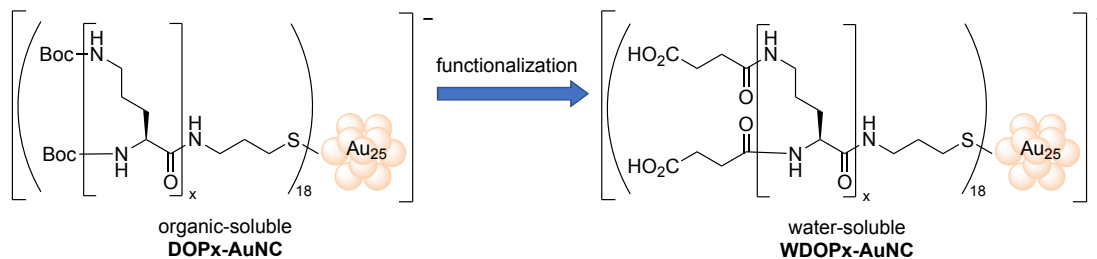


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Thiolate-protected gold nanoclusters (AuNCs) of precise molecular formulas have been investigated as catalysts due to their higher relative surface area than conventional gold nanoparticles. However, the strong gold–sulfur bonds of thiolate ligands brought about “catalyst poison” to diminish the catalytic activity. Recently, we reported that peptide dendron thiolate ligands generate a hydrogen-bonding supramolecular reaction field on the surface of Au₂₅ nanocluster, enhancing the reaction turnover in photocatalytic oxidation of amino alcohols through intermolecular hydrogen bonds between ligands and substrates.¹ In order to improve catalytic turnover further, we designed water-soluble peptide dendron thiolate ligands acting as supramolecular reaction field in water, enabling the efficient encapsulation of hydrophobic substrates from aqueous media and release of hydrophilic products from the reaction field. Based on this concept, we synthesized water-soluble [Au₂₅(SR)₁₈][−] nanoclusters bearing hydrogen-bonding supramolecular reaction field.

The peptide dendron thiol ligands were synthesized from previously reported Boc-protected dendritic ornithine peptide thioacetates **DOPx-SAc** (x denotes the generation of peptide dendrons).¹ Au₂₅ nanoclusters were synthesized by conventional reduction method using methyl ester-terminated thiols and purified by silica gel column chromatography. Finally, all the terminal methyl groups were deprotected to afford the desired water-soluble AuNCs **WDOPx-AuNC**. The reference Au₂₅ nanocluster bearing non-peptidyl thiolate ligands was also synthesized by the similar synthetic procedure using methyl 3-mercaptopropionate. In this presentation, we will report the synthesis of the water-soluble AuNCs **WDOPx-AuNC** and the effect of hydrogen-bonding supramolecular reaction field in catalytic reactions.



1. Isozaki, K.; Nakamura, M.; *et al.* *ACS Catal.* **2021**, *11*, 13180–13187.