

## Supporting Information

### Triangular and Tetrahedral Array of Silver(I) Ions by a Novel Disk-Shaped Tridentate Ligand: Dynamic Control of Coordination Equilibrium of the Silver(I) Complexes

Shuichi Hiraoka,<sup>†</sup> Tao, Yi,<sup>†</sup> Motoo Shiro,<sup>‡</sup> and Mitsuhiko Shionoya\*,<sup>†</sup>

<sup>†</sup> Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

<sup>‡</sup> Rigaku Corporation, 3-9-12 Matsubaracho, Akishima, Tokyo 196-8666, Japan

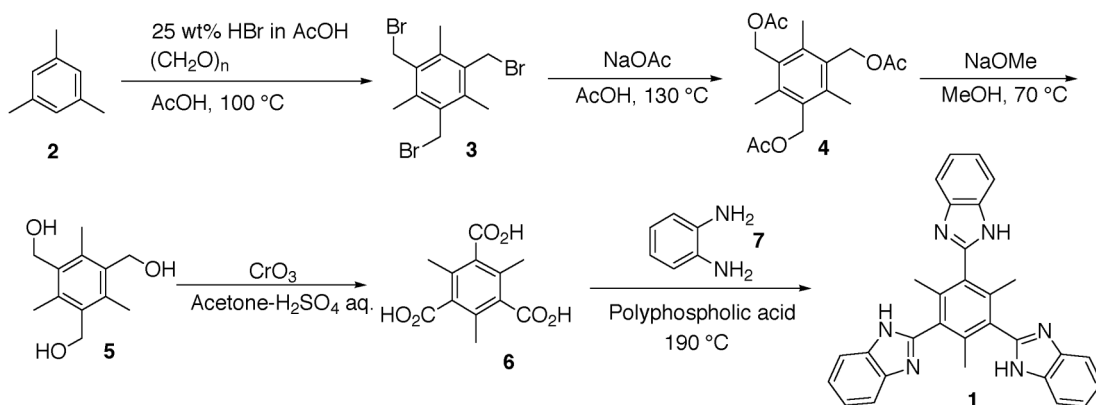
#### Contents

• Preparation of <b>1</b>	.....page S2
• Formation of the Ag <sub>4</sub> <b>1</b> <sub>4</sub> ·(OTf) <sub>4</sub> and Ag <sub>3</sub> <b>1</b> <sub>2</sub> ·(OTf) <sub>3</sub> complexes	.....page S3
• ESI mass spectrum of the Ag <sub>4</sub> <b>1</b> <sub>4</sub> complex (Figure S1)	.....page S3
• ESI mass spectrum of the Ag <sub>3</sub> <b>1</b> <sub>2</sub> complex (Figure S2)	.....page S4
• <sup>19</sup> F NMR spectrum of silver(I) complexes (Figure S3)	.....page S4

## Preparation of 1,3,5-Tribenzimidazolyl-2,4,6-trimethyl benzene (**1**)

Tridentate ligand **1** was prepared starting from mesitylene **2** in 5 steps (Scheme S1). Synthetic details of **6** from **2** are reported in the following literature: Kolotuchin, S. V., Thiessen, P. A., Fenlon, E. E., Wilson, S. R., Loweth, Colin J., Zimmerman, S. C. *Chem. Eur. J.* **1999**, 5, 2537-2547.

Scheme S1



## Preparation of **1** from **6**

2,4,6-Trimethylbenzene-1,3,5-tricarboxylic acid **6** (2.5 g, 10 mmol) and 1,2-diaminobenzene (3.7 g, 34 mmol) were added to polyphosphoric acid (30 mL), and the mixture was stirred at 190 °C for 16 h. The resulting gray solution was allowed to cool down to 100 °C and then poured into ice with vigorous stirring. The gray solid formed was collected, then was neutralized by stirring in a saturated solution of sodium bicarbonate overnight. The raw solid product was collected and washed with water, acetone, and chloroform, respectively. The solid was dissolved in 1 N HCl (50 mL) and filtered, and then the acidic solution was neutralized with 1 N NaOH. The precipitation was collected, washed with water and dried in vacuo, to obtain a light gray solid of 3.02 g (yield 64.5%). Mp > 240 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 12.70 (s, 3 H), 7.69 (d, *J* = 7.7 Hz, 3H), 7.54 (d, *J* = 7.7 Hz, 3H), 7.24 (dd, *J* = 7.7, 7.7 Hz, 3H), 7.21 (dd, *J* = 7.7, 7.7 Hz, 3H), 1.88 (s, 9H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 150.6, 143.5, 138.5, 134.2, 130.6, 122.3, 121.3, 119.0, 111.3. IR (KBr) ν 3175, 3050, 1410, 1270, 740 cm<sup>-1</sup>. MS (FAB) *m/z* exact mass M<sup>+</sup> 469.2164, C<sub>30</sub>H<sub>25</sub>N<sub>6</sub> requires 469.2141.

### Formation of $\text{Ag}_4\mathbf{1}_4\cdot(\text{OTf})_4$

$\text{AgOTf}$  (0.021 mmol, 5.4 mg) was added to  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$  (0.5 mL, 1/1, v/v) solution of **1** (0.021 mmol, 10.0 mg) and the mixture was stand at room temperature for 5 min.  $^1\text{H}$  NMR spectrum showed the quantitative formation of the  $\text{Ag}_4\mathbf{1}_4$  complex.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$ , 1/1, v/v)  $\delta$  7.52 (d,  $J = 8.8$  Hz, 12H), 7.23 (dd,  $J = 8.8, 8.8$  Hz, 12H), 7.09 (d,  $J = 8.8$  Hz, 12H), 6.77 (dd,  $J = 8.8, 8.8$  Hz, 12H), 1.87 (s, 36H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$ , 1/1, v/v)  $\delta$  156.1, 145.9, 144.4, 137.5, 132.7, 127.5, 126.5, 124.1 (q,  $J = 316.6$  Hz), 122.5, 115.8, 21.9. ESI-MS ( $\text{CH}_3\text{OH}$ )  $m/z = 818.4$  [ $\text{Ag}_4\mathbf{1}_4\cdot(\text{OTf})$ ] $^{3+}$ , 1302.3 [ $\text{Ag}_4\mathbf{1}_4\cdot(\text{OTf})_2$ ] $^{2+}$ .

### Formation of $\text{Ag}_3\mathbf{1}_2\cdot(\text{OTf})_3$

$\text{AgOTf}$  (0.021 mmol, 8.2 mg) was added to  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$  (0.5 mL, 1/1, v/v) solution of **1** (0.021 mmol, 10.0 mg) and the mixture was stand at room temperature for 5 min.  $^1\text{H}$  NMR spectrum showed the quantitative formation of the  $\text{Ag}_3\mathbf{1}_2$  complex.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$ , 1/1, v/v)  $\delta$  8.09 (d,  $J = 8.8$  Hz, 6H), 7.76 (d,  $J = 8.8$  Hz, 6H), 7.64 (dd,  $J = 8.8, 8.8$  Hz, 6H), 7.57 (dd,  $J = 8.8, 8.8$  Hz, 6H), 2.09 (s, 18H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$ , 1/1, v/v)  $\delta$  154.8, 145.9, 145.0, 136.9, 132.5, 128.7, 124.1 (q,  $J = 316.6$  Hz), 121.8, 116.9, 21.7. ESI-MS ( $\text{CH}_3\text{OH}$ )  $m/z = 420.3$  [ $\text{Ag}_3\mathbf{1}_2$ ] $^{3+}$ , 648.1 [ $\text{Ag}_3\mathbf{1}_2\cdot\text{OH}\cdot\text{H}_2\text{O}$ ] $^{2+}$ , 705.0 [ $\text{Ag}_3\mathbf{1}_2\cdot(\text{OTf})$ ] $^{2+}$ , 1559.0 [ $\text{Ag}_3\mathbf{1}_2\cdot(\text{OTf})_2$ ] $^{+}$ .

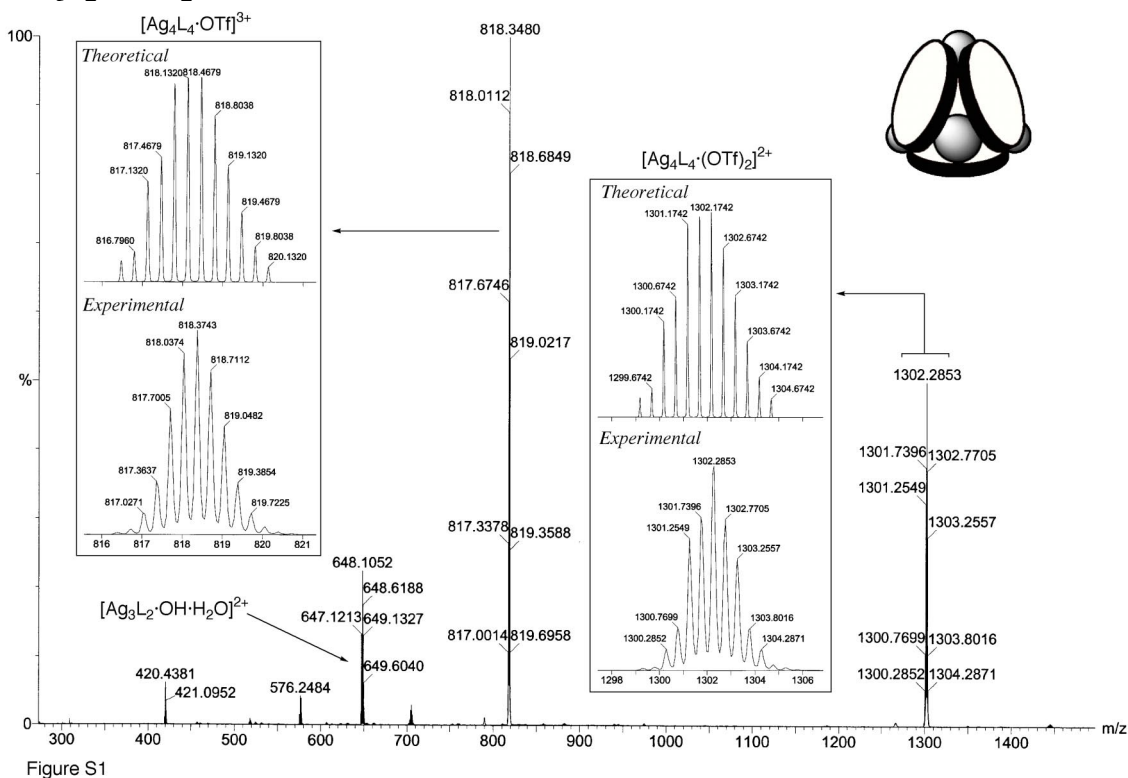


Figure S1

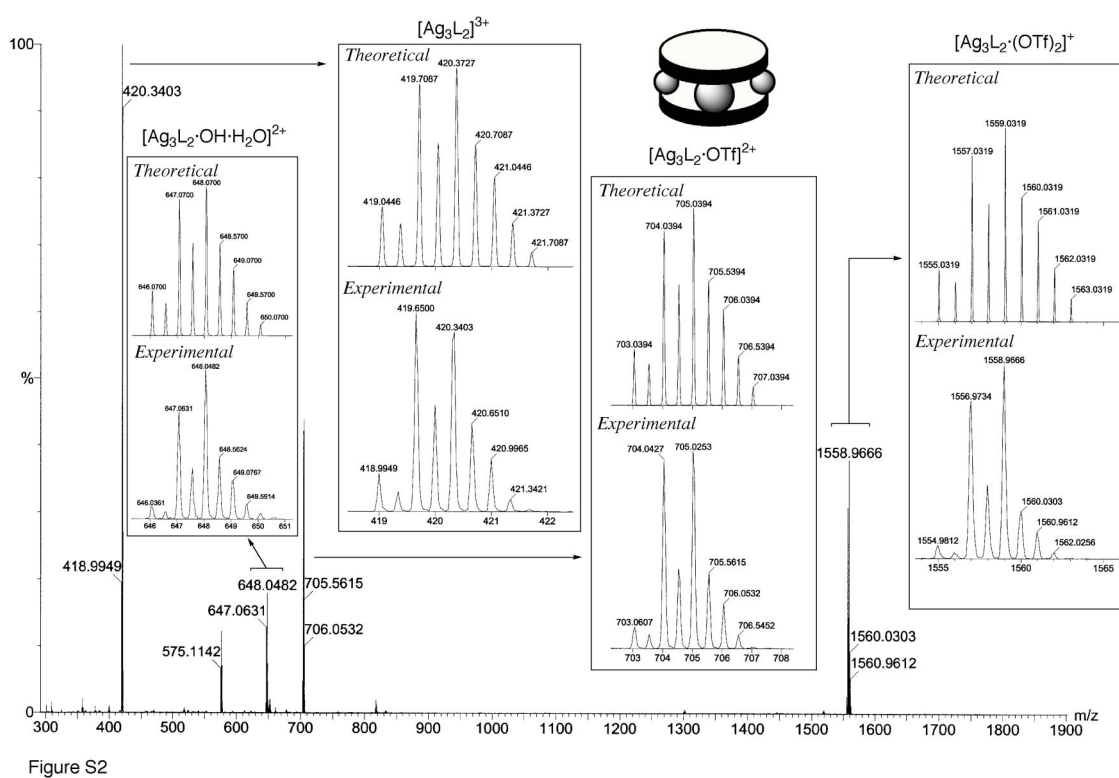


Figure S2

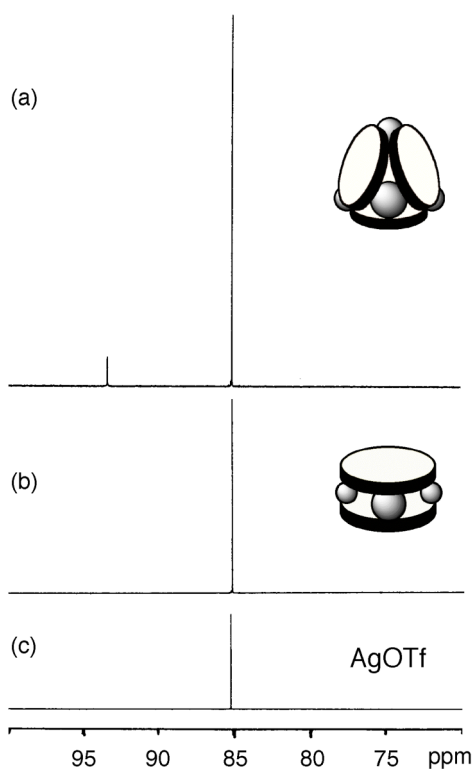


Figure S3. Comparison of  $^{19}\text{F}$  NMR spectra for silver complexes in  $\text{CD}_3\text{OD}$ ; (a)  $\text{Ag}_4\mathbf{1}_4\cdot(\text{OTf})_4$ , (b)  $\text{Ag}_3\mathbf{1}_2\cdot(\text{OTf})_3$ , and (c)  $\text{AgOTf}$ . The Chemical shifts were measured as downfield shifts from  $\text{C}_6\text{F}_6$  that was used as an internal standard.