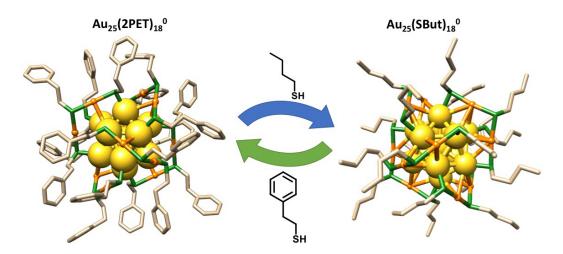
¹H-NMR and MALDI investigation of thiol-exchange reaction in Au₂₅(SR)₁₈ cluster

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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 $Au_{25}(SC_2H_4Ph)_{18}$ exchange with butane thiol and vice versa $(Au_{25}(SButane)_{18}$ exchange with HSC_2H_4Ph , Figure 1). By these studies, were possible to understand: 1) the affinity of different thiol ligands towards the 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.



- [1] H. Häkkinen, Nat. Chem., 2012, 4, 443-55.
- [2] T. Ni, M. Tofanelli, B. Philips, C. J. Ackerson, *Inorg. Chem.*, **2014**, 53, 6500-6502.
- [3] P. Pengo, C. Bazzo, M. Boccalon, L. Pasquato, *Chem. Commun.*, **2015**, 51, 3204–3207.