Toward two-dimensional superatomic honeycomb structures. evaluation of [Ge9(Si(SiMe3))3]- as source of GeGe9-cluster building Blocks for Extended Materials

Muñoz-Castro A.

Takahashi K.

Inspired by recent experimental realizations of two-dimensional (2D) metals and alloys, we theoretically investigate plausible formation of new germanium frameworks based on the aggregation of ligand-decorated GeGe9 clusters. Here, we explore the formation of single-, double-, and triply connected arrays of species with Zintl-ion core of GeGe9 leading to the formation of dimers ([Ge9R2]2 2-), hexamers ([Ge9R]6 6-), and two-dimensional arrays ([M3{GeGe9}3]?; M = Li, Cs). This can be potentially addressed by the controlled removal of ligands from the [Ge9{Si-(SiMe3)3}3]- monoanion acting as the source of GeGe9 building blocks. Our results reveal that the bonding between different GeGe9 cores is favorable and covalent in nature as a localized 2c-2e Ge-Ge exobond. The extended two-dimensional {GeGe9}? array designed as [M3{GeGe9}3]? with M = Li, Cs in periodic boundary conditions is energetically stable. The resulting layered Ge-structure has similar stability as that of germanene. It exhibits large pores with radius of 5.23 A between the three-connected GeGe9 clusters. Hence, it can be considered as a the first superatomic honeycomb structure proposed to date. This 2D material exhibit a small band gap in contrast to the 2D germanene which has no such gap. Hence, the two-dimensional GeGe9 cluster-based compound would have potential for a tunable bandgap material. The use of Geclusters is suggested as an interesting approach to obtain nanomaterials accessing to novel alleotropes.