

## [ $m \times n$ ] Metal Ion Arrays Templated by Coordination Cages

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**Abstract:** Three-dimensional  $m \times n$  arrays of metal ion clusters can be assembled as aromatic stacks of planar polynuclear metal complexes within columnar coordination cages. The polynuclear complexes and cage height program the final array structures of the metal ion clusters. Cyclic trinuclear Au(I) complexes ( $m = 3$ ) assembled into trigonal prismatic arrays ( $n = 1-3$ ) within the cages and the array structures were clearly shown by X-ray crystallographic analysis. A silver-sandwiched hetero-Au<sub>3</sub>-Ag-Au<sub>3</sub> cluster was also prepared by treating a hexanuclear Au<sub>3</sub>-Au<sub>3</sub> cluster with Ag(I) ion.

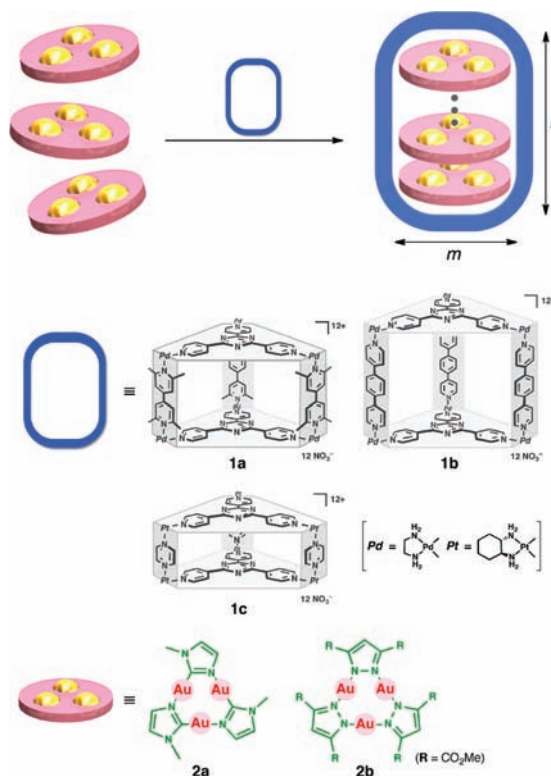
Clusters of metal ions can exhibit multiple metal-metal interactions and give rise to unique properties.<sup>1</sup> Methods for generating discrete linear arrays<sup>2</sup> or two-dimensional grids<sup>3a</sup> or layers<sup>3b,c</sup> exist but are often lengthy and tedious. To date there exist no reliable, simple methods for generating discrete three-dimensional (3D) polynuclear metal ion arrays in which the number and spacing of metal ions can be precisely controlled. Here we demonstrate that 3D arrays of metal ion clusters can be obtained easily using self-assembled organic-pillared cages **1** as templates for columnar stacks of planar polynuclear metal complexes (Scheme 1).<sup>4</sup> The number of metal ions ( $m \times n$ ) in the clusters is determined by number of ions in each polynuclear complex ( $m$ ) and the encapsulation number ( $n$ ), which is controlled by changing the length of the pillar ligands of the organic cage.

In this work, using cyclic trinuclear ( $m = 3$ ) Au(I) complexes **2**,<sup>5</sup> we assembled [ $3 \times 2$ ] and [ $3 \times 3$ ] Au(I) clusters along the  $C_3$  axis of cage **1** to form 3D columnar metal arrays. These polynuclear metal complexes are distinguishable from conventional  $m \times n$ -type polynuclear complexes (e.g., prismatic [Pt<sub>3</sub>(CO)<sub>6</sub>]<sub>*n*</sub><sup>2-</sup> oligomers<sup>6</sup>) in that the stacking number is strictly defined by the cage template.

Imidazolate-bridged trinuclear Au(I) complex **2a** (33.5 mg, 0.040 mmol) was suspended in an aqueous solution of cage **1a** (10 mM, 1.0 mL) at 60 °C for 2 h.<sup>7</sup> After removal of the residual excess guest, the quantitative conversion to inclusion complex **1a**·(**2a**)<sub>2</sub> was confirmed by NMR analysis (Figure 1b,c). In the <sup>1</sup>H NMR spectrum, the signals of guest **2a** were shifted upfield as a result of shielding by the aromatic panels of **1a**, and two sets of signals were observed for cage **1a** and guest **2a** in a ~1:1 ratio; the same and opposite orientations of the two enclathrated **2a** complexes are possible and diastereomeric.<sup>8</sup> Assignment of the signals to diastereomeric host-guest complexes was supported by the observation of identical diffusion coefficients for the two species ( $D = 1.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) in diffusion-ordered NMR spectroscopy (DOSY). Cold-spray ionization mass spectrometry (CSI-MS) also confirmed a single, stable solution structure of complex **1a**·(**2a**)<sub>2</sub> with a molecular weight of 4674.4 Da.

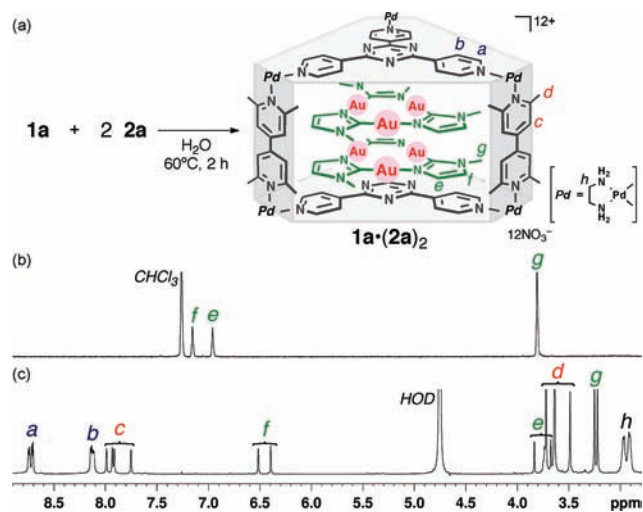
Next, we constructed [ $3 \times 3$ ] Au(I) clusters within cage **1b**. Triple stacks of electron-rich aromatics (donor, D) are unfavorable because of electrostatic repulsion, and the electron-poor triazine

**Scheme 1.** (top) Schematic Representation of Three-Dimensional Arrays of Metal Ion Clusters within Coordination Cages **1**; (bottom) Accumulated Trinuclear Au(I) Complexes **2**

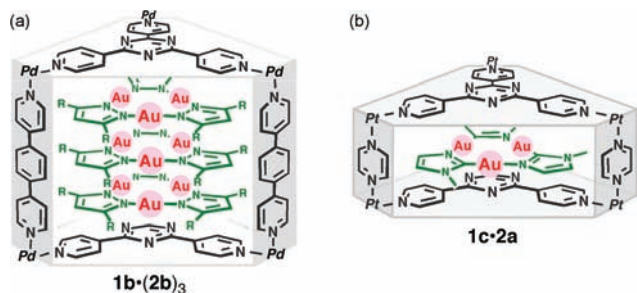


panel (acceptor, A) of cage **1** is typically inserted during self-assembly to form an alternating A-D-A-D-A stack.<sup>4c,9</sup> To circumvent the insertion of the triazine panel, we designed the electron-deficient trinuclear Au(I) complex **2b**<sup>10</sup> with electron-withdrawing ester groups, and when **2b** used as the template in the formation of cage **1b**, the desired inclusion complex **1b**·(**2b**)<sub>3</sub> formed (Figure 2a). As expected, the three guests within cage **1b** appeared as two sets of signals in a 2:1 ratio in the NMR spectrum (see the Supporting Information).

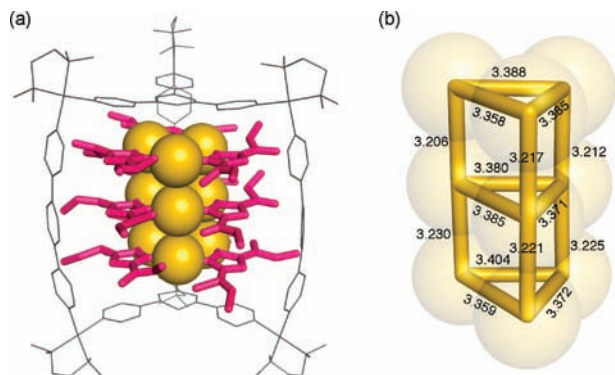
The structure of the [ $3 \times 3$ ] Au(I) cluster was unambiguously determined by X-ray crystallographic analysis of the analogous complex **1b'**·(**2b**)<sub>3</sub> (Figure 3a).<sup>11</sup> The gold atoms of **2b** are arranged in an eclipsed, pseudo- $D_{3h}$  symmetry<sup>12</sup> rather than a twisted, offset  $D_3$  symmetry and form an extended trigonal prism in spite of the unfavorable steric repulsion between side chains (Figure 3b). Intermolecular aurophilic Au...Au interactions are clearly visible, as the intermolecular Au...Au distances range from 3.206 to 3.230 Å, which are significantly shorter than the sum of the van der Waals radii (3.6 Å).<sup>13</sup> Trinuclear Au(I) complexes usually form offset stacks in the crystalline state, with only two of the three Au(I) ions participating in intermolecular Au...Au interactions;<sup>14</sup> thus, the



**Figure 1.** (a) Formation of a  $[3 \times 2]$  Au(I) cluster within cage **1a** [inclusion complex  $1a \cdot (2a)_2$ ]. (b, c)  $^1\text{H}$  NMR spectra (500 MHz, 300 K) of (b) trinuclear Au(I) complex **2a** (in  $\text{CDCl}_3$ ) and (c) inclusion complex  $1a \cdot (2a)_2$  (in  $\text{D}_2\text{O}$ ).

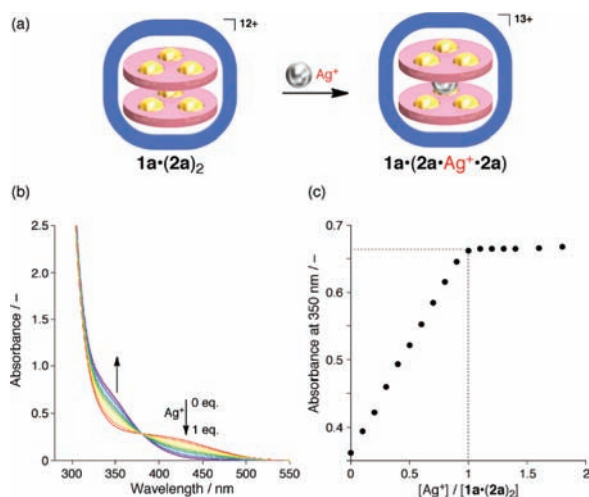


**Figure 2.** Chemical structures of (a) a  $[3 \times 3]$  Au(I) cluster within cage **1b** [inclusion complex  $1b \cdot (2b)_3$ ] and (b) a  $[3 \times 1]$  Au(I) cluster within cage **1c** (inclusion complex  $1c \cdot 2a$ ).



**Figure 3.** (a) X-ray crystal structure of  $1b \cdot (2b)_3$ . (b) Highlight of the trigonal prismatic array of the  $[3 \times 3]$  Au(I) cluster. Intra- and intermolecular Au–Au distances are given in Å.

columnar array of nine Au(I) ions is due not solely to  $\text{Au} \cdots \text{Au}$  interactions but also to the involvement of symmetry constraints imposed by the  $D_{3h}$  symmetry of cage **1b'**. Host–guest aromatic–aromatic stacking interactions between guest **2b** and host **1b'** are also clearly present in the crystal structure, as the two triazine panels of cage **1b'** clamp down upon the  $(2b)_3$  cluster, resulting in severe distortion of the rigid pillar ligand. For the sake of completeness, the simplest  $[3 \times 1]$  Au(I) cluster **1c·2a** was also prepared. Cage **1c**, with pyrazines as pillar ligands, bound **2a** to form the inclusion complex **1c·2a** (Figure 2b).



**Figure 4.** (a) Schematic representation of the insertion of one Ag(I) ion into complex  $1a \cdot (2a)_2$ . (b) Change in the absorption spectra of complex  $1a \cdot (2a)_2$  as the concentration of  $\text{AgNO}_3$  was varied.  $[1a \cdot (2a)_2] = 0.10 \text{ mM}$  in  $\text{H}_2\text{O}$  (1 cm cell, 3.2 mL). (c) Spectrophotometric titration curve of complex  $1a \cdot (2a)_2$  with  $\text{AgNO}_3$  in  $\text{H}_2\text{O}$  ( $\lambda = 350 \text{ nm}$ ).

Polynuclear Au(I) complexes involving  $\text{Au(I)} \cdots \text{Au(I)}$  interactions often display characteristic emissions in the visible region,<sup>15</sup> but all of the Au clusters in cages **1a–c** were nonemissive, as cage **1** strongly absorbs light with  $\lambda < 350 \text{ nm}$  and host–guest interactions can also efficiently quench guest emission.<sup>16</sup>

The addition of metal ions to trimeric Au(I) clusters to form  $\text{Au}_3\text{–M–Au}_3$  sandwich complexes has been observed only in the solid state,<sup>17</sup> yet within cage **1a**, Ag(I) ions entered the pair of trimeric  $\text{Au}_3$  clusters (**2a**)<sub>2</sub> to form a  $\text{Au}_3\text{–Ag–Au}_3$  “sandwich” in aqueous solution at room temperature (Figure 4). When an aqueous solution of complex  $1a \cdot (2a)_2$  (0.10 mM, 3.2 mL) was titrated with aqueous  $\text{AgNO}_3$  (8.0 mM, 0–0.040 mL), the orange solution gradually turned pale-yellow (Figure 4b). UV–vis spectra clearly indicated the uptake of Ag(I) ions in a 1:1 ratio (Figure 4c). The  $^1\text{H}$  NMR signals of **2a** shifted downfield ( $\Delta\delta \approx 0.3 \text{ ppm}$ ), but the two entrapped guests remained equivalent and retained  $D_{3h}$  symmetry. Since the cage framework is highly positive (12+), electrostatic repulsion precludes a simple associative complex, and the NMR and UV data are best rationalized by a structure in which the Ag(I) ion is bound between the  $\text{Au}_3$  units of guests **2a** in a  $\text{Au}_3\text{–Ag–Au}_3$  cluster.

The  $\text{Ag}^+$  ion was irreversibly bound and chemically inert within  $1a \cdot (2a)_2$ ;  $\text{AgCl}$  precipitation was not observed upon addition of 10 equiv of  $\text{NH}_4\text{Cl}$ , nor were photoreduced Ag(0) colloids formed under UV irradiation. The binding of  $\text{Ag}^+$  ions by  $1a \cdot (2a)_2$  is specific; the binding of alkali metal ions was not observed.

In summary, we have successfully constructed a matrixlike 3D array of metal clusters using self-assembled columnar coordination cages as templates for the stacking of polynuclear metal complexes. The height and width of the metal array can be determined by judicious choices of the precursor metal complexes and the organic pillar ligands. This method is simple and widely applicable to a variety of planar metal complexes and will allow straightforward access to unprecedented homo- and heterometallic clusters.

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**Supporting Information Available:** Experimental procedures, physical properties, and crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) The crystal structure revealed that the trigonal prism array is slightly twisted, which strictly speaking gives D<sub>3</sub> rather than D<sub>3h</sub> symmetry.
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