N-Heterocyclic Carbenes as Novel Ligands for Surfaces, Nanoparticles and Nanoclusters

N-heterocyclic carbenes (NHCs) are carbon-based organic molecules that have been extensively employed as ligands for transition metal complexes for the past twenty years. They form stable metal complexes that can be used under conditions where other complexes would decompose. Despite their widespread use in transition metal chemistry, until recently, the employment of NHCs on metal surfaces has remained largely unexplored. This presentation will focus on the use of NHCs as novel ligands to functionalize planar metallic surfaces, curved gold nanoparticles and nanoclusters. We developed novel methods for the synthesis of air-stable benzimidazolium bicarbonates as single-source NHC precursors that were used to form high-quality films on gold surfaces. This enabled the facile preparation of identical monolayers to those formed using free NHCs but in the air, using undried solvents, with a single component precursor. Subsequently, we employed this simple generation of NHC monolayers to prepare various gold biosensors and functionalize other metals such as copper, platinum, and magnesium enabling unprecedented insight into structure-property relationships. In addition, we described the synthesis of amphiphilic NHC-functionalized gold nanoparticles where their self-assembly in polar solvents allowed the tuning of the collective optical properties and boosted the overall stability. Furthermore, we reported the first examples of gold superatoms, known as nanoclusters, protected by NHCs either by a displacement reaction or by the direct reduction NHC-gold complexes. The resulting NHC-phosphine-protected Au$_{11}$ clusters were significantly stable and electrocatalytically activate toward the reduction of CO$_2$ whereas the all NHC-stabilized Au$_{13}$ clusters had exceptionally high photoluminescence greater than the most luminescent ligand-protected Au$_{13}$ superatom cluster. We also obtained first crystal structures of this new class of materials and showed the effect of the NHCs design on the cluster properties.