Potential energy surface study of X@Si\textsubscript{32}X\textsuperscript{−}_{44} (X=Cl, Br) clusters to decipher the stabilization process of Si\textsubscript{20} fullerene

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Efforts toward stabilization of the Si\textsubscript{20} fullerene through different schemes have failed despite several theoretical predictions. However, recently Tillmann \textit{et. al.} succeeded to stabilize the Si\textsubscript{20} fullerene through exohedral decoration with eight Cl substituents and twelve SiCl\textsubscript{3} groups on the surface and enclosing Cl\textsuperscript{−} ion. A deeper understanding on what factors lead to stabilization will open the path for stabilizing other systems of interest. Here, we employ the minima hopping method within density functional theory to understand the potential energy surface. The study shows that the exo-endo halide decoration of the cage alters the glassy nature of the potential energy surface of pure cage to structure seeker. Further analysis of different properties of the global minima, reveal that the extra electron instead of residing on the central encapsulated atom in the cage, is distributed on the cage and increases the encapsulation energy; thereby stabilizing the system. We also provide estimates of the stability for different kind of exo-endo halide decorations and their feasible realization in experiments.

1 Introduction

The discovery of C\textsubscript{60} fullerene in 1985 marks an important milestone in nanosciences.\textsuperscript{3} Since then, many experimental and theoretical efforts had been made to find fullerene structures made out of non-carbon materials for various applications.\textsuperscript{2,4} Lately, boron based fullerene structure, borospherene B\textsubscript{40} was discovered by Zhai \textit{et al.} in 2014.\textsuperscript{5} As both C and Si both are Group-IV elements without any d orbitals, the Si structures are expected to be similar to their carbon counterparts. Few examples include linear polysilanes, silicon nanosheets and nanotubes.\textsuperscript{6,10}

Since C\textsubscript{20} forms the smallest known fullerene, Si\textsubscript{20} clusters were widely studied.\textsuperscript{11} While C atoms can easily adjust their valence states to participate single, double and triple bonds, Si strongly favors sp\textsuperscript{3} hybridization in connection with single bonds and this inherent constraint leads to the instability of the Si\textsubscript{20} fullerene.\textsuperscript{12}

Endohedral doping of Si\textsubscript{20} cages with metal atoms, M@Si\textsubscript{20} was believed for a while to stabilize the cage like geometries. However systematic structure prediction studies show that this strategy fails.\textsuperscript{13,14} The second approach was based on the introduction of exohedral substituents to fully saturate all four silicon valencies. The Si\textsubscript{20}H\textsubscript{20} dodecahedron configuration has been identified as the global minima.\textsuperscript{15,16} In this context, as a third approach, a combination of both techniques was considered which should lead to a stable M@Si\textsubscript{20}H\textsubscript{20} where M=metal/halide.\textsuperscript{17,18}

The embedding energy of the endohedral dopants in the hydrogenated cages was found to be smaller than for the bare endohedrally doped fullerene due to weak interaction between the dopant and the cage.\textsuperscript{20} Other than that, such surface passivated endohedrally doped fullerenes proposed in theoretical calculations have very weak interactions among each other and might therefore be stable building blocks for novel materials. It was also predicted that the halide ions, especially Br\textsuperscript{−}, are ideally suited for the synthesis of Si\textsubscript{20}H\textsubscript{20}.\textsuperscript{19} However, no such system have been observed in experiments till date.

In our recent study on Si\textsubscript{20}H\textsubscript{20}\textsuperscript{−}, we found that its potential energy surface(PES) is complex. The spontaneous formation of Si\textsubscript{20}H\textsubscript{20} by condensation is unlikely to occur because the time scale for finding the global minimum is much longer then the time scale for competing processes such as fragmentation or fusion.

Recently, Tillmann \textit{et. al.} have developed a one step synthesis protocol by which the Si\textsubscript{20} dodecahedral core can be stabilized and hence, realized in experiments. The resulting structure is the [Cl@Si\textsubscript{32}Cl\textsubscript{44}]\textsuperscript{−}, which consists of a Si\textsubscript{20} dodecahedral core with an endohedral Cl\textsuperscript{−} ion and exohedrally decorated with 8 Cl and 12 SiCl\textsubscript{3} groups.\textsuperscript{21} Their DFT studies on different possible exohedral decoration with Cl and SiCl\textsubscript{3} of the Si\textsubscript{20} cage structure...
provides valuable information about the role of the exohedral decoration on the energetics of the synthesized structure. Later, Vargas et al. \cite{22} investigated the role of the central halide ion in stabilizing the system based on energy decomposition and multipole analysis.

The study of PES can provide estimate of the synthesizability of a desired compound, the barrier height required to cross and time-scale to synthesize the compound. As explained earlier in Ref.\cite{21}, why it is not feasible to synthesize Si$_{20}$H$_{20}$ and opposite for C$_{60}$. Thus, the PES is equally important as the properties of the synthesized structure. The two studies Ref.\cite{22} and Ref.\cite{23} have focussed primarily on the cage structure of Cl@Si$_{32}$Cl$_{44}$ and the role of either exohedral or endohedral substituents in stabilizing the system. However, the role of the PES in making the synthesis of [Cl@Si$_{32}$Cl$_{44}$]$^-$ feasible have not been explored yet. Apart from PES, the studies do not address the impact of different combination of exohedral-endohedral decoration of Si$_{20}$ cage and the extra electron in its stabilization.

In this work, the minima hopping method\cite{24} was used to explore the potential energy surface(PES) of Si$_{20}$ with different endohedral-exohedral decorations. The runs generated in total 500 distinct structures, which can be classified into fragmented and non-fragmented structures. Distance-energy plots constructed for these structures were used to understand the nature of the PES. In addition, a detailed analysis of the charge density, stability and reactivity of the ground state configuration was conducted. Based on a model of the central halide ion trapped in a spherical potential well, we elucidate the role of exo-endo decorations along with negative charge in the stabilization process.

## 2 Computational Methodology:

In order to explore the potential energy surface(PES) of the system of interest, the minima hopping method (MHM) was employed\cite{21,22,24,25,26,27}. The PES is explored by performing consecutive short molecular dynamics escape steps followed by local geometry relaxations, thereby exploiting the Bell-Evans-Polanyi principle\cite{26}. The relaxed structures are accepted or rejected based on the threshold set on the energy difference. The transformation pathways were found by the minima hopping guided path search (MHGPS)\cite{27}.

To identify the structural difference between two configurations and removing the duplicate structures, we have used fingerprint method based on overlap matrix constructed from atom centered Gaussian type orbitals\cite{28}. More details on the method can be found in the appendix.

All the ab-initio simulation have been performed at the level of density functional theory (DFT) as implemented in BigDFT\cite{29}. This code uses Daubechies wavelets as a basis set. The atoms were described by the soft Goedecker-type norm-conserving pseudopotentials with non-linear core correction\cite{30,31} for the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional\cite{32}. The Libxc library\cite{33} coupled with BigDFT was used to evaluate the PBE functionals. A grid spacing of 0.4 Bohr was used. Convergence parameters in BigDFT were set such that total energy differences were converged up to $10^{-4}$ eV and all configurations were relaxed until the maximal force component on any atom reached the noise level of the calculation, which was of the order of 1 meV/Å.

The difference in charge density($\Delta\rho$) and electron localization function(ELF)\cite{34} was calculated using the VASP code\cite{35}. The atoms were described by the Projector Augmented Wave potentials as provided in VASP for the PBE functional. In order to mimic the systems under study in free boundary condition, a uniform box of dimension $20 \times 20 \times 20$ Å$^3$ was used. This is the minimum box size required to prevent self interaction between the clusters. For geometric optimization, a energy cut-off of 350 eV was used and for ELF calculation 600 eV.

## 3 Results and Discussion:

![Fig. 1](image) The configurational energy spectrum of (a) [Cl@Si$_{32}$Cl$_{44}$]$^-$ and (b) [Br@Si$_{32}$Br$_{44}$]$^-$, along with the figures of the ground state configuration and next 3 lowest energy structures. The Si, Cl and Br atoms are shown by blue, green and brown sphere, respectively.

### 3.1 Structure, Geometry and Energetics

A natural starting point of our investigation is the $[\text{Cl}@\text{Si}_{32}\text{Cl}_{44}]^-$ symmetric cage structure, experimentally realized by Tillmann et al.\cite{22} in 2015. This $[\text{Cl}@\text{Si}_{32}\text{Cl}_{44}]^-$ symmetric structure with D$_{2h}$ symmetry is made of a Si$_{20}$ dodecahedral core consisting of 20 vertices forming 12 pentagons. Among the 20 vertices, 12 are capped by SiCl$_3$ groups arranged in pairs and forming the vertices of an octahedron and the remaining 8 are capped with Cl atom. The structure also has an endohedrally doped Cl$^-$ ion. The Si atoms of the cage capped with Cl are represented as Si$_0$ and SiCl$_3$ decorated Si as Si$_1$.

To rapidly perform an exhaustive configurational search of the PES of $[\text{Cl}@\text{Si}_{32}\text{Cl}_{44}]^-$, we carried out MHM runs starting from different configurations; the reported experimental structure and few new configurations were created by exchanging the position of the decorative Cl atoms and SiCl$_3$ groups. Starting from these
different configurations and after removing the similar structures found in different MHM runs through fingerprint distance, we were left with ~500 distinct structures. These structures lie in the energy range $0 \text{ eV} \leq \Delta E \leq 17 \text{ eV}$ w.r.t. the lowest energy structure of $[\text{Cl}@\text{Si}_{32}\text{Cl}_{44}]^–$.

We also carried out investigation on the PES of $[\text{Br}@\text{Si}_{32}\text{Br}_{44}]^−$. The 500 structures obtained for $[\text{Cl}@\text{Si}_{32}\text{Cl}_{44}]^−$ were used as templates for generating structures of $[\text{Br}@\text{Si}_{32}\text{Br}_{44}]^−$ by replacing the Cl atoms with Br and post-relaxing them. As Cl and Br are chemically similar, the $[\text{Br}@\text{Si}_{32}\text{Br}_{44}]^−$ structures easily relaxed without significant distortion and are in the energy range $0 \text{ eV} \leq \Delta E \leq 12 \text{ eV}$ w.r.t. the lowest energy structure of $[\text{Br}@\text{Si}_{32}\text{Br}_{44}]^−$.

The low energy structures generally consist of Si$_{20}$ dodecahedron with diverse arrangement of the Cl and SiCl$_3$ groups on its vertices. However, the high energy structures consist of mostly fragmented structures along with distorted cage structures. In most cases among the fragmented structures, the SiCl$_3$ gets fragmented to form a free SiCl$_3$ with the remaining Cl attached to the Si atom of the cage. This feature of structural motif vs energetic ordering appear to be common in both $[\text{Cl}@\text{Si}_{32}\text{Cl}_{44}]^−$ and $[\text{Br}@\text{Si}_{32}\text{Br}_{44}]^−$.

Based on this two distinct structural motif, the whole structure set can be classified into fragmented and non-fragmented structures. The fragmented structures start to appear at $\Delta E = 1.48 \text{ eV}$ and $\Delta E = 0.96 \text{ eV}$ for $[\text{Cl}@\text{Si}_{32}\text{Cl}_{44}]^−$ and $[\text{Br}@\text{Si}_{32}\text{Br}_{44}]^−$ respectively. Above this energy range, both fragmented and non-fragmented structures can be found. Beyond $\Delta E \geq 4 \text{ eV}$, only the fragmented structures can be found in both $[\text{Cl}@\text{Si}_{32}\text{Cl}_{44}]^−$ and $[\text{Br}@\text{Si}_{32}\text{Br}_{44}]^−$.

The low energy spectrum of $[\text{Cl}@\text{Si}_{32}\text{Cl}_{44}]^−$ and $[\text{Br}@\text{Si}_{32}\text{Br}_{44}]^−$, which consists of primarily non-fragmented structures is shown in Fig. 1(a) and Fig. 1(b) respectively w.r.t. their corresponding lowest energy structure. Along with this, their 4 lowest energy structures are shown in Fig. 1. Among the predicted $[\text{Cl}@\text{Si}_{32}\text{Cl}_{44}]^{−1}$ clusters, the experimentally observed cage structure with D$_{2h}$ symmetry was found to be the lowest energy structure, where the central Cl$^−$ ion is located at the center of the cage. This theoretical observation also holds true for the $[\text{Br}@\text{Si}_{32}\text{Br}_{44}]^−$ clusters. The distance between the central Cl$^−$ ion and Si from the Si$_{20}$ dodecahedron cage is $\sim$3.28-3.39 Å which is comparable to the experimental values of 3.32-3.38 Å. In case of the central Br$^−$ ion in the $[\text{Br}@\text{Si}_{32}\text{Br}_{44}]^−$ cage structure, the distance is 3.31-3.40 Å. Thus, the central halide ion to cage distance is similar in both cases.

The other low energy structures have different arrangements of Si$_0$ and Si$_1$ on pentagons of the cage. Tillmann et. al through DFT calculation on different decoration of Si$_{20}$ cage with increasing number of SiCl$_3$ units have found that the ideal arrangement would be that in the pentagon, two consecutive vertices are to be occupied by SiCl$_3$ units, their immediate neighbouring vertices by Cl atom and the remaining vertex by a SiCl$_3$ group. Deviation from this symmetric arrangement of Si$_0$ was found to cost energy of the structures. This is in agreement with our observations.

The second lowest energy isomer of $[\text{Cl}@\text{Si}_{32}\text{Cl}_{44}]^−$ and $[\text{Br}@\text{Si}_{32}\text{Br}_{44}]^−$ are 0.25 eV and 0.37 eV higher than their ground state respectively. This isomer has one non-ideal pentagon consisting of 4 SiCl$_3$ groups and 1 Cl atom. The third lowest has two non-ideal pentagons and the fourth lowest with three non-ideal pentagons. Thus, shifting away from the ideal pentagonal arrangement for Cl and SiCl$_3$ leads to an increase in energy. However, with more non-ideal pentagons, the situation gets complicated as there are many possible decorative arrangements on these pentagons and their relative energetic ordering is not straightforward to understand. At a certain point in high energy spectrum, the cage structure starts to release SiCl$_3$ with the vertices replaced by Cl atoms. The very high energy structures have completely destroyed cages and free SiCl$_3$ molecules.

The structures of $[\text{Cl}@\text{Si}_{32}\text{Cl}_{44}]^−$ and $[\text{Br}@\text{Si}_{32}\text{Br}_{44}]^−$ are found to have intermediate to large HOMO-LUMO gaps. Our calculations of 10 lowest energy structures of $[\text{Cl}@\text{Si}_{32}\text{Cl}_{44}]^−$ and $[\text{Br}@\text{Si}_{32}\text{Br}_{44}]^−$ at the level of semilocal DFT are found to be in the range 1.7-2.0 eV and 2.0-2.4 eV respectively. No specific trends have been found among the HOMO-LUMO gap of different structures. The HOMO-LUMO gaps can be found in the SI.

### 3.2 Fingerprint Distance-Energy

Apart from the energy ranking of the predicted structures, we also tried to seek insight into the nature of the PES through fingerprint-distance(DE) vs energy plots. In such a plot, the energy difference($\Delta E$) is plotted against the fingerprint distance w.r.t. the ground state structure.

The DE plots of both $[\text{Cl}@\text{Si}_{32}\text{Cl}_{44}]^−$ (open orange square) and $[\text{Br}@\text{Si}_{32}\text{Br}_{44}]^−$ (open blue circle) in the Fig. 2. The energy and the fingerprint distance w.r.t. the lowest energy configuration for each case. For any structure one can find another structure that is more similar to the ground state and that is in nearly all cases lower or in a few cases slightly higher in energy. Hence, on gains quasi continuously energy by moving toward the ground state. The arrow is meant as a guide to the eye, indicating the average driving force.
not too far in the configurational distance. This suggests that the barrier for jumping from the first metastable structure into the ground state is relatively small and that there is, in general, a strong driving force towards the ground state. The fragmented structures have been removed while constructing the distance-energy plot.

In contrast, the structures of Si\textsubscript{20} are found to have small \(\Delta E\) w.r.t. the putative global minima as shown in SI. Details about the generation of Si\textsubscript{20} structures are provided in the SI. Also, Si\textsubscript{20} structures with similar energies are found with both small and large fingerprint distance. This points to the fact that one can easily get trapped in one of the local minima and would need to cross barriers of different heights to fall into the global minima. These features are characteristics of a glassy system. This comparative analysis reveals the interesting fact that the exo-endo decoration of Si\textsubscript{20} not only stabilizes the dodecahedron cage but also alters the PES in such a manner that it changes from glassy to structure seeker.

In order to assess the possibility and reaction time at higher temperature, we estimated the Boltzmann probabilities as a function of temperature for the 10 lowest energy structures of [Cl@Si\textsubscript{32}Cl\textsubscript{4}]- and [Br@Si\textsubscript{32}Br\textsubscript{4}]-. The details of the calculation of the Boltzmann probability plot and the figure (Fig. 1 in appendix) is provided in appendix. The Boltzmann probabilities show that the ground state structure of [Br@Si\textsubscript{32}Br\textsubscript{4}]- is dominant until \(\sim 1200 \text{ K}\) and for [Cl@Si\textsubscript{32}Cl\textsubscript{4}]- until \(\sim 800 \text{ K}\). At higher temperatures, other low energy structures start to emerge.

Hence, considering 800 K as the upper limit, the time required for transition at 800 K is around 0.2 msec. Since, the experimental synthesis was carried out in a solvent medium the actual barrier height could be considerably lower than our calculated height.

### 3.4 Bonding and ELF Analysis

![Figure 4](image)

**Fig. 4** a) Charge density difference between neutral and charged Cl@Si\textsubscript{32}Cl\textsubscript{4}, b) ELF of [Cl@Si\textsubscript{32}Cl\textsubscript{4}]- at \(\eta=0.88\). The Si and Cl atoms are shown by blue and green sphere, respectively.

In order to investigate where the extra electron added to the [Cl@Si\textsubscript{32}Cl\textsubscript{4}]- is localized, the \(\Delta \rho\) between the [Cl@Si\textsubscript{32}Cl\textsubscript{4}]- and [Cl@Si\textsubscript{32}Cl\textsubscript{4}+] is shown in Fig 4(a) where, the yellow colour indicates the presence of extra electronic charge and blue electron deficiency. The plot shows that when an electron is added, it doesn’t reside on the central Cl atom. Rather, the Si as well as Cl atoms of the Si\textsubscript{0} decoration on the cage gain some electronic charge at the expense of losing electronic charge from Si atoms with Si\textsubscript{1} decoration. There is no significant difference in the charge density of the Cl in the SiCl\textsubscript{3} groups in Si\textsubscript{1} decoration.

The ELF of [Cl@Si\textsubscript{32}Cl\textsubscript{4}]- at isosurface value of 0.88 is shown in Fig 4(b). The circular lobes on the Cl atoms indicate the presence of lone pair electrons on them.

### 3.5 Dissociation and Coalescence

The analysis carried out above on the PES and on ground state configuration of [Cl@Si\textsubscript{32}Cl\textsubscript{4}]- doesn’t necessarily shed light on its reactivity. In order to understand its reactive/inert nature, we accessed if it is stable against dissociation or coalescence.

Fragmentation of [Cl@Si\textsubscript{32}Cl\textsubscript{4}]- has been observed in the laser-desorption ionization(LDI) MS(-) experiments. As mentioned earlier, the SiCl\textsubscript{3} group fragments to form a free SiCl\textsubscript{2} molecule and the remaining Cl atom gets adsorbed on the Si atom of the Si\textsubscript{20} cage. A major fragmentation cascade is observed due...
to the extrusions of such SiCl$_2$ groups. Similar structures also were found in our MHM search. Through our DFT calculation, we found that the ground state configuration is found to be local minimum and stable under dissociation of one SiCl$_2$ and two SiCl$_2$ groups with dissociation energy 1.49 and 2.70 eV, respectively. The dissociation energy is defined as the difference between the cluster and the individual components of the fragmented parts of the cluster under vacuum condition.

The issue of coalescence of the ground minimum of [Cl@Si$_{12}$Cl$_{44}$]$^-$ and [Br@Si$_{12}$Br$_{44}$]$^-$ was addressed by estimating the energy required to form dimers. The dimers were created by bringing the ground state configuration in proximity for three different relative orientation (see appendix) and relaxing them without any constraint. It turns out that both the [Cl@Si$_{12}$Cl$_{44}$]$^-$ and [Br@Si$_{12}$Br$_{44}$]$^-$ are chemically inert and repel each other, as indicated by their positive binding energy of dimer. The binding energy of the dimer is defined as the difference between the energy of the dimer and the energy of the monomers. The factor leading to repulsion is the presence of lone pair electrons on peripheral Cl atoms as shown in ELF analysis (Fig. 4).

3.6 Exohedral and Endohedral Substituents

The complex dependency of different exohedral and endohedral decorations along with the extra electron in stabilizing the Si$_{20}$ cage makes their understanding challenging. Vargas et. al. through energy decomposition analysis tried to decipher the role of substituents and suggested alternative halide based substituents which can stabilize the cage. Though such analysis are useful, they are complicated and often not easy to decipher.

The central halide ion in the cage can be considered to be a particle trapped in a spherical potential well. Considering this simple picture, one can easily assimilate the combined effect of the exohedra/endohedral substituents and the additional electron to a single quantity i.e., the curvature of the potential.

For our tests we considered [Cl@Si$_{12}$Cl$_{44}$]$^{-1}$, [Cl@Si$_{12}$Cl$_{44}$], [Br@Si$_{12}$Cl$_{44}$]$^{-1}$, [Cl@Si$_{20}$H$_{20}$]$^{-1}$ and [Br@Si$_{12}$Br$_{44}$]$^{-1}$ cases. The radius of the cage is different for different decorations. The change in energy $\Delta E$(eV) w.r.t. displacement(Å) of the central atom of the cage shows that the potential of the charged and neutral case are on top of each other for all the systems, giving clear indication that the extra electron on the structure does not effect the stability of the center atom (see appendix). The curvature of the systems with central Br ion is larger than the ones with central Cl ion. This is due to the large ionic radius of Br as compared to Cl confined in the cage structure of similar diameter. The large ionic radius leads to steep increase in potential w.r.t. displacement. Hence, the potential is influenced by the substituents and not by the extra electron.

As evident from above, the spring constant K of the potential for [Cl@Si$_{12}$Cl$_{44}$] remains approximately same for both the neutral and charged system. However, the encapsulation energy(E.E.) increases by factor of ~1.84 for charged system as compared to neutral case. The extra stabilization due to addition of an electron is also supported by the large electron affinity. This behavior holds true for other endo-exo decoration of Si$_{20}$ dodecahedron considered. The electron affinity depends only on the exohedral substituents. The values for different decorations are provided in the SI. Thus, the extra electron doesn’t lead to increase in interaction between the central atom and the cage, rather goes to the cage and stabilizes it.

4 Conclusion

In conclusion, through exploration of the PES of [Cl@Si$_{12}$Cl$_{44}$]$^-1$ and [Br@Si$_{12}$Br$_{44}$]$^-1$, we found that the experimentally observed symmetric cage structure is the putative global minima. The exo-endodelic decoration of Si$_{20}$ cage with Cl and SiCl$_2$ transforms the nature of PES from glassy to structure seeker. At room temperature the symmetric cage structure is the most viable isomer during synthesis. However, at higher temperature, other isomers would start to emerge. The ground state minimum is stable against dissociation and coalescence. Our stability analysis suggests that the experimental efforts could be oriented towards the synthesis of the hypothetical counterpart [Br@Si$_{12}$Br$_{44}$]$^-1$ of [Cl@Si$_{12}$Cl$_{44}$]$^-1$.

The $\Delta$ shown in Fig. 4 coupled with the central atom displacement study modeled into a particle trapped in a spherical potential well clearly indicate that the extra electron instead of residing on the central halide atom, gets distributed on the cage and stabilizes it by increasing the inter-atomic interaction within the cage. rather between the central atom and the cage. As a result of this, the extra electron leads to significant increase in encapsulation energy, thereby making the combined system more stable.

Conflicts of interest

There are no conflicts to declare.

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**A Finger print method:**

The configurational fingerprints are given by the eigenvalues of an overlap matrix $O_{ij}$.

$$O_{ij} = \int \phi_i^*(r)\phi_j^*(r)dr$$  \hspace{1cm} (1)

where $\phi_i$ are the Gaussian type orbitals centered on the atom at position $r_i$ and is given by

$$\phi_i^j(r) \propto (x-x_i)^{l_x}(y-y_i)^{l_y}(z-z_i)^{l_z}\exp(-\alpha_i|\mathbf{r}-\mathbf{r}_i|^2)$$  \hspace{1cm} (2)

Here $l=(l_x, l_y, l_z)$ is an angular momentum $L=l_x+l_y+l_z$. The orbitals are classified depending on their value of $L$. i.e., $s$-type orbital is $L=0$, $p$-type orbital is $L=1$, or $d$-type orbital is $L=3$. $\alpha_i$ is the orbital width and they are inversely proportional to the covalent radius of the atoms on which the orbitals are centered on. The structural difference is given by the root mean square difference of the two fingerprint vectors. This fingerprint distance is invariant under translations, rotations, reflections as well as under the permutation of the atomic indices.

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*Fig. 5* The Boltzmann probability distribution of 5 lowest energy structures of $[\text{Cl@Si}_{32}\text{Cl}_{44}]^{-}$ (bottom panel) and The Boltzmann probability have been estimated for 10 lowest energy structures.
Dimers are constructed by adding two GS configurations along X, Z and X-Y directions. Here we show the structures which are formed by adding the GS configurations along X and X-Y direction.

| System       | Gap in Ångstrom |
|--------------|-----------------|
| Si\(_{32}\)Cl\(_{45}^-\) | 6.736           |
| Si\(_{32}\)Cl\(_{45}^+\) | 6.787           |
| Si\(_{32}\)Cl\(_{44}\)Br\(^-\) | 6.749           |
| Si\(_{32}\)Br\(_{45}\)\(^-\) | 6.679           |
| Si\(_{20}\)H\(_{20}\)Cl\(^-\) | 6.629           |

Table 1 Diameter of the gap in the X-Y plane.

Distance Energy (DE) plot of Si\(_{20}\) clusters. The fingerprint distances and energy differences are calculated with respect to the ground state configuration. There is no driving force towards the ground state.

**B Exohedral and Endohedral Substituents**

Based on this simplistic picture of a particle trapped in a 1D-potential, we estimated the spring constant of the quadratic potential. The potential can be easily constructed by obtaining the energy difference as a function of displacement, where the reference energy is the energy of the geometrically relaxed structure. During the displacement of the central atom, the whole structure is kept fixed and only scf runs were done to obtain the total energy. In addition we also calculated encapsulation energy (E.E.) and electron affinity (E.A.). Encapsulation energy is given by:

\[
\text{E.E.} = E_{\text{system}} - E_{\text{cage}} - E_{\text{central atom}}
\]
where $E_{\text{system}}$ is the energy of the whole system cage + center anion (neutral or charged), $E_{\text{cage}}$ energy of the empty cage without the central atom and $E_{\text{central anion}}$ energy of the central halogen (neutral or charged state). Electron affinity (E.A.) is given by

$$E.A. = E_{\text{neutral system}} - E_{\text{charged system}}$$  \hspace{1cm} (4)

where $E_{\text{charged system}}$ is the energy of the charged cage and $E_{\text{neutral system}}$ is the energy of the charged cage.

The E.E., spring constant $K$ and E.A. of these systems are listed in Table 2. As seen above in the Fig 8 and also from the $K$ values, they are similar for charged and neutral states. The E.E. sheds light on the role of the extra electron, i.e. it reduces the total energy, making it more stable and is also supported by the large E.A. Its also interesting to note that the E.A. is not effected by the type of central halide ion, but rather by the exohedral decoration.

| System       | E.E. (eV) | K (eV/Å$^2$) | E.A. (eV) |
|--------------|-----------|--------------|-----------|
| Cl@Si$_{32}$Cl$_{44}$ | -2.34   | 2.16         | 2.08(X,Y,Z) | 5.68 |
| Br@Si$_{32}$Cl$_{44}$ | -1.87   | 2.91         | 2.82       | 5.68 |
| Cl@Si$_{32}$Br$_{44}$ | -2.48   | 1.89         | 1.90       | 5.43 |
| Br@Si$_{32}$Br$_{44}$ | -2.03   | 2.62         | 2.60       | 5.44 |
| Cl@Si$_{20}$H$_{20}$  | -0.07   | 2.70         | 2.69       | 0.16 |
| Br@Si$_{20}$H$_{20}$  | -0.05   | 3.82         | 3.81       | 0.16 |
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Fig. 8 Change in total energy $\Delta E$(eV) as a function of displacement ($\Delta x$) in Å of the center atom for different combination of exohedral and endohedral decoration in the Si$_{20}$ dodecahedron cage. The reference energy for each case was the total energy of the ground state structure and the reference length for the displacement was the radius of the cage for corresponding decoration. The cage structure was kept fixed during the displacement of the center atom.