Supporting Information

For

Ligand- and Anion-Directed Supramolecular Assembly of Exo-Coordinated Mercury(II) Halide Complexes with O_2S_2-Donor Macrocycles

So Young Lee, Sunhong Park, Hyun Jee Kim, Jong Hwa Jung* and Shim Sung Lee*

Department of Chemistry and Research Institute of Natural Sciences, Gyeongsang National University, Jinju 660-701, Korea

Experimental

Synthesis and characterization of $\mathbf{L^2}$:

Cesium carbonate (12.00 g, 36.8 mmol) was dissolved in DMF (1000 mL) in a 3-liter round-bottom flask. 1,3-Propanedithiol (1.33 g, 12.4 mmol) and dichloride[S1] (4.0 g, 12.3 mmol) was dissolved in DMF (30 mL) and this solution added to a 50-mL glass syringe. Under a nitrogen atmosphere, the contents of the syringe was added dropwise (a rate of 0.6 mL h^{-1}) into a DMF solution of Cs_2CO_3 at 45-50 °C for 50 h. The reaction mixture was rapidly stirred for a further 10 h, allowed to cool to room temperature, then filtered. The filtrate was evaporated and the residue was partitioned between water and dichloromethane. The aqueous phase was separated and extracted with two further portions of dichloromethane. The combined organic phases were dried with anhydrous sodium sulfate and then evaporated to dryness. The flash column chromatography (SiO_2; *n*-hexane-ethyl acetate 9.5:0.5) afforded the product as a white solid in 38% yield. M.p. 82-84 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.89-7.26 (*m*, 8 H, Ar), 4.31 (*t*, *J* = 5.8 Hz, 4 H, ArOCH_2), 3.73 (*s*, 4 H, ArCH_2S), 2.32 (*t*, *J* = 5.8 Hz, 4 H, OCH_2CH$_2$), 2.29 (*t*, *J* = 7.2Hz, 4 H, SCH_2CH$_2$), 1.35 (*q*, *J* = 7.2 Hz, 2 H, SCH$_2$CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) 157.01, 131.33, 128.68, 127.70, 121.22, 112.68, 64.46, 30.96, 30.73, 30.22, 29.40; IR (KBr disk) 2909.97, 2339.51, 1665.30, 1602.47, 1514.79, 1467.94, 1426.78, 1396.21, 1298.53 cm^{-1}; Mass spectrum *m/z* 360 (M, 65 %), 286 (4), 254 (100), 253 (3), 226 (2), 212 (6), 195 (5), 162 (5), 147 (80), 133 (30), 107 (54), 91 (82), 78 (40),77 (20), 65(5), Anal. Calcd for $C_{20}H_{24}O_2S_2$: C, 66.63; H, 6.71; S, 17.79. Found: C, 66.38; H, 6.73; S, 17.66.

References

S1. Atkinson, I. M.; Lindoy, L. F.; Matthews, O. A.; Meehan, G. V.; Sobolev, A. N.; White, A. H. *Aust. J. Chem.* **1994**, *47*, 1155.

Analytical data of 1, $[Hg_2(\mathbf{L^1})_2Cl_4]$. M.p. 138-140 °C. IR (KBr disk) 3002.96, 2929.67, 1598.88, 1585.38, 1488.94, 1452.30, 1404.08, 1290.29, 1228.57, 1190.00, 1164.92, 1103.21, 1070.42, 1051.13, 923.84, 827.41, 771.47, 748.33, 673.11 cm^{-1}; $[Hg_2(\mathbf{L^1})_2Cl_4]$: Anal. Calcd: C, 36.19; H, 3.74; S, 10.51; Found: C, 35.80; H, 3.34; S, 10.62%.

Analytical data of 2, $[Hg(\mathbf{L^1})I_2]$. M.p. 157-159 °C. IR (KBr disk) 2925.81, 1593.09, 1583.45, 1488.94, 1446.51, 1404.08, 1192.22, 1245.93, 1226.64, 1184.21, 1107.06, 1064.63, 927.70, 829.33, 783.05, 757.97, 682.75 cm^{-1}; $[Hg(\mathbf{L^1})I_2]$: Anal. Calcd: C, 27.87; H, 2.59; S, 8.19; Found: C, 27.48; H, 2.56; S, 8.15%. Mass spectrum *m/z* (ESI) 661.8 $[Hg(\mathbf{L^1})I_2\text{-}I]^+$.

Analytical data of 3, $[Hg(\mathbf{L^2})Cl_2]_n$. M.p. 271-274 °C. IR (KBr disk) 2924.23, 1598.88, 1490.87, 1253.64, 1238.21, 1105.14, 1053.06, 752.19 cm^{-1}; $[Hg(\mathbf{L^2})Cl_2]_n$: Anal. Calcd: C, 38.25; H, 4.20; S, 10.15; Found: C, 38.01; H, 3.83; S, 10.15%.

Analytical data of 4a, $[Hg(\mathbf{L^2})Br_2]_n$. M.p. 160-163 °C. IR (KBr disk) 2915.01, 1596.95, 1488.94, 1253.64, 1234.36, 1103.21, 1049.20, 752.19 cm^{-1}; $[Hg(\mathbf{L^2})Br_2]_n$: Anal. Calcd: C, 33.51; H, 3.71; S, 8.94; Found: C, 33.32; H, 3.36; S, 8.89%.

Analytical data of 4b, $[Hg(\mathbf{L^2})I_2]_n$. M.p 156-157 °C. IR (KBr disk) 2945.81, 1598.88, 1488.94, 1452.30, 1411.80, 1294.15, 1238.21, 1105.14, 1053.06, 1024.13, 968.20, 750.26 cm^{-1}; $[Hg(\mathbf{L^2})I_2]_n$: Anal. Calcd: C, 29.54; H, 3.17; S, 7.94; Found: C, 29.48; H, 2.97; S, 7.87%.

Crystallographic Structure Determinations

All data were collected on a Bruker Smart diffractometer equipped with a graphite monochromated Mo Kα (λ = 0.71073 Å) radiation source and a CCD detector. The 45 frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The first 50 frames were retaken after complete data collection. The crystal showed no significant decay. The frame data were processed to give structure factors using the SAINT.[S2] The structure was solved by direct methods

and refined by full matrix least squares methods on F^2 for all data using SHELXTL software.[S3] The non-hydrogen atoms were refined anisotropically.

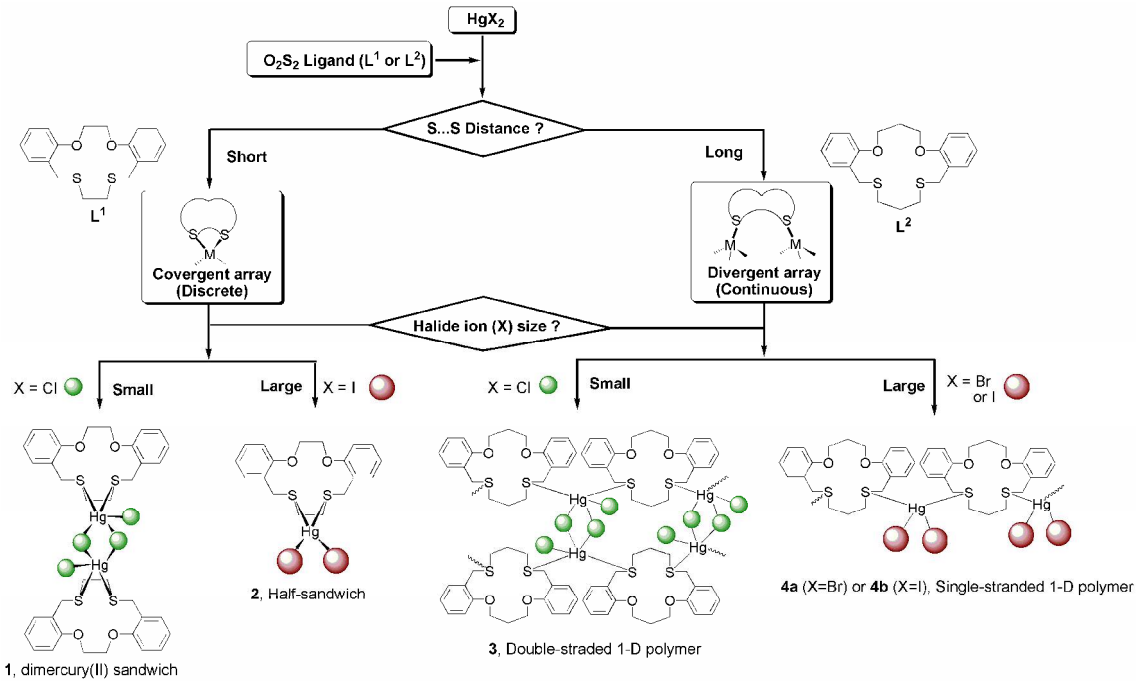
References

S2. Bruker, SMART and SAINT: *Area Detector Control and Integration Software Ver. 5.0*; Bruker Analytical X-ray Instruments: Madison, Wisconsin, 1998.

S3. Bruker, SHELXTL: *Structure Determination Programs Ver. 5.16*; Bruker Analytical X-ray Instruments: Madison, Wisconsin, 1998.

Table S1. Crystal and experimental data

	L²	**1**	**2**	**3**	**4a**	**4b**
Formula	$C_{20}H_{24}O_2S_2$	$C_{18}H_{20}Cl_2HgO_2S_2$	$C_{18}H_{20}HgI_2O_2S_2$	$C_{20}H_{24}Cl_2HgO_2S_2$	$C_{20}H_{24}Br_2HgO_2S_2$	$C_{20}H_{24}HgI_2O_2S_2$
Formula weight	360.51	603.95	786.85	632.00	720.92	814.90
Temperature	173(2) K	173(2) K	173(2) K	173(2) K	173(2) K	173(2) K
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$	P-1	Cc	Cc
Z	4	4	8	2	4	4
a (Å)	11.6616(6)	11.6016(5)	18.3775(8)	9.4924(10)	8.5707(8)	8.5589(5)
b (Å)	11.3384(6)	8.0991(4)	11.5386(5)	11.5543(13)	13.9847(14)	13.9339(7)
c (Å)	14.1323(8)	21.5623(10)	21.4632(10)	12.3437(14)	19.1698(18)	20.1922(11)
α (°)	90	90	90	107.791(2)	90	90
β (°)	96.6480(10)	97.9210(10)	106.1140(10)	98.997(2)	97.691(2)	96.6290(10)
γ (°)	90	90	90	114.183(2)	90	90
V (Å^3)	1856.06(17)	2006.72(16)	4372.5(3)	1112.5(2)	2277.0(4)	2392.0(2)
D_x (g/cm^3)	1.290	1.999	2.391	1.887	2.103	2.263
$2\theta_{max}$ (°)	55.00	55.00	55.00	54.00	56.58	54.00
R	0.0337	0.0222	0.0533	0.0488	0.0385	0.0173
wR	0.0831	0.0527	0.0955	0.1264	0.0685	0.0406
No. of reflection used [$>2\sigma(I)$]	4207 [R_{int} = 0.0476]	4502 [R_{int} = 0.0280]	4936 [R_{int} = 0.0531]	4640 [R_{int} = 0.0335]	3781 [R_{int} = 0.0591]	4510 [R_{int} = 0.0191]
Diffractometer	Bruker SMART CCD system	Bruker SMART CCD system	Bruker SMART CCD system	Bruker SMART CCD system	Bruker SMART CCD system	Bruker SMART CCD system
Structure determination	SHELXTL	SHELXTL	SHELXTL	SHELXTL	SHELXTL	SHELXTL
Refinement	full-matrix	full-matrix	full-matrix	full-matrix	full-matrix	full-matrix



Scheme S1. Ligand- and anion-directed assembly of exo-coordinated mercury(II) halide complexes with O_2S_2-donor macrocycles

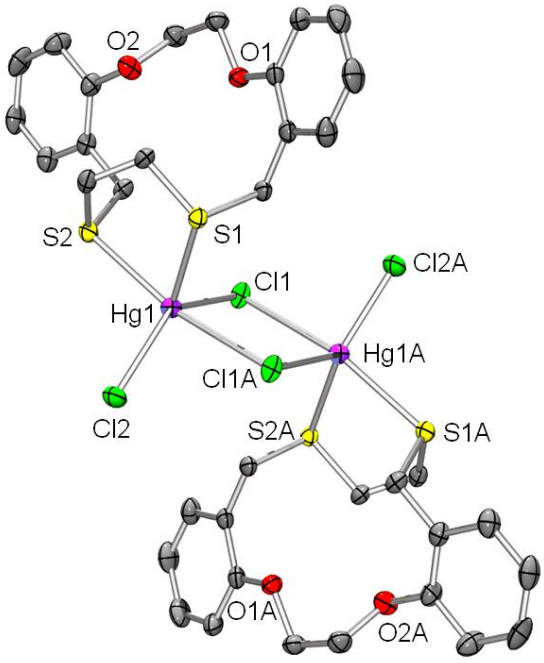


Figure S1. Dimercury(II) sandwich structure of **1**, $[Hg_2(\mathbf{L^1})_2Cl_4]$. Hydrogen atoms are omitted. Selected bond distances (Å) and bond angles (°): Hg(1)-Cl(1) 2.5216(8), Hg(1)-Cl(2) 2.3671(9), Hg(1)-S(2) 2.7197(8), Hg(1)-S(1) 2.5611(8), Hg(1)-Cl(1)A 3.0320(8). S(2)-Hg(1)-S(1) 83.69(2), Cl(2)-Hg(1)-Cl(1) 119.47(3), Cl(2)-Hg(1)-S(1) 137.02(3), Cl(1)-Hg(1)-S(2) 100.59(3), Hg(1)-Cl(1)-Hg(1)A 95.02(2), S(2)-Hg(1)-Cl(1)A 164.32 (2), Cl(2)-Hg(1)-Cl(1)A 92.56 (3), [symmetry operations: (A) 2 - *x*, - *y*,- *z*].

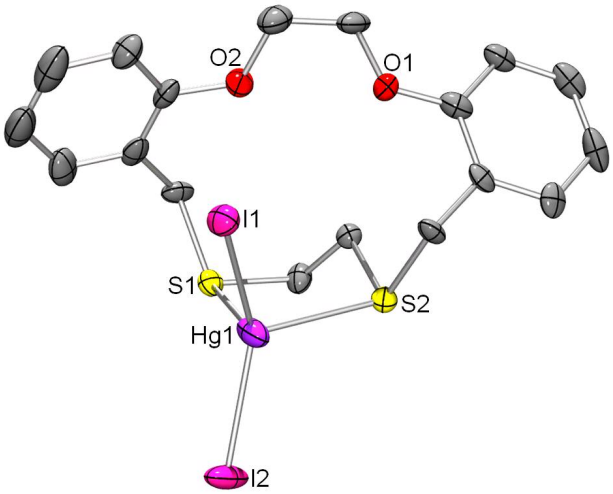


Figure S2. Half-sandwich structure of **2**, [Hg(**L**^{1})I_2]. Hydrogen atoms are omitted. Selected bond distances (Å) and bond angles (°): Hg(1)-I(1) 2.6434(7), Hg(1)-I(2) 2.6589(8), Hg(1)-S(1) 2.924(2), Hg(1)-S(2) 2.690(2). I(1)-Hg(1)-I(2) 145.87(3), I(1)-Hg(1)-S(2) 107.71(5), I(2)-Hg(1)-S(2) 103.37(5), I(1)-Hg(1)-S(1) 112.58(5), I(2)-Hg(1)-S(1) 86.08(5), S(2)-Hg(1)-S(1) 80.21(6).

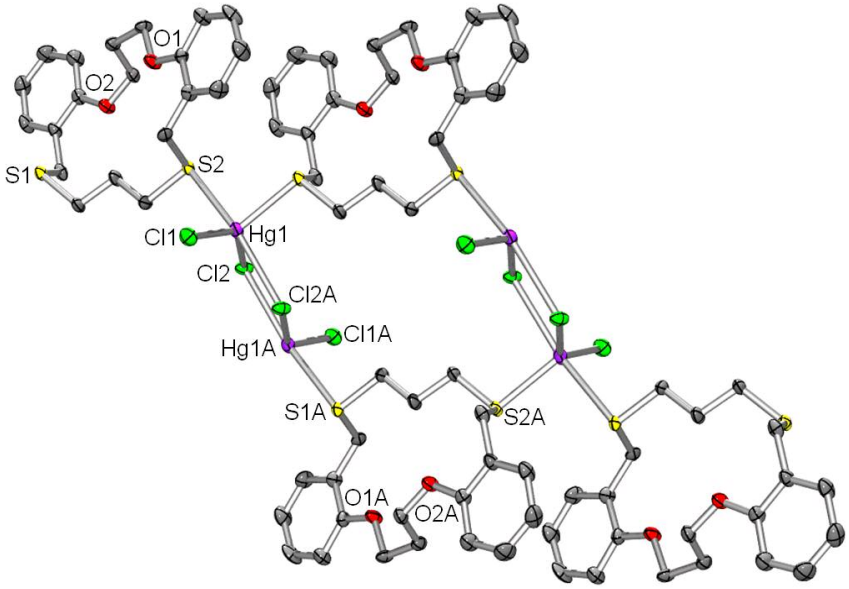


Figure S3. Double-stranded 1-D polymeric structure of **3**, $[Hg(\mathbf{L}^{2})Cl_2]_n$. Hydrogen atoms are omitted. Selected bond distances (Å) and bond angles (°): Hg(1)-Cl(1) 2.393(2), Hg(1)-Cl(2) 2.474(2), Hg(1)-S(2) 2.8694(19), Hg(1)-Cl(2)A 2.9653(19), Cl(2)-Hg(1)A 2.9653(19). Cl(1)-Hg(1)-Cl(2) 133.81(7), Cl(1)-Hg(1)-S(2) 94.23(7), Cl(2)-Hg(1)-S(2) 86.69(6), Cl(1)-Hg(1)-Cl(2)A 88.39(7), Cl(2)-Hg(1)-Cl(2)A 83.84(6), S(2)-Hg(1)-Cl(2)A 169.04(5), Hg(1)-Cl(2)-Hg(1)A 96.16(6). [symmetry operations: (A) - *x* - 1,- *y* + 1,- *z*].

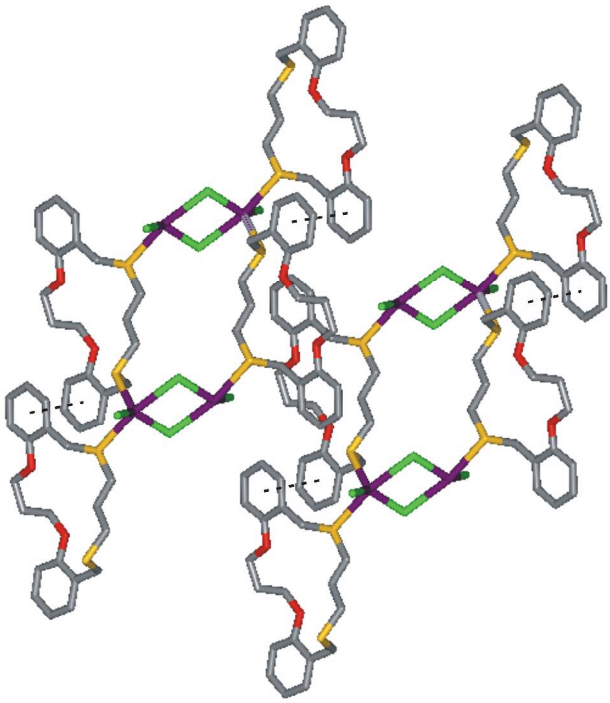


Figure S4. Packing diagram of **3** showing π-π stacking interactions (dashed lines, 4.352 Å and 5.86°).

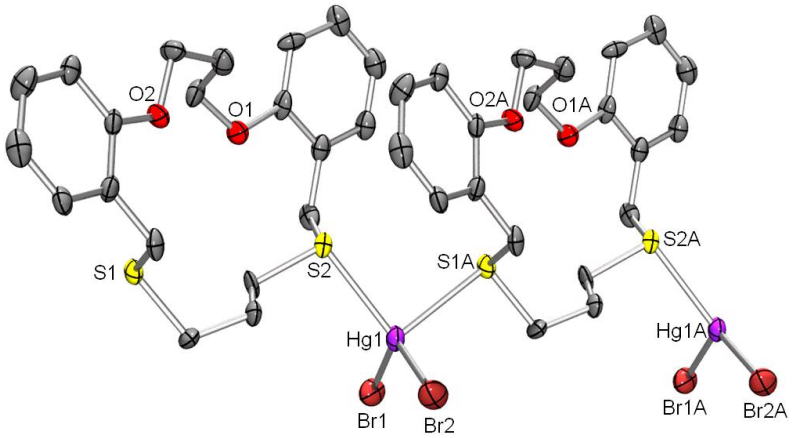


Figure S5. Single-stranded 1-D polymeric structure of **4a**, $[Hg(\mathbf{L^2})Br_2]_n$. Hydrogen atoms are omitted. Selected bond distances (Å) and bond angles (°): Hg(1)-Br(1) 2.5452(14), Hg(1)-Br(2) 2.5093(13), Hg(1)-S(1)A 2.679(3) Hg(1)-S(2) 2.574(2). Br(2)-Hg(1)-Br(1) 125.06(4), Br(2)-Hg(1)-S(2) 113.78(7), Br(1)-Hg(1)-S(2) 111.67(7), Br(2)-Hg(1)-S(1)A 103.31(7), Br(1)-Hg(1)-S(1)A 101.31(7), S(2)-Hg(1)-S(1)A 95.55(8), [symmetry operations: (A) *x* - 1, *y*, *z*].

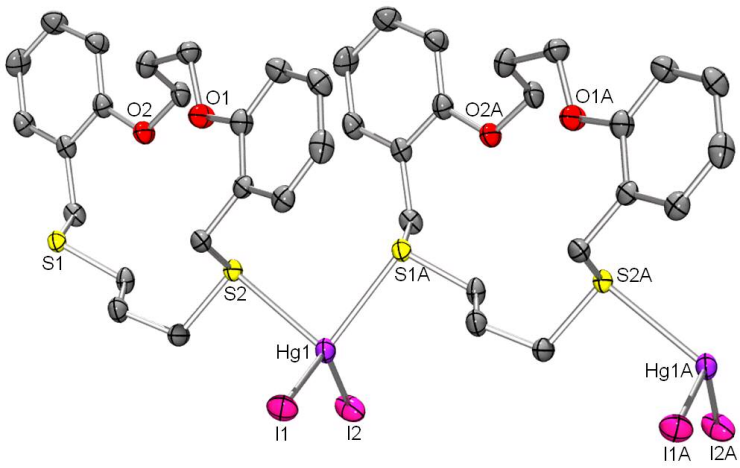


Figure S6. Single-stranded 1-D polymeric structures of **4b**, $[Hg(\mathbf{L}^2)I_2]_n$. Hydrogen atoms are omitted. Selected bond distances (Å) and bond angles (°): Hg(1)-S(2) 2.6206(10), Hg(1)-S(1)A 2.7185(10), Hg(1)-I(1) 2.6898(4), Hg(1)-I(2) 2.6665(3). S(2)-Hg(1)-I(2) 114.84(2), S(2)-Hg(1)-I(1) 109.62(2), I(2)-Hg(1)-I(1) 127.853(14), S(2)-Hg(1)-S(1)A 91.99(3), I(2)-Hg(1)-S(1)A 104.06(2), I(1)-Hg(1)-S(1)A 100.15(2), [symmetry operations: (A) *x* - 1, *y*, *z*].