Electronic Supplementary Material (ESI) for Dalton Transactions


# Electronic Supporting Information for

# Argentivorous Molecules having Two Kinds of Aromatic Side-Arms: Intramolecular Competition between Side-Arms

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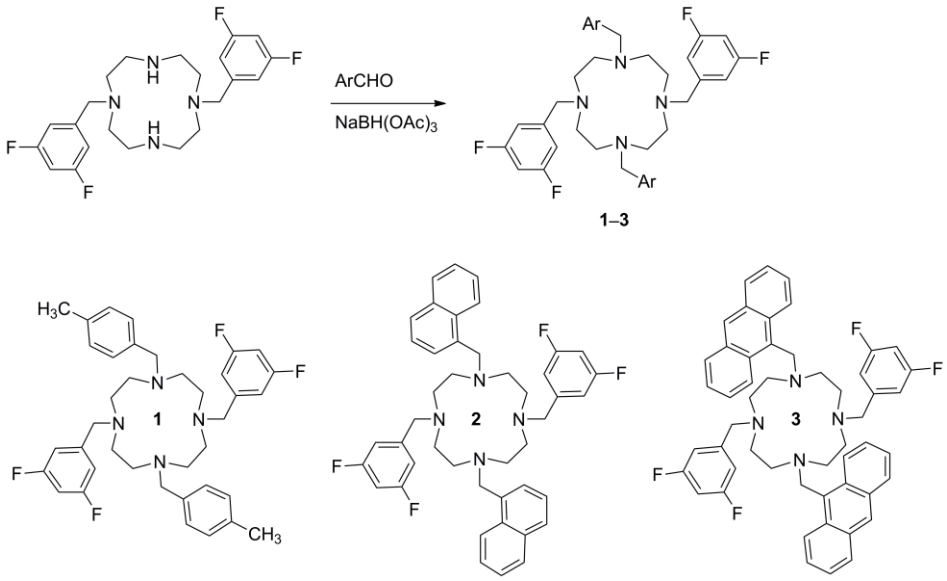


**Figure S1**. Synthetic scheme.

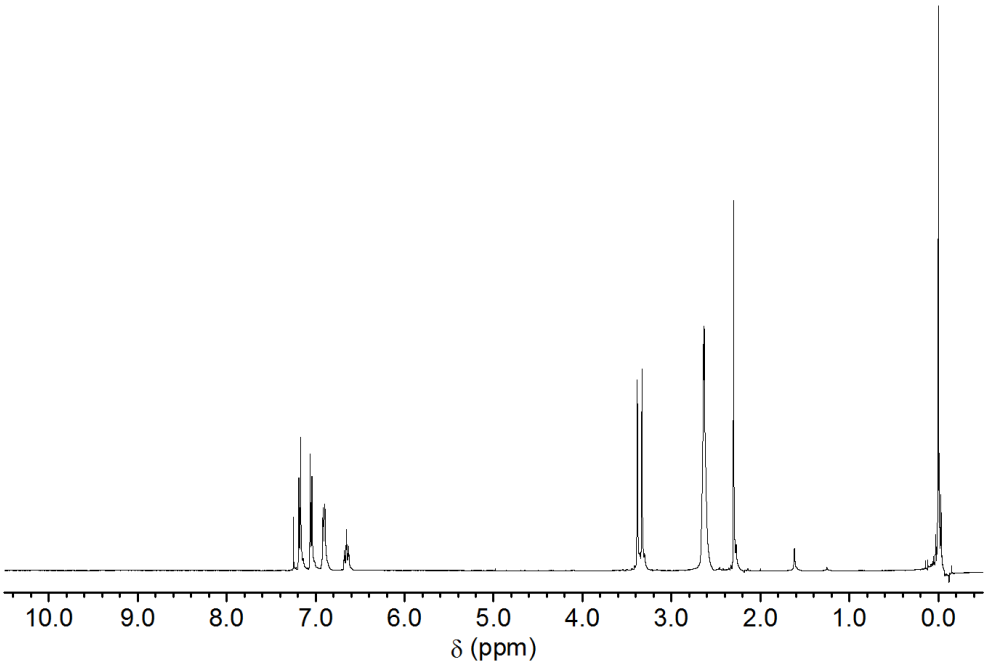


**Figure S2**. $^{1}$H NMR spectrum of **1** in $CDCl_3$.

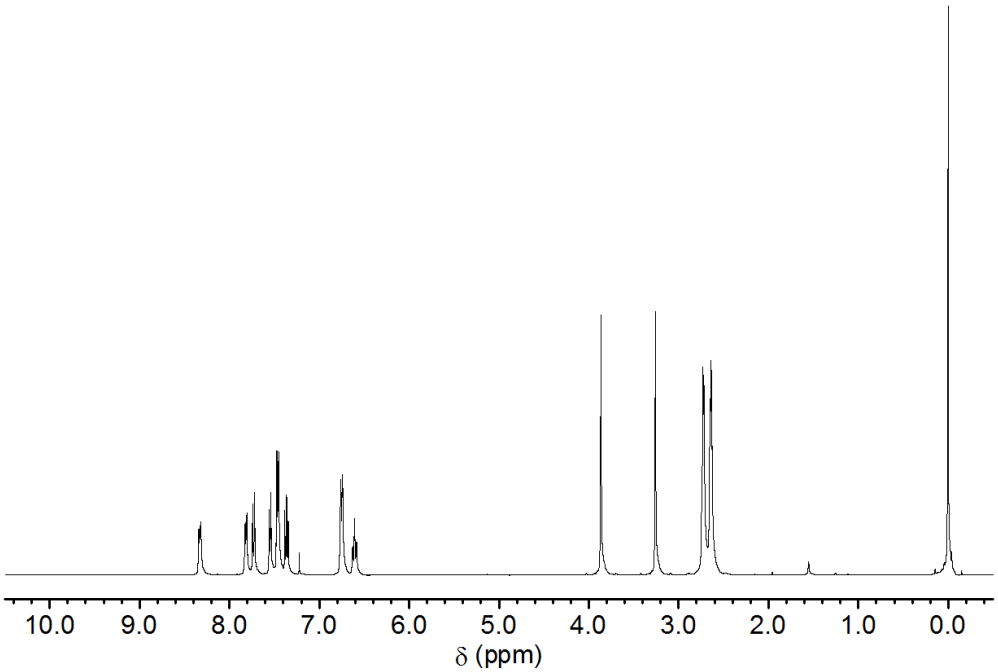


**Figure S3**. $^{1}$H NMR spectrum of **2** in $CDCl_3$.

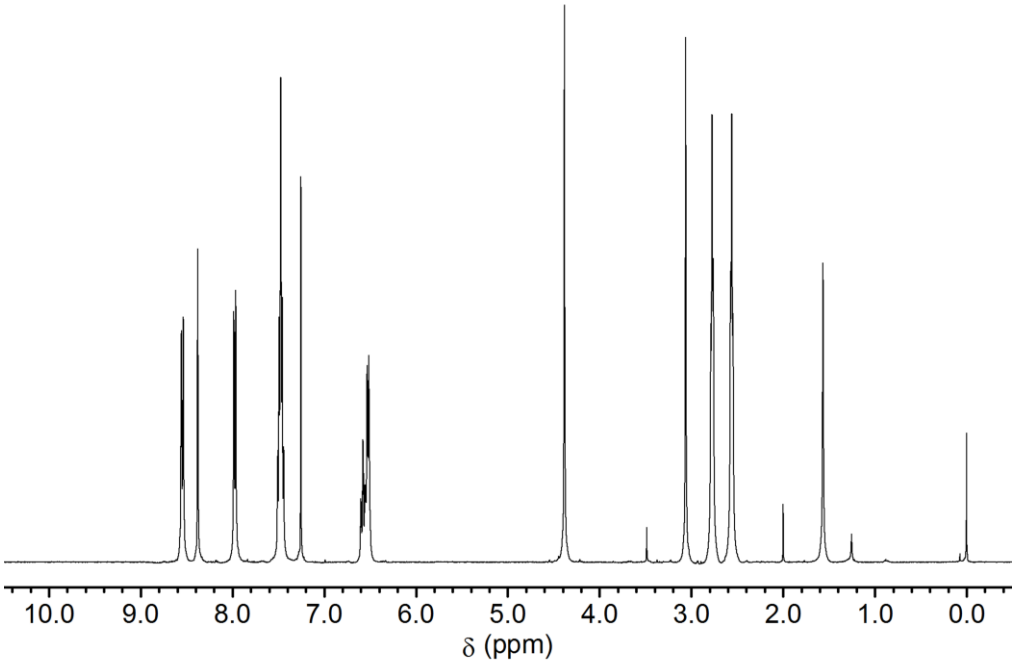


**Figure S4**. $^{1}$H NMR spectrum of **3** in $CDCl_3$.

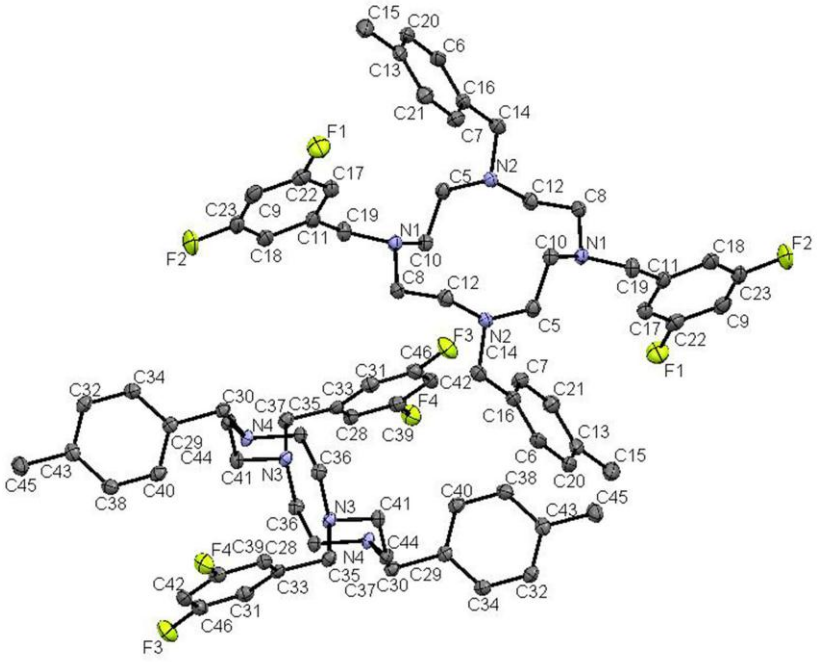


**Figure S5**. X-ray structure of **1** (50% probability lebel). Hydrogen atoms omitted.

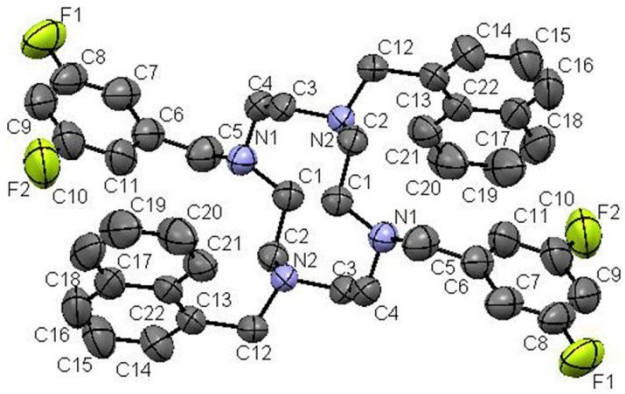


**Figure S6**. X-ray structure of **2** (50% probability lebel). Hydrogen atoms omitted.

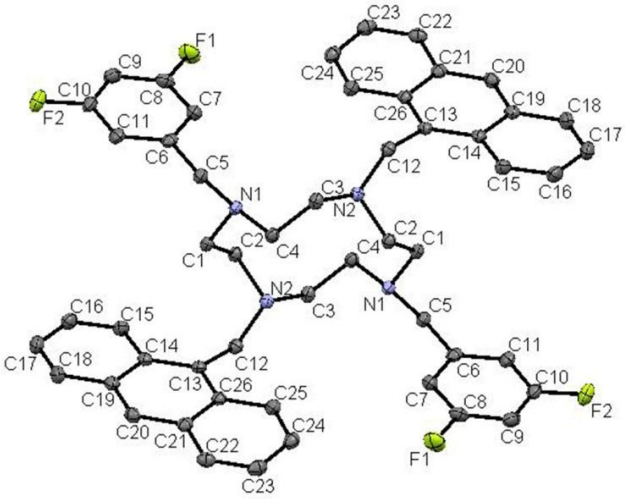


**Figure S7**. X-ray structure of **3** (50% probability lebel). Hydrogen atoms omitted.

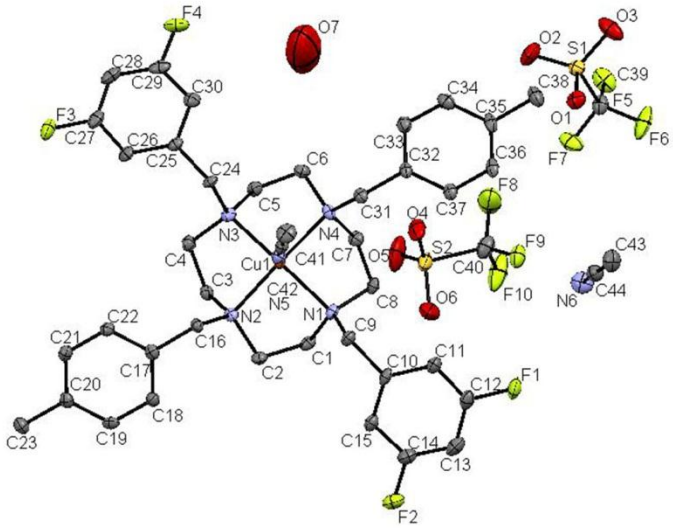


**Figure S8**. X-ray structure of **1**/Cu($CF_3SO_3$)$_2$ complex (50% probability lebel). Hydrogen atoms omitted.

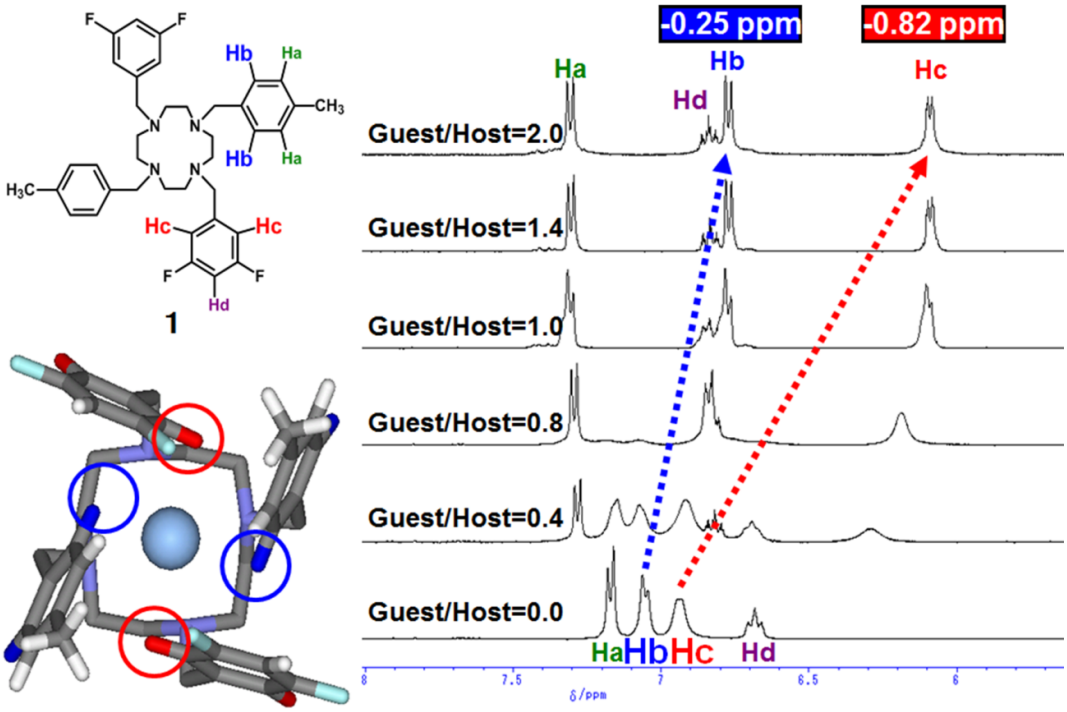


**Figure S9.** $Ag^{+}$-ion-induced $^{1}H$ NMR spectral changes of **1** (in $CD_2Cl_2/CD_3OD$).

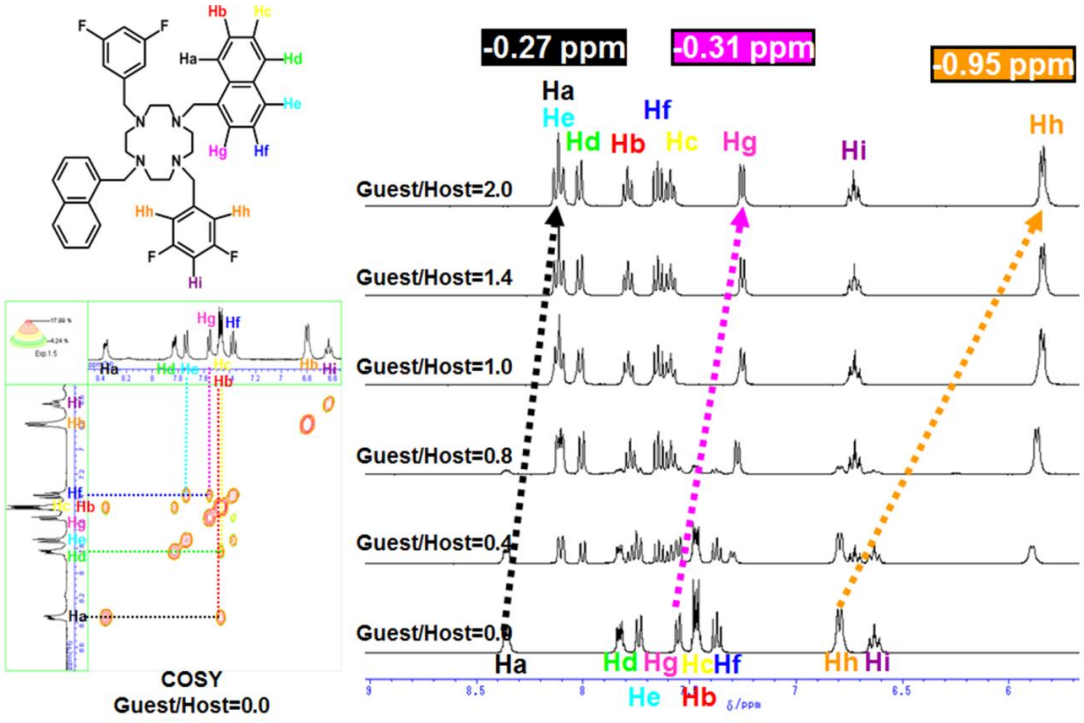


**Figure S10.** $Ag^{+}$-ion-induced $^{1}H$ NMR spectral changes of **2** (in $CD_2Cl_2/CD_3OD$).

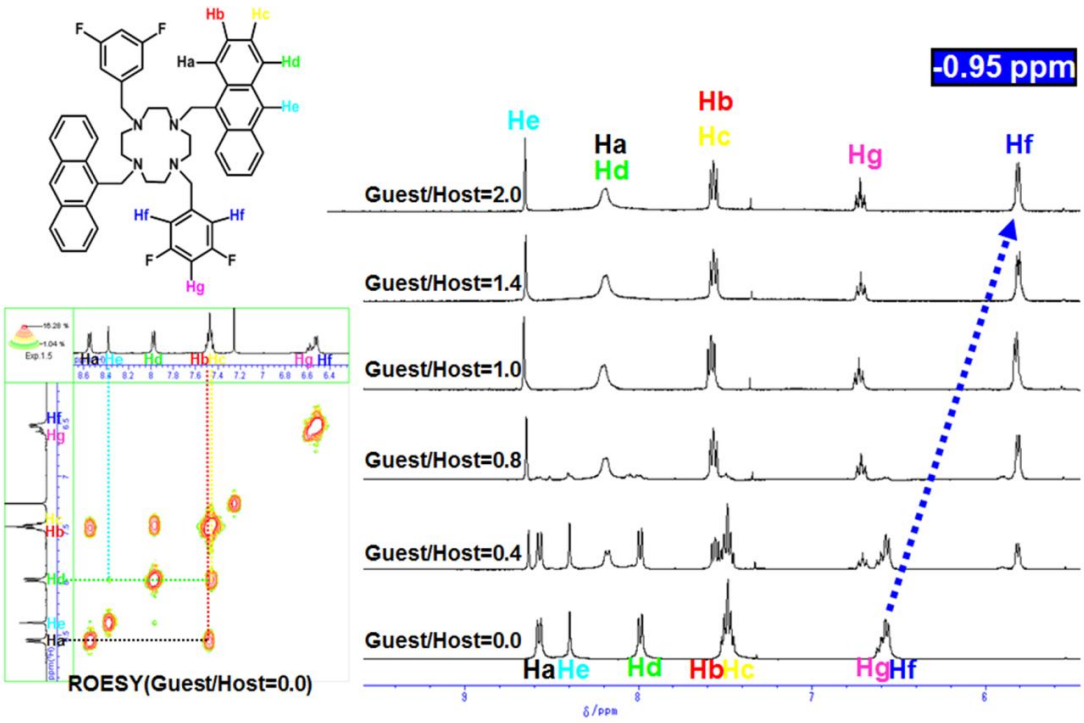


**Figure S11.** $Ag^{+}$-ion-induced $^{1}H$ NMR spectral changes of **3** (in $CD_2Cl_2/CD_3OD$).

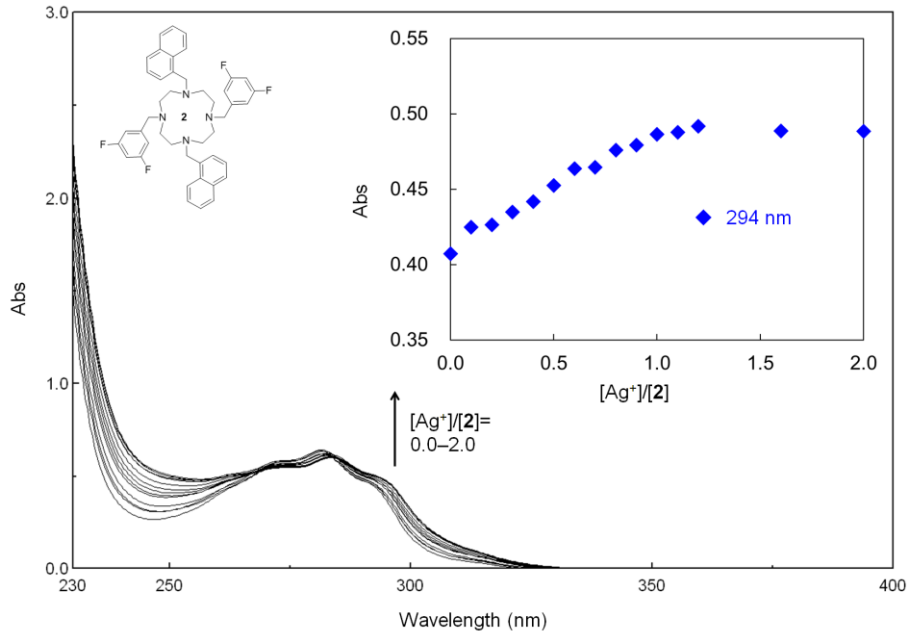


**Figure S12.** $Ag^{+}$-ion-induced UV-vis spectral changes of **2**. [**2**] = 1.0 x $10^{-4}$ mol/L ($CH_3CN$).

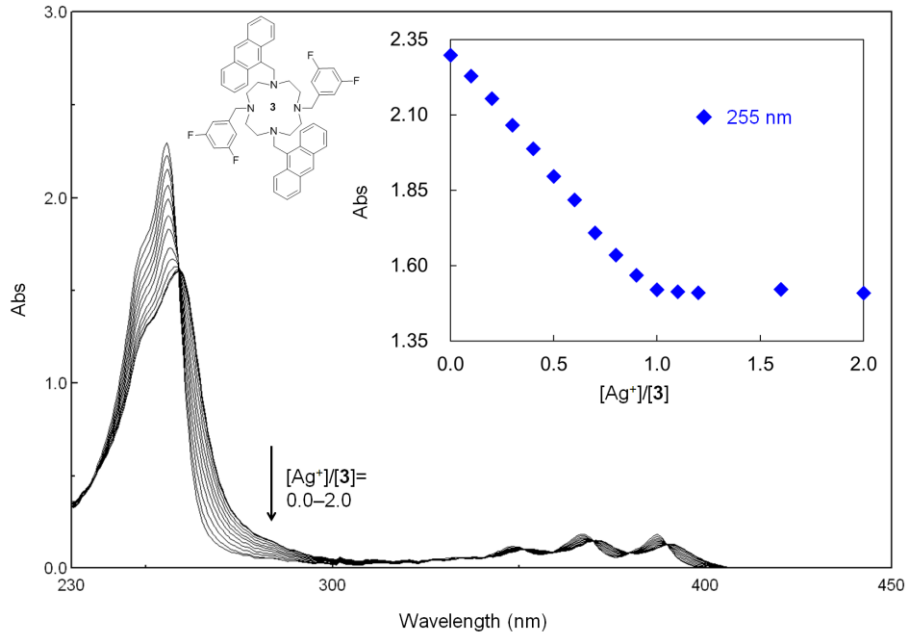


**Figure S13.** $Ag^{+}$-ion-induced UV-vis spectral changes of **3**. [**3**] = 1.0 x $10^{-4}$ mol/L ($CH_3CN$).

| | A | B | C | D | E | F | G | H | I | J |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | xt | A_obs | | | ML | Xfree | A_calc | diff^2 | | |
| 2 | 0.0 | 0.24958 | 0.000102058 | 0.0001021 | 0 | 1 | 0.24958 | 0 | | |
| 3 | 0.1 | 0.26437 | 0.000112238 | 9.194E-05 | 1.015E-05 | 0.9002812 | 0.2622698 | 4.411E-06 | | |
| 4 | 0.2 | 0.28235 | 0.000122418 | 8.183E-05 | 2.03E-05 | 0.8006322 | 0.2749508 | 5.475E-05 | | |
| 5 | 0.3 | 0.28941 | 0.000132598 | 7.174E-05 | 3.043E-05 | 0.7010824 | 0.2876191 | 3.207E-06 | | |
| 6 | 0.4 | 0.30668 | 0.000142778 | 6.168E-05 | 4.055E-05 | 0.6016806 | 0.3002685 | 4.111E-05 | | |
| 7 | 0.5 | 0.31752 | 0.000152958 | 5.167E-05 | 5.064E-05 | 0.5025133 | 0.3128882 | 2.145E-05 | | |
| 8 | 0.6 | 0.32518 | 0.000163138 | 4.174E-05 | 6.07E-05 | 0.4037491 | 0.3254565 | 7.645E-08 | | |
| 9 | 0.7 | 0.33747 | 0.000173318 | 3.197E-05 | 7.067E-05 | 0.3057641 | 0.3379257 | 2.076E-07 | | |
| 10 | 0.8 | 0.34700 | 0.000183498 | 2.257E-05 | 8.047E-05 | 0.2095748 | 0.3501663 | 1.003E-05 | | |
| 11 | 0.9 | 0.35747 | 0.000193678 | 1.427E-05 | 8.97E-05 | 0.1188261 | 0.3617147 | 1.802E-05 | | |
| 12 | 1.0 | 0.37018 | 0.000203858 | 1.026E-05 | 9.68E-05 | 0.0491321 | 0.3705836 | 1.629E-07 | | 0.37018 |
| 13 | 1.1 | 0.37708 | 0.000214038 | 1.464E-05 | 9.97E-05 | 0.0206142 | 0.3742127 | 8.221E-06 | | 0.37708 |
| 14 | 1.2 | 0.37616 | 0.000224218 | 2.303E-05 | 0.0001006 | 0.011842 | 0.375329 | 6.905E-07 | | 0.37616 |
| 15 | 1.6 | 0.37721 | 0.000264938 | 6.219E-05 | 0.0001014 | 0.0041843 | 0.3763035 | 8.217E-07 | | 0.37721 |
| 16 | 2.0 | 0.38355 | 0.000305658 | 0.0001026 | 0.0001015 | 0.0025259 | 0.3765146 | 4.95E-05 | | 0.38355 |
| 17 | | | | | | | | 0.0002126 | | 0.38 |
| 18 | K | 3869385.24 | 6.59 | 0.0002126 | | | | | | |
| 19 | d_comp | 0.376836 | | | | | | | | |
| 20 | Lt | 1.02E-04 | | | | | | | | |

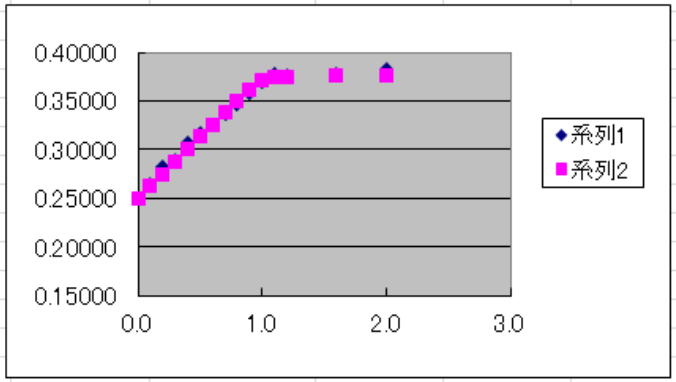


**Figure S14**. Nonlinear least-squares analyses of the titration profiles of **1**.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | xt | A_obs | | | ML | Xfree | A_calc | diff^2 | | |
| 2 | 0.0 | 2.75549 | 5.00044E-05 | 5E-05 | 0 | 1 | 2.75549 | 0 | | |
| 3 | 0.1 | 2.81545 | 5.50044E-05 | 4.501E-05 | 5E-06 | 0.9000099 | 2.7903204 | 0.0006315 | | |
| 4 | 0.2 | 2.85820 | 6.00044E-05 | 4.001E-05 | 9.999E-06 | 0.8000222 | 2.8251499 | 0.0010923 | | |
| 5 | 0.3 | 2.89636 | 6.50044E-05 | 3.501E-05 | 1.5E-05 | 0.700038 | 2.8599782 | 0.0013236 | | |
| 6 | 0.4 | 2.93362 | 7.00044E-05 | 3.001E-05 | 2E-05 | 0.6000591 | 2.8948046 | 0.0015066 | | |
| 7 | 0.5 | 2.95967 | 7.50044E-05 | 2.501E-05 | 2.5E-05 | 0.5000886 | 2.9296281 | 0.0009025 | | |
| 8 | 0.6 | 2.99129 | 8.00044E-05 | 2.002E-05 | 2.999E-05 | 0.4001329 | 2.9644465 | 0.0007206 | | |
| 9 | 0.7 | 3.00929 | 8.50044E-05 | 1.503E-05 | 3.499E-05 | 0.3002067 | 2.9992546 | 0.0001007 | | |
| 10 | 0.8 | 3.05159 | 9.00044E-05 | 1.004E-05 | 3.998E-05 | 0.2003539 | 3.0340371 | 0.0003081 | | 3.09246 |
| 11 | 0.9 | 3.08280 | 9.50044E-05 | 5.084E-06 | 4.496E-05 | 0.1007911 | 3.0687186 | 0.0001983 | | 3.10904 |
| 12 | 1.0 | 3.09246 | 0.000100004 | 9.417E-07 | 4.953E-05 | 0.0093722 | 3.1005633 | 6.566E-05 | | 3.10914 |
| 13 | 1.1 | 3.10904 | 0.000105004 | 5.092E-06 | 4.996E-05 | 0.0008782 | 3.1035221 | 3.045E-05 | | 3.10894 |
| 14 | 1.2 | 3.10914 | 0.000110004 | 1.005E-05 | 4.998E-05 | 0.0004422 | 3.103674 | 2.988E-05 | | |
| 15 | 1.6 | 3.10894 | 0.000130004 | 3.002E-05 | 4.999E-05 | 0.0001477 | 3.1037765 | 2.666E-05 | | |
| 16 | 2.0 | 3.09956 | 0.000150004 | 5.001E-05 | 5E-05 | 8.865E-05 | 3.1037971 | 1.795E-05 | | |
| 17 | | | | | | | | 0.0069549 | | |
| 18 | K | 225557079 | 8.35 | 0.0069549 | | | | | | |
| 19 | d_comp | 3.10383 | | | | | | | | |
| 20 | Lt | 5.00E-05 | | | | | | | | |
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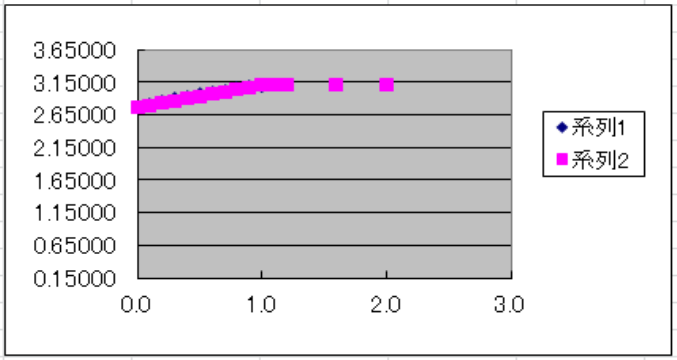


**Figure S15**. Nonlinear least-squares analyses of the titration profiles of **2**.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | xt | A_obs | | | ML | Xfree | A_calc | diff^2 | | | |
| 2 | 0 | 2.29708 | 1.00001E-05 | 1E-05 | 0 | 1 | 2.29708 | 0 | | | |
| 3 | 0.1 | 2.22822 | 1.10001E-05 | 9E-06 | 1E-06 | 0.900001 | 2.218768 | 8.934E-05 | | | |
| 4 | 0.2 | 2.15262 | 1.20001E-05 | 8E-06 | 2E-06 | 0.8000022 | 2.1404561 | 0.000148 | | | |
| 5 | 0.3 | 2.06479 | 1.30001E-05 | 7E-06 | 3E-06 | 0.7000038 | 2.0621446 | 6.998E-06 | | | |
| 6 | 0.4 | 1.98649 | 1.40001E-05 | 6E-06 | 4E-06 | 0.6000059 | 1.9838334 | 7.057E-06 | | | |
| 7 | 0.5 | 1.89498 | 1.50001E-05 | 5E-06 | 5E-06 | 0.5000089 | 1.9055229 | 0.0001112 | | | |
| 8 | 0.6 | 1.81675 | 1.60001E-05 | 4E-06 | 6E-06 | 0.4000133 | 1.8272136 | 0.0001095 | | | |
| 9 | 0.7 | 1.7079 | 1.70001E-05 | 3.001E-06 | 7E-06 | 0.3000207 | 1.7489066 | 0.0016815 | | | |
| 10 | 0.8 | 1.63426 | 1.80001E-05 | 2.001E-06 | 8E-06 | 0.2000355 | 1.6706054 | 0.001321 | | | |
| 11 | 0.9 | 1.56723 | 1.90001E-05 | 1.002E-06 | 8.999E-06 | 0.1000797 | 1.5923272 | 0.0006299 | | | |
| 12 | 1 | 1.5194 | 2.00001E-05 | 5.955E-08 | 9.97E-06 | 0.0029729 | 1.5162802 | 9.733E-06 | | | |
| 13 | 1.1 | 1.51205 | 2.10001E-05 | 1.002E-06 | 9.999E-06 | 8.856E-05 | 1.5140214 | 3.886E-06 | | | |
| 14 | 1.2 | 1.50957 | 2.20001E-05 | 2.001E-06 | 1E-05 | 4.431E-05 | 1.5139867 | 1.951E-05 | | | |
| 15 | 1.6 | 1.52036 | 2.60001E-05 | 6E-06 | 1E-05 | 1.477E-05 | 1.5139636 | 4.091E-05 | 180000000 | 8.26 | 0.000449431 |
| 16 | 2 | 1.50838 | 3.00001E-05 | 1E-05 | 1E-05 | 8.865E-06 | 1.5139589 | 3.112E-05 | 200000000 | 8.30 | 0.000449394 |
| 17 | | | | | | | | 0.0042096 | 250000000 | 8.40 | 0.000449349 |
| 18 | K | 1.1281E+10 | 10.05 | 0.0042096 | | | | | 275000000 | 8.44 | 0.000449342 |
| 19 | d_comp | 1.513952 | | | | | | | 290000000 | 8.46 | 0.000449340 |
| 20 | Lt | 1.00E-05 | | | | | | | 295000000 | 8.47 | 0.00044934 |
| 21 | | | | | | | | | 300000000 | 8.48 | 0.000449340 |
| 22 | | | | | | | | | 305000000 | 8.48 | 0.000449341 |
| 23 | | | | | | | | | 310000000 | 8.49 | 0.000449341 |
| 24 | | | | | | | | | 325000000 | 8.51 | 0.000449343 |
| 25 | | | | | | | | | 350000000 | 8.54 | 0.000449348 |
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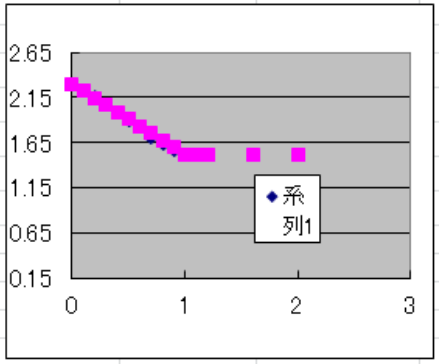


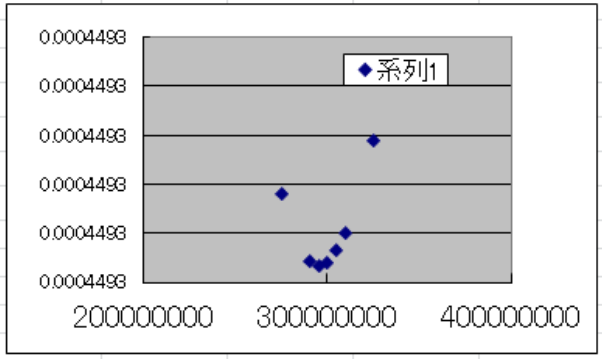


**Figure S16**. Nonlinear least-squares analyses of the titration profiles of **3**.

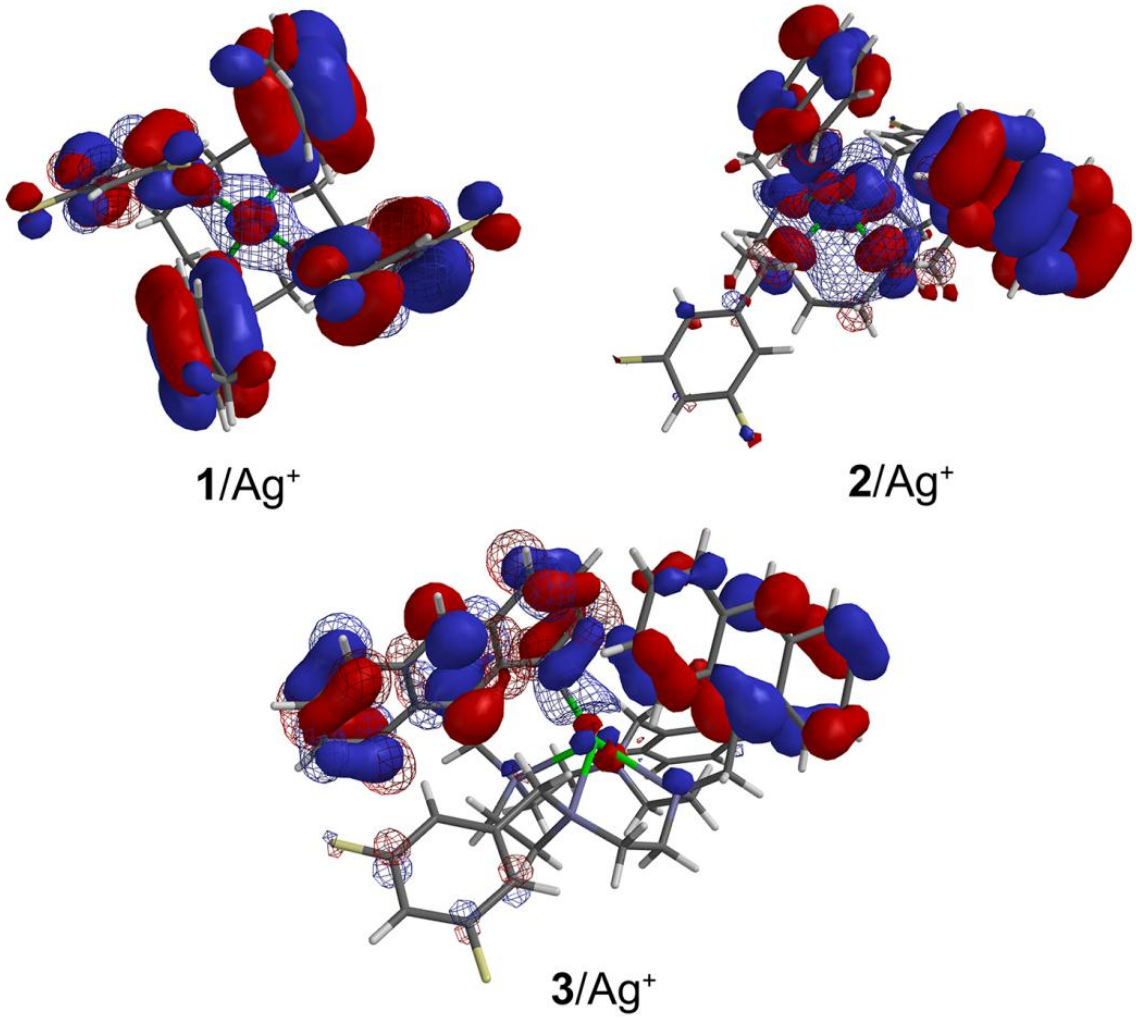


**Figure S14**. The LUMOs and HOMOs calculated by the DFT methods [B3LYP/3-21G(*)] using the X-ray structures of the $Ag^+$ complexes with **1**–**2** (Isosurface value is 0.032 au).

**1**/$Ag^+$ complx, LUMO (mesh) and HOMO[–4], HOMO[–5], HOMO[–6] , HOMO[–7] (solid).

**2**$Ag^+$ complx, LUMO[+9] (mesh) and HOMO[–2], HOMO[–4], HOMO[–7] (solid).

**3**/$Ag^+$ complx, LUMO[+6] (mesh) and HOMO[-5], HOMO[-6], HOMO[-7], HOMO[-8] (solid).