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Stimuli-Responsive and Structure-Adaptive Three-Dimensional Gold(I) Cluster Cages Constructed via "De-aurophilic" Interaction Strategy

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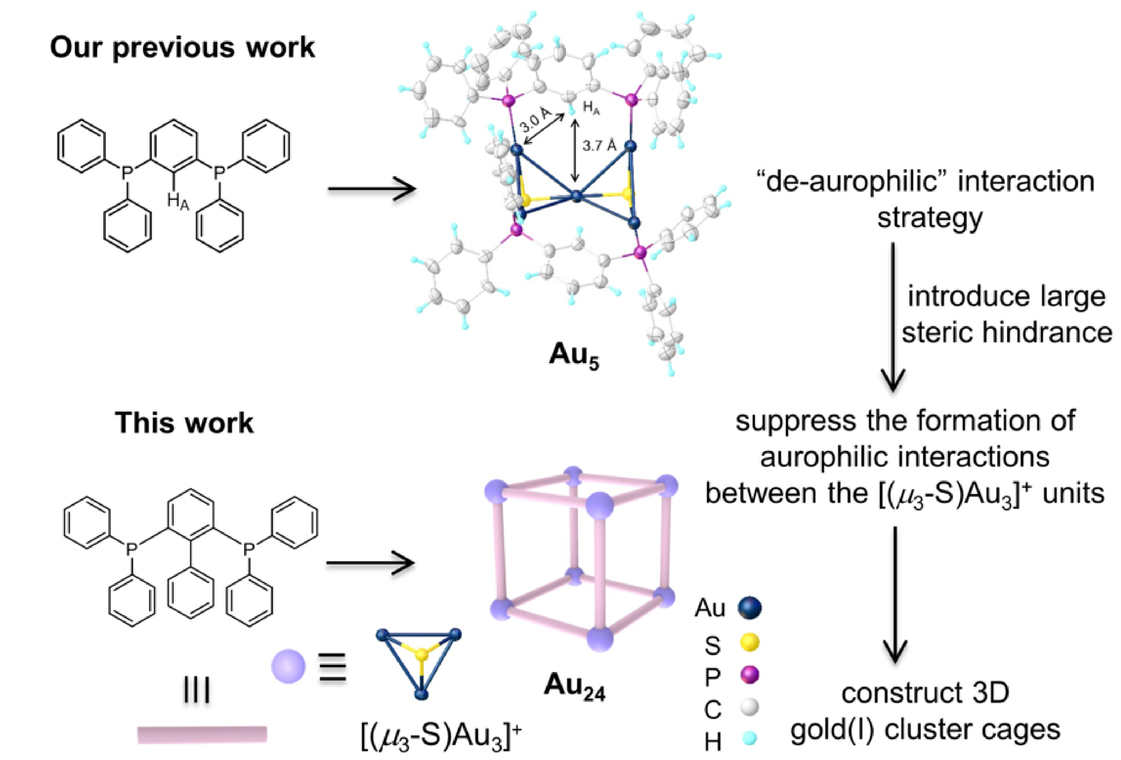
Abstract

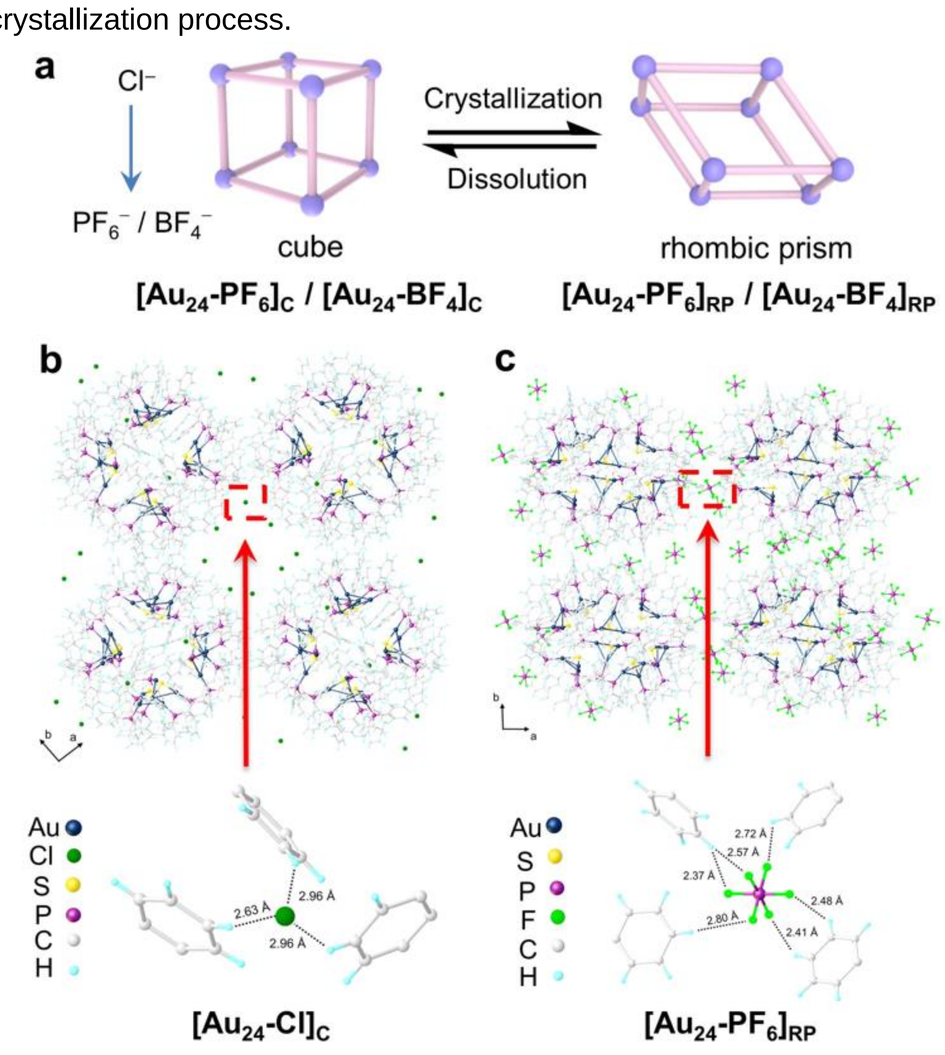
Self-assembly of three-dimensional (3D) metallo-supramolecular cages has drawn increasing attention for their potential to interconvert between different architectures due to the dynamic and reversible features of the coordination bond. While gold(I) clusters have attracted much interest due to their propensity to exhibit aurophilic interactions, the construction of 3D gold(I) cluster cages has remained a challenging and daunting task. Here, we proposed a "de-aurophilic" interaction strategy, which involves the prevention of aurophilic interaction formation between the basic $[(m_3\text{-}S)Au_3]^+$ units, to construct 3D gold(I) cluster cages. Through the judicious design of diphosphine ligands, an unprecedented class of gold(I) cluster cages with adaptive structures has been constructed. These gold(I) cluster cages are found to show intriguing stimuli-responsive structure transformation and interconversion. This work not only provides a strategy for the design and construction of novel 3D supramolecular cages based on cluster nodes, but also offers a paradigm to study the stimuli-responsive structural interconversion between the unique structures of these gold(I) cluster cages.

Rational Design Strategy of Gold(I) Cluster Cages



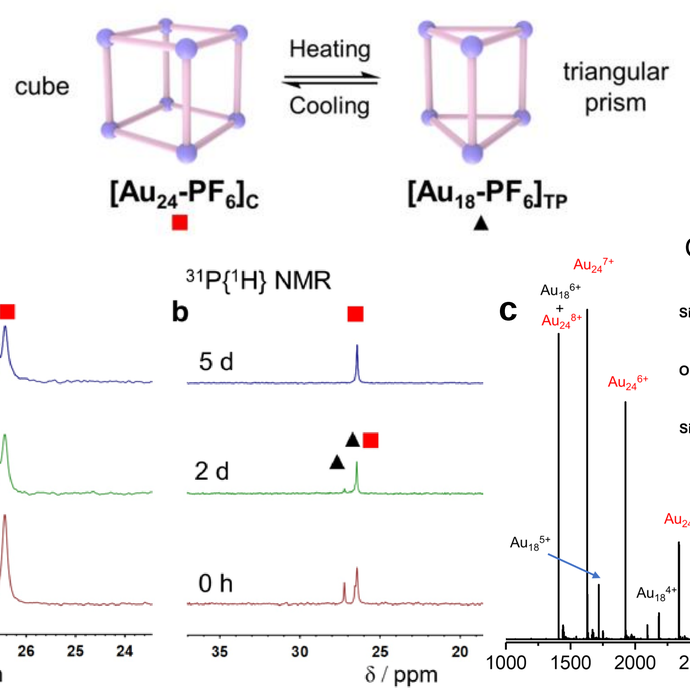
Anion-Induced Structural Transformation from the Cube to the Rhombic Prism

The rhombic prism structures of $\mathbf{[Au_{24}\text{-}PF_6]_{RP}}$ / $\mathbf{[Au_{24}\text{-}BF_4]_{RP}}$ show a larger number of hydrogen bonds and stronger hydrogen bonding between the cations and anions than the cubic structure of $\mathbf{[Au_{24}\text{-}Cl]_C}$. Therefore, a change of the counterions from Cl^- to PF_6^- or BF_4^- would result in structural transformation from a cubic structure to a rhombic prism structure during the crystallization process.



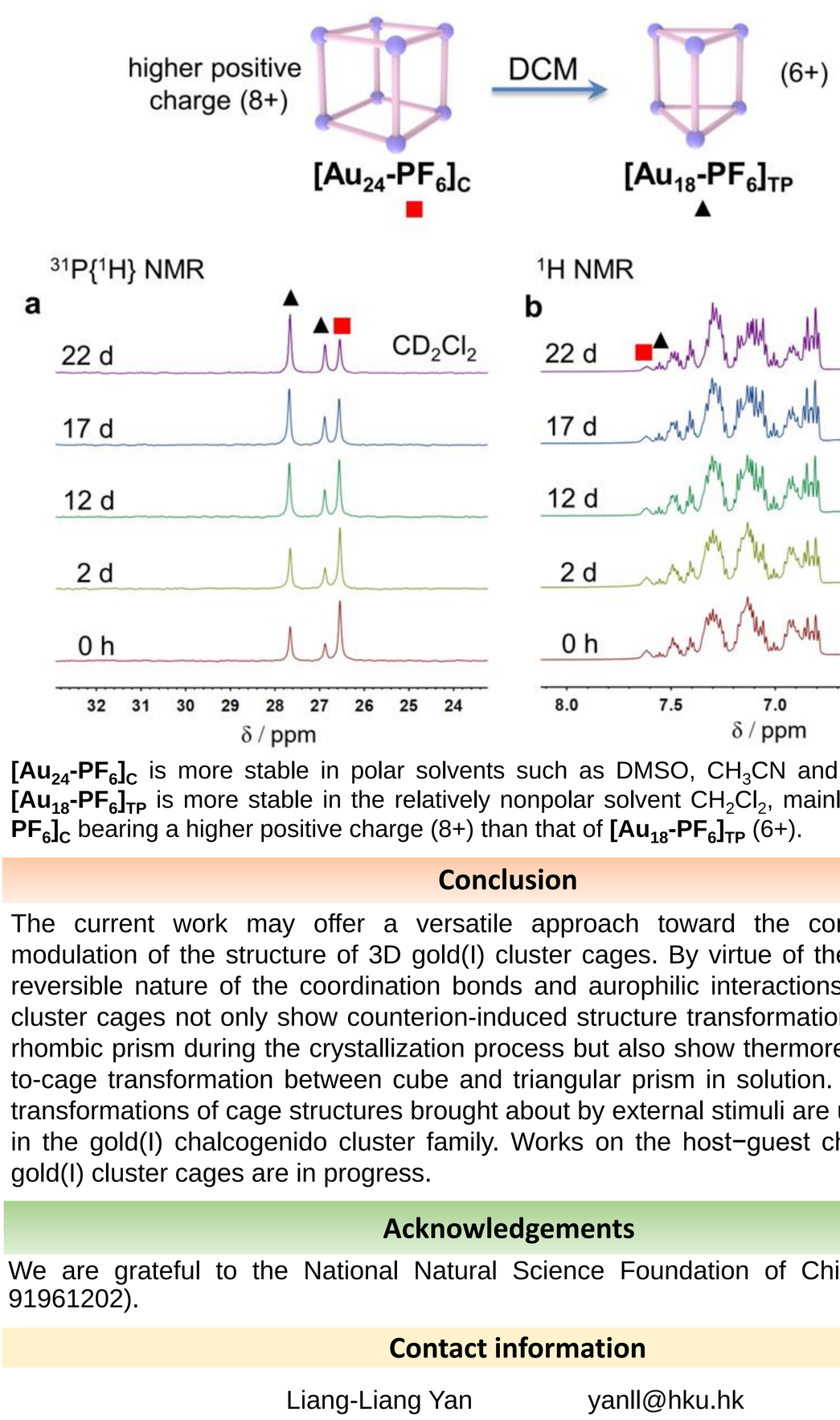
(a) Reversible structural conversion between cube and rhombic prism. Packing diagram of (b) $\mathbf{[Au_{24}\text{-}Cl]_C}$ and (c) $\mathbf{[Au_{24}\text{-}PF_6]_{RP}}$.

Temperature-Induced Reversible Structural Transformation between the Cubic Cage and the Triangular Prism Cage



(a) $^{31}P\{^1H\}$ NMR spectral change of $\mathbf{[Au_{24}\text{-}PF_6]_C}$ before and after heating in CD_3CN. (b) $^{31}P\{^1H\}$ NMR spectral change of a mixture $\mathbf{[Au_{24}\text{-}PF_6]_C}$ and $\mathbf{[Au_{18}\text{-}PF_6]_{TP}}$ with time at room temperature in CD_3CN. (c) CSI-MS of the mixture of $\mathbf{[Au_{24}\text{-}PF_6]_C}$ and $\mathbf{[Au_{18}\text{-}PF_6]_{TP}}$.

Solvent-Mediated Structural Conversion



$\mathbf{[Au_{24}\text{-}PF_6]_C}$ is more stable in polar solvents such as DMSO, CH_3CN and acetone, while $\mathbf{[Au_{18}\text{-}PF_6]_{TP}}$ is more stable in the relatively nonpolar solvent CH_2Cl_2, mainly due to $\mathbf{[Au_{24}\text{-}PF_6]_C}$ bearing a higher positive charge (8+) than that of $\mathbf{[Au_{18}\text{-}PF_6]_{TP}}$ (6+).

Conclusion

The current work may offer a versatile approach toward the construction and modulation of the structure of 3D gold(I) cluster cages. By virtue of the dynamic and reversible nature of the coordination bonds and aurophilic interactions, these gold(I) cluster cages not only show counterion-induced structure transformation from cube to rhombic prism during the crystallization process but also show thermoreversible cage-to-cage transformation between cube and triangular prism in solution. Such dynamic transformations of cage structures brought about by external stimuli are unprecedented in the gold(I) chalcogenido cluster family. Works on the host−guest chemistry of 3D gold(I) cluster cages are in progress.

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