Bare and ligand protected planar hexacoordinate silicon in SiSb₃M₃⁺ (M = Ca, Sr, Ba) clusters†

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The occurrence of planar hexacoordination is very rare in main group elements. We report here a class of clusters containing a planar hexacoordinate silicon (phSi) with the formula SiSb₃M₃⁺ (M = Ca, Sr, Ba), which have D₃h (1A₁) symmetry in their global minimum structure. The unique ability of heavier alkali-earth atoms to use their vacant d atomic orbitals in bonding effectively stabilizes the peripheral ring and is responsible for covalent interaction with the Si center. Although the interaction between Si and Sb is significantly stronger than the Si–M one, sizable stabilization energies (∼27.4 to −35.4 kcal mol⁻¹) also originated from the combined electrostatic and covalent attraction between Si and M centers. The lighter homologues, SiE₃M₃⁺ (E = N, P, As; M = Ca, Sr, Ba) clusters, also possess similar D₃h symmetric structures as the global minima. However, the repulsive electrostatic interaction between Si and M dominates over covalent attraction making the Si–M contacts repulsive in nature. Most interestingly, the planarity of the phSi core and the attractive nature of all the six contacts of phSi are maintained in N-heterocyclic carbene (NHC) and benzene (Bz) bound SiSb₃M₃(NHC)₆ and SiSb₃M₃(Bz)₆⁺ (M = Ca, Sr, Ba) complexes. Therefore, bare and ligand-protected SiSb₃M₃⁺ clusters are suitable candidates for gas-phase detection and large-scale synthesis, respectively.

Exploring the bonding capacity of main-group elements (such as carbon or silicon) beyond the traditional tetrahedral concept has been a fascinating subject in chemistry for five decades. The 1970 pioneering work of Hoffmann and coworkers1 initiated the field of planar tetracoordinate carbons (ptCs), or more generally, planar hypercoordinate carbons. The past 50 years have witnessed the design and characterization of an array of ptC and planar pentacoordinate carbon (ppC) species.2–14 However, it turned out to be rather challenging to go beyond ptC and ppC systems. The celebrated CB₆²⁻ cluster and relevant systems20–26 were merely model systems because C avoids planar hypercoordination in such systems.25,26 In 2012, the first genuine global minimum D₃h, CO₄Li⁺⁺ cluster was reported to have six interactions with carbon in planar form, although electrostatic repulsion between positively charged phC and Li centers and the absence of any significant orbital interaction between them make this hexacoordinate assignment questionable.12 It was only very recently that a series of planar hexacoordinate carbon (phC) species, CE₃M₃⁺ (E = S–Te; M = Li–Cs), were designed computationally by the groups of Tiznado and Merino (Fig. 1; left panel),27 in which there exist pure electrostatic interactions between the negative C³⁻ center and positive M⁺⁺ ligands. These phC clusters were achieved following the so-called “proper polarization of ligand” strategy.

The concept of planar hypercoordinate carbons has been naturally extended to their next heavier congener, silicon-based systems. Although the steric repulsion between ligands decreases due to the larger size, the strength of π- and σ-bonding between the central atom and peripheral ligands dramatically decreases, which is crucial for stability. Planar tetracoordinate silicon (ptSi) was first experimentally observed in a pentatomic C₅₄SiAl₄⁺ cluster by Wang and coworkers in 2000.28 Very recently, this topic got a huge boost by the room-temperature large-scale syntheses of complexes containing a ptSi unit.29 A recent computational study also predicted the global minimum of SiMg₂Y⁺ (Y = In, Tl) and SiMg₂In₂ to have unprecedented planar pentacoordinate Si (ppSi) units.23 Planar hexacoordinate Si (phSi) systems seem to be even more difficult to stabilize. Previously, a C₅₄ symmetric Cu₄H₄Si cluster was predicted as the true minimum,30 albeit its potential energy surface was not fully explored. A kinetically viable phSi (SiAl₄⁻, Mg₄H₄⁺) cluster cation was also predicted.36 However, these phSi

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systems\textsuperscript{24,25} are only local minima and not likely to be observed experimentally. In 2018, the group of Chen identified the Ca\textsubscript{3}Si\textsubscript{2}\textsuperscript{2–} building block containing a ppSi center and constructed an infinite CaSi monolayer, which is essentially a two-dimensional lattice of the Ca\textsubscript{3}Si\textsubscript{2} motif.\textsuperscript{26} Thus, it is still an open question to achieve a phSi atom to date.

Herein we have tried to find the correct combination towards a phSi system as the most stable isomer. Gratifyingly, we found a series of clusters, SiE\textsubscript{3}M\textsubscript{3}\textsuperscript{+} \((E = N, P, As, Sb; M = Ca, Sr, Ba)\), having planar \(D_{3h}\) symmetry with Si at the center of the six membered ring, as true global minimum forms. Si–E bonds are very strong in all the clusters, and alkaline-earth metals interact with the Si center by employing their d orbitals. However, electrostatic repulsion originated from the positively charged Si and M centers for \(E = N, P, As\) dominates over attractive covalent interaction, making individual Si–M contacts repulsive in nature. This makes the assignment of \(\text{SiE}_{3}M_{3}\textsuperscript{+} \((E = N, P, As; M = Ca, Sr, Ba)\)\) as genuine phSi somewhat skeptical. \(\text{SiSb}_{3}M_{3}\textsuperscript{+} \((M = Ca, Sr, Ba)\)\) clusters are the sole candidates which possess genuine phSi centers as both electrostatic and covalent interactions in Si–M bonding becomes substantial. Along this line, we consider the combinations of \(\text{SiE}_{3}M_{3}\textsuperscript{+} \((E = N, P, As, Sb; M = Be, Mg, Ca, Sr, Ba)\)\) as genuine phSi systems.

Two major computational efforts were made before reaching our title phSi clusters. The first one is to examine \(\text{SiE}_{3}M_{3}\textsuperscript{+} \((E = S–Po; M = Li–Cs)\)\) clusters, which adopt \(D_{3h}\) or \(C_{3v}\) structures as true minima (see Table S1 in ESI†) being isoelectronic to the previous phC \(\text{CE}_{3}M_{3}\textsuperscript{+} \((E = S–Po; M = Li–Cs)\)\) clusters. In the \(\text{SiE}_{3}M_{3}\textsuperscript{+} \((E = S–Po; M = Li–Cs)\)\) clusters, the Si center always carries a positive charge ranging from 0.01 to +1.03\(|e|\), in contrast to the corresponding phC species (see Fig. 1). Thus, electrostatic interactions between the Si\textsuperscript{5+} and M\textsuperscript{5+} centers would be repulsive (Fig. 1). Given that the possibility of covalent interaction with an alkali metal is minimal, it would be a matter of debate whether they could be called true coordination. A second effort is to tune the electronegativity difference between Si and M centers so that the covalent contribution in Si–M bonding becomes substantial. Along this line, we consider the combinations of \(\text{SiE}_{3}M_{3}\textsuperscript{+} \((E = N, P, As, Sb; M = Be, Mg, Ca, Sr, Ba)\)\) as genuine phSi systems. The results in Fig. S1† show that for \(E = Be\) and Mg, the phSi geometry has a large out-of-plane imaginary frequency mode, which indicates a size mismatch between the Si center and peripheral E\textsubscript{3}M\textsubscript{3} \((E = N–Bi; M = Be, Mg)\) ring. On the other hand, the use of larger \(M = Ca, Sr, Ba\) atoms effectively expands the size of the cavity and eventually leads to perfect planar geometry with Si atoms at the center as minima. In the case of \(\text{SiBi}_{3}M_{3}\textsuperscript{+}\), the planar isomer possesses a small imaginary frequency for \(M = Ca\). Although planar \(\text{SiBi}_{3}S_{3}\textsuperscript{+}\) and \(\text{SiBi}_{3}B_{3}\textsuperscript{+}\) are true minima, they are 2.2 and 2.5 kcal mol\textsuperscript{−1} higher in energy than the lowest energy isomer, respectively (Fig. S2†).

Fig. 1 The pictorial depiction of previously reported phC \(\text{CE}_{3}M_{3}\textsuperscript{+} \((E = S–Te; M = Li–Cs)\)\) clusters and the present \(\text{SiE}_{3}M_{3}\textsuperscript{+} \((E = S–Te; M = N–Sb; M = Li–Cs and Ca–Ba)\) clusters. Herein the solid and dashed lines represent covalent and ionic bonding, respectively. The opposite double arrows illustrate electrostatic repulsion.

### Table 1

<table>
<thead>
<tr>
<th>(E)</th>
<th>(r_{N-E})</th>
<th>(r_{N-Ca})</th>
<th>(r_{E-Ca})</th>
<th>(q_{N})</th>
<th>(q_{E})</th>
<th>(q_{Ca})</th>
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<tr>
<td>N</td>
<td>1.669</td>
<td>2.555</td>
<td>2.246</td>
<td>1.57</td>
<td>−1.93</td>
<td>1.74</td>
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<tr>
<td></td>
<td>(1.14)</td>
<td>(0.12)</td>
<td>(0.02)</td>
<td>(0.01)</td>
<td>(0.13)</td>
<td>(0.05)</td>
</tr>
<tr>
<td>P</td>
<td>2.180</td>
<td>2.935</td>
<td>2.640</td>
<td>0.25</td>
<td>−1.42</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td>(1.34)</td>
<td>(1.11)</td>
<td>(0.14)</td>
<td>(0.13)</td>
<td>(0.03)</td>
<td>(0.27)</td>
</tr>
<tr>
<td></td>
<td>(1.33)</td>
<td>(1.10)</td>
<td>(0.03)</td>
<td>(0.05)</td>
<td>(0.03)</td>
<td>(0.29)</td>
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<tr>
<td>Sb</td>
<td>2.538</td>
<td>3.155</td>
<td>2.896</td>
<td>−0.39</td>
<td>−1.16</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>(1.29)</td>
<td>(1.01)</td>
<td>(0.04)</td>
<td>(0.01)</td>
<td>(0.18)</td>
<td>(0.08)</td>
</tr>
</tbody>
</table>
= N, P, As, Sb; M = Ca, Sr, Ba) clusters. Relative energies (in kcal mol\(^{-1}\)) are shown at the single-point CCSD(T)/def2-TZVP/PBE0/def2-TZVP level, followed by a zero-energy correction at PBE0. The values from left to right refer to Ca, Sr, and Ba in sequence. The group symmetries and electronic states are also given.

Born–Oppenheimer molecular dynamics (BOMD) simulations at room temperature (298 K), taking SiE3Ca3 clusters as additional isomers. The global minimum structure is a D\(_{3h}\) symmetric phSi with an \(^1\)A\(_1\) electronic state for all the twelve cases. The second lowest energy isomer, a ppSi, is located more than 49 kcal mol\(^{-1}\) above phSi for E = N. This relative energy between the most stable and nearest energy isomer gradually decreases upon moving from N to Sb. In the case of SiSb3Ca\(_3\) clusters, the second-lowest energy isomer is 4.6–6.1 kcal mol\(^{-1}\) higher in energy than phSi. The nearest triplet state isomer is very high in energy (by 36–53 kcal mol\(^{-1}\), Fig. S3–S6) with respect to the global minimum.

Born–Oppenheimer molecular dynamics (BOMD) simulations at room temperature (298 K), taking SiE3Ca\(_3\) clusters as additional isomers. The global minimum structure is a D\(_{3h}\) symmetric phSi with an \(^1\)A\(_1\) electronic state for all the twelve cases. The second lowest energy isomer, a ppSi, is located more than 49 kcal mol\(^{-1}\) above phSi for E = N. This relative energy between the most stable and nearest energy isomer gradually decreases upon moving from N to Sb. In the case of SiSb3Ca\(_3\) clusters, the second-lowest energy isomer is 4.6–6.1 kcal mol\(^{-1}\) higher in energy than phSi. The nearest triplet state isomer is very high in energy (by 36–53 kcal mol\(^{-1}\), Fig. S3–S6) with respect to the global minimum.

The values in parentheses are the percentage contributions to total attractive interactions (\(\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}\)). The values in parentheses are the percentage contributions to the total orbital interaction \(\Delta E_{\text{orb}}\).

Fig. 2. The structures of low-lying isomers of SiE3M\(_3\) (E = N, P, As, Sb; M = Ca, Sr, Ba) clusters. Relative energies (in kcal mol\(^{-1}\)) are shown at the single-point CCSD(T)/def2-TZVP/PBE0/def2-TZVP level, followed by a zero-energy correction at PBE0. The values from left to right refer to Ca, Sr, and Ba in sequence. The group symmetries and electronic states are also given.

### Table 2. The EDA-NOCV results of the SiE3Ca\(_3\) cluster using Ca\(^{+}\) (D, 4s\(^1\)) + SiE3Ca\(_2\) (D) as interacting fragments at the PBE0/TZ2P-ZORA/PBE0/def2-TZVP level. All energy values are in kcal mol\(^{-1}\).

<table>
<thead>
<tr>
<th>Energy term</th>
<th>Interaction</th>
<th>(\Delta E_{\text{int}})</th>
<th>(\Delta E_{\text{Pauli}})</th>
<th>(\Delta E_{\text{elstat}})</th>
<th>(\Delta E_{\text{orb}})</th>
</tr>
</thead>
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<tr>
<td>(\Delta E_{\text{elstat}})</td>
<td>SiE3Ca(_2)–Ca(^{+})(s) electron-sharing σ-bond</td>
<td>-192.9</td>
<td>139.8</td>
<td>-162.0 (48.7%)</td>
<td>-170.7 (51.3%)</td>
</tr>
<tr>
<td>(\Delta E_{\text{orb}})</td>
<td>SiE3Ca(_2) \to Ca(^{+})(d) π(^+-) donation</td>
<td>-32.9 (19.3%)</td>
<td>-32.0 (21.1%)</td>
<td>-32.0 (21.1%)</td>
<td>-32.0 (21.1%)</td>
</tr>
<tr>
<td>(\Delta E_{\text{orb}})</td>
<td>SiE3Ca(_2) \to Ca(^{+})(d) σ-bond</td>
<td>-13.1 (7.7%)</td>
<td>-11.9 (7.8%)</td>
<td>-11.9 (7.8%)</td>
<td>-11.9 (7.8%)</td>
</tr>
<tr>
<td>(\Delta E_{\text{orb}})</td>
<td>SiE3Ca(_2) \to Ca(^{+})(d) π(^+) donation</td>
<td>-12.3 (7.2%)</td>
<td>-12.2 (8.0%)</td>
<td>-12.2 (8.0%)</td>
<td>-12.2 (8.0%)</td>
</tr>
<tr>
<td>(\Delta E_{\text{orb}})</td>
<td>SiE3Ca(_2) \to Ca(^{+})(d) δ-bond</td>
<td>-8.1 (4.7%)</td>
<td>-9.9 (6.5%)</td>
<td>-9.9 (6.5%)</td>
<td>-9.9 (6.5%)</td>
</tr>
</tbody>
</table>

\(a\) The values in parentheses are the percentage contributions to total attractive interactions (\(\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}\)). \(b\) The values in parentheses are the percentage contributions to the total orbital interaction \(\Delta E_{\text{orb}}\).
the Mayer bond order (MBO), which can be seen as a generalization of WBIs and is more acceptable since the approach of WBI calculations assumes orthonormal conditions of basis functions while the MBO considers an overlap matrix. The MBO values for the Si–M links are now sizable (0.13–0.18). These values are reasonable considering the large difference in electronegativity between Si and M, and, therefore, only a very polar bond is expected between them. In fact, the calculations of WBIs after orthogonalization of basis functions by the Löwdin method gives significantly large bond orders (0.48–0.55), which is known to overestimate the bond orders somewhat. The above results indicate that the presence of covalent bonding cannot be ruled out only by looking at WBI values.

Our following argument regarding the presence of covalent Si–M bonding is based on energy decomposition analysis (EDA) in combination with natural orbital for chemical valence (NOCV) theory. We first performed EDA by taking Ca and SiE₃Ca² in different charge and electronic states as interacting fragments to get the optimum fragmentation scheme that suits the best to describe the bonding situation (see Tables S6–S9†). The size of orbital interaction ($\Delta E_{\text{orb}}$) is used as a probe.²⁸ For all cases, Ca⁺ (D, 4s¹) and SiE₃Ca₂ (D) in their doublet spin states turn out to be the best schemes, which give the lowest $\Delta E_{\text{orb}}$ value. Table 2 shows the numerical results of EDA-NOCV calculations. The relative contribution of electrostatic and orbital terms shows that the interaction between Ca⁺ and SiE₃Ca₂ is a bit more covalent in nature than electrostatic. The intrinsic interaction energy ($\Delta E_{\text{int}}$) between the two fragments gradually diminishes upon moving from E = N to its heavier homologues. Both decreased electrostatic and orbital interactions are responsible for such a reduction in $\Delta E_{\text{int}}$.

The decomposition of $\Delta E_{\text{orb}}$ into pair-wise orbital interaction $\Delta E_{\text{orb}(n)}$ in Table 2 and the corresponding deformation densities $\Delta \rho(n)$ provide us with the most important information about

![Fig. 3](https://example.com/fig3.png)

**Fig. 3** Plot of the deformation densities, $\Delta \rho(1)–(5)$ corresponding to $\Delta E_{\text{orb}(1)–(5)}$ and the related interacting orbitals of the fragments in the SiN₃Ca₅⁺ cluster at the PBE0/TZ2P-ZORA/PBE0/def2-TZVP level. The orbital energy values are in kcal mol⁻¹. The charge flow of the deformation densities is from red to blue. The isovalue for $\Delta \rho(1)$ is 0.001 au and for the rest is 0.0005 au.
wise interactions. The s orbital of Ca⁺ takes part in the electron-transfer coupling of unpaired electrons of Ca⁺ and SiE₃Ca₂. The results of adaptive natural density partitioning (AdNDP) analysis also corroborate this, where M centers are connected through 7c-2e π-bonds (see Fig. S10†).

Another aspect is to check the nature of electrostatic interaction between Si and M. The natural charges in Table 1 shows significant electron transfer from M to E centers that imposes a positive partial charge of 1.7[e]. The E centers possess large negative charges (ranging from -1.2 to -1.9[e]), which decrease with the reduction in electronegativity of E. For a given M, with the variation of E, a drastic change in partial charge on Si is noted. For E = N, the Si center carries a high positive charge (1.6[e]), which is greatly reduced upon moving to E = P (0.3[e]). For E = As, the Si center becomes almost neutral, and eventually, it possesses a negative charge for E = Sb. Therefore, the electrostatic repulsion between Si and M should be largely reduced from N to As, and finally for SiSb₃M₃⁺, the electrostatic interaction between Si and M should be attractive. Note that the energy partitioning scheme in EDA-NOCV taking Ca⁺ + SiE₃Ca₂ provides combined energy contributions for one M–Si contact and two M–E contacts. This argument based on point charges is further verified by the energy components obtained in interacting quantum atom (IQA) analysis, which shows that the covalent (V_Coval) part of the Si–Ca interaction is attractive (ranging between −4.6 and −11.6 kcal mol⁻¹) in all cases. However, the electrostatic (ionic, V_Ionic) part is highly repulsive for E = N, P, As, making the overall interaction repulsive. Such electrostatic repulsion is sharply reduced in moving from N to
As, and finally, for E = Sb, it becomes attractive (see Tables S10–S12†). Thus, the SiSb₃M₃⁺ cluster presents a case in which covalent bonding is robust and ionic interaction between Si and M centers is attractive in nature. If we look at the interatomic interaction energies (V_{total}) for Si–M bonds and M–E bonds, it can be understood that the repulsive energy in Si–M bonds is largely overcompensated by two M–E bonds, even for E = N. This is the reason why electrostatic repulsion between Si and M centers does not result in a very large Si–M bond distance. Nevertheless, repulsive Si–M contacts in SiE₃M₃⁺ (E = N, P, As) make hexacoordination assignment skeptical. SiSb₃M₃⁺ clusters should be considered to possess phSi convincingly. Note that the IUPAC definition of coordination number only demands “the number of other atoms directly linked to that specified atom”, but does not say about the overall nature of interaction between them. In SiSb₃M₃⁺, phSi is linked to three Sb atoms through strong covalent bonds and is bound to three M atoms through ionic interaction in combination with a weaker covalent interaction. These clusters are only weakly aromatic because of such polar electronic distribution (see Fig. S11†).

The next challenge is to protect the reactive centers of phSi clusters with bulky ligands, which is required for large scale synthesis. This is not an easy task since slight external perturbation of most of the planar hypercoordinate atom species could result in a loss in planarity. Few years ago, the groups of Ding and Merino⁵⁵ reported Ca₃MX₃ (M = Zr, Hf; X = F–I, C₂H₅) where ppC is sandwiched and protected by a metallocene framework. Therefore, the presence of X groups is mandatory to provide the electronic stabilization in ppC. In the present cases, surprisingly, SiSb₃M₃⁺ clusters are found to maintain the planarity around hexagons even after the coordination of M centers with six N-heterocyclic carbene (NHC) and benzene (Bz) ligands forming SiSb₃M₃(NHC)₆⁺ and SiSb₃M₃(Bz)₆⁺ (M = Ca, Sr, Ba) complexes, respectively (see Fig. 4). These complexes are highly stable against ligand dissociation as reflected by the high bond dissociation energy (D_e = 236.1 (Ca), 203.9 (Sr) and 171.3 (Ba) kcal mol⁻¹) for SiSb₃M₃(NHC)₆⁺ → SiSb₃M₃⁺ + 6NHC and D_e = 153.8 (Ca), 128.0 (Sr) and 114.0 (Ba) kcal mol⁻¹ for SiSb₃M₃(Bz)₆⁺ → SiSb₃M₃⁺ + 6Bz. The Si–M bond distances are slightly elongated because of coordination with the ligands. But the results of ICA given in Table S13† show that Si–M bonds have attractive interaction energies ranging between −20.0 and −32.4 kcal mol⁻¹. Therefore, the planarity of the phSi core and the attractive nature of all the six contacts of phSi are maintained in ligand-bound SiSb₃M₃(NHC)₆⁺ and SiSb₃M₃(Bz)₆⁺ (M = Ca, Sr, Ba) complexes.

In summary, we have theoretically achieved the first series of planar hexacoordinate silicon (phSi) clusters, SiSb₃M₃⁺ (M = Ca, Sr, Ba), by exploring their potential energy surfaces. These phSi systems are both thermodynamically and kinetically stable. The global minimum structures of SiE₃M₃⁺ (E = N, P, As, Sb) clusters have a D₃h symmetry with the 1A1g electronic state. The ability of the heavier alkaline-earth metals (Ca–Ba) to utilize their d orbitals in chemical bonding is a key factor that underlies the stability of these systems. The Ca–Ba ligands form weak covalent bonding with Si centers through their d orbitals, mimicking transition metals. The electronic charge distribution and ICA analysis show that electrostatic interaction in the Si–Ca links is essentially repulsive in SiN₃M₃⁺, but it sharply reduces with the decrease in electronegativity of E. Eventually, a sizable electrostatic attractive interaction exists between Si and M centers in SiSb₃M₃⁺, leading to a truly unprecedented phSi bonding motif that is held together by both covalent bonding and attractive ionic interaction. For SiE₃M₃⁺ (E = N, P, As) clusters, the electrostatic repulsion between Si and M dominates over covalent interaction, making Si–M contacts repulsive in nature. Most interestingly, the planarity of the phSi core and the attractive nature of all the six contacts of phSi are maintained in N-heterocyclic carbene (NHC) and benzene (Bz) bound SiSb₃M₃(NHC)₆⁺ and SiSb₃M₃(Bz)₆⁺ (M = Ca, Sr, Ba) complexes. Therefore, such clusters protected by bulky ligands would be suitable candidates for large scale synthesis in the presence of bulky counter-ions. Recent experimental reports on pSi systems have already stimulated much curiosity within the community, and the present results would undoubtedly act as a stimulus to it.

Data availability

Computational details, extra data and the Cartesian coordinates for all compounds are provided in the ESI† accompanying this paper.

Author contributions

JCG, H-JZ, Z-hC, SP, and GM designed the works and concepts, analyzed the data, wrote the draft, and finalized it. CC and M-hW performed the global minima searching. L-YF and L-QZ performed NBO and ICA. SP performed EDA-NOCV. All authors took part in the discussions and approved the final version.

Conflicts of interest

The authors declare no conflict of interest.

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