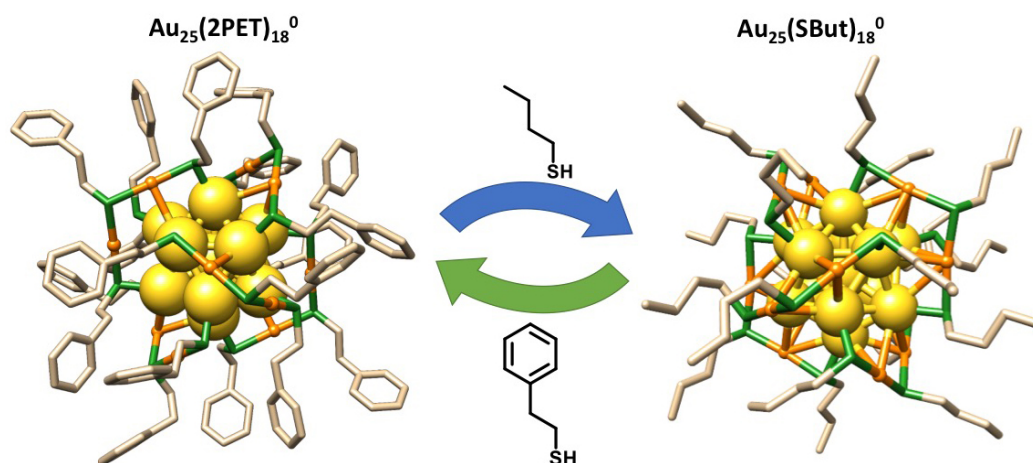


**$^1\text{H-NMR}$  and MALDI investigation of thiol-exchange reaction in  $\text{Au}_{25}(\text{SR})_{18}$  cluster**G. Salassa<sup>1</sup><sup>1</sup>University of Geneva, <sup>2</sup>Univeristá di Padova, <sup>3</sup>Université de Gêneve

Small thiol protected gold nanoparticles (< 2nm), also known as gold cluster, are self-assembled systems formed by Au(0) core and a thiol protecting monolayer. The latter is fundamental not only for stabilization and solubility of the clusters themselves, but also is the principal responsible for their reactivity.[1] One of the most frequent reactions used to functionalized the monolayer are the thiol-exchange reactions.[2]. These reactions usually present difficulties in controlling the number of substitutions and the reaction time can vary from minutes to days. In this study we investigated the thiol-exchange reaction using nuclear magnetic resonance (NMR) spectroscopy and MALDI analysis.[3] Kinetic studies were performed on  $\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}$  exchange with butane thiol and vice versa ( $\text{Au}_{25}(\text{SBut})_{18}$  exchange with  $\text{HSC}_2\text{H}_4\text{Ph}$ , Figure 1). By these studies, were possible to understand: 1) the affinity of different thiol ligands towards the  $\text{Au}_{25}$  cluster, 2) calculating the number of thiols exchange, 3) the position of exchange and 4) obtaining the relative binding constants. From this information was possible to gain a clearer picture on the mechanism of this reaction that can help in fine-tuning the functionality of the monolayer.



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