Modification of Monolayer Protected Gold Clusters (MPCs) via the Curtius Rearrangement

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Monolayer protected clusters (MPCs) are composed of organic molecules chemically adsorbed to the surface of metallic nanoparticles. MPCs are receiving much attention for possible use as chemical and biochemical sensors, as catalysts, and as photoimaging devices. It is the chemical interactions of the organic functionality on the MPCs which give the clusters specific properties suitable for such applications. Our interests lie in investigations directed towards understanding how anchoring the substrate to a surface affects its reactivity, and how one can control the reactivity for selected chemical modifications in these environments. In this study, we prepared a 2 nm Au MPC modified with a long alkyl chain containing a terminal acyl azide functional group. Upon exposure to ultraviolet light or heat, the acyl azide group undergoes the Curtius Rearrangement, in which molecular nitrogen is lost and an isocyanate is formed, as shown below. The isocyanate readily reacts with a variety of nucleophiles such as amines and alcohols and thus opens up the possibly of selected and controlled modification to MPC surfaces. The synthesis and reactivity of this newly formed MPC will be discussed.

The Curtius Rearrangement