

## Supporting Information

### Positive Homotropic Allosteric Binding of Silver(I) Ions in Multidentate Azacalixpyridine Macrocycles: Effect on the Formation and Stabilization of Silver Nanoparticles

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#### Synthesis

All commercially available chemicals were used without further purification. Methylazacalix[*n*]pyridines (**Py**[*n*], *n* = 8 and 9) and methylazacalix[2]arene[6]pyridine (**Py**[6]**Ph**[2]) were synthesized according to the literature method by the fragment coupling protocol between terminal dibrominated and diaminated linear oligomers.<sup>1</sup> Linear pyridine oligomers **L-Py**[*n*] (*n* = 1, 3, 5 and 7) were also synthesized according to the reported methods.<sup>1</sup> Solvents used in this study were processed by standard procedures.

**Synthesis of [Ag<sub>3</sub>(Py[8])(CF<sub>3</sub>SO<sub>3</sub>)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (**1**).** In a 10 mL round-bottom flask, methylazacalix[8]pyridine (**Py**[8], 17.0 mg, 0.02 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 ml) at room temperature. Then a CH<sub>3</sub>OH solution (2 mL) of AgCF<sub>3</sub>SO<sub>3</sub> (15.4 mg, 0.06 mmol) was added under stirring. The mixture was further stirred for two hours. The solution was then filtered and the filtrate was diffused by diethyl ether in the dark. Yellow crystals of **1** were obtained in 81% yield based on the **Py**[8] ligand. Elemental analysis for **1**·H<sub>2</sub>O: C<sub>51</sub>H<sub>50</sub>Ag<sub>3</sub>F<sub>9</sub>N<sub>16</sub>O<sub>10</sub>S<sub>3</sub>, found (calcd): C, 37.24 (37.40); 3.09 (3.07); N, 13.42 (13.68).

**Synthesis of [(H<sub>2</sub>O)@{Ag<sub>3</sub>(Py[9])}] (CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>·1.5(Et<sub>2</sub>O) (**2**).** The method for the synthesis of **2** was similar to that for complex **1**, but employed **Py**[9] instead of **Py**[8]. Colorless crystals of complex **2** were deposited in 48% yield based on the **Py**[9] ligand. Microcrystals subjected to elemental analysis were purified by diffusion of

diethyl ether into the CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> (v:v = 1:1) solution of **2**. Elemental analysis for [Ag<sub>3</sub>(Py[9])](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>·(CH<sub>3</sub>CN)·(CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>)<sub>0.5</sub>: C<sub>61</sub>H<sub>62</sub>Ag<sub>3</sub>F<sub>9</sub>N<sub>19</sub>O<sub>9.5</sub>S<sub>3</sub>, found (calcd): C, 40.87 (40.61); H, 3.53 (3.46); N, 14.97 (14.75).

**Synthesis of Py[8]-Ag.** Diluted solution containing both AgSO<sub>3</sub>CF<sub>3</sub> (10<sup>-4</sup> M) and Py[8] (3.3·10<sup>-5</sup> M) (would generate complex **1** *in situ*) was freshly prepared in mixed solvent of CH<sub>3</sub>OH and CH<sub>2</sub>Cl<sub>2</sub> (v:v = 9:1) and stored in the dark before use. NaBH<sub>3</sub>CN solid (5 mg) was added rapidly to the solution (5 ml) under vigorous stirring at room temperature and a pale yellow solution could be achieved in a few minutes which can keep its color and solution homogeneity over one month.

**Synthesis of Py[9]-Ag.** The method for the synthesis of Py[9]-Ag was similar to that for Py[8]-Ag, but employed Py[9] instead of Py[8].

### X-ray crystallographic analysis

Data for complex **1** was collected at 173 K with Mo-*K*α radiation (λ = 0.71073 Å) on a Rigaku Saturn 724+ CCD diffractometer with frames of oscillation range 0.5 °. Data for complexes **2** was collected at 153 K with Cu-*K*α radiation (λ = 1.54184 Å) on an Agilent SuperNova diffractometer equipped with an Atlas CCD detector with frames of oscillation range 1 °. All structures were solved by direct methods, and non-hydrogen atoms were located from difference Fourier maps. All non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on *F*<sup>2</sup> by using the SHELXTL program unless otherwise noticed.<sup>2</sup> All figures were drawn by using X-seed program.<sup>3</sup>

Crystal data for [Ag<sub>3</sub>(Py[8])(CF<sub>3</sub>SO<sub>3</sub>)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (**1**): C<sub>51</sub>H<sub>48</sub>Ag<sub>3</sub>F<sub>9</sub>N<sub>16</sub>O<sub>9</sub>S<sub>3</sub>, *M* = 1619.84, triclinic, space group *P*-1 (No. 2), *a* = 13.158 (3) Å, *b* = 13.945(3) Å, *c* = 16.183(3) Å, α = 97.30(3) °, β = 90.51(3) °, γ = 94.38(3) °, *V* = 2936.0(10) Å<sup>3</sup>, *Z* = 2, *T* = 173 K, *D*<sub>c</sub> = 1.832 g/cm<sup>-3</sup>. The structure, refined on *F*<sup>2</sup>, converged for 13313 unique reflections (*R*<sub>int</sub> = 0.1275) and 9754 observed reflections with *I* > 2σ(*I*) to give *R*<sub>1</sub> = 0.0930 and *wR*<sub>2</sub> = 0.2301 and a goodness-of-fit = 1.105.

Crystal data for [(H<sub>2</sub>O)@{Ag<sub>3</sub>(Py[9])}](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>·1.5(Et<sub>2</sub>O) (**2**): The structure of **2** was refined with 1.5 diethyl ether molecules and a water molecule in the asymmetric unit. C<sub>63</sub>H<sub>69</sub>Ag<sub>3</sub>F<sub>9</sub>N<sub>18</sub>O<sub>11.5</sub>S<sub>3</sub>, *M* = 1853.15, triclinic, space group *P*-1 (No. 2), *a* = 13.1897(7) Å, *b* = 13.7061(8) Å, *c* = 20.5215(11) Å, α = 94.475(4) °, β = 90.360(4) °, γ = 104.014(5) °, *V* = 3587.3(3) Å<sup>3</sup>, *Z* = 2, *T* = 153 K, *D*<sub>c</sub> = 1.716 g/cm<sup>-3</sup>. The structure, refined on *F*<sup>2</sup>, converged for 13900 unique reflections (*R*<sub>int</sub> = 0.0459) and 10061 observed reflections with *I* > 2σ(*I*) to give *R*<sub>1</sub> = 0.0627 and *wR*<sub>2</sub> = 0.1726 and

a goodness-of-fit = 1.023. Silver atom Ag2 is disordered at two positions with a refined site-occupancy ratio of 0.92:0.08. Silver atom Ag3 is disordered over two separated positions in the refined ratio of 0.72:0.28. Each of the total three triflate anions is disorder at two positions with a refined site ratio of 0.61:0.39, 0.46:0.54 and 0.67:0.33 for triflate group S1, S2 and S3 respectively. Carbon atom C58 together with H58A and H58B was disordered at two positions with a site-occupancy ratio of 0.67:0.33.

### TEM characterization

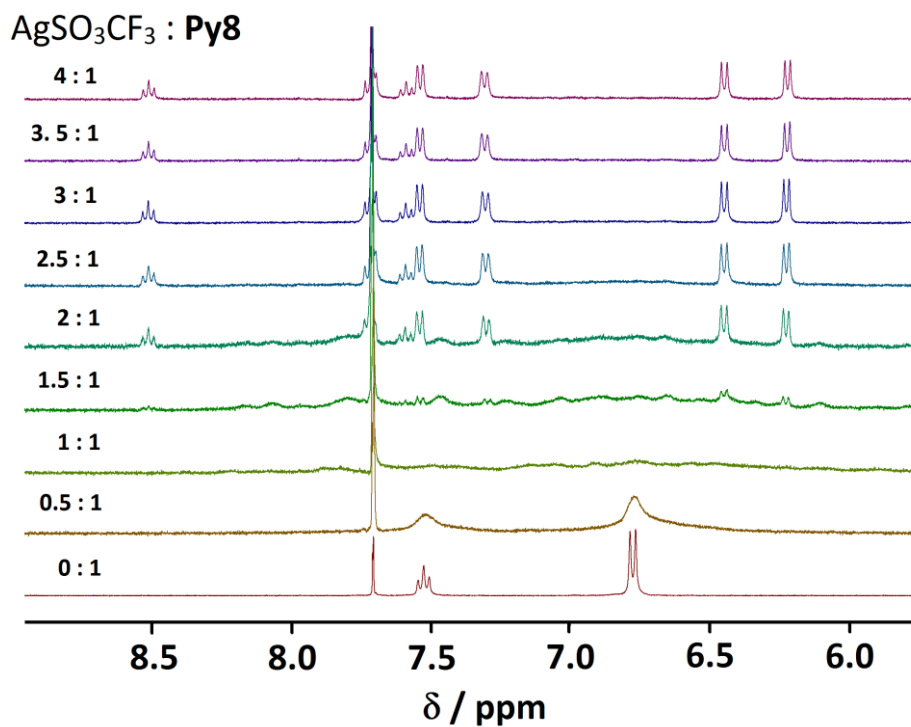
The morphology of **Py[8]-Ag** and **Py[9]-Ag** were determined on a Hitachi H-800 transmission electron microscope. The SAED pattern of **Py[8]-Ag** were taken by a JEOL JEM-2010 high-resolution transmission electron microscope.

### Hill plot

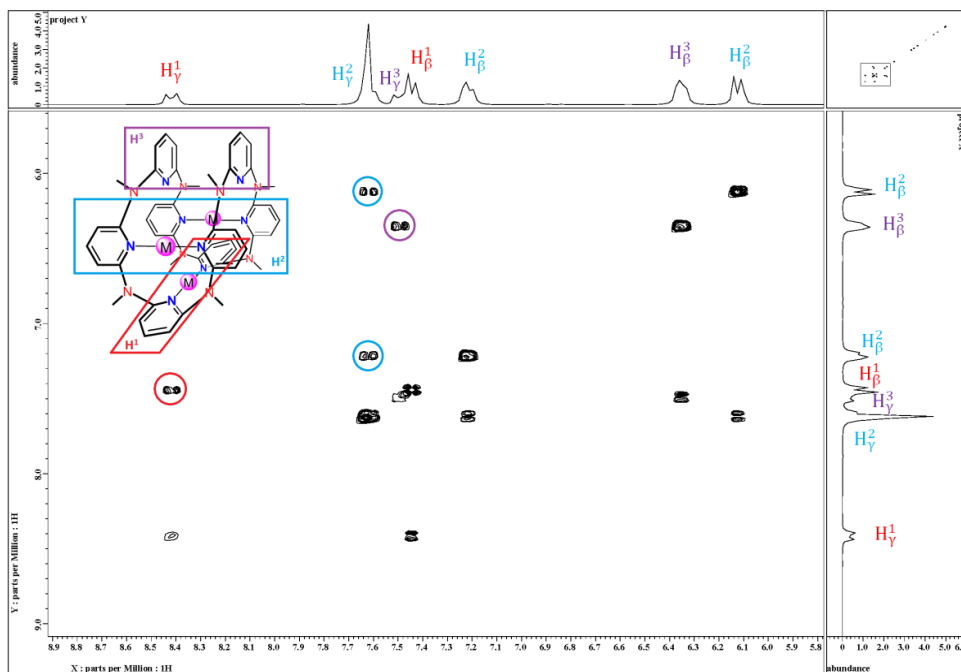
In the Hill equation:  $\log(Y/1-Y) = n\log[Ag^+] + \log K$ ,  $Y$  is the fractional saturation of the host **Py[n]** and  $K$  and  $n$  are the association constant and Hill coefficient, respectively. Herein, we assume the concentration of free silver ions  $[Ag^+]$  equals to the total silver concentration. The fractional saturation  $Y$  was calculated from the relative decrease of UV peak at 327 nm for **Py[8]** and 334 nm for **Py[9]** along with the silver ion concentration increasing from 0 to 3 equivalents relative to the macrocycles. The absorption variation at 327 nm or 334 nm was normalized on the basis of the total absorption change by the equation  $Y = \Delta\text{abs}/\Delta\text{abs}(\text{max})$ .

### References

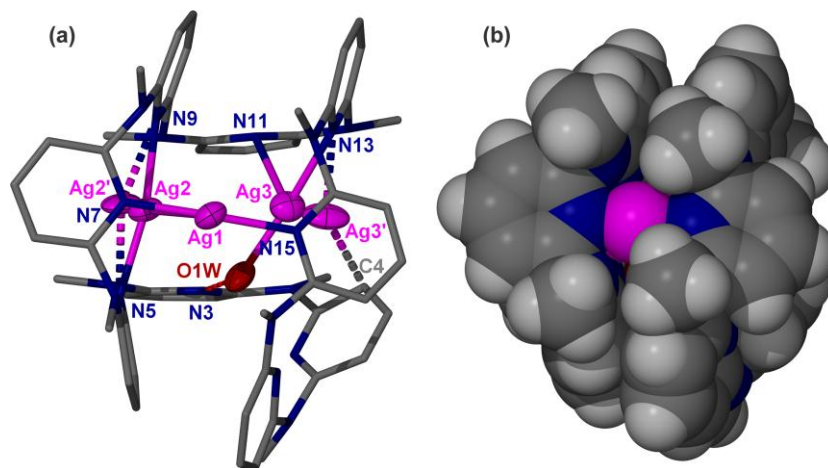
- (1) E.-X. Zhang, D.-X. Wang, Q.-Y. Zheng, M.-X. Wang, *Org. Lett.* **2008**, *10*, 2565-2568.
- (2) G. M. Sheldrick, SHELXL-97 (Univ. Göttingen, 1997).
- (3) (a) L. J. Barbour, *J. Supramol. Chem.* **2001**, *1*, 189. (b) J. L. Atwood, L. J. Barbour, *Cryst. Growth Des.* **2003**, *3*, 3-8.



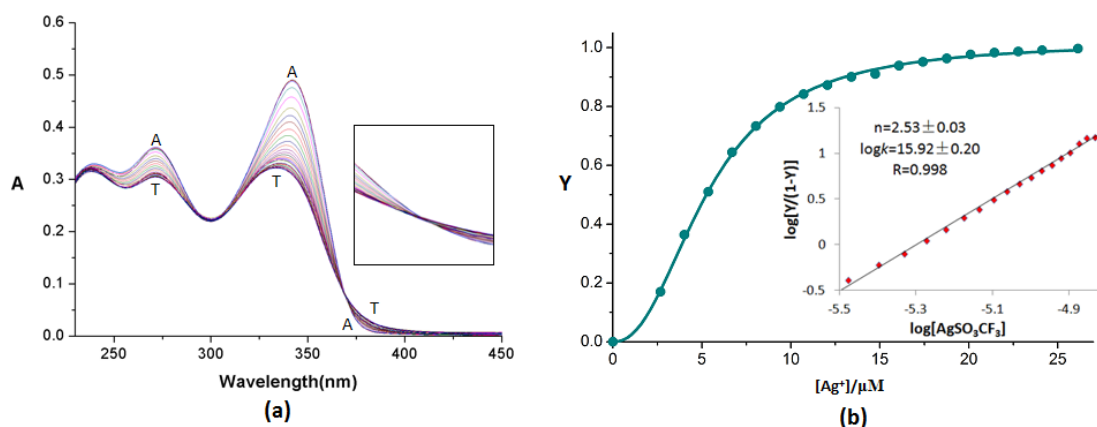
**Figure S1.** Partial <sup>1</sup>H NMR spectra (400 MHz,  $\nu(\text{CDCl}_3) : \nu(\text{CD}_3\text{OD}) = 1:1$ ) of Py[8] in its silver triflate titration experiment at  $-60^\circ\text{C}$ .



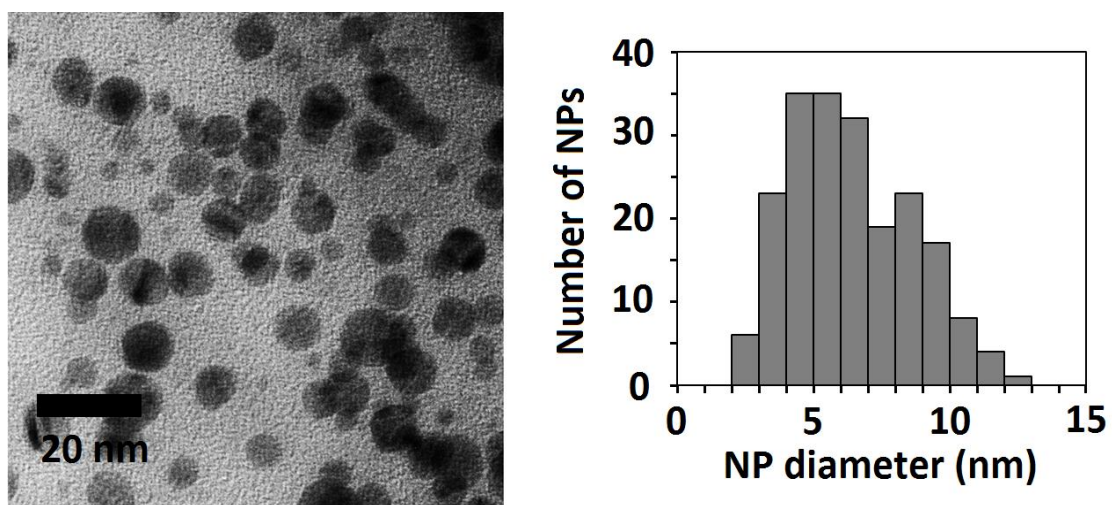
**Figure S2.** Partial <sup>1</sup>H-COSY spectrum of **1** in a mixed solvent of CDCl<sub>3</sub> and CD<sub>3</sub>OD ( $\nu:\nu = 1:1$ ) at  $-60^\circ\text{C}$ .



**Figure S3.** (a) Crystal structure of complex  $[(\text{H}_2\text{O})@(\text{Ag}_3(\text{Py}[\mathbf{9}]))] (\text{CF}_3\text{SO}_3)_3 \cdot 1.5(\text{Et}_2\text{O})$  (**2**) with partial atom labeling (50% probability for silver atoms). Hydrogen atoms and triflate groups are omitted for clarity. Silver atoms Ag2 and Ag3 each is disordered at two positions, whose coordination environments are shown in dashed lines. Selected bond lengths and distances ( $\text{\AA}$ ): Ag1-N7 2.144 (6); Ag1-N15 2.134(6); Ag2-N5 2.228(5); Ag2-N9 2.234(5); Ag2'-N5 2.320(15); Ag2'-N9 2.281(14); Ag3-N11 2.635(6); Ag3-N13 2.211(6); Ag3-O1W 2.098(5); Ag3'-N13 2.177(6); Ag3'-C4 2.454(8); Ag1...Ag2 3.210(3). (b) Metallacage structure in **2** shown in space-filling model. Color scheme for atoms: Ag, purple; C, black; H, gray; N, blue; O, red.



**Figure S4.** (a) UV-vis titration curves of **Py[9]** ( $6.7 \mu\text{M}$ ) with  $\text{AgSO}_3\text{CF}_3$  (from 0 to  $26.8 \mu\text{M}$ , a $\rightarrow$ t, step  $0.67 \mu\text{M}$ ) in a mixed solvent of  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{OH}$  (v:v = 1:1) at 298 K. (b) Binding isotherm and Hill plot for the binding of  $\text{AgSO}_3\text{CF}_3$  with **Py[9]** based on the absorption at 334 nm.



**Figure S5.** TEM images (left) and the size distribution (right) of the **Py[9]-Ag** nanoparticles sample.