Thin-film formation of thiolate-protected Au_{25} cluster through inter-cluster covalent linking

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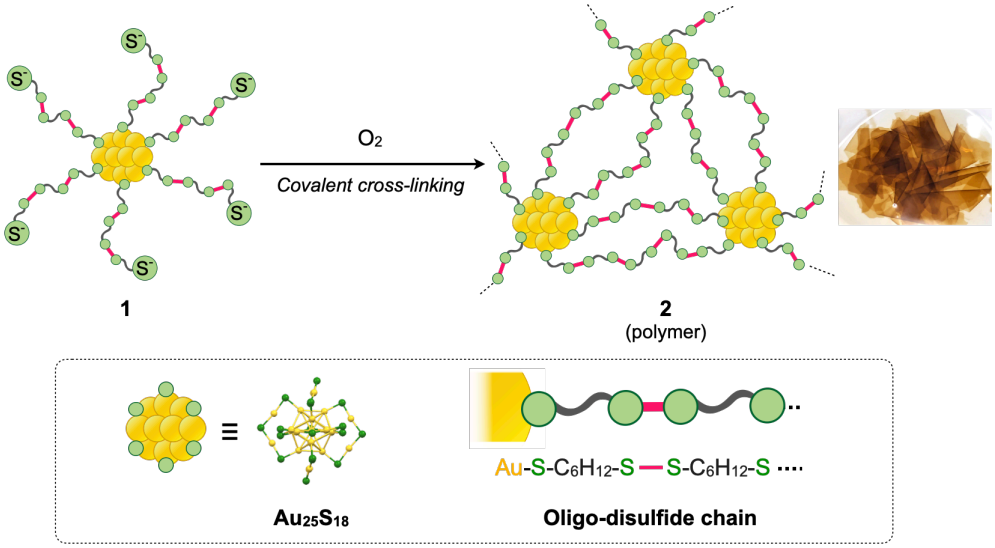
Ligand protected gold clusters show unique optical and catalytic properties, and thus they have great potentials for solid materials.[1] In such situations, an incorporation of cluster compounds into films is one of the promising strategies for further applications. However, preparation of cluster-based film is limited to dispersion of cluster compounds into polymer matrices, which inhibits the emergence of unique cluster-based properties.[2] In this study, we present a facile synthesis of thiolated-Au_{25} cluster film, in which the clusters are covalently cross-linked with retention of the original Au_{25} framework.

We first synthesized 1,6-hexanedithiolate-protected Au_{25} cluster by a conventional method. After purification, absorption spectrum showed the characteristic pattern of $Au_{25}S_{18}$ framework. In addition, elemental analysis and ^{1}H-NMR measurements revealed that the cluster surface is coated with oligo-disulfide chains derived from 1,6-hexanedithiols, having thiolate anions (S^-) at the terminal of the chains (**1**). The as-synthesized Au_{25} cluster (**1**) is soluble in common organic solvents, however, it turned into insoluble polymer films (**2**) upon the exposure to oxygen in solid state. This film formation is associated with the inter-cluster covalent cross-linking as a result of the oxidation of the terminal thiolates. We also demonstrated that the obtained Au_{25} film can be used as a photosensitizer for singlet oxygen generation and an adsorbent for small organic molecules.



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