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## Supporting Information

### **A Chromogenic Macrocycle Exhibiting Cation-Selective and Anion-Controlled Color Change: An Approach to Understanding Structure-Color Relationships**

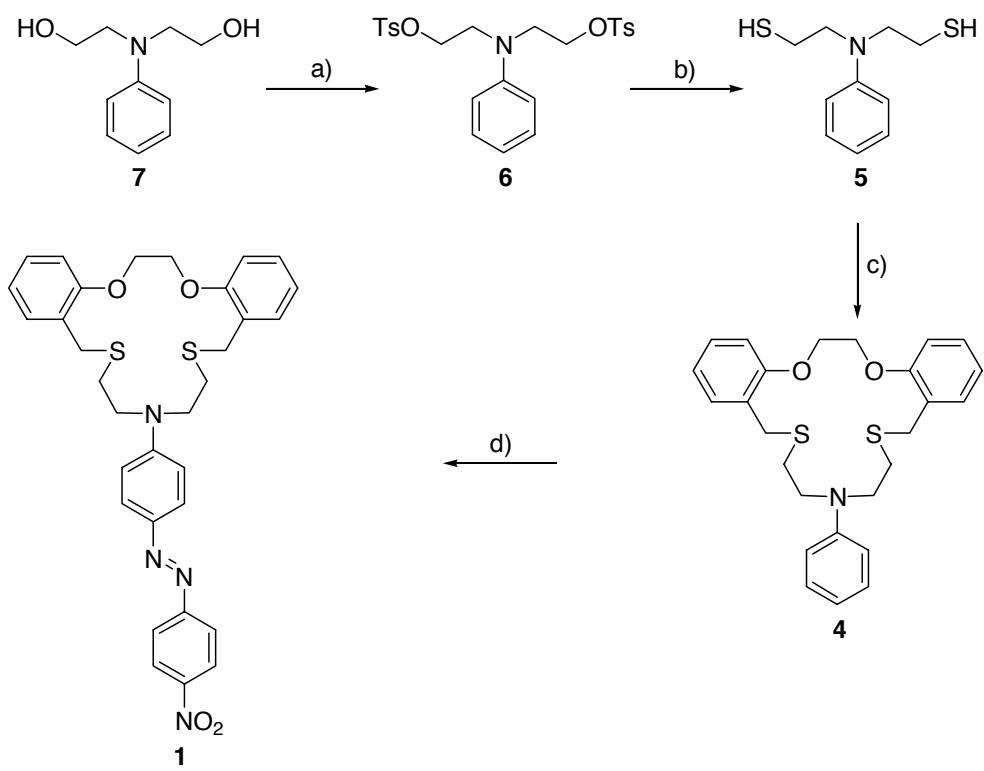
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**Scheme S1.** Synthesis of the azo-coupled macrocycle **1**: a) *p*-TsCl, pyridine, 82%; b) thiourea, NaHCO<sub>3</sub>, EtOH, H<sub>2</sub>O; c) 1,2-bis(2-(chloromethyl)phenoxy)ethane, Cs<sub>2</sub>CO<sub>3</sub>, DMF, 48%; d) diazonium salt, DMF, 88%.

To a solution of *N,N'*-phenyldiethanolamine **7** (25.0 g, 138 mmol) in dry pyridine (33 mL) at 0 °C was slowly added *para*-toluenesulfonyl chloride (31.5 mL, 333 mmol). As the reaction mixture was allowed to reach rt, the reaction became slightly exothermic. After 3 h, the clear yellow mixture was slowly poured into 500 mL of fast stirring ice-water, giving a solid. Recrystallization from ethanol/toluene yielded **6**, 2,2'-(phenylazanediyl)bis(ethane-2,1-diy)bis(4-methylbenzenesulfonate) as a colorless crystalline solid (55.21 g, 81.7%). The analysis data of **6** obtained from different route have been reported [*J. Organometal. Chem.*, **2001**, 626, 221–226].

To a solution of **6** (30.0 g, 67.2 mmol) in ethanol (100 mL), thiourea (9.32 g, 122.54 mmol) was added. The reaction mixture was refluxed for 2 h, then concentrated and saturated NaHCO<sub>3</sub> (*aq.* 60 mL) was added. The mixture was refluxed for 3 h. After cooling to rt, CHCl<sub>3</sub> (50 mL) were added, and the organic layer was separated and dried over MgSO<sub>4</sub>. Removal of the organic solvent in vacuo afforded **5**, 2,2'-(phenylazanediyl) diethanethiol as a colorless oil (87%). Due to the instability of **5**, no further purification was done.

**4** was synthesized under high dilution employing the cyclization procedure. Cesium carbonate (5.70 g, 17.50 mmol) was dissolved in DMF (1500 mL) in a 3-L round-bottom flask. **5** (4.0 g, 13.46 mmol) and 1,2-bis(2-(chloromethyl)phenoxy) ethane (10.05 g, 47.1 mmol) were dissolved in DMF (30 mL) and placed in a 50-mL glass syringe. Under a nitrogen atmosphere, the contents of the syringe were added dropwise at regular speed (a rate of 10 mL h<sup>-1</sup>) into the DMF solution by the aid of microprocessor controlled syringe pump at 45–50 °C for 5 h. The mixture was kept for a further 10 h. After cooling to rt the reaction mixture was filtered and evaporated. Water (100 mL) was added, and the mixture was extracted with 3 × 70 mL of dichloromethane. The organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was removed to give a yellow oil. Flash column chromatography (SiO<sub>2</sub>, *n*-hexane : dichloromethane /1 : 1, R<sub>f</sub>=0.3) afforded the product as a white solid in 48% yield (2.75 g). m.p. 124 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ= 7.43 (d, <sup>2</sup>J (H,H) =7.5 Hz, 2H; Ar-H), 7.23 (t, <sup>3</sup>J (H,H) = 5.5 Hz, 2H; Ar-H), 7.12 (t, <sup>3</sup>J (H,H) = 7.5 Hz, 2H; Ar-H), 6.98 (d, <sup>2</sup>J (H,H) = 5.5 Hz, 2H; Ar-H), 6.93 (t, <sup>3</sup>J (H,H) = 7.0 Hz, 2H; Ar-H), 6.62 (t, <sup>3</sup>J (H,H) = 7.0 Hz, 1H; Ar-H), 6.51 (d, <sup>2</sup>J (H,H) = 8.0 Hz, 2H; Ar-H), 4.39 (s, 4H; CH<sub>2</sub>), 3.87 (s, 4H; CH<sub>2</sub>), 3.52 (t, <sup>3</sup>J (H,H) = 7.5 Hz, 4H; CH<sub>2</sub>), 2.61 (t, <sup>3</sup>J (H,H) = 7.5 Hz, 4H; CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ= 156.4, 146.7, 130.9, 129.3, 128.3, 127.5, 121.6, 116.1, 111.9, 67.6, 51.9, 29.1, 28.6; IR (KBr): ν = 1343 cm<sup>-1</sup> (Ar-N), 1256 cm<sup>-1</sup> (C-N);

HRMS: m/z (%): 451.1639 [M<sup>+</sup>]: Cald for C<sub>26</sub>H<sub>29</sub>NO<sub>2</sub>S<sub>2</sub> 451.1640; Elemental analysis calcd (%) for C<sub>26</sub>H<sub>29</sub>NO<sub>2</sub>S<sub>2</sub>: C 69.14, H 6.47, N 3.10, S 14.20; found: C 68.92, H 5.98, N 3.03, S 13.94.

**1** was synthesized from reaction of **4** and diazonium salt. The diazonium salt of 4-nitroaniline (0.2 g, 1.44 mmol) was prepared by adding an aqueous solution of sodium nitrite (0.13 g, 1.87 mmol) dropwise into a homogeneous mixture of 0.03 mL of sulfuric acid and 1 mL of glacial acetic acid. The mixture was stirred at 0 °C for 5 min. The diazonium salt solution was added dropwise into a solution of **4** (0.50 g, 1.11 mmol) in 50 mL of DMF at 0 °C. The solution was stirred for an additional 12 h at 0 °C. CHCl<sub>3</sub> (50 mL) and water (50 mL) were added, and the organic layer was separated and dried over MgSO<sub>4</sub>. Removal of the organic solvent in vacuo afforded a red oil. Column chromatography on silica gel with *n*-hexane: dichloromethane (1:3) as eluent (*R*<sub>f</sub> = 0.18) provided **1** as a red crystalline solid in 88% yield. m.p. 150 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 8.34 (d, <sup>2</sup>J (H,H) = 9.0 Hz, 2H; Ar-H), 7.93 (d, <sup>2</sup>J (H,H) = 9.0 Hz, 2H; Ar-H), 7.83 (d, <sup>2</sup>J (H,H) = 9.0 Hz, 2H; Ar-H), 7.48 (d, <sup>2</sup>J (H,H) = 7.5 Hz, 2H; Ar-H), 7.28 (t, 2H; Ar-H), 7.05 (t, <sup>3</sup>J (H,H) = 7.5 Hz, 2H; Ar-H), 7.03 (t, <sup>3</sup>J (H,H) = 7.0 Hz, 2H; Ar-H), 6.60 (d, <sup>2</sup>J (H,H) = 9.5 Hz, 2H; Ar-H), 4.40 (s, 4H; CH<sub>2</sub>), 3.91 (s, 4H; CH<sub>2</sub>), 3.71 (t, <sup>3</sup>J (H,H) = 7.5 Hz, 4H; CH<sub>2</sub>), 2.61 (t, <sup>3</sup>J (H,H) = 7.5 Hz, 4H; CH<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C, TMS) δ = 156.8, 156.4, 150.5, 143.9, 131.0, 128.5, 127.0, 126.2, 124.7, 122.6, 121.8, 112.0, 111.6, 67.7, 52.2, 29.0, 28.2; IR (KBr): ν = 1517, 1328 cm<sup>-1</sup> (NO<sub>2</sub>), 1387 cm<sup>-1</sup> (Ar-N), 1241 cm<sup>-1</sup> (C-N); HRMS: m/z (%): 600.1868 [M<sup>+</sup>]: Cald for C<sub>32</sub>H<sub>32</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub> 600.1865; Elemental analysis calcd (%) for C<sub>32</sub>H<sub>32</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>: C 63.98, H 5.37, N 9.33, S 10.67; found: C 64.01, H 5.06, N 9.04, S 10.62.

Pale-yellow complex **2**, [Hg(**1**)ClO<sub>4</sub>](ClO<sub>4</sub>) was prepared as following. Benzene (1 mL) was layered above dichloromathane solution (3 mL) of **1** (25 mg, 41.6 mmol) and then methanol solution (3 mL) of Hg(ClO<sub>4</sub>)<sub>2</sub> (14.3 mg, 41.6 mmol) was layered on the benzene. On standing for a week at rt the pale-yellow crystals of **2** suitable for X-ray analysis was afforded.

Red-colored complex **3**, [Hg(**1**)I<sub>2</sub>]<sub>2</sub> was prepared as following. A methanol solution (3 mL) of HgI<sub>2</sub> (18.9mg, 41.6mmol) was layered above dichloromathane solution (3 mL) of **1** (25 mg, 41.6 mmol). On standing for a week at rt the red crystals of **3** suitable for X-ray analysis was afforded.

## Crystallographic Structure Determinations

All data were collected on a Bruker Smart diffractometer equipped with a graphite monochromated Mo K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) 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.<sup>1</sup> The structure was solved by direct methods and refined by full matrix least squares methods on  $F^2$  for all data using SHELXTL software.<sup>2</sup> The non-hydrogen atoms were refined anisotropically. The carbon atom C19 in **2** show relatively large thermal displacement parameters; attempts to resolve the atoms as partial occupancy could not be done sensibly. The hydrogen atoms were placed in calculated positions and refined with a riding model with  $U_{\text{iso}}$  constrained to be 1.2 times  $U_{\text{eq}}$  of the parent atom.

## **References**

1. Bruker, SMART and SAINT: *Area Detector Control and Integration Software Ver. 5.0*; Bruker Analytical X-ray Instruments: Madison, Wisconsin, 1998.
2. Bruker, SHELXTL: *Structure Determination Programs Ver. 5.16*; Bruker Analytical X-ray Instruments: Madison, Wisconsin, 1998.

**Table S1.** Crystal data and structure refinement for **2**, [Hg(1)ClO<sub>4</sub>](ClO<sub>4</sub>)

Empirical formula	C <sub>32</sub> H <sub>32</sub> Cl <sub>2</sub> Hg N <sub>4</sub> O <sub>12</sub> S <sub>2</sub>	
Formula weight	1000.23	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 22.880(5) Å	α= 90°.
	b = 25.666(6) Å	β= 123.552(5)°.
	c = 14.578(3) Å	γ= 90°.
Volume	7134(3) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.862 Mg/m <sup>3</sup>	
Absorption coefficient	4.651 mm <sup>-1</sup>	
F(000)	3952	
Crystal size	0.30 x 0.10 x 0.10 mm <sup>3</sup>	
Theta range for data collection	1.33 to 27.00°.	
Index ranges	-29<=h<=27, -29<=k<=32, -18<=l<=18	
Reflections collected	20435	
Independent reflections	7418 [R(int) = 0.1551]	
Completeness to theta = 27.00°	95.2 %	
Absorption correction	Empirical SADABS	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	7418 / 0 / 478	
Goodness-of-fit on F <sup>2</sup>	0.992	
Final R indices [I>2sigma(I)]	R1 = 0.0622, wR2 = 0.1254	
R indices (all data)	R1 = 0.2073, wR2 = 0.1982	
Largest diff. peak and hole	1.005 and -2.485 e.Å <sup>-3</sup>	

**Table S2.** Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **2**,  $[\text{Hg(1)ClO}_4](\text{ClO}_4)$ 

Hg(1)-S(1)	2.424(4)	Hg(1)-S(2)	2.434(4)
Hg(1)-O(8)	2.494(10)	Hg(1)-N(1)	2.672(11)
S(1)-C(10)	1.823(15)	S(1)-C(9)	1.841(15)
S(2)-C(26)	1.811(14)	S(2)-C(25)	1.846(14)
O(1)-C(32)	1.410(17)	O(1)-C(1)	1.439(16)
O(2)-C(2)	1.399(16)	O(2)-C(3)	1.402(16)
O(3)-N(4)	1.19(2)	O(4)-N(4)	1.18(2)
N(1)-C(12)	1.436(17)	N(1)-C(24)	1.477(17)
N(1)-C(11)	1.506(16)	N(2)-N(3)	1.158(18)
N(2)-C(15)	1.52(2)	N(3)-C(18)	1.58(3)
N(4)-C(21)	1.46(3)	C(1)-C(2)	1.51(2)
C(3)-C(4)	1.37(2)	C(3)-C(8)	1.38(2)
C(4)-C(5)	1.40(2)	C(5)-C(6)	1.38(3)
C(6)-C(7)	1.39(2)	C(7)-C(8)	1.37(2)
C(8)-C(9)	1.49(2)	C(10)-C(11)	1.509(19)
C(12)-C(17)	1.38(2)	C(12)-C(13)	1.395(19)
C(13)-C(14)	1.38(2)	C(14)-C(15)	1.34(2)
C(15)-C(16)	1.35(2)	C(16)-C(17)	1.39(2)
C(18)-C(19)	1.32(3)	C(18)-C(23)	1.34(3)
C(19)-C(20)	1.42(3)	C(20)-C(21)	1.39(3)
C(21)-C(22)	1.29(3)	C(22)-C(23)	1.41(3)
C(24)-C(25)	1.485(19)	C(26)-C(27)	1.530(19)
C(27)-C(32)	1.372(19)	C(27)-C(28)	1.378(19)
C(28)-C(29)	1.41(2)	C(29)-C(30)	1.33(2)
C(30)-C(31)	1.43(2)	C(31)-C(32)	1.34(2)
Cl(1)-O(5)	1.399(12)	Cl(1)-O(7)	1.414(11)
Cl(1)-O(8)	1.426(11)	Cl(1)-O(6)	1.428(12)
Cl(2)-O(11)	1.428(10)	Cl(2)-O(9)	1.431(9)
Cl(2)-O(12)	1.438(10)	Cl(2)-O(10)	1.444(11)
S(1)-Hg(1)-S(2)	151.85(13)	S(1)-Hg(1)-O(8)	100.0(3)
S(2)-Hg(1)-O(8)	99.5(3)	S(1)-Hg(1)-N(1)	80.3(3)
S(2)-Hg(1)-N(1)	79.6(3)	O(8)-Hg(1)-N(1)	178.2(4)
C(10)-S(1)-C(9)	102.6(7)	C(10)-S(1)-Hg(1)	99.9(5)
C(9)-S(1)-Hg(1)	112.0(5)	C(26)-S(2)-C(25)	100.4(7)
C(26)-S(2)-Hg(1)	106.6(5)	C(25)-S(2)-Hg(1)	101.6(5)
C(32)-O(1)-C(1)	116.0(11)	C(2)-O(2)-C(3)	116.5(12)
C(12)-N(1)-C(24)	112.7(12)	C(12)-N(1)-C(11)	112.1(11)
C(24)-N(1)-C(11)	113.4(11)	C(12)-N(1)-Hg(1)	116.8(8)
C(24)-N(1)-Hg(1)	98.7(8)	C(11)-N(1)-Hg(1)	102.1(8)

N(3)-N(2)-C(15)	101.4(18)	N(2)-N(3)-C(18)	103.0(18)
O(4)-N(4)-O(3)	125(3)	O(4)-N(4)-C(21)	119(3)
O(3)-N(4)-C(21)	116(3)	O(1)-C(1)-C(2)	108.0(12)
O(2)-C(2)-C(1)	109.1(13)	C(4)-C(3)-C(8)	122.2(15)
C(4)-C(3)-O(2)	122.6(15)	C(8)-C(3)-O(2)	115.1(15)
C(3)-C(4)-C(5)	121.0(17)	C(6)-C(5)-C(4)	117.1(19)
C(5)-C(6)-C(7)	120.9(17)	C(8)-C(7)-C(6)	121.6(17)
C(7)-C(8)-C(3)	117.1(16)	C(7)-C(8)-C(9)	120.9(16)
C(3)-C(8)-C(9)	121.9(14)	C(8)-C(9)-S(1)	117.6(11)
C(11)-C(10)-S(1)	112.7(10)	N(1)-C(11)-C(10)	111.7(11)
C(17)-C(12)-C(13)	115.9(15)	C(17)-C(12)-N(1)	125.3(13)
C(13)-C(12)-N(1)	118.8(14)	C(14)-C(13)-C(12)	121.2(16)
C(15)-C(14)-C(13)	119.9(17)	C(14)-C(15)-C(16)	122.5(18)
C(14)-C(15)-N(2)	108.4(16)	C(16)-C(15)-N(2)	129.1(19)
C(15)-C(16)-C(17)	117.1(17)	C(12)-C(17)-C(16)	123.4(15)
C(19)-C(18)-C(23)	120(2)	C(19)-C(18)-N(3)	122(2)
C(23)-C(18)-N(3)	117(2)	C(18)-C(19)-C(20)	122(2)
C(21)-C(20)-C(19)	118(2)	C(22)-C(21)-C(20)	119(2)
C(22)-C(21)-N(4)	119(2)	C(20)-C(21)-N(4)	122(3)
C(21)-C(22)-C(23)	124(2)	C(18)-C(23)-C(22)	118(2)
N(1)-C(24)-C(25)	112.7(11)	C(24)-C(25)-S(2)	113.6(11)
C(27)-C(26)-S(2)	108.2(10)	C(32)-C(27)-C(28)	117.9(14)
C(32)-C(27)-C(26)	122.0(13)	C(28)-C(27)-C(26)	119.9(14)
C(27)-C(28)-C(29)	119.1(15)	C(30)-C(29)-C(28)	122.7(16)
C(29)-C(30)-C(31)	117.1(16)	C(32)-C(31)-C(30)	119.9(15)
C(31)-C(32)-C(27)	123.0(15)	C(31)-C(32)-O(1)	123.1(13)
C(27)-C(32)-O(1)	113.8(13)	O(5)-Cl(1)-O(7)	107.1(9)
O(5)-Cl(1)-O(8)	110.0(9)	O(7)-Cl(1)-O(8)	111.0(7)
O(5)-Cl(1)-O(6)	109.9(10)	O(7)-Cl(1)-O(6)	110.8(8)
O(8)-Cl(1)-O(6)	108.1(8)	Cl(1)-O(8)-Hg(1)	128.5(7)
O(11)-Cl(2)-O(9)	108.0(7)	O(11)-Cl(2)-O(12)	109.7(7)
O(9)-Cl(2)-O(12)	110.0(6)	O(11)-Cl(2)-O(10)	109.3(7)
O(9)-Cl(2)-O(10)	109.4(7)	O(12)-Cl(2)-O(10)	110.4(6)

Symmetry transformations used to generate equivalent atoms:

**Table S3.** Crystal data and structure refinement for **3**, [Hg(1)I<sub>2</sub>]<sub>2</sub>

Empirical formula	C <sub>64</sub> H <sub>64</sub> Hg <sub>2</sub> I <sub>4</sub> N <sub>8</sub> O <sub>8</sub> S <sub>4</sub>	
Formula weight	2110.25	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.3042(11) Å	α= 90°.
	b = 36.375(4) Å	β= 100.603(2)°.
	c = 8.3764(8) Å	γ= 90°.
Volume	3385.5(6) Å <sup>3</sup>	
Z	2	
Density (calculated)	2.070 Mg/m <sup>3</sup>	
Absorption coefficient	6.536 mm <sup>-1</sup>	
F(000)	2008	
Crystal size	0.40 x 0.20 x 0.15 mm <sup>3</sup>	
Theta range for data collection	1.12 to 27.00°.	
Index ranges	-14<=h<=12, -46<=k<=46, -10<=l<=10	
Reflections collected	20468	
Independent reflections	7342 [R(int) = 0.0626]	
Completeness to theta = 27.00°	99.1 %	
Absorption correction	Empirical SADABS	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	7342 / 0 / 406	
Goodness-of-fit on F <sup>2</sup>	1.124	
Final R indices [I>2sigma(I)]	R1 = 0.0435, wR2 = 0.1063	
R indices (all data)	R1 = 0.0734, wR2 = 0.1283	
Largest diff. peak and hole	1.201 and -2.174 e.Å <sup>-3</sup>	

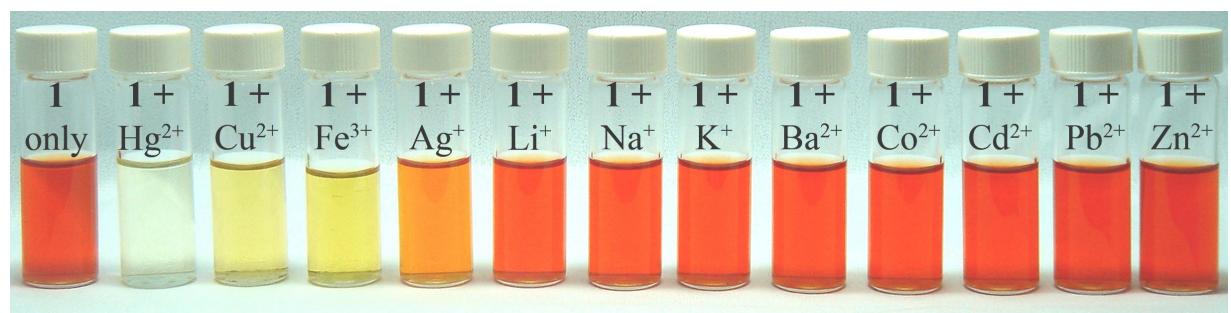
**Table S4.** Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **3**,  $[\text{Hg(1)}\text{L}_2]_2$ 

Hg-S(1)	2.5983(18)	Hg-I(2)	2.6920(6)
Hg-I(1)#1	2.7080(6)	Hg-I(1)	3.1541(7)
I(1)-Hg#1	2.7080(6)	S(1)-C(10)	1.829(7)
S(1)-C(9)	1.848(7)	S(2)-C(25)	1.825(8)
S(2)-C(26)	1.827(7)	O(1)-C(32)	1.359(8)
O(1)-C(1)	1.422(9)	O(2)-C(3)	1.354(8)
O(2)-C(2)	1.440(8)	O(3)-N(4)	1.222(9)
O(4)-N(4)	1.235(9)	N(1)-C(12)	1.383(10)
N(1)-C(24)	1.454(10)	N(1)-C(11)	1.455(9)
N(2)-N(3)	1.272(9)	N(2)-C(15)	1.410(9)
N(3)-C(18)	1.427(10)	N(4)-C(21)	1.466(9)
C(1)-C(2)	1.505(10)	C(3)-C(4)	1.407(10)
C(3)-C(8)	1.432(10)	C(4)-C(5)	1.375(11)
C(5)-C(6)	1.372(11)	C(6)-C(7)	1.404(11)
C(7)-C(8)	1.369(10)	C(8)-C(9)	1.507(10)
C(10)-C(11)	1.552(9)	C(12)-C(13)	1.406(11)
C(12)-C(17)	1.410(10)	C(13)-C(14)	1.385(11)
C(14)-C(15)	1.401(11)	C(15)-C(16)	1.396(11)
C(16)-C(17)	1.384(10)	C(18)-C(23)	1.389(11)
C(18)-C(19)	1.410(11)	C(19)-C(20)	1.369(11)
C(20)-C(21)	1.382(11)	C(21)-C(22)	1.387(11)
C(22)-C(23)	1.418(10)	C(24)-C(25)	1.529(11)
C(26)-C(27)	1.495(10)	C(27)-C(28)	1.382(10)
C(27)-C(32)	1.390(10)	C(28)-C(29)	1.395(11)
C(29)-C(30)	1.378(11)	C(30)-C(31)	1.398(11)
C(31)-C(32)	1.404(10)		
S(1)-Hg-I(2)	108.90(4)	S(1)-Hg-I(1)#1	118.01(4)
I(2)-Hg-I(1)#1	129.25(2)	S(1)-Hg-I(1)	102.60(4)
I(2)-Hg-I(1)	97.72(2)	I(1)#1-Hg-I(1)	90.291(18)
Hg#1-I(1)-Hg	89.709(18)	C(10)-S(1)-C(9)	99.6(3)
C(10)-S(1)-Hg	102.1(2)	C(9)-S(1)-Hg	107.5(3)
C(25)-S(2)-C(26)	102.7(4)	C(32)-O(1)-C(1)	119.0(6)
C(3)-O(2)-C(2)	118.1(6)	C(12)-N(1)-C(24)	120.8(6)
C(12)-N(1)-C(11)	121.6(6)	C(24)-N(1)-C(11)	117.4(6)
N(3)-N(2)-C(15)	112.9(6)	N(2)-N(3)-C(18)	113.5(6)
O(3)-N(4)-O(4)	123.4(7)	O(3)-N(4)-C(21)	118.3(7)
O(4)-N(4)-C(21)	118.3(7)	O(1)-C(1)-C(2)	107.2(6)
O(2)-C(2)-C(1)	106.3(6)	O(2)-C(3)-C(4)	125.9(6)
O(2)-C(3)-C(8)	114.8(6)	C(4)-C(3)-C(8)	119.3(6)

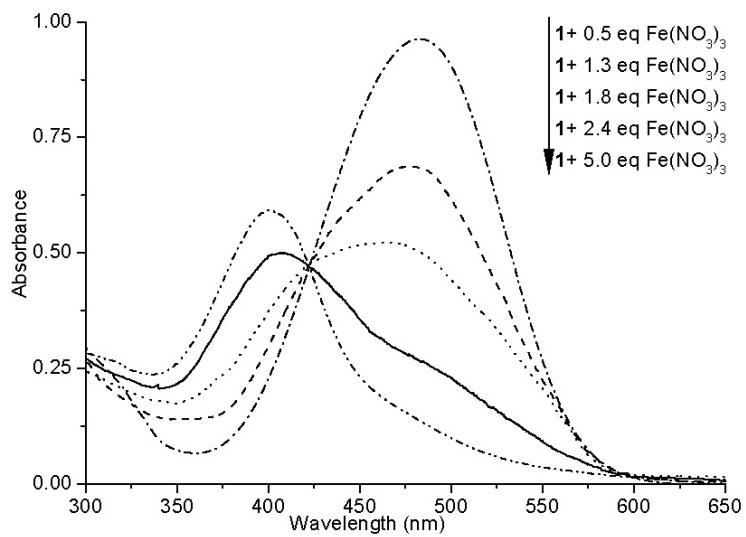
C(5)-C(4)-C(3)	119.0(7)	C(6)-C(5)-C(4)	122.2(8)
C(5)-C(6)-C(7)	119.5(7)	C(8)-C(7)-C(6)	120.5(7)
C(7)-C(8)-C(3)	119.5(7)	C(7)-C(8)-C(9)	122.3(7)
C(3)-C(8)-C(9)	118.1(6)	C(8)-C(9)-S(1)	110.8(5)
C(11)-C(10)-S(1)	110.4(5)	N(1)-C(11)-C(10)	112.0(6)
N(1)-C(12)-C(13)	121.8(7)	N(1)-C(12)-C(17)	121.8(7)
C(13)-C(12)-C(17)	116.4(7)	C(14)-C(13)-C(12)	122.0(7)
C(13)-C(14)-C(15)	120.7(7)	C(16)-C(15)-C(14)	118.1(7)
C(16)-C(15)-N(2)	117.5(7)	C(14)-C(15)-N(2)	124.4(7)
C(17)-C(16)-C(15)	121.0(7)	C(16)-C(17)-C(12)	121.8(7)
C(23)-C(18)-C(19)	119.6(7)	C(23)-C(18)-N(3)	125.1(7)
C(19)-C(18)-N(3)	115.2(7)	C(20)-C(19)-C(18)	121.1(8)
C(19)-C(20)-C(21)	119.0(7)	C(20)-C(21)-C(22)	122.1(7)
C(20)-C(21)-N(4)	119.5(7)	C(22)-C(21)-N(4)	118.4(7)
C(21)-C(22)-C(23)	118.7(7)	C(18)-C(23)-C(22)	119.4(7)
N(1)-C(24)-C(25)	114.0(6)	C(24)-C(25)-S(2)	111.1(6)
C(27)-C(26)-S(2)	112.4(5)	C(28)-C(27)-C(32)	119.3(7)
C(28)-C(27)-C(26)	120.5(7)	C(32)-C(27)-C(26)	120.2(6)
C(27)-C(28)-C(29)	121.6(7)	C(30)-C(29)-C(28)	118.6(7)
C(29)-C(30)-C(31)	121.4(7)	C(30)-C(31)-C(32)	118.9(7)
O(1)-C(32)-C(27)	115.3(6)	O(1)-C(32)-C(31)	124.5(7)
C(27)-C(32)-C(31)	120.3(7)		

Symmetry transformations used to generate equivalent atoms:

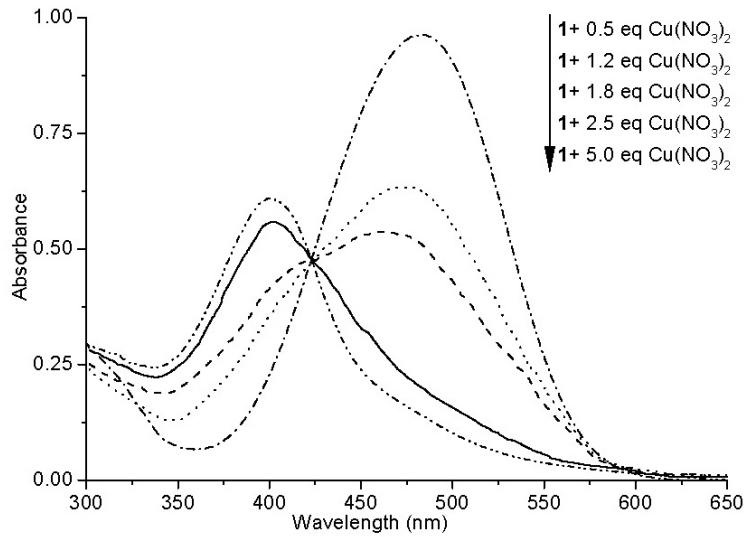
#1 -x,-y+1,-z+2



**Figure S1.** Metal-induced color changes of **1** in acetonitrile (5 equiv of metal nitrate was added).



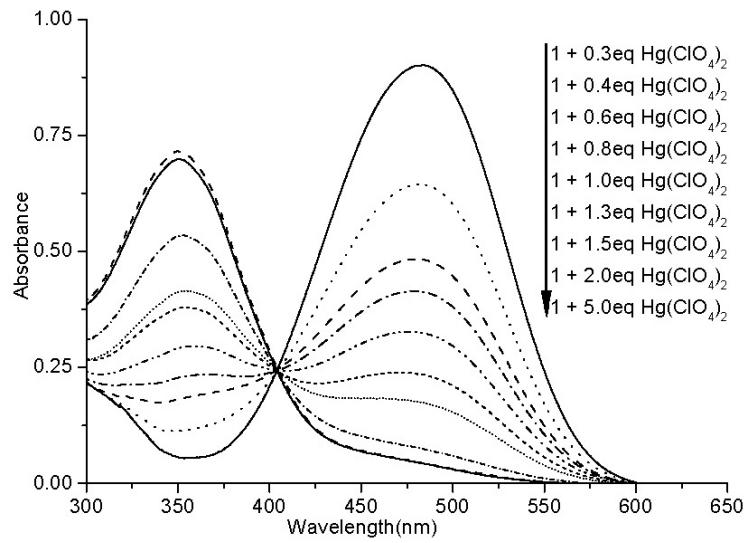
**Figure S2.** UV/Vis titrations of **1** (0.30 mM) with  $\text{Fe}(\text{NO}_3)_3$  (0-5.0 equiv) in acetonitrile.



**Figure S3.** UV/Vis titrations of **1** (0.30 mM) with  $\text{Cu}(\text{NO}_3)_2$  (0-5.0 equiv) in acetonitrile.

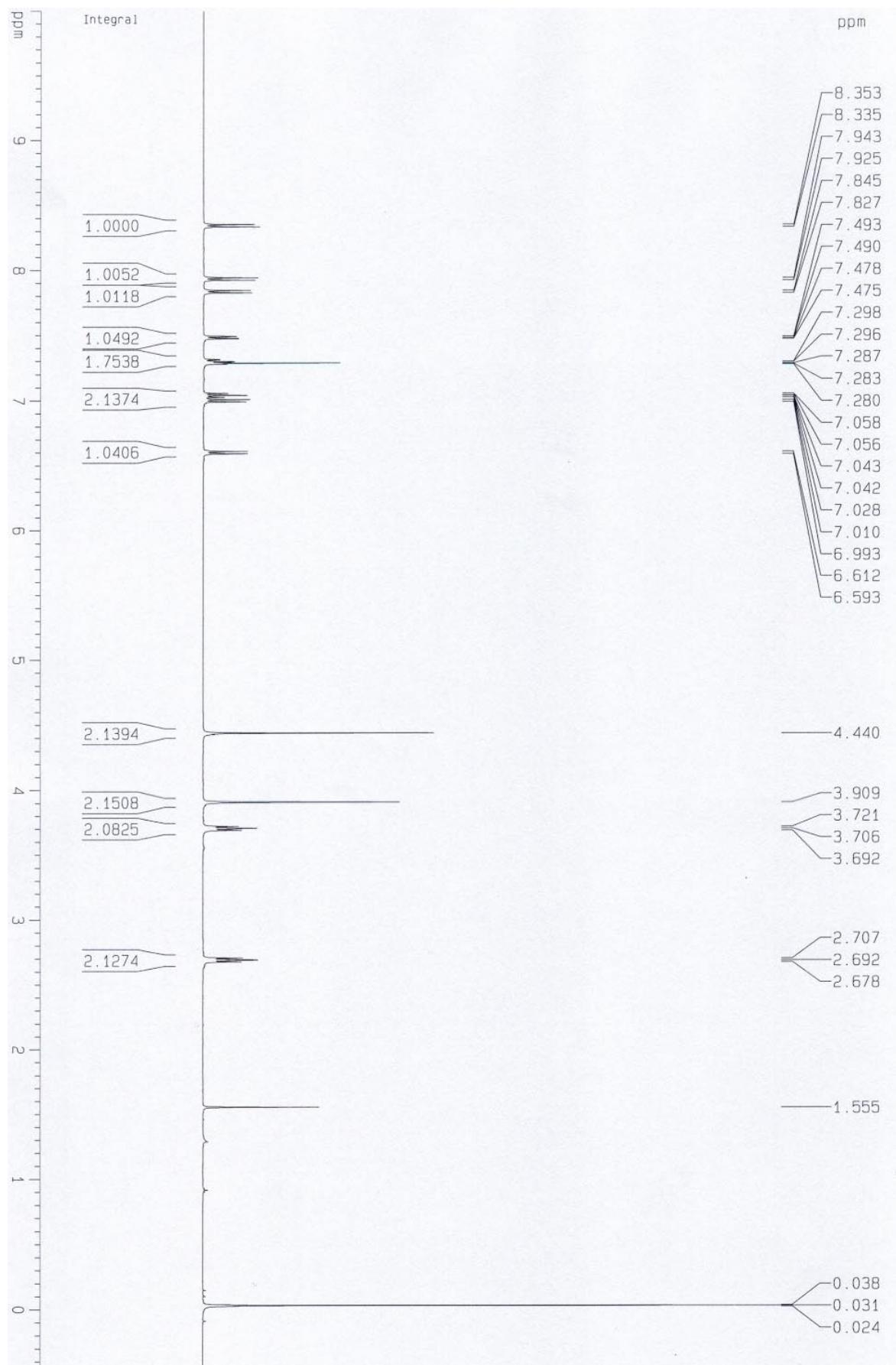


**Figure S4.** Anion-controlled color changes of **1** in acetonitrile (5 equiv of mercury(II) salt was added).

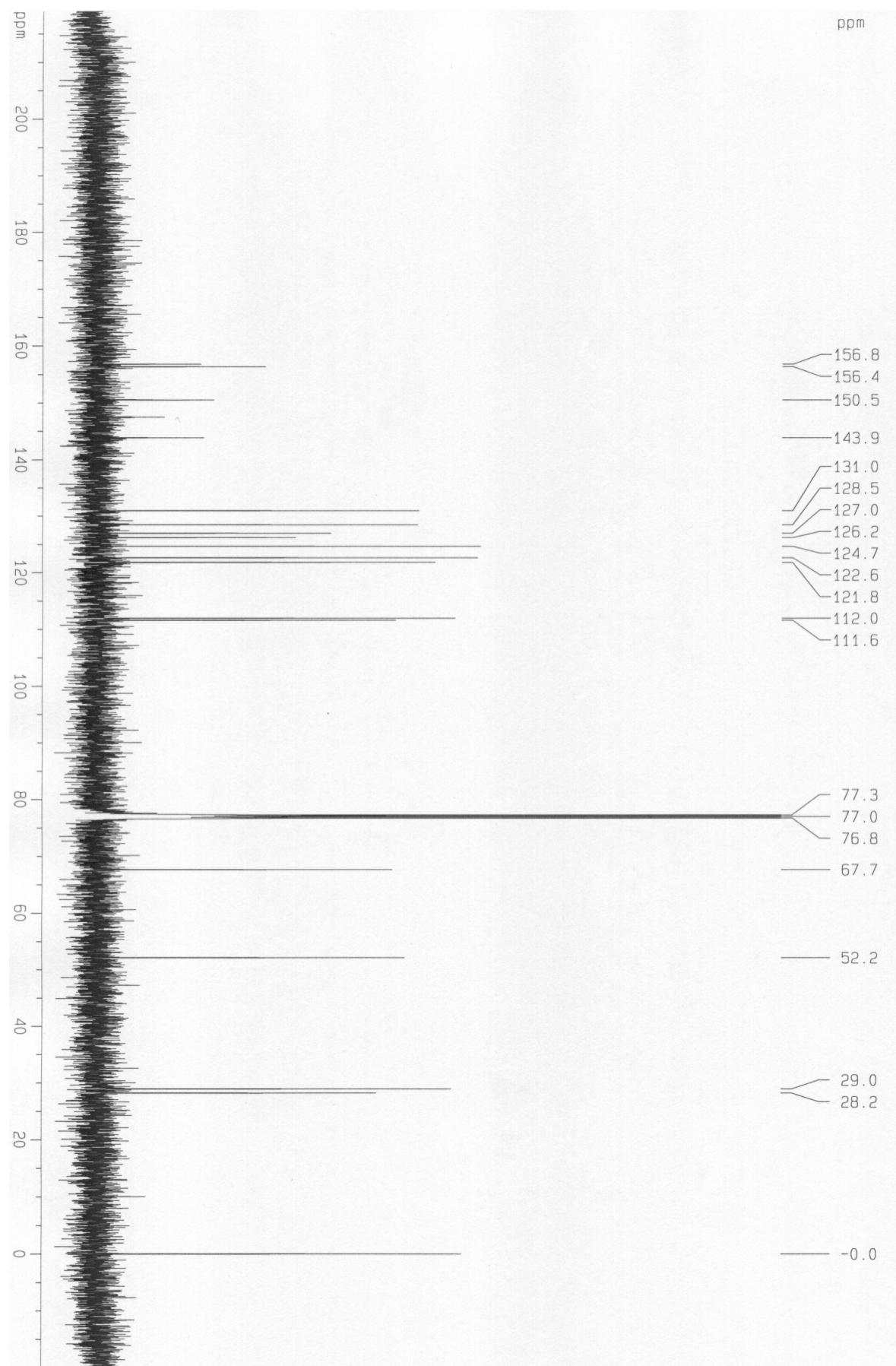


**Figure S5.** UV/Vis titrations of **1** (0.30 mM) with  $\text{Hg}(\text{ClO}_4)_2$  (0-5.0 equiv) in acetonitrile.

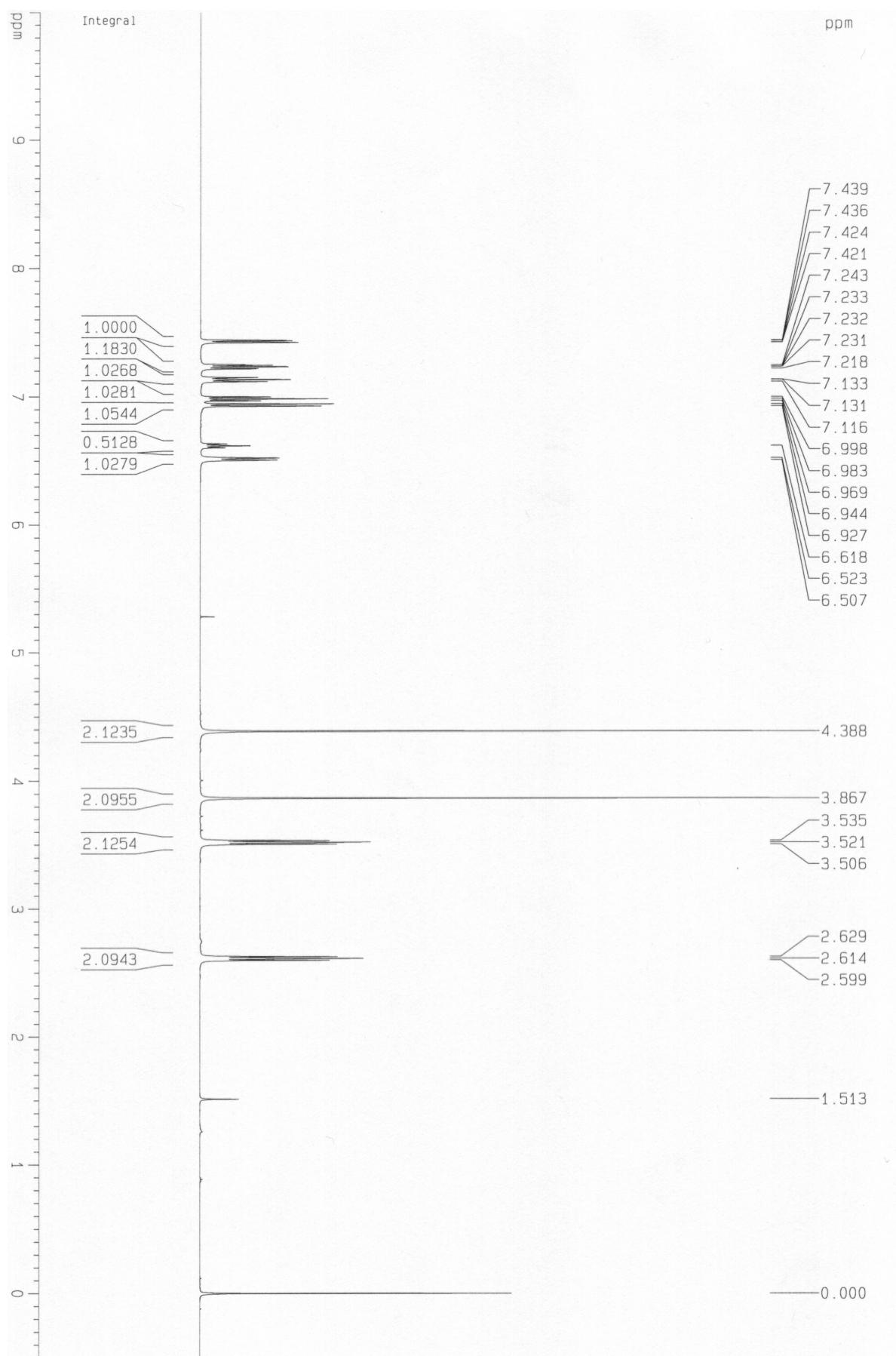
**Figure S6.**  $^1\text{H}$  NMR spectrum of **1**



**Figure S7.**  $^{13}\text{C}$  NMR spectrum of **1**



**Figure S8.**  $^1\text{H}$  NMR spectrum of **4**



**Figure S9.**  $^{13}\text{C}$  NMR spectrum of **4**

