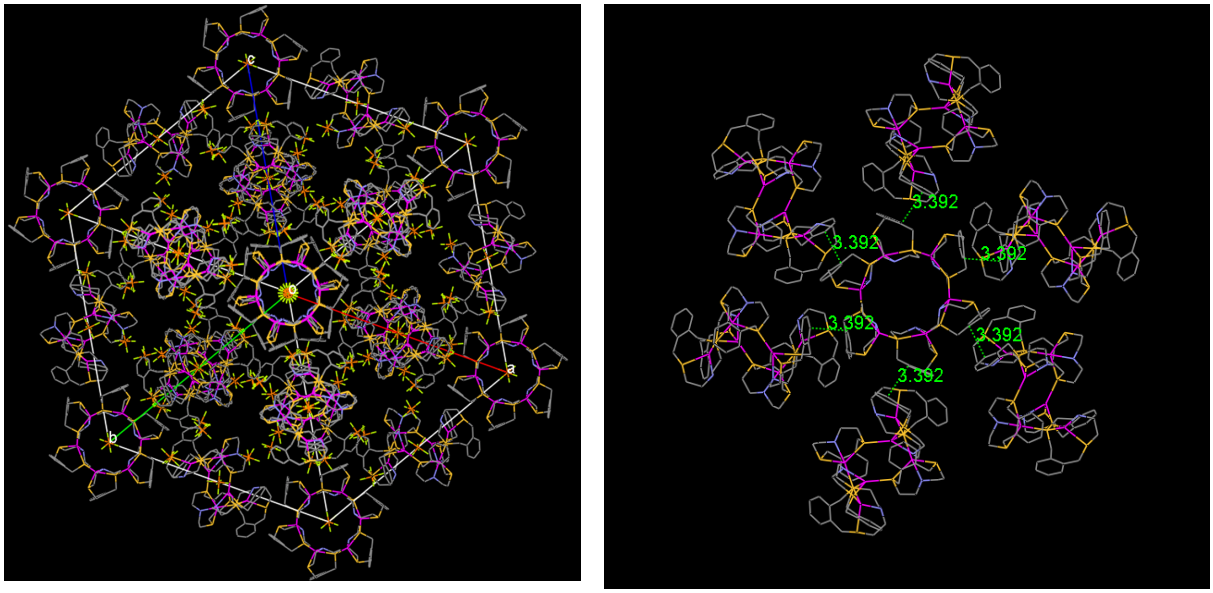
Table S1 Crystal and experimental data

	1	**2**	**3a**	**3b**	**4**
Formula	$C_{72}H_{102}Ag_6F_{36}N_6P_6S_{12}$	$C_{55}H_{76}Ag_3F_{18}N_4P_3S_8$	$C_{12}H_{17}Br_4Hg_2NS_2$	$C_{12}H_{17}Hg_2I_4NS_2$	$C_{12}H_{17}Br_4Hg_2NS_2$
Formula weight	2953.36	1808.20	960.21	1148.17	960.21
Temperature (K)	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	Cubic	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Ia*-3*d*	*P*1	*Pbca*	*Pbca*	$P2_1/c$
Z	16	1	8	8	4
a (Å)	36.322(3)	11.4605(5)	18.2813(8)	18.9518(19)	13.5645(11)
b (Å)	36.322(3)	11.6121(6)	8.1124(4)	8.5212(9)	11.9094(10)
c (Å)	36.322(3)	13.1785(6)	26.4524(12)	27.755(3)	12.4053(10)
α (°)	90	90.294(1)	90	90	90
β (°)	90	99.549(1)	90	90	104.114(2)
γ (°)	90	94.075(1)	90	90	90
V (Å^3)	47921(8)	1724.87(14)	3923.0(3)	4482.2(8)	1943.5(3)
D_x (g/cm^3)	1.637	1.741	3.251	3.403	3.282
$2\theta_{max}$ (°)	56.92	54	56.56	54	53
R	0.0433	0.0535	0.0463	0.0427	0.0778
wR	0.1194	0.1340	0.1018	0.1084	0.1129
GOF	1.112	1.049	1.016	1.118	1.002
No. of reflection used [>2σ(*I*)]	5010 [R_{int} = 0.1461]	8741 [R_{int} = 0.0118]	4740 [R_{int} = 0.1028]	4888 [R_{int} = 0.0589]	3943 [R_{int} = 0.0857]
Diffractometer	Bruker SMART CCD	Bruker SMART CCD	Bruker SMART CCD	Bruker SMART CCD	Bruker SMART CCD
Structure determination	SHELXTL	SHELXTL	SHELXTL	SHELXTL	SHELXTL
Refinement	full-matrix	full-matrix	full-matrix	full-matrix	full-matrix



(a) (b)

Fig. S7 Molecular structure of **1**, $[Ag_6(\mathbf{L}^1)_6(PF_6)](PF_6)_5$: (a) top view (Ortep) and (b) general view (ball-and-stick, the anion at the centre was removed). Thermal ellipsoids are drawn at the 30% probability level. Symmetry operations: (A) $1/2 - x, 1/2 + y, z$, (B) $-1/2 + x, y, 1/2 - z$, (C) $1/2 - x, -y, 1/2 + z$, (D) $-1/2 + x, 1/2 - y, -z$, (E) $1 - x, -y, -z$.



(a) (b)

Fig. S8 (a) Packing diagram and (b) the π-π stacking interactions (dashed lines) of **1**, $[Ag_6(\mathbf{L}^1)_6(PF_6)](PF_6)_5$.

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

Ag1-N1	2.338(3)	S1-Ag1B	2.452(1)
Ag1-S1A	2.452(1)	Ag1-S2	2.613(1)
Ag1-S1	2.614(1)		
N1-Ag1-S1A	144.2(1)	N1-Ag1-S1	79.8(1)
S1A-Ag1-S1	117.6(1)	N1-Ag1-S2	80.0(1)
S1A-Ag1-S2	116.8(1)	S1-Ag1-S2	110.9(1)
Ag1B-S1-Ag1	137.0(1)		

Symmetry Code: (A) $1/2 - x, 1/2 + y, z$, (B) $-1/2 + x, y, 1/2 - z$.

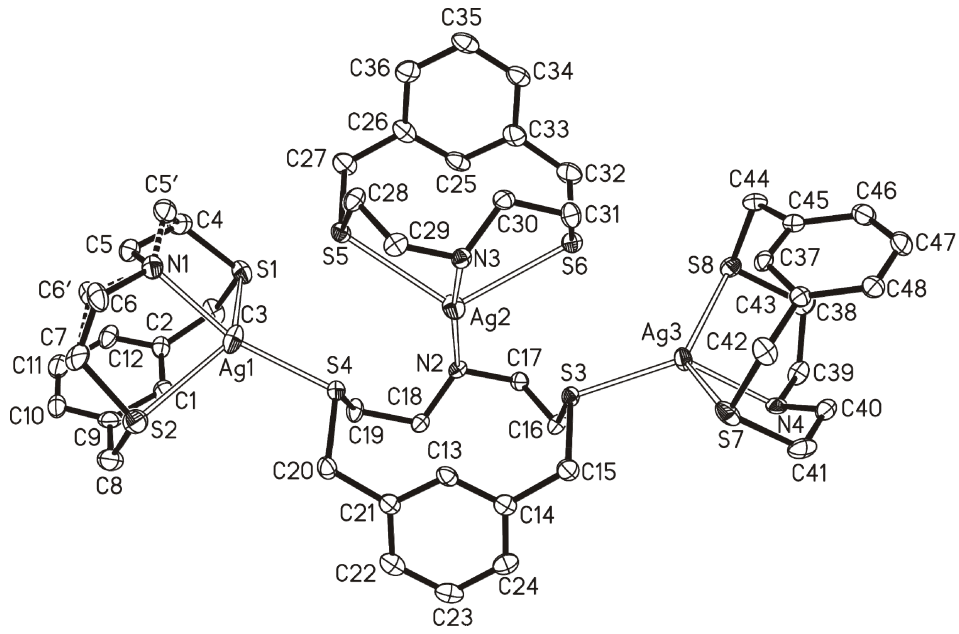


Fig. S9 Molecular structure of **2**, $[Ag_3(\mathbf{L}^2)_4](PF_6)_3 \cdot C_6H_5CH_3$. Hydrogen atoms, noncoordinating anions and solvent are omitted. Thermal ellipsoids are drawn at the 30% probability level.

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

Ag1-N1	2.315(8)	Ag1-S4	2.486(2)
Ag1-S1	2.761(2)	Ag1-S2	2.773(2)
Ag2-N2	2.269(6)	Ag2-N3	2.280(6)
Ag2-S5	2.900(2)	Ag2-S6	2.928(2)
Ag3-N4	2.352(7)	Ag3-S3	2.516(2)
Ag3-S8	2.669(2)	Ag3-S7	2.708(2)
N1-Ag1-S4	156.2(2)	S4-Ag1-S1	108.2(1)
N1-Ag1-S1	80.2(2)	N1-Ag1-S2	79.8 (2)
S4-Ag1-S2	109.4(1)	S1-Ag1-S2	127.6(1)
N2-Ag2-N3	166.3(2)	N2-Ag2-S5	114.3(2)
N3-Ag2-S5	77.2(2)	N2-Ag2-S6	101.0(2)
N3-Ag2-S6	78.5(2)	S5-Ag2-S6	118.1(1)
N4-Ag3-S3	132.2(2)	N4-Ag3-S8	79.8(2)
S3-Ag3-S8	127.8(1)	N4-Ag3-S7	80.0(2)
S3-Ag3-S7	100.1(1)	S8-Ag3-S7	129.0(1)

$[Ag_3(\mathbf{L}^2)_4]^{3+}$ (calc. 425.7)

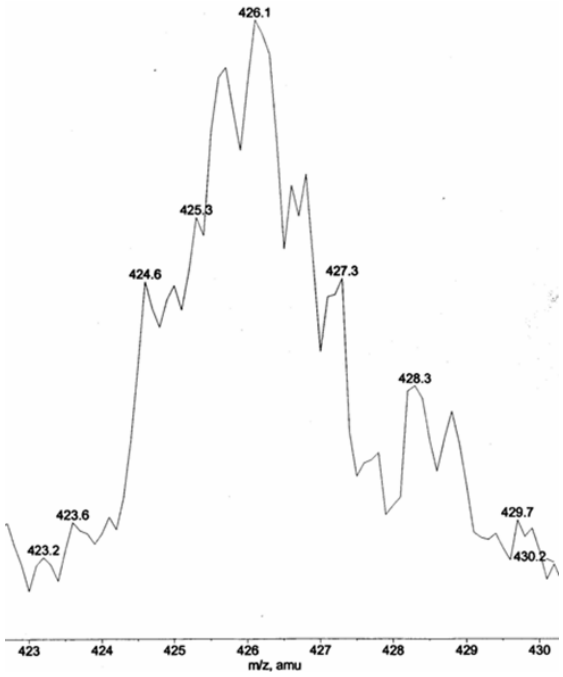


Fig. S10 Partial ESI-mass spectrum of **2** showing the existence of $[Ag_3(\mathbf{L}^2)_4]^{3+}$ species.

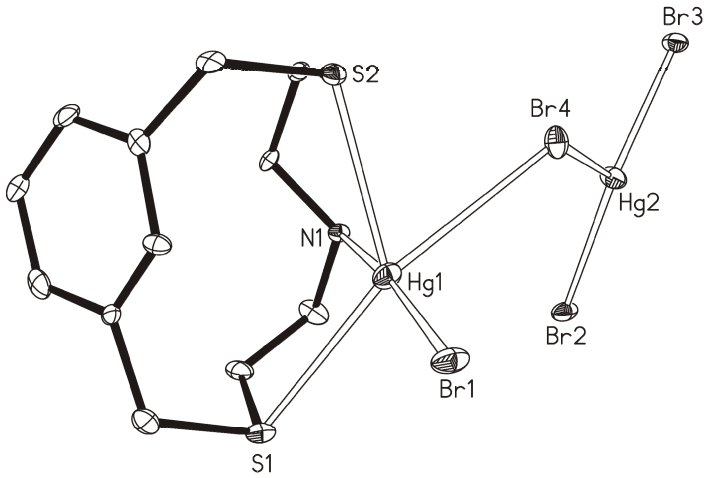


Fig. S11 Asymmetric unit of **3a**, $[Hg_2(\mathbf{L}^2)Br_4]_n$. Hydrogen atoms are omitted. Thermal ellipsoids are drawn at the 30% probability level.

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

Hg1-N1	2.198(8)	Hg1-S2	2.864(3)
Hg1-Br1	2.439(1)	Hg1-S1	2.928(3)
Hg2-Br2	2.527(1)	Hg2-Br3	2.541(1)
Hg2-Br4	2.600(1)	Br2-Hg2B	2.978(1)
Hg2-Br2A	2.978(1)		
N1-Hg1-Br1	170.8(2)	Br1-Hg1-S2	109.3(1)
N1-Hg1-S2	79.8(2)	N1-Hg1-S1	78.6(2)
Br1-Hg1-S1	94.2(1)	S2-Hg1-S1	127.6(1)
Br2-Hg2-Br3	131.8(1)	Br2-Hg2-Br4	118.3(1)
Br3-Hg2-Br4	107.9(1)	Br2-Hg2-Br2A	94.6(1)
Br3-Hg2-Br2A	89.6(1)	Br4-Hg2-Br2B	100.6(1)
Hg2-Br2-Hg2B	99.6(1)		

Symmetry Code: (A) - *x* -1/2, *y* + 1/2, *z*, (B) - *x* - 1/2, *y* - 1/2, *z*.

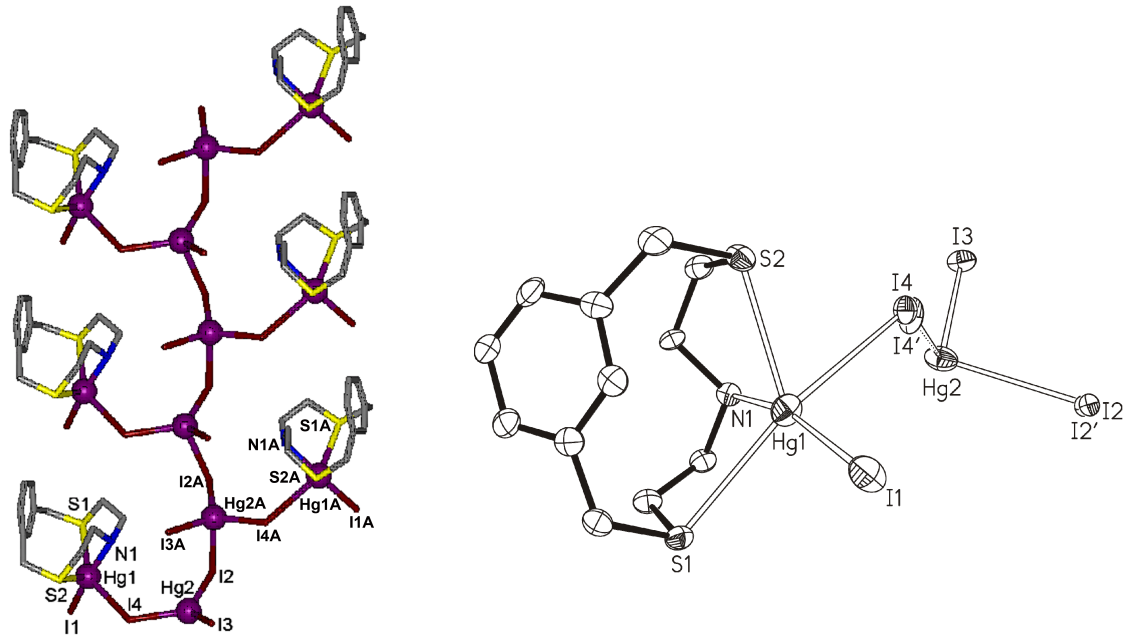
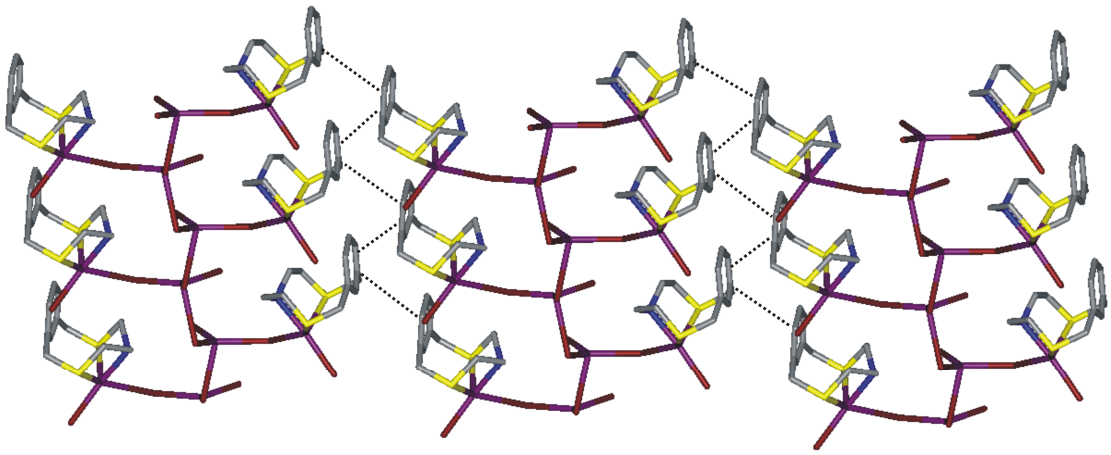


Fig. S12 (a) Leaf-shaped infinite 1D structure and (b) asymmetric unit of **3b**, $[Hg_2(\mathbf{L}^2)I_4]_n$. Thermal ellipsoids are drawn at the 30% probability level. Symmetry operations: (A) - *x* - 1/2, *y* + 1/2, *z*.

Table S5 Selected bond lengths (Å) and bond angles (º) for **3b**

Hg1-N1	2.224(9)	Hg1-I1	2.6003(11)
Hg1-S2	2.855(3)	Hg1-S1	3.012(3)
Hg2-I3	2.7029(10)	Hg2-I2A	2.716(15)
Hg2-I4	2.709(16)	Hg2-I2	3.147(15)
I2-Hg2B	2.716(15)		
N1-Hg1-I1	162.7(2)	N1-Hg1-S2	79.6(2)
I1-Hg1-S2	117.73(8)	N1-Hg1-S1	76.3(2)
I1-Hg1-S1	92.22(7)	S2-Hg1-S1	123.09(9)
I3-Hg2-I2A	120.9(3)	I3-Hg2-I4	111.6(3)
I2A-Hg2-I4	122.7(3)	I3-Hg2-I2	98.9(3)
I2A-Hg2-I2	97.6(3)	I4-Hg2-I2	99.9(4)
Hg2B-I2-Hg2	98.5(4)		

Symmetry Code: (A) - *x* - 1/2, *y* + 1/2, *z*, (B) - *x* -1/2, *y* - 1/2, *z*.



(a)

(b)

Fig. S13 (a) Packing diagram, showing π-π stacking interactions (dashed lines) and (b) projection of the 1D chain for **3**, $[Hg_2(\mathbf{L}^2)X_4]_n$ (**3a**: X = Br and **3b**: X = I) along the a-axis.

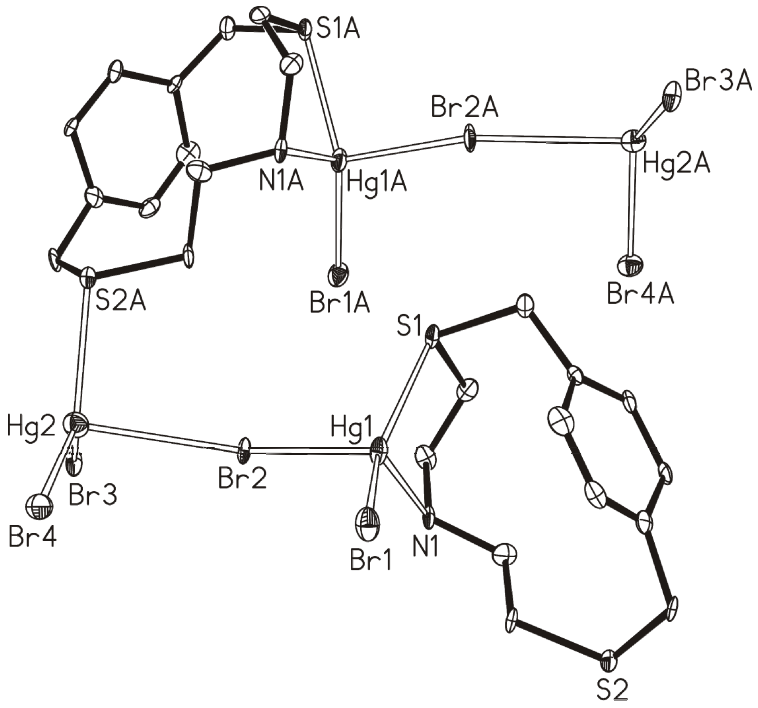


Fig. S14 Coordination environment of **4**, $[Hg_2(\mathbf{L}^3)Br_4]_n$. Thermal ellipsoids are drawn at the 30% probability level. Thermal ellipsoids are drawn at the 30% probability level. Symmetry operations: (A) - *x* + 2, *y* + 1/2, - *z* + 1/2.

Table S6 Selected bond lengths (Å) and bond angles (º) for **4**

Hg1-N1	2.393(15)	Hg1-Br1	2.494(2)
Hg1-S1	2.524(4)	Hg1-Br2	2.687(2)
Hg2-Br4	2.483(2)	Hg2-Br3	2.557(2)
Hg2-S2A	2.601(4)	Hg2-Br2	2.997(2)
S2-Hg2B	2.601(4)		
N1-Hg1-Br1	119.0(3)	N1-Hg1-S1	83.8(4)
Br1-Hg1-S1	144.4(1)	N1-Hg1-Br2	88.0(3)
Br1-Hg1-Br2	110.3(1)	S1-Hg1-Br2	96.6 (1)
Br4-Hg2-Br3	127.3(1)	Br4-Hg2-S2A	123.2(1)
Br3-Hg2-S2A	108.0(1)	Br4-Hg2-Br2	94.0(1)
Br3-Hg2-Br2	93.9(1)	S2A-Hg2-Br2	94.5(1)
Hg1-Br2-Hg2	149.0(1)		

Symmetry Code: (A) - *x* + 2, *y* + 1/2, - *z* + 1/2, (B) - *x* + 2, *y* - 1/2, - *z* + 1/2.