Photoreactivity on Monolayer Protected Nanoparticles: Norrish Type I vs. Norrish-Yang Type II

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Monolayer-protected nanoparticles (MPNs) are composed of nanometer-sized colloidal metal cores surrounded by organic substrates chemically adsorbed to the surface. It is the nature of the organic substrate that gives an MPN its specific properties, which opens up the possibility for their use in chemical and biochemical sensing, catalysis, and molecular recognition. It is of interest to study how the incorporation of an organic substrate into the MPN environment affects its mobility and reactivity. Our group utilizes the photochemical reactions of organic substrates in order to probe the MPN environment.[1,2,3]

Previous studies in our laboratory have shown that the Norrish-Yang type II photochemical reaction of an aryl ketone anchored to the MPN surface results in the exclusive generation of the fragmentation product (Scheme 1) and the conversion to product depends on the size of the MPN core[1,4]. The mobility constraints imposed on the aryl ketone as it is incorporated into the MPN environment were assumed to be the reason for the reaction selectivity and incomplete reactions, but the aryl ketone probe employed in these studies offered no more information in this regard.

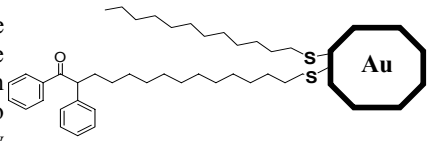
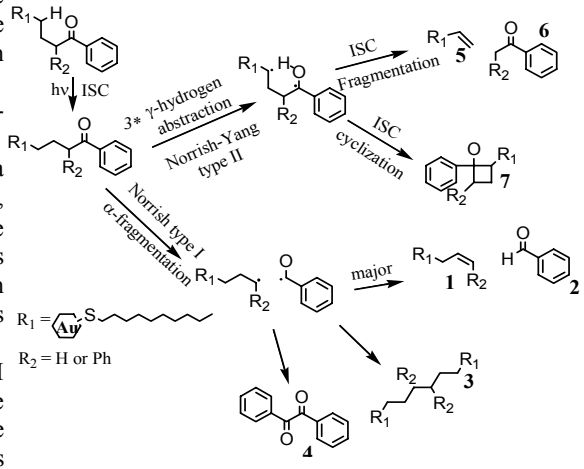


Figure 1: Aryl ketone probed to the MPNP

The aryl ketone probe utilized in this study is 14-mercapto-1,2-diphenyl-tetradecanone.

As highlighted in Scheme 1, this aryl ketone can undergo a conformationally demanding reaction, the Norrish-Yang type II, or a less demanding α-fragmentation reaction, the Norrish type I, from the same excited state. The product distribution of this reaction on the MPN surface can be compared to that in solution in order to elucidate how the MPN environment influences reactivity.

In solution, the probe undergoes the Norrish-Yang type II photoreaction. In contrast, when anchored to the MPN, the Norrish type I photoreaction is more dominant. In addition, the acyl radical that is generated in the Norrish I reaction causes cleavage of the substrates on the MPN surface and increases the size of the gold core.



Scheme 1: Norrish type I vs. Norrish-Yang type II photoreactions

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