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ORIGINAL PAPER

Trends in the formation of aggregates and crystals from M@Si$_{16}$ clusters: a study from first principle calculations

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Abstract We have shown recently that the ground state and low-lying energy isomers of the endohedral M@Si$_{16}$ clusters ($M = \text{Sc}^-$, Ti, V$^+$) have a nearly spherical cage-like symmetry with a closed shell electronic structure which conforms them as exceptional stable entities. This is manifested, among other properties, by a large Homo–Lumo gap about 2 eV which suggest the possibility of using these clusters as basic units (superatoms) to construct optoelectronic materials. As a first step in that direction, we have studied in this work, by means of first principles calculations, the trends in the formation of [Ti@Si$_{16}$]$_n$, [Sc@Si$_{16}$K]$_n$, and [V@Si$_{16}$F]$_n$ aggregates as their size increases, going from linear to planar to three dimensional arrangements. The most favorable configurations for $n \geq 2$ are those formed from the fullerene-like D$_{4d}$ isomer of M@Si$_{16}$, instead of the ground state Frank–Kasper T$_d$ structure of the isolated M@Si$_{16}$ unit, joined by Si–Si bonds between the Si atoms of the square faces. In all cases the Homo–Lumo gap for the most favorable structure decrease with the size n. Trends for the binding energy, dipole moment, and other electronic properties are also discussed. Several crystal structures constructed from these superatom,

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supermolecules, and aggregates have been tested and preliminary results are summarily commented.

Keywords Cluster-assembled materials · Artificial atoms · Nanoparticles · Superatoms · Clusters · Hierarchical assembly · Nanocrystals · Superlattices · Self-assembly

1 Introduction

The interest in the study of small atomic clusters is growing in present times motivated for their potential usage as building blocks for new functional materials and devices at the nanoscale. To achieve this goal is of paramount importance to investigate how the system geometry depends on the interparticle coupling and how it affects the physical properties of the systems. Chemically stable building blocks which interact weakly among themselves and with other clusters of the same material should have a closed electron configuration with a large energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The other important factor determining the cluster stability is the atomic geometry. Thus, the cooperative effects between electronic and geometrical factors can provide a guiding principle for designing stable building-block clusters. In a previous work [1] we have determined from first-principle calculations the geometrical and electronic structure of the low-laying energy isomers of $\mathrm{M@Si}_n$ clusters ($M = \mathrm{Sc}^-$, Ti, V^+) in the range $n = 14$–18, see Fig. 1. In that work we obtained a good agreement with the experimental results obtained by Nakajima and coworkers [2–5] for the the endohedral character and extra stability of $\mathrm{M@Si}_{16}$ clusters, as well as for their electron affinity and Homo–Lumo gap. For the ground state geometry of these clusters we obtained a distorted Frank–Kasper T_d structure in agreement with a previous calculation for $\mathrm{Ti@Si}_{16}$ by Kumar and coworkers [6].

Furthermore, we provided in ref. [1] an interpretation of the electronic structure and orbital projected density of states (PDOS) of $\mathrm{M@Si}_{16}$ clusters in the context of the spherical shell model perturbed by the crystalline field of the underlying ionic geometry. That fact has been confirmed recently by the angular dependent photo-electron spectroscopy experiments of von Issendorf and coworkers [7]. The model rest on the following assumptions:

1. For an empty spherical cage, the $\mathrm{O}^+(3)$ states have predominantly zero radial nodes: $1s, 1p, 1d, 1f, 1g, 1h, \ldots$
2. *l-selection rule*: only those M orbitals transforming in the same *irrep* of the point group of the cluster can be mixed in a given bonding state.
3. The covalent bonding in $\mathrm{M@Si}_{16}$ results from the hybridization of the empty-cage states and the valence states of endohedral-atom having equal angular momentum l.

Thus, the $\mathrm{V@Si}_{16}^+$ cluster has 68 valence electrons (64 from Si and 4 from V^+) in the single-particle spherical shells $1s, 1p, 1d, 1f, 2s, 1g, 2p, 2d$, which suffer different splitting depending on the ionic geometry. For the ground state T_d symmetry, with Homo–Lumo gap 2.25 eV, the splitting is $s(a1)$, $p(t2)$, $d(t2+e)$, $f(a2+t1+t2)$,

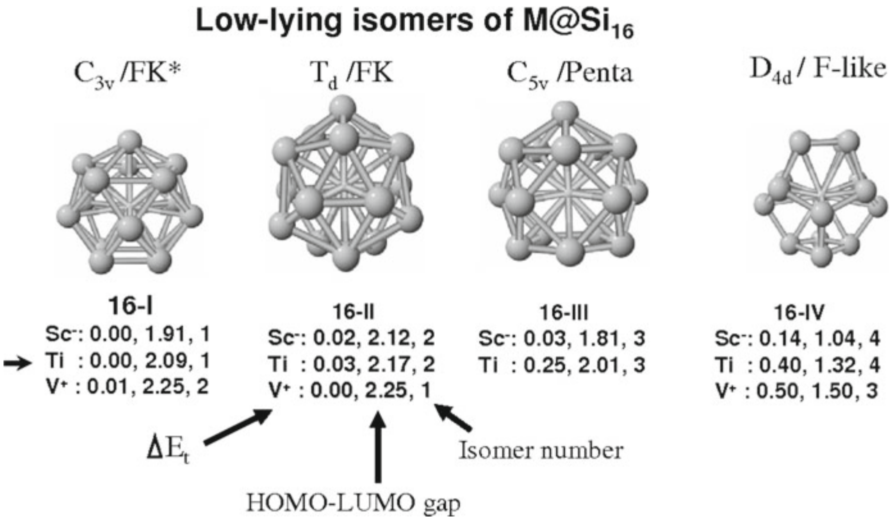


Fig. 1 Geometry of the several low-lying energy isomers of M@Si_{16} clusters. Below each structure is given, for the three types of atom-impurity, the total energy difference (eV) with respect to the lowest energy configuration, the Homo–Lumo gap (eV), and ordinal number of the isomer. Notice that the Homo–Lumo gap of the 16-IV isomer is considerably smaller than for the others

$g(a1+e+t1+t2)$, $h(e+t1+2t2)$, $i(a1+a2+e+t1+2t2), \ldots$, which can easily be recognized in our calculated PDOS for that isomer [1]. The XAS experiments of ref. [7] show agrement with our PDOS for that T_d FK isomer (16-I of Fig. 1), but not for that of the D_{4d} f-like geometry of V@Si_{16}^{+}, which is 0.5 eV above the ground state and have a smaller Homo–Lumo gap 1.50 eV.

The construction of new optoelectronic materials by assembling molecules of the type V@Si_{16}X with X = halogen atom, or Sc@Si_{16}Y with Y = alkali atom, was suggested by Nakajima and coworkers [4] assuming that the large Homo–Lumo gap of the ionic superatom can be maintained in the range of ∼2 eV when the ionic supermolecule is formed and a solid phase is eventually grown after them. For the Ti@Si_{16} superatom, has been shown in a calculation by Pacheco et al. [8] the possible survivance at room conditions of a meta-stable hcp solid formed from the FK ground state.

Before to explore the stability of meta-stable bulk phases of materials composed of M@Si_{16}Z super-atoms we study in this paper the more favorable structures of the aggregates $[\mathrm{Ti@Si_{16}}]_n$, $[\mathrm{Sc@Si_{16}K}]_n$, and $[\mathrm{V@Si_{16}F}]_n$ formed from cage-like M@Si_{16} clusters. In the Sect. 2 is described our computational approach. In Sects. 3–5 we present and discuss the results for aggregates of Ti, Sc^{-}, and V^{+} doped Si_{16} cluster, respectively. In Sect. 6 are presented a few preliminary results for extended 1D, 2D, and 3D systems formed from these superatoms, supermolecules, and aggregates. In Sect. 7 we summarize our results.

2 Computational procedure

We have used the density functional theory [9] (DFT) code Siesta [10] within the generalized gradient approximation as parameterized by Perdew, Burke and

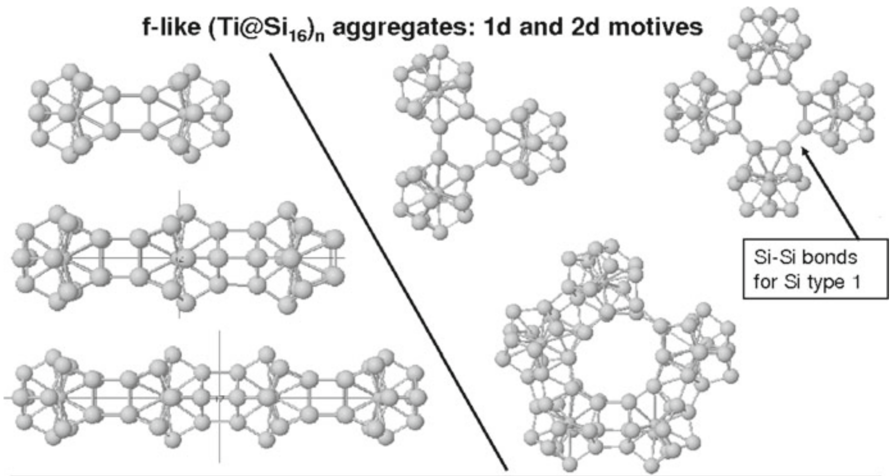
Ernzerhof [11] for the exchange-correlation effects. Details about the pseudopotentials and basis sets are the same as in our previous work [1]. Specifically, we used norm conserving scalar relativistic pseudopotentials [12] in their fully nonlocal form [13], generated from the atomic valence configuration $3s^2 3p^2$ for Si (with core radii 1.9 a.u. for s and p orbitals), and the semi-core valence configuration $4s^2 3p^6 3d^n$ for Sc ($n = 1$), Ti ($n = 2$), and V ($n = 3$) (all of them with core radii, in a.u., 2.57, 1.08, and 1.37 for s, p, and d orbitals, respectively). For K (F) we used the configuration $4s^1 (2s^2 2p^5)$ with core radius 3.64 (1.39) a.u. for all s, p, and d valence orbitals. In the present calculations we used a double-ζ basis s, p (for Si) and s, p, d (for M), with single polarization d (for Si) and p for M, having maximum cutoff radius, in a.u., 7.47 (Si), 8.85 (Sc), 8.45 (Ti), and 8.08 (V). The basis set and pseudopotentials of M atoms were used and tested before in refs. [14,15]. The matrix elements of the self-consistent potential are evaluated by integration in a uniform grid with double zeta plus polarization (DZP) basis. The grid fineness is controlled by the energy cutoff of the plane waves that can be represented in it without aliasing (120 Ry in this work).

The equilibrium geometries result from an unconstrained conjugate-gradient structural relaxation using the DFT forces. We try out several initial structures for each cluster (typically more than twenty) until the force on each atom was smaller than 0.010 eV/Å. A $4 \times 4 \times 4$ Monkhorst pack grid was used for bulk calculations of SC, BCC, FCC, NaCl, CsCl, and hcp structures.

3 $[\mathrm{Ti@Si_{16}}]_n$ aggregates

In Fig. 2 are represented the minimum energy $[\mathrm{Ti@Si_{16}}]_n$ aggregates with $n \leq 4$ formed from the D_{4d} f-like $\mathrm{Ti@Si_{16}}$ superatom and with one- and two-dimensional arrangements. The binding energy (eV) (with respect to the fully separated units), Homo–Lumo gap (eV), and dipole moment (Debye) for different sizes (n) and arrangements (chain and planar) are given in the inset. The dimer ($n = 2$) is formed preferably by means four Si–Si bonds between Si atoms of the type 1, that is, Si atoms belonging to the square basis of the D_{4d} superatom. Notice that the units in the dimer are specular images the one of the other. This dimer has ∼1 eV deeper total energy than a compact equilibrium configuration of $\mathrm{Ti_2@Si_{32}}$ which was fully optimized after an initial icosahedral I_h geometry of $\mathrm{Si_{32}}$. This fact give us confidence in the reliability of the aggregation of $\mathrm{Ti@Si_{16}}$ superatoms to form larger complexes.

Several low lying energy isomers of the dimer in Fig. 2 were found. One of them is formed by twisting 90° one of the two $\mathrm{Ti@Si_{16}} D_{4d}$ units around the molecular axe of the dimer. It is possible to grown linear chains from $n = 2$ to $n = 3, 4$ aggregates by adding adding a specular unit or dimer, respectively, as represented in Fig. 2. Other possibilities, among many others, is to add 90° twisted units, or alternating specular with twisted dimer units. The planar configurations for $n = 3$ and 4 have smaller binding energy per unit than the linear ones. These 2D aggregates are formed by Si–Si bonds between the Si atoms of the square basis in the D_{4d} isomer of $\mathrm{Ti@Si_{16}}$. Comparing the binding energy per Si–Si bond of the 1D and 2D $n = 3$–4 aggregates we see that the planar configuration is favorable. For $n = 5$ the five Ti dopant atoms



n	2	3	4	5	6	7	8
E_b (eV)	2.016	4.030	5.196	11.167			
E_b (eV)	**2.016**	**4.111**	**6.091**	**8.074**	**10.060**	**12.789**	**15.089**
Gap (eV)	0.57	0.24	0.31	0.13			
Gap (chain)	**0.57**	**0.46**	**0.36**	**0.30**	**0.24**	**0.07**	**0.01**
Dipole (D)	0.019	0.275	0.003	2.197			
Dipole (chain)	**0.019**	**1.135**	**0.655**	**0.846**	**1.051**	**9.480**	**9.540**

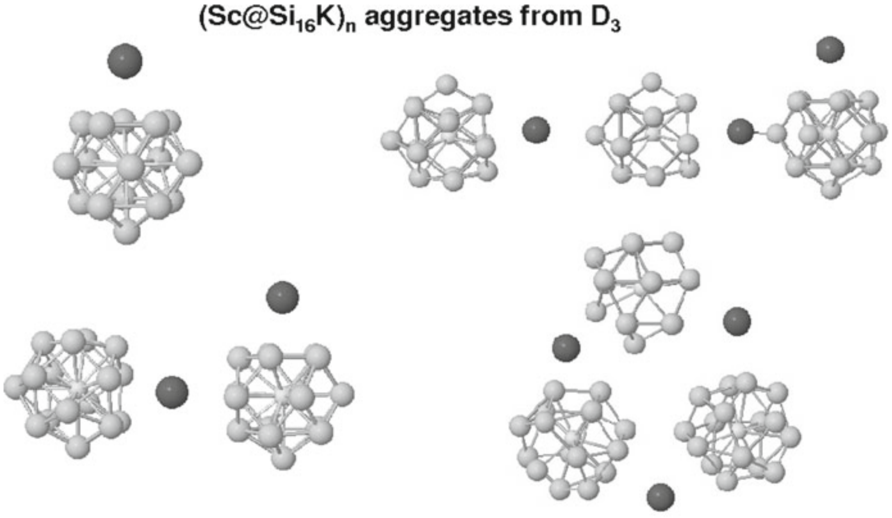
Fig. 2 One-(*left*) and two-(*right*) dimensional arrangements of $[\mathrm{Ti@Si}_{16}]_n$ aggregates formed from the $\mathrm{D}_{4\mathrm{d}}$ f-like Ti@Si_{16} superatom. The binding between superatoms occurs by means Si–Si bonds between Si atoms of the type 1, that is, Si atoms belonging to the square basis of the cluster, except for the planar $n = 5$ aggregate, where Si–Si bonds involving Si type two atoms are also involved. The binding energy (eV), Homo–Lumo gap (eV), and dipole moment (Debye) for different sizes (n) and arrangements (chain and planar) are given in the inset

form a non regular planar pentagon, and are formed Si–Si bond between type-2 Si atoms. The regular pentagon is a low lying energy isomer.

The Homo–Lumo gap in both, 1D and 2D structures, decreases as the size increases. Thus the transition to the metallic state is reached for very few basic units. The study of the PDOS of these aggregates is in progress. Interestingly, one can see that the planar $n = 3$ and 4 aggregates can be taken as units to form infinite surfaces with honeycomb and simple square structures, respectively. Growing these $n = 3$–4 units in the normal direction to the plane can be formed other type of wires resembling nanotubes. We will study these systems in the near future.

4 $[\mathrm{Sc@Si}_{16}\mathrm{K}]_n$ aggregates

In Fig. 3 are represented the $[\mathrm{Sc@Si}_{16}-\mathrm{K}]_n$ aggregates of supermolecular Sc@$\mathrm{Si}_{16}-$K units formed from the 16-III Sc@Si_{16}^{-} cluster bonded to a K atom. The Sc@Si_{16}K supermolecule is formed by capping the K atom on the pentagonal basis of an isomer of Sc@Si_{16}^{-} with only 30 meV higher energy than the Frank–Kasper ground state. The $[\mathrm{Sc@Si}_{16}\mathrm{K}]_n$ aggregates ($n = 1$–3) formed from that supermolecule prefer



n	1	2	3 chain	3 triangle
E_b (eV)		0.444	0.885	1.91
Gap (eV)	**1.72**	**0.653**	**0.210**	**1.40**
Dipole (D)	11.73	22.42	39.57	4.66
Sc-Sc (Å)		10.284	10.44-10.98	8.75-9.08

Fig. 3 $[Sc@Si_{16} - K]_n$ aggregates of supermolecular $Sc@Si_{16} - K$ units formed from the 16-III $O_{5v}Sc@Si_{16}^-$ cluster bonded to a K atom. The binding between supermolecules is mediated by the K atom. For $n = 3$ are given two configurations, linear (*right up*) and planar (*right down*). The binding energy (eV), Homo–Lumo gap (eV), dipole moment (Debye), and distance Sc–Sc (Å) for $n \leq 3$ are given in the *inset*

non-linear compact configurations, with the highest coordination of the K atoms. Other competitive equilibrium aggregates with linear configuration for $n \geq 2$ are formed from molecular units composed of the C_{3v} and T_d isomers. The formation of aggregates from fullerene-like D_{4d} isomer of $Sc@Si_{16}^-$ plus the K atom is in progress and preliminary results show interesting trend to be reported elsewhere.

The possibility of a endohedral ScK molecule inside of Si_{16} cage configurations have been also considered.

5 $[V@Si_{16}F]_n$ aggregates

The molecule F_2 dissociate on all isomers and positions of $V@Si_{16}^+$ in agreement with experiments [4]. The highest dissociation energy is 8.25 eV.

In Fig. 4 are given the $[V@Si_{16} - F]_n$ aggregates of supermolecular $V@Si_{16} - F$ units formed from the D_{4d} f-like $V@Si_{16}^-$ cluster bonded to a F atom. The binding between superatoms occurs by means of Si–Si bonds between Si atoms of the type 1, that is, Si atoms belonging to the square basis of the cluster, as well as Si–Si bonds

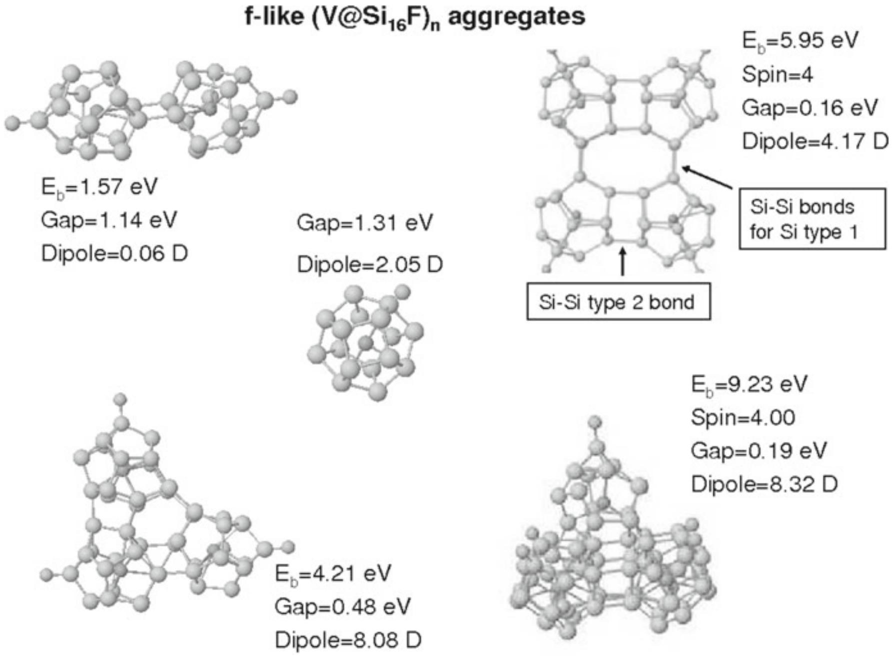


Fig. 4 $[V@Si_{16}-F]_n$ aggregates of supermolecular $V@Si_{16}-F$ units formed from the D_{4d} f-like $V@Si_{16}^-$ cluster bonded to a F atom. The binding between superatoms occurs by means of Si–Si bonds between Si atoms of the type 1, that is, Si atoms belonging to the square basis of the cluster, as well as Si–Si bonds between Si type 2 atoms. The binding energy (eV), Homo–Lumo gap (eV), dipole moment (Debye), and magnetic moment (μ_B) (only for $n = 4$–5) are given beside

between Si type 2 atoms. The binding energy (eV), Homo–Lumo gap (eV), dipole moment (Debye), and magnetic moment (μ_B) (only for $n = 4$–5) are also given.

The most stable $V@Si_{16}F$ supermolecule is formed by bonding the F atom on a Si atom of a square basis in the fullerene-like D_{4d} isomer of $V@Si_{16}^-$. The $[V@Si_{16}F]_n$ aggregates ($n = 1$–5) formed from that supermolecule prefer planar configurations up to $n = 4$, with the smallest coordination of the F atoms. Contrary to $Ti@Si_{16}$ aggregates, the ground state for $n = 2$ is bonded having the two units inverted with respect to the center of the two Si–Si bonds. Interesting chains and nano-tubes can be formed from the $n = 4$ aggregate. The low lying isomer of the $n = 3$ aggregate with only Si–Si bonds between type-1 Si atoms can be grown along the aggregate axis to obtain a 1D infinite wire.

6 Crystals from $M@Si_{16} - X$ supermolecular units

We have calculated several crystal phases having the $Ti@Si_{16}$ superatom as basic unit. For the BCC case, we obtained that the FK isomer, with T_d symmetry, reaches a meta-stable minimum with ~1.5 eV cohesive energy at ~8.5 Å unit–unit distance, whereas the f-like D_{4d} isomer lead to a deeper minimum with ~5.5 eV cohesive energy at

~8.0 Å unit–unit distance. The orientation of the cluster in the cell has a controllable effect.

Similar calculations have been performed for FCC, BCC, and SC crystals using the Sc@Si_{16}K supermolecule with the FK isomer isomer of the Sc@Si_{16} component as the basic unit. Other bulk structures with the NaCl and CsCl structures were tested. The most stable structure is, however, NaCl with the f-like isomer.

In the case of the f-like V@Si_{16}F supermolecule, the largest cohesive energy is obtained for the NaCl–FCC crystal. The orientation of the super-atom in the cell play an important role. The initial geometry of the super-atom suffers strong deformations when approaching the minimum of the energy-volume plot. The PDOS for this meta-stable structure shows an interesting metallic character with a tendency to ferromagnetism in the distribution of the *d*-electrons of Vanadium.

7 Summary and outlook

The doped M@Si_{16} clusters with $M = Sc^-$, Ti, and V^+, having 68 valence electrons, are more stable (magic) than those with neighbor sizes ($n = 15, 17$) because they adopt a nearly spherical geometry allowing hybridization of the *d* orbital of the endohedral M and the *d* orbital of the spherical Si cage. This calculated features are in agrement with experiments [4,7].

For [Ti@Si_{16}]$_n$ we have obtained equilibrium structures for one dimensional (1D) linear chains, two dimensional networks having triangular (2D-T) and square (2D-S) motifs, and three dimensional (3D) arrangements. Some of these arrangements can be seen as units to form infinite 1D, 2D, and 3D periodic systems. We have studied the relative stability of these [Ti@Si_{16}]$_n$ arrangements in order to determine the minimum size *n* to evolve from 1D to 2D to 3D systems.

The Sc@Si_{16}K supermolecule is formed by capping the K atom on the pentagonal basis of an isomer of Sc@Si_{16}^- with only 30 meV higher energy than the Frank–Kasper ground state. The [Sc@Si_{16}K]$_n$ aggregates ($n = 1$–3) formed from that supermolecule prefer non-linear compact configurations, with the highest coordination of the K atoms. Other competitive equilibrium aggregates with linear configuration for $n \geq 2$ are formed from molecular units composed of the fullerene-like D_{4d} isomer of Sc@Si_{16}^- plus the K atom.

The most stable V@Si_{16}F supermolecule is formed by bonding the F atom on a Si atom of a square basis in the fullerene-like D_{4d} isomer of V@Si_{16}^-. The [V@Si_{16}F]$_n$ aggregates ($n = 1$–5) formed from that supermolecule prefer planar configurations up to $n = 4$, with the smallest coordination of the F atoms. Interesting chains and nano-tubes can be formed from the $n = 4$ aggregate.

Ti@Si_{16} and V@Si_{16}F with f-like units form meta-stable bcc and NaCl crystals, respectively, whereas Sc@Si_{16}K prefers a fcc (NaCl) structure formed with the f-like supermolecule. The orientation of the super-atom in the cell play an important role. The PDOS of fcc–NaCl structure of V@Si_{16}F at the Fermi energy is very high indicating an unstable phase. The Homo–Lumo gap of the finite aggregates decreases when the size increases, and the 3D bulk phases are generally metallic. Thus, bulk materials assembled from these aggregates are not of interest for optoelectronic devices.

However, the study of the stability and magnetic properties of 1D and 2D infinite systems formed from the M@Si_{16}Z superatom and supermolecules considered in this work is in progress, and promise a big amount of unexpected properties.

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