

Living Libraries of Intermetallic Superatoms

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Intermetallics of metals of very different properties (M/E) can potentially substitute industrial catalysts based on rare and precious metals.^[1] To realize this opportunity, atom-precise/-efficient catalyst design is required at the size regime of ≤ 1 nm, where every metal atom ‘counts’. We discovered a novel way to generate ‘living libraries’ of meta-stable, all-hydrocarbon ligated clusters $[M_aE_b](R)_n$. Such clusters are molecular counterparts of the solid state M/E materials.^[2] The electronic structure of the clusters’ “superatomic” valence shell controls stability and reactivity.^[3,4]

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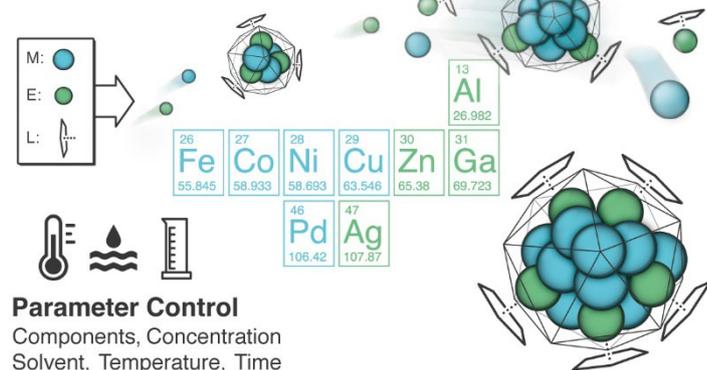


Figure 1. The term ‘living’ highlights the properties of an evolving library, which we define as a dynamic mixture of clusters, growth species and additives. A living library has typically not reached chemical equilibrium. Its distribution of clusters (i.e. different M/E compositions, nuclearity and structure, including isomers) can be highly sensitive to perturbation, which includes the interaction with reactants to be trapped or converted at metal atoms exposed at the cluster surface.^[5]

These cluster libraries are populated with interrelated species, transient and highly reactive as well as more accessible but less reactive ones. The clusters are generated by multivariate sets of initial components and library evolution conditions, which factors relate to chemical networks of nucleation, growth and degradation reactions, to additive association, dissociation, to metal-atom site activation (e.g. by ligand de-protection) and to reactions with small molecules at the cluster surface (e.g. H_2 , CO_2 , H_2O , O_2 , NO_x , small hydrocarbons). The cluster libraries may allow for efficient probing elementary reaction steps related to catalytic transformation of small molecules directly from the mixture without size-focusing or isolating defined clusters in a first step.

Our wet-chemical bottom-up approach to intermetallic clusters and superatoms is deeply rooted in the organometallic coordination chemistry of transition metal complexes $[ML_n]$ with low coordinate group-12 and group-13 compounds ER acting as ligands and as well as cluster growth components.^[6,7] We have been working in this area now for about 30 years. The presentation will be an account of our progress over time and it will highlight some key results on our way coming closer to realize the vision of a ‘superatom coordination chemistry for catalysis’.

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