Theoretical investigation in preparing water-soluble $Au_{25-n}M_n$ (M = Au, Ag, Cu, Pd, Pt) Nanoclusters with atomic precision

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Ultrasmall (< 2 nm), water-soluble noble metal nanoclusters have shown great potential in bio-imaging, diagnosis, and therapy for heavy ills (such as cancer, Parkinson's disease *etc.*). Benefiting from the small size, the atomic composition of these clusters has been well elucidated by ESI-MS, and EXAFS *etc*. Fantastic size effect was observed, that is, the physical-chemical properties and the physiologic functional of these nanoclusters are highly dependent on their atomic size (mainly the number of metal atoms). However, the precise atomic structure, and especially the metal-metal or metal-ligand binding modes of these clusters, have been rarely reported to date. The ambiguity in atomic structure remarkably limited the investigation on their structure-property correlations and the practical application.
In the regime of the "precision to precision" protocols[1,2], we herein used density functional theory (DFT) calculations to probe the thermodynamic plausibility and inherent determinants in synthesizing atomically precise, water-soluble clusters via the framework-maintained two-phase ligand exchange method. A series of rod-like $Au_{25-n}M_n$ (M = Au, Ag, Cu, Pd, Pt) clusters with the same framework but varied ligands and metal composition were chosen as the modeling reactants, and cysteine was used as the modeling water-soluble ligand (). It was found that the acidity of reaction conditions remarkably affect the thermodynamic facility of the ligand exchange reactions. Ligand effect (structural distortion and acidity) dominates the overall thermodynamic facility of the ligand exchange reaction, while the number and type of dopped metal atom(s) can only slightly adjust the reaction rates.

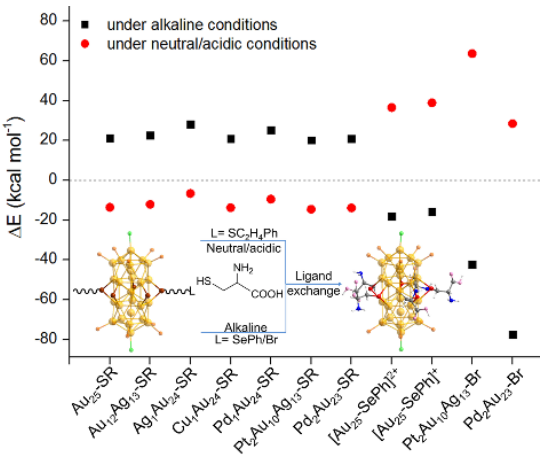

Figure 1: The framework-maintained ligand exchange of $Au_{25-n}M_n$ nanoclusters.

References

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2. M. Rambukwella, S. Burrage, M. Neubrander, O. Baseggio, E. Aprà, M. Stener, A. Fortunelli, A. Dass, *J. Phys. Chem. Lett.* **8** (2017), 1530.