## Transferrring oxygen and electrons and recycling plastics - many facets of coordination chemistry with N donor ligands

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The reactivity of the enzyme tyrosinase involves both the ortho-hydroxylation of phenols as well as the oxidation of ortho-catechols to ortho-quinones. Tyrosinase harnesses the oxidative power of O<sub>2</sub> for these transformations, activating the molecule from its triplet state and controlling its reactivity as a  $\mu$ - $\eta^2$ : $\eta^2$ -peroxidodicopper(II) (**P**) complex. The reaction mechanism has been studied on the real enzyme as well as using model systems, only few of which show catalytic activity. The Herres-Pawlis group has achieved this with bis(pyrazolyl)methane (BPM) ligands, showing unprecedented reactivity, extending the substrate scope beyond that of tyrosinase itself. We tune BPM ligands tune with respect to their electronic properties by introducing different para-substituents in the third (pyridinyl)donor, showing dramatic effect on thermal stability of the P complex, as well as hydroxylation rates of phenolic substrates. The thermal decay product of such a BPM ligated **P** complex could be crystallized for the first time, showing the hydroxylation of an aliphatic tBu group. This reactivity is heavily influenced by the third donor's electronic properties and is uncommon for P complexes, it is observed primarily for the energetically close lying bis- $\mu$ -oxido-dicopper(III) (O) isomer. A P/O-isomerization is proposed, supported by DFT simulations of different conformers and transition states, as well as activation parameters and Marcus reorganization energies of electron transfer reactions. Furthermore, the catalytic activity is determined by isolating phenazines, a stable species derived from ortho-quinones formed by tyrosinase-like reactivity of the new complexes.

In the second part of the talk, the focus lies on bioplastics and the recycling of polyesters. Industrial plastic production follows a linear economic model in which customized polymers are designed and disposed of in landfills, incinerators or in the environment after single usage. Furthermore, 79.4% of all plastics in 2023 are made from fossil raw materials. The problem of environmental pollution from plastic waste and the associated new approach to establishing a circular plastics economy is leading to a growing demand for environmentally friendly, biobased alternatives. Polylactide (PLA) is one of the most promising bio-based, biodegradable bioplastics already being used as a packaging material. In the industrial production of PLA, a toxic catalyst (tin(II) bis(2-ethylhexanoate), [Sn(oct)<sub>2</sub>]) is currently used and remains in the polymer. The challenge is to replace Sn(oct)<sub>2</sub> with an environmentally friendly catalyst and incorporate it in the depolymerization of PLA to path the way towards a circular economy.

We present a new highly active zinc hybrid guanidine catalyst for lactide and caprolactone polymerization. Particularly outstanding are the similar polymerization rates. Metal guanidine catalysts known from literature have so far shown a significantly higher activity in lactide polymerization. For the first time, a catalyst with activities of the same order of magnitude is presented here. The catalyst is also highly active in the chemical recycling of PLA, polycaprolactone (PCL) and polyethylene terephthalate (PET). Its reusability in recycling is particularly noteworthy (figure 1). The introduced catalyst combines polymerization and depolymerization and is therefore an interesting candidate for a circular plastics economy.