# Activity Improvement by Immobilization and Protection of Artificial Imine Reductase on Silica Nanoparticles 

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Artificial metalloenzymes (ArMs) are hybrid catalysts created by a non-covalent incorporation of an organometallic cofactor within a host protein scaffold.1,2 Such system based on the biotinstreptavidin technology combines organometallic and enzymatic catalysis, 3,4 and can therefore catalyze multiple chemical processes. With the aim of immobilizing Artificial Transfer Hydrogenase (ATHase) on silica nanoparticles (SNPs) and performing NAD+ regeneration in situ, we selected the enantioselective transfer hydrogenation of cyclic imines as a model reaction.


Various lyophilized streptavidin isoforms were pre-incubated with the biotinylated iridium cofactor to obtain the functional artificial metalloenzymes, which were embedded within a protective organosilica layer 5 yielding active SNPs.


Upon immobilization and protection of streptavidin mutants on the SNPs, the resulting nanoparticles display increased TON (46'000)6 for the salsolidine precursor reduction, with the possibility to recycle the active catalyst. This protected system is able to retain its activity in presence of various cellular debris without any treating agent. The concentration of the active $\mathrm{Cp}{ }^{*} \mathrm{Ir}$ catalyst was determined by means of ICP-MS measurements.

1. Ward, T. R., Acc. Chem. Res. 2011, 44, 47.
2. Lu, Y., et al, Nature 2009, 460, 855.
3. Dürrenberger, M., et al. Angew. Chem. Int. Ed. 2011, 50, 3026.
4. Köhler V., et al. Nature Chem. 2013, 5, 93.
5. Cumbo, A., et al. Nat. Commun. 2013, 4.
6. Hestericová, M., et al. Chem. Commun. 2016, 52, 9462.
