Electronic supplementary information

for

Benzothiazole-coupled NS_4-donor macrocycle and its complexation-based dual-channel sensing for Hg^{2+}: the influence of anions and structure-function relationship

Yelim Lee, Joon Rae Kim, Eunji Lee*

Department of Chemistry, Gangneung-Wonju National University, Gangneung 25457, South Korea

Experimental

Synthesis of 2. The compound **2** was prepared via the modified procedure of the reported method in the literature[S1]. To a stirred solution of $POCl_3$ (5.14 mL, 55.2 mmol) and DMF (1.86 mL, 22.1 mmol) in a round-bottom flask, was added *N*-Phenyldiethanolamine (2.00 g, 11.0 mmol). The mixture was stirred at 80 °C for 12 h and then the resulting solution was poured into ice water. The resulting pale-brown precipitate was collected by filtration, washed with water and diethyl ether, and dried in a vacuum oven. Yield: 75 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (*s*, 1 H, C*H*O), 7.78 (*d*, 2 H, Ar), 6.75 (*d*, 2 H, Ar), 3.85 (*t*, 4 H, N*CH*$_2$CH$_2$Cl), 3.67 (*t*, 4 H, NCH$_2$*CH*$_2$Cl). Mass spectrum: *m/z* = 246.08 $[C_{11}H_{14}Cl_2NO]^+$ (calcd 246.05).

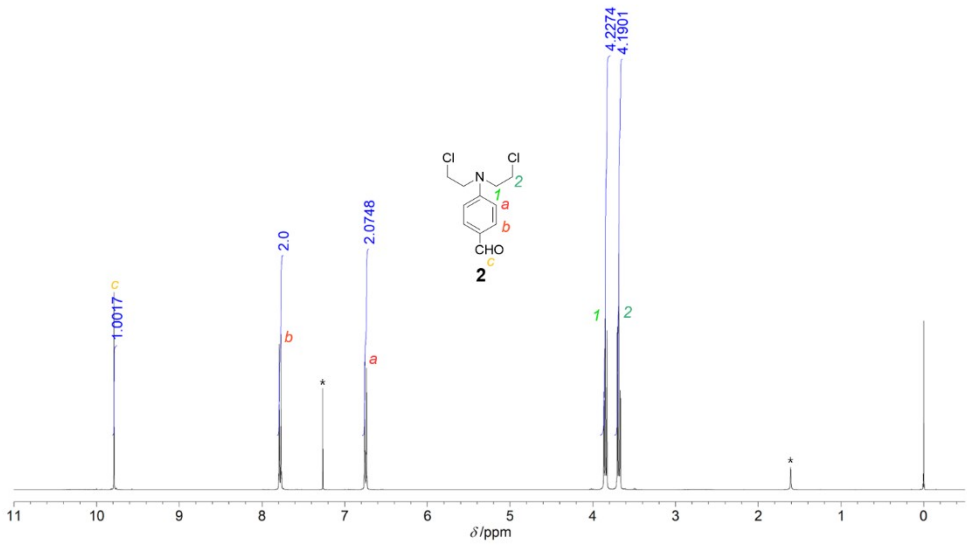
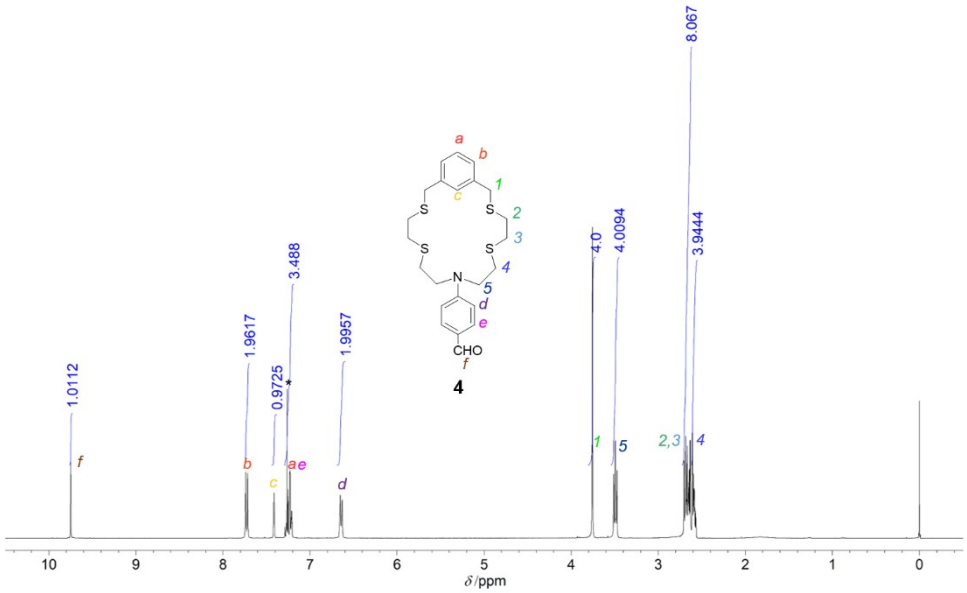
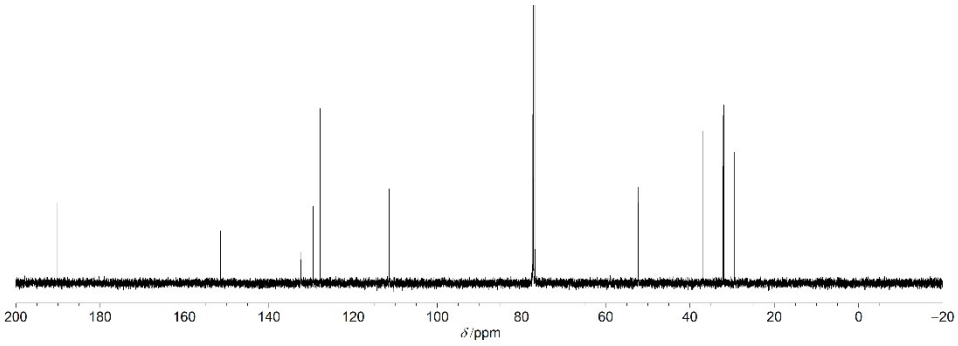


Fig. S1 ^{1}H-NMR spectra of **2** in $CDCl_3$.

Synthesis of 3. The compound **3** was prepared via the modified procedure of the reported method in the literature[S2]. Thiourea (1.09 g, 14.3 mmol) was added to a solution of *m*-xylylenebis(1-chloro-3-thiapropane)[S2] (1.04 g, 3.53 mmol) in ethanol (100 mL). The reaction mixture was refluxed for 3 h, allowed to cool to room temperature, and then evaporated. 100 mL of saturated $NaHCO_3$ was added and then the mixture was refluxed a further 3 h. After cooling to room temperature, the mixture was partitioned between water and chloroform. The combined organic phases were dried with anhydrous sodium sulfate and then evaporated to dryness. Crude product a yellow oil was used for the next reaction after drying without purification.

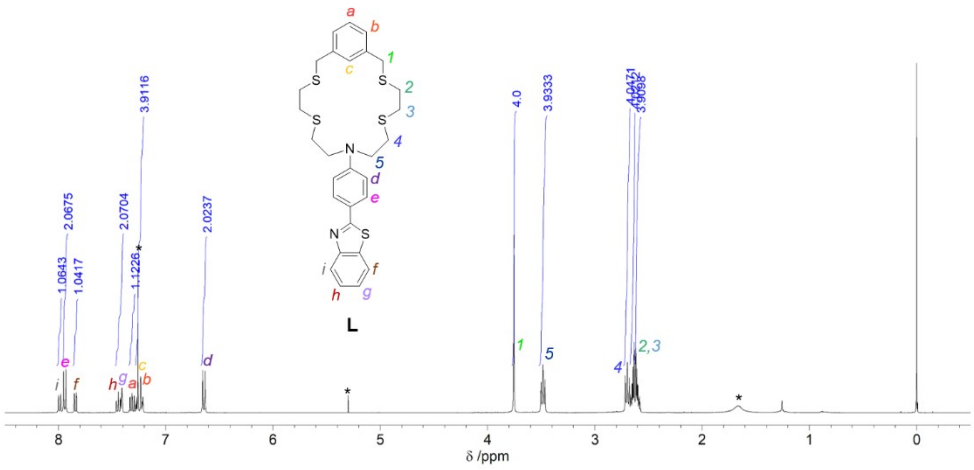


(a)

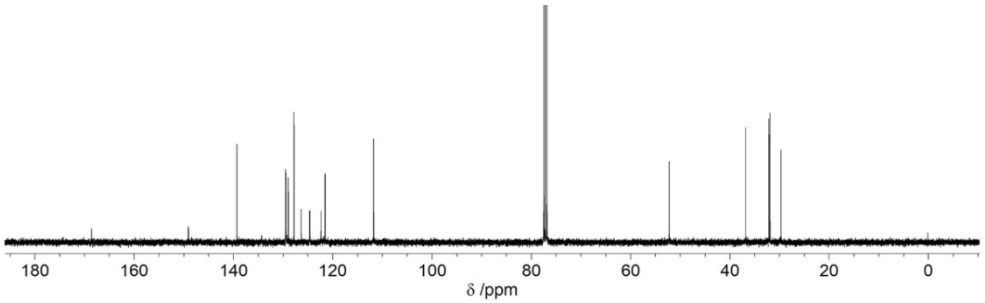


(b)

Fig. S2 (a) ^{1}H- and (b) ^{13}C-NMR spectra of **4** in $CDCl_3$.



(a)



(b)

Fig. S3 (a) ^{1}H- and (b) ^{13}C-NMR spectra of **L** in $CDCl_3$

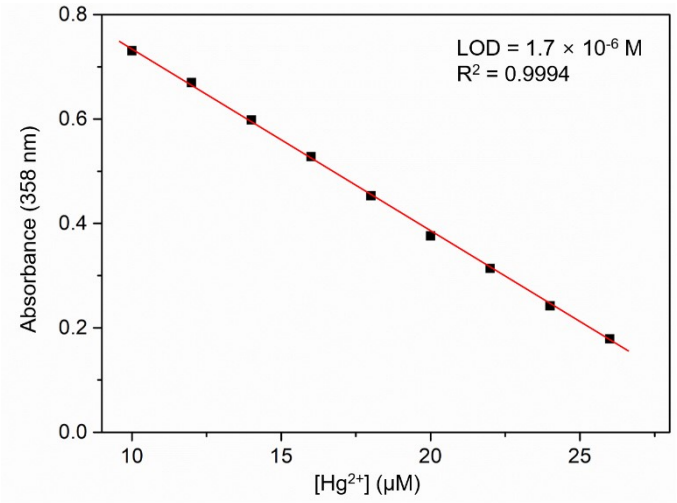
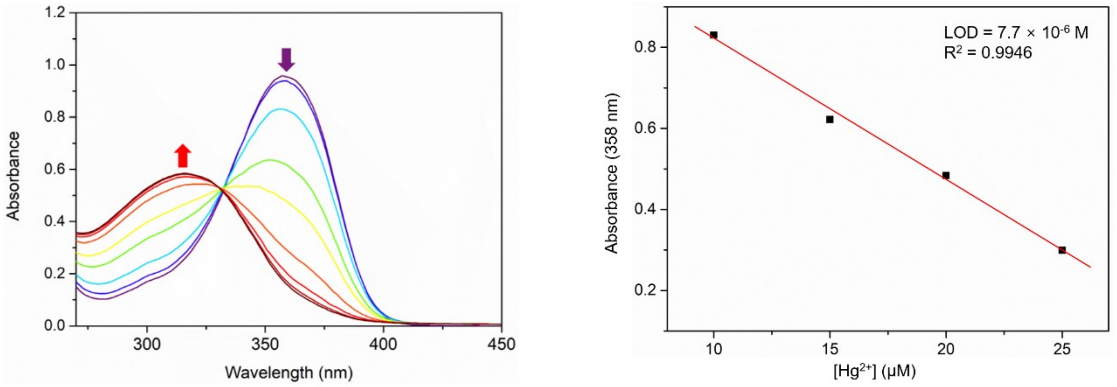
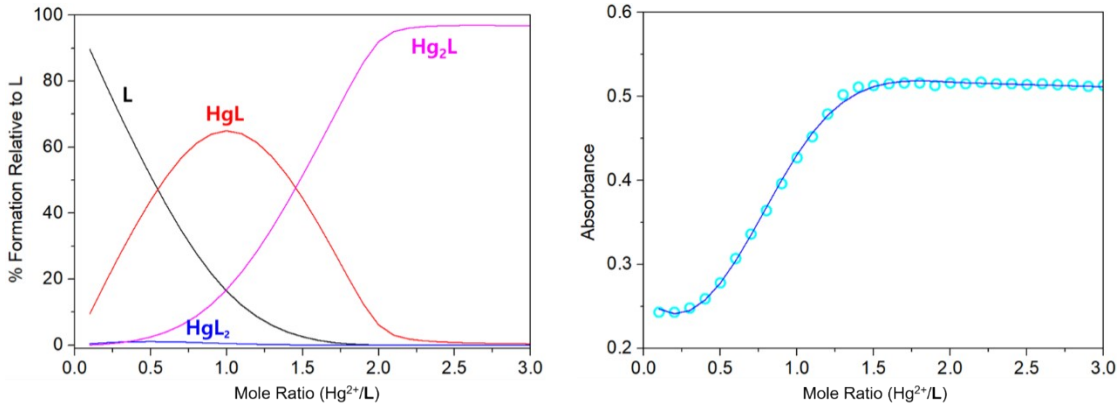


Fig. S4 Linear fitting for the $[Hg^{2+}]$ vs A from the UV-vis spectra of **L** in EtOH/DMSO (v/v, 9:1).



(a) (b)

Fig. S5 (a) UV-vis spectra of **L** (2.0×10^{-5} M) with mercury(II) perchlorate (10–25 uM) in 95%EtOH/DMSO (v/v, 9:1). (b) Linear fitting for the $[Hg^{2+}]$ vs A from the UV-vis spectra of **L** in the presence of $Hg(ClO_4)_2$.



(a) (b)

Fig. S6 Curve-fitting for UV-vis titration data to determine the stability constants for the complexations of **L** with $Hg(ClO_4)_2$ using HyperSpec software by employing the multiple binding model including 1:2, 1:1 and 2:1 (metal-to-ligand) ratios: (a) species distribution diagram and (b) HyperSpec output (○: experimental values, solid line: theoretical fit).

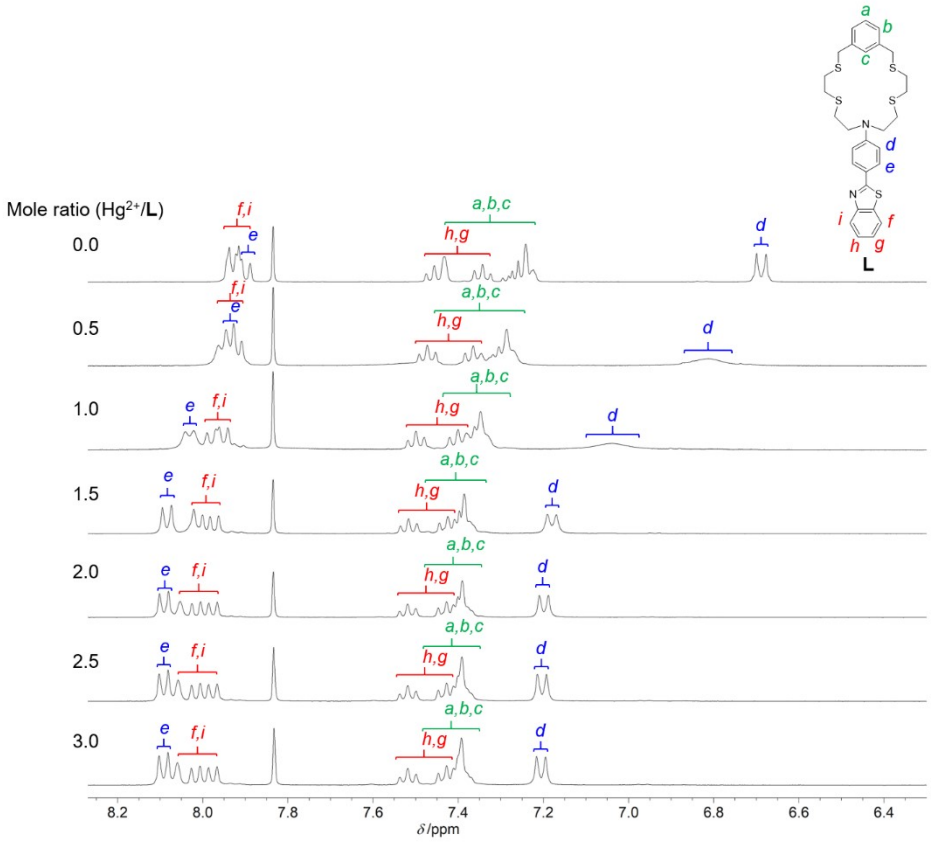


Fig. S7 Comparative NMR spectra (aromatic region) of **L** in the presence of $Hg(ClO_4)_2$ (0-2.0 equiv) in $CDCl_3$/DMSO-d_6 (v/v, 5:2).

X-ray crystallographic analysis

All data were collected on a Bruker D8 Venture PHOTON III M14 diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) generated by a rotating anode. Data collection, data reduction, and semiempirical absorption correction were carried out using the software package APEX2.[S3] All of the calculations for the structure determination were carried out using the SHELXTL package.[S4] In all cases, all nonhydrogen atoms were refined anisotropically and all hydrogen atoms were placed in idealised positions and refined isotropically in a riding manner along with their respective parent atoms. Relevant crystal data collection and refinement data for the crystal structures are summarised in Table S1. CCDC 2281697 (**L**) and 2281698 (HgI_2 complex) contain 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.

Table S1. Crystal and Experimental Data and Refinement Parameters

	L	$[Hg_2(\mathbf{L})I_4]$
Formula	$C_{29}H_{32}N_2S_5$	$C_{29}H_{32}Hg_2I_4N_2S_5$
Formula weight	568.86	1477.64
Temperature	223(2)	223(2)
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	$P2_1/n$
Z	2	4
a (Å)	9.831(5)	8.6176(2)
b (Å)	10.536(6)	19.1568(4)
c (Å)	14.817(8)	22.9808(4)
α (°)	90.682(17)	90
β (°)	91.831(15)	94.7210(10)
γ (°)	110.896(15)	90
V (Å^3)	1432.6(13)	3780.93(14)
D_{calc} (g/cm^3)	1.319	2.596
$2\theta_{max}$ (°)	52.00	52.00
Goodness-of-fit on F^2	1.032	1.038
R_1, wR_2 [$I > 2\sigma(I)$]	0.0671, 0.1895	0.0310, 0.0677
R_1, wR_2 [all data]	0.1161, 0.2291	0.0406, 0.0717
No. of reflection used [>2σ(*I*)]	7046 [R_{int} = 0.0643]	7435 [R_{int} = 0.0431]
Refinement	full-matrix	full-matrix

Table S2 Selected bond lengths (Å) and bond angles (°) for $[Hg_2(\mathbf{L})I_4]$

Hg1-I1	2.643(1)	Hg2-I3	2.610(1)
Hg1-I2	2.620(1)	Hg2-I4	2.642(1)
Hg1-S1	2.813(2)	Hg2-S3	2.886(2)
Hg1-S2	2.792(2)	Hg2-S4	2.861(2)
I1-Hg1-I2	144.3(2)	I3-Hg2-I4	154.8(2)
I2-Hg1-S2	106.4(1)	I3-Hg2-S4	98.1(1)
I1-Hg1-S2	102.5(1)	I4-Hg2-S4	101.4(1)
I2-Hg1-S1	103.5(1)	I3-Hg2-S3	112.7(1)
I1-Hg1-S1	101.8(1)	I4-Hg2-S3	87.6(1)
S1-Hg1-S2	79.7(1)	S3-Hg2-S4	76.0(1)

References

S1. J. Massin, W. Dayoub, J.-C. Mulatier, C. Aronica, Y. Bretonniere and C. Andraud, *Chem. Mater*., 2011, **23**, 862−873.

S2. J. Buter, R. M. Kellogg and F. V. Bolhuisb, *J. Chem. Soc., Chem. Commun.*, 1990, 282−284.

S3. *Bruker, APEX2 Version 2009.1-0 Data collection and Processing Software,* Bruker AXS Inc., Madison, Wisconsin, U.S.A., 2008.

S4. *Bruker, SHELXTL-PC Version 6.22 Program for Solution and Refinement of Crystal Structures,* Bruker AXS Inc., Madison, Wisconsin, U.S.A., 2008.