

## Striking Confinement Effect: $\text{AuCl}_4^-$ Binding to Amines in a Nanocage Cavity

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### Supporting Information

#### 1. Preparation of nanocages

Siloxane nanocages were prepared according to the method described by Suh,<sup>1</sup> starting with micelles of (triethoxysilyl)propylcetylcarbamate, followed by controlled hydrolysis and condensation, further shell cross-linking with dimethyldimethoxysilane and capping with trimethylmethoxysilane. Finally, the carbamate bonds were cleaved with methanol. The propylamine groups inside the nanocages were quantified by reaction with ninhydrin.

#### 2. Cyclic Voltammetry

Data were collected with a CHI 900 Electrochemical Scanning Microscope (CH Instruments Inc.) in a one-compartment cell using a glassy carbon working electrode (diameter=3mm), a platinum wire counter electrode and a Ag/AgCl reference electrode. Before carrying out a measurement, N<sub>2</sub> was flowed through the solution for 10 minutes at a rate of 2 mL/min using a stainless steel needle. NaCl or NaClO<sub>4</sub> (Aldrich, ≥ 98.0 %) at a concentration of 0.1 M were used as supporting electrolytes in methanol/water (4.4% H<sub>2</sub>O) and methanol (0.1% H<sub>2</sub>O) solutions, respectively. The working electrode was scanned at 0.1V/s over the range 1.1 to -0.4 V vs Ag/AgCl.

#### 3. X-ray absorption Spectroscopy (XAS)

Experiments were carried out at the bending magnet beamline 5-BMD of the Dupont-Northwestern-Dow Collaborative Access Team (DND-CAT) at the Advanced Photon Source in Argonne National Laboratory. The Si(111) monochromator was detuned by 30% at the Au L<sub>III</sub> edge (11919 eV) to minimize contributions from harmonics. The spectra were collected in the fluorescence mode from solution samples in polyethylene cylindrical cells (diameter=1 cm, volume=1 cm<sup>3</sup>) sealed with Parafilm M (Alcan, Inc.).

Phase shifts, backscattering amplitudes, and XANES references were obtained experimentally from the following reference compounds: AuCl<sub>3</sub> (Aldrich, 99.99+%) for Au(III)–Cl, Au(OH)<sub>3</sub> (Aldrich) for Au(III)–O, Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Aldrich, 99.995%) for Au(III)-N and Au foil for Au(0) and Au–Au. Both the XANES and EXAFS data were analyzed by standard procedures using the WINSAX97 software.

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4. UV-VIS absorption spectra were recorded on a Spectronic Genesys 2 spectrometer. The optical path length was 1.0 or 0.1 cm, depending on the solution concentration. Deionized distilled water or methanol was used as reference.

5. pH calculation of a nm-size water droplet containing one hydroxyl ion:

The concentration of hydroxyl ions in a solution composed of one molecule of the ion in a nm-size water droplet was calculated, assuming the pH in the droplet can be defined the same way as in bulk solution, its value is calculated for different droplet sizes.

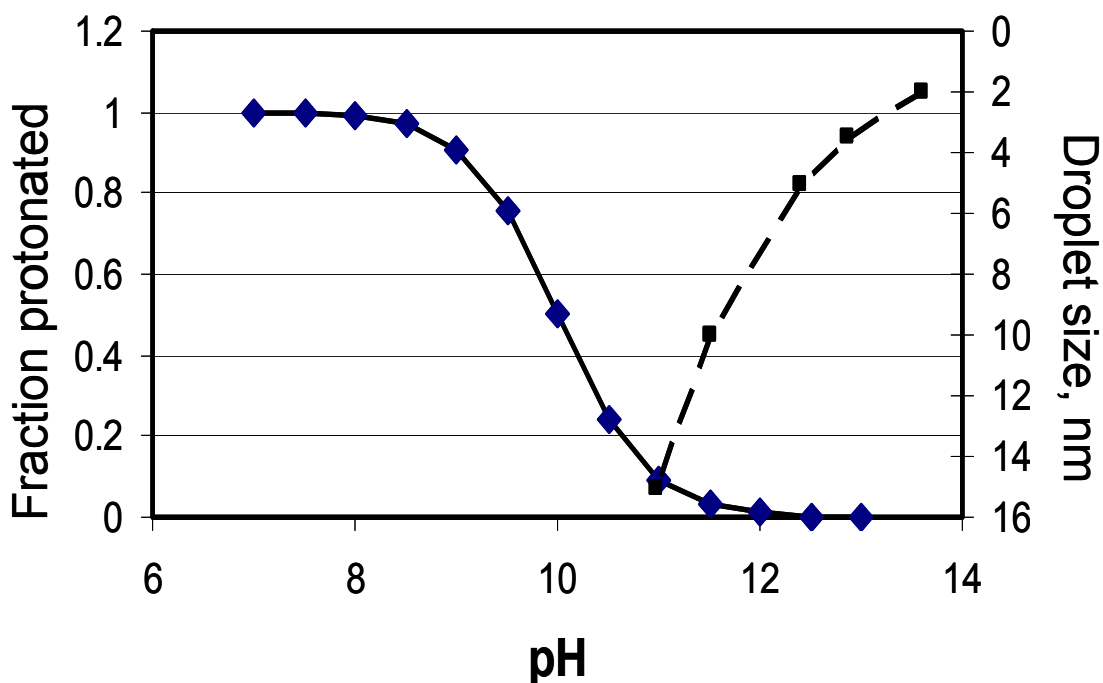


Figure S1. (blue diamond) Fraction of protonated amine of  $pK = 10$  as a function of pH, and (black square) pH of a droplet of water containing one molecule of hydroxyl ion as a function of droplet diameter.

6. UV-vis spectra of  $\text{AuCl}_4^-$  at different pHs.

These spectra were collected for solutions containing  $72 \mu\text{M}$   $\text{HAuCl}_4$  and various amounts of NaOH or HCl to adjust the pH. Additional NaCl was added to yield a Cl/Au ratio of 1070. The spectra were monitored as a function of time until no further changes could be detected. The final spectra after 5 h and the pH of the solution immediately after collecting the spectra are shown in Fig. S2.

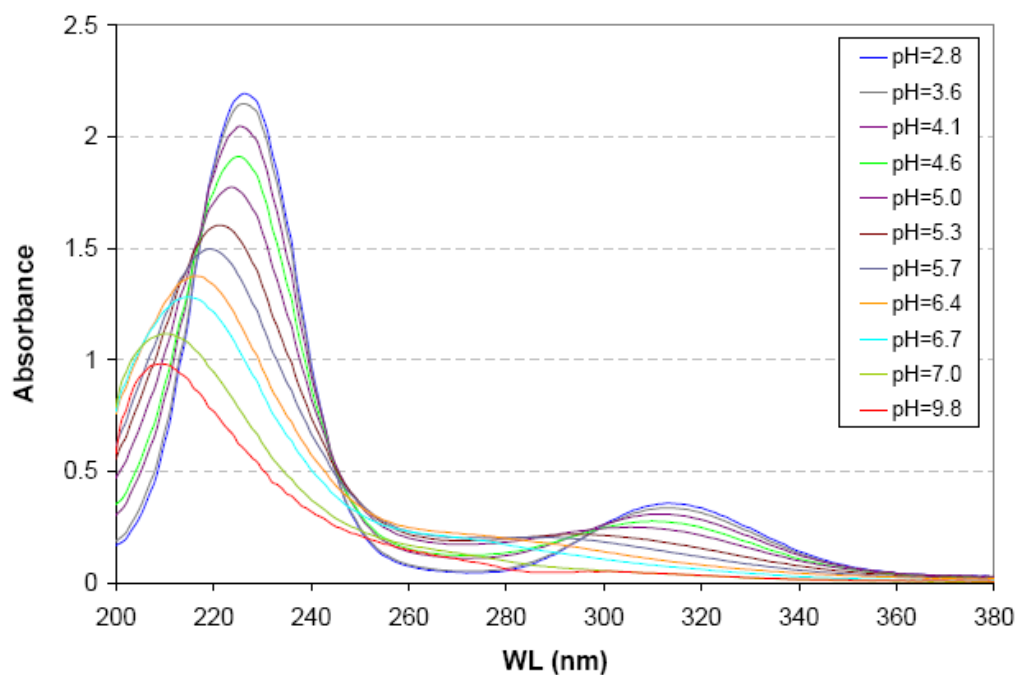


Figure S2. UV-vis spectra of 72  $\mu\text{M}$   $\text{HAuCl}_4$  solutions at different pHs adjusted with NaOH.

7. Correlation between Au-Cl coordination number and extinction coefficient at 227 nm. From the known hydrolysis constants<sup>2-6</sup> (Table S1) and concentration of  $\text{AuCl}_4^-$ , total  $\text{Cl}^-$  concentration, and pH, the distribution of various  $\text{AuCl}_x(\text{OH})_{4-x}^-$  species could be calculated. Table S2 shows one set of results with total Au(III) concentration of 72  $\mu\text{M}$ . From the distribution of Au species, the population-weighted average Au-Cl coordination (CN) was calculated:

$$\text{CN} = \sum_{x=1}^4 x F_{\text{AuCl}_x(\text{OH})_{4-x}^-}$$

where F is the mole fraction of Au in that speciation.

Table S1. Hydrolysis constants and their corresponding reactions.

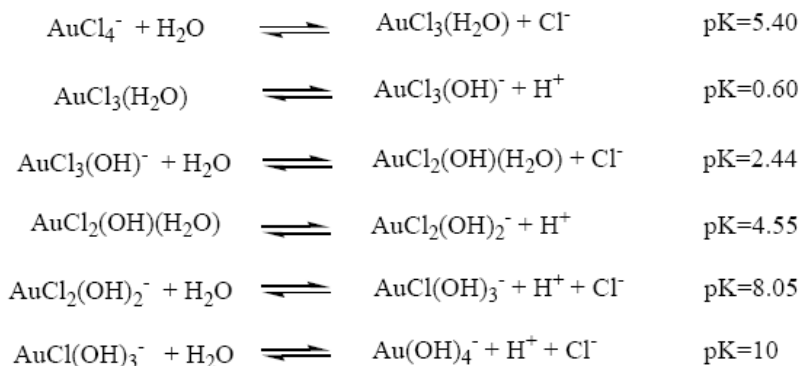


Table S2. Molar extinction coefficient and the corresponding calculated distribution of various  $\text{AuCl}_x(\text{OH})_{4-x}$  species in an aqueous solution at different pH.  $[\text{Au(III)}] = 72 \text{ } \mu\text{M}$ ,  $\text{Cl}/\text{Au} = 1070$ .

| pH   | Abs<br>(226nm) | $\epsilon \times 10^4$<br>( $\text{M}^{-1} \text{cm}^{-1}$ ) | $\chi F_{\text{AuCl}_x(\text{OH})_{4-x}}$ |                              |                                |                              | Au-Cl<br>CN |
|------|----------------|--------------------------------------------------------------|-------------------------------------------|------------------------------|--------------------------------|------------------------------|-------------|
|      |                |                                                              | $\text{AuCl}_4^-$                         | $\text{AuCl}_3(\text{OH})^-$ | $\text{AuCl}_2(\text{OH})_2^-$ | $\text{AuCl}(\text{OH})_3^-$ |             |
| 2.8  | 2.192          | 3.040                                                        | 3.97                                      | 0.02                         | 0.00                           | 0.00                         | 3.99        |
| 3.6  | 2.147          | 2.978                                                        | 3.81                                      | 0.14                         | 0.00                           | 0.00                         | 3.95        |
| 3.8  | 2.132          | 2.957                                                        | 3.70                                      | 0.21                         | 0.01                           | 0.00                         | 3.92        |
| 4.1  | 2.044          | 2.835                                                        | 3.45                                      | 0.39                         | 0.02                           | 0.00                         | 3.85        |
| 4.3  | 2.038          | 2.827                                                        | 3.18                                      | 0.57                         | 0.03                           | 0.00                         | 3.78        |
| 4.6  | 1.906          | 2.644                                                        | 2.63                                      | 0.94                         | 0.06                           | 0.00                         | 3.63        |
| 5    | 1.743          | 2.417                                                        | 1.66                                      | 1.50                         | 0.17                           | 0.00                         | 3.33        |
| 5.3  | 1.518          | 2.105                                                        | 0.97                                      | 1.75                         | 0.34                           | 0.00                         | 3.07        |
| 5.5  | 1.422          | 1.972                                                        | 0.62                                      | 1.75                         | 0.51                           | 0.01                         | 2.88        |
| 5.7  | 1.344          | 1.864                                                        | 0.36                                      | 1.61                         | 0.71                           | 0.02                         | 2.70        |
| 6.4  | 1.137          | 1.577                                                        | 0.03                                      | 0.60                         | 1.25                           | 0.17                         | 2.04        |
| 6.7  | 1.012          | 1.404                                                        | 0.01                                      | 0.28                         | 1.18                           | 0.31                         | 1.78        |
| 7    | 0.756          | 1.049                                                        | 0.00                                      | 0.11                         | 0.92                           | 0.49                         | 1.53        |
| 7.2  | 0.642          | 0.890                                                        | 0.00                                      | 0.05                         | 0.72                           | 0.61                         | 1.38        |
| 7.4  | 0.64           | 0.888                                                        | 0.00                                      | 0.03                         | 0.52                           | 0.71                         | 1.26        |
| 9    | 0.538          | 0.746                                                        | 0.00                                      | 0.00                         | 0.01                           | 0.45                         | 0.46        |
| 9.4  | 0.578          | 0.802                                                        | 0.00                                      | 0.00                         | 0.00                           | 0.25                         | 0.25        |
| 9.8  | 0.606          | 0.840                                                        | 0.00                                      | 0.00                         | 0.00                           | 0.12                         | 0.12        |
| 9.9  | 0.599          | 0.831                                                        | 0.00                                      | 0.00                         | 0.00                           | 0.09                         | 0.09        |
| 11.6 | 0.51           | 0.707                                                        | 0.00                                      | 0.00                         | 0.00                           | 0.00                         | 0.00        |

In the UV-vis spectra in Figure S2, the bands at 227 and 313 nm are characteristic of  $\text{AuCl}_4^-$  solutions in water and methanol. The band at 227 nm corresponds to the  $^1\text{A}_{1g} \rightarrow ^1\text{E}_u(\text{a})$  ligand-to-metal charge-transfer transition (LMCT),<sup>7</sup> which shifts to higher energies as  $\text{OH}^-$  or  $-\text{NH}_2$  displaces  $\text{Cl}^-$  from the Au(III) inner-coordination sphere and reduces the absorption intensity at 227 nm.

Using the extinction coefficient from the UV-vis spectra and the CN either from calculation or from EXAFS results, a correlation between the average Au-Cl coordination and the extinction coefficient at 227 nm was derived (Fig. S3). This correlation was found to be applicable for experiments using two different Au concentrations, with or without addition of NaCl to increase the Cl/Au ratio to 1070, and in water or methanol solution.

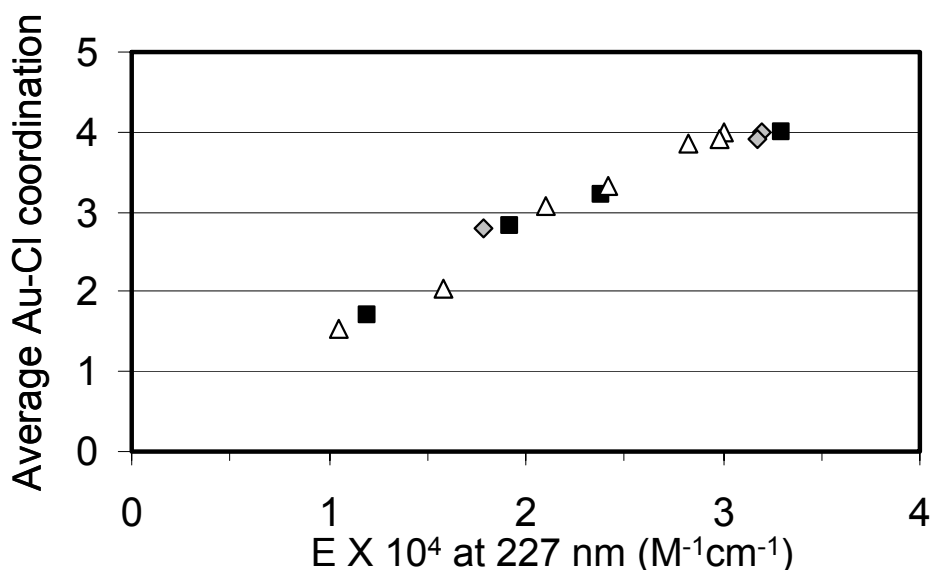


Figure S3. Correlation between Au-Cl coordination and extinction coefficient at 227 nm. Open triangles: 72  $\mu\text{M}$  Au(III) in water, from UV-vis; filled square: 426  $\mu\text{M}$  Au(III) in water, from UV-vis; grey diamond: 426  $\mu\text{M}$  Au(III) in methanol, from EXAFS and UV-vis.

#### 8. Analysis of EXAFS data.

X-ray absorption spectroscopy allowed direct measurement of changes in the Au(III) inner-coordination sphere resulting from the displacement of chloride by  $-\text{NH}_2$  or  $\text{OH}^-$  because chloride is a much stronger scatterer than either N or O. The collected data were analyzed using the standard analysis procedure for the WINXAS97 software. The coordination parameters were obtained by a least square fit in  $k$ - and  $r$ -space of the isolated multiple-shell,  $k^2$  weighted Fourier transform data. These parameters include the coordination number, the bond distance, the Debye-Waller factor, and  $E_0$ . Since the scattering factors for N and O and the Au-O and Au-N bond lengths are similar, they are not distinguished by the EXAFS data. Therefore, changes in the Au-Cl coordination due to solvolysis were independently determined, as described in the text.

On the other hand, the differences between Au-Cl and Au-N are substantial, and can be readily detected in both the real and the imaginary components of the Fourier transformed data, as shown in Figure S4 for the same three samples as in Figure 1 in the text. The magnitude of the Fourier Transform also showed a decrease in Au-Cl coordination for sample C. We estimate that the uncertainty in the changes in the coordination number is about 0.1. Thus, a change of the Au-Cl coordination number of unity is well beyond uncertainty.

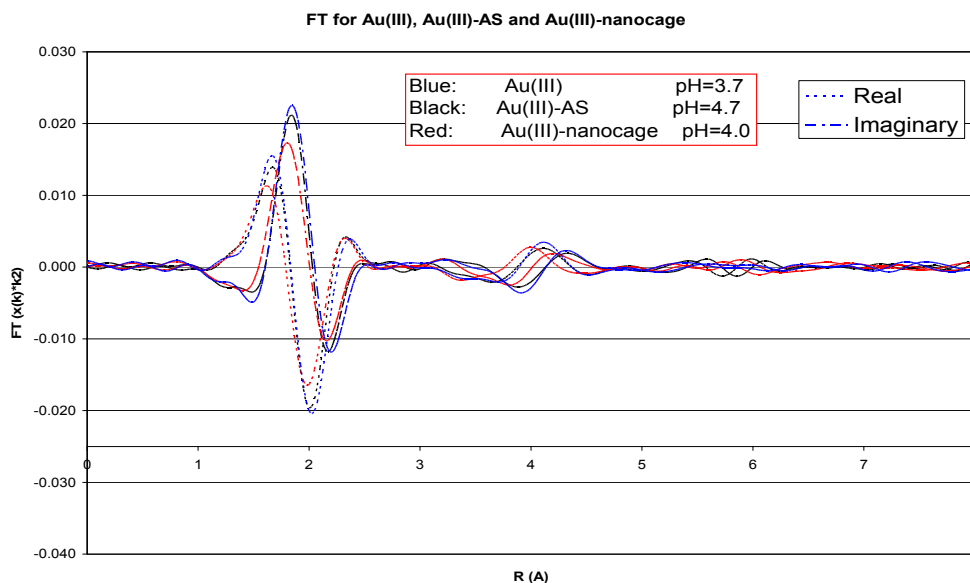


Figure S4. The real and imaginary components of the Fourier transform of the data corresponding the three samples in Figure 1. The red curves are distinctly different from the blue and black curves, clearly indicating a change in the coordination parameters.

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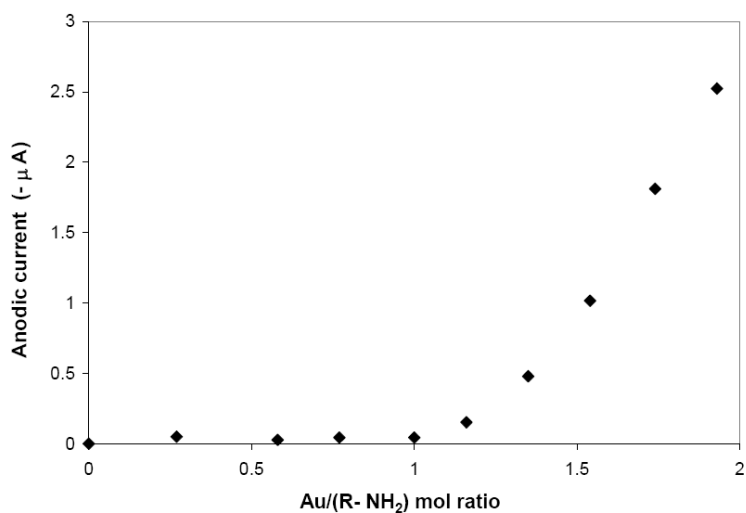


Figure S5. Magnitude of anodic current during the oxidative scan in cyclic voltammetry of various concentrations of  $\text{AuCl}_4^-$  in methanol solution (4.4%  $\text{H}_2\text{O}$ ) containing 42  $\mu\text{M}$  amines in nanocages and  $\log[\text{H}^+] = -7.4$ . Scan rate 0.1 V/s, Ag/AgCl reference electrode, 0.11 M NaCl supporting electrolyte.

## References

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