Enhancing Diversity in Ligand-Stabilized, Atomically Precise Gold Clusters

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Atomically precise gold nanoclusters (Au NCs) are a class of well defined molecules featuring a core of gold atoms stabilized by a ligand shell. These molecules have been demonstrated to exhibit excellent properties such as high chemical and electrochemical stability, photoluminescence and chirality, which can be potentially exploited in numerous applications (optics,[1] nanomedicine,[2] catalysis,[3]…). This variety of properties is generally related to the availability of different types of ligands and ligand combinations, which from the more common thiolates and phosphines have been recently extended to carbon-based ligands, such as alkynyls or N-heterocyclic carbenes (NHCs). However, access to new organometallic clusters of this kind is still impeded by the limited availability of reliable, high-yielding synthetic methodologies.

To overcome this hurdle, we have embarked in a systematic study of the reactivity of well known and preformed Au NCs with carbon-based ligands/ligand precursors displaying different electronic and steric features, in order to spread light on the formation of Au NCs featuring Au-C bonds and on their molecular physico-chemical properties. This strategy has proved useful to enable access to peculiar Au NCs which cannot be formed otherwise via direct methods. Indeed, we have recently succeeded in synthesizing new classes of mixed PPh_3 and NHC ligated Au NCs through a reaction sequence which allows to control both composition and nuclearity.[4] We have also disclosed the preparation of the first NHC-stabilized Au NC bearing gold-methyl bonds.[5] In this contribution, highlights will be provided on the electrochemical,[6] optical and medicinal properties of these Au NCs, as well as on the effect of tailored ligand substitutions in the cluster shell.

To further expand the possibility to selectively prepare novel organometallic AuNCs with engineered properties, we are also investigating the synthesis of Au NCs stabilized by alternative neutral carbon-based ligands, such as isonitriles, which to the best of our knowledge represent a novelty in the field. Preliminary results in this direction will be reported as well.

(1) Liu, Z. et al. Adv. Mater. 2024, 36 (8), 2309073.

(2) Lin, Z. et al. Adv. Func. Mater. 2021, 31 (51), 2105662.

(3) Higaki, T. et al. Angew. Chem. Int. Ed. 2019, 131 (25), 8377–8388.

(4) Bevilacqua, M. et al. Inorg. Chem. 2023, 62 (4), 1383–1393.

(5) Bevilacqua, M. et al. Eur. J. Inorg. Chem. 2024, e202400351

(6) Reato, M. et al. Electrochimica Acta 2025, DOI 10.1016/j.electacta.2025.147562