A Molecular Precursor Approach to Tailored Cluster Synthesis

The reactivity of E-Si bonds (E = S, Se, Te) can be exploited in d-block metaltrimethylsilylchalcogenolates [M-E-SiMe₃] to access ternary M-E-M' clusters when such coordination complexes are reacted with a second metal source. Using *N*-heterocyclic carbene (NHC) ligands it is possible to prepare thermally stable [(NHC)M-ESiMe₃] that can be used for the preparation of *isostructural* homo- and heterometallic group 11 – group 16 clusters.[1,2] The NHCs effectively stabilize the formed polymetallic assemblies and, when merged with the rich luminescence features of heterometallic group 11-chalcogenide clusters, they offer an ability to probe composition/structure/property relationships. This has enabled series of clusters [(NHC)₄M₄M'₄(μ_3 -E)₄] (M = Cu, Au; M' = Cu, Ag, Au) to be prepared where systematic replacement of the metals and/or chalcogen is possible. Phosphorescence is observed from all clusters and emission energies can be varied based on the choice of metal and chalcogen within structurally identical cluster cores. Higher nuclearity cluster frameworks are also accessible using this approach.[3]

[1] J. Am. Chem. Soc., **2017**, 139, 14045-14048.

[2] Inorg. Chem., **2019**, 58, 5838-5848.

[3] Dalton Trans., **2020**, 49, 593-597.