Cage-like La₄B₂₄ and Core-Shell La₄B₂₉⁰⁺⁻⁻⁻⁻ : perfect spherically aromatic tetrahedral metallo-borospherenes

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Abstract
Cage-like and core-shell metallo-borospherenes exhibit interesting structures and bonding. Based on extensive global searches and first-principles, theory calculations, we predict herein the perfect tetrahedral cage-like T₄ld La₄B₂₄ (1) and core-shell T₄ld La₄B₂₉ (2), T₄ld La₄B₂₉⁺ (3), and T₄ld La₄B₂₅ (4) which all possess the same geometrical symmetry as their carbon fullerene counterpart T₄Td C₇₄, with four equivalent interconnected B₆ triangles on the cage surface and four nona-coordinate La centers in four conjoined η⁶ B₉ rings. In these tetra-La-doped boron complexes, La₄[B@B₄@B₂₄]₀/⁻/⁻/⁻ (2 3 4) in the structural motif of 1 + 4 + 28 contain a B-centered tetrahedral T₄ld B@B₄ core in a La-decorated tetrahedral La₄B₂₄ shell, with the negatively charged tetra-coordinate B⁻ at the center being the boron analog of tetrahedral C in T₄d CH₄ (B⁻ ~ C). Detailed orbital and bonding analyses indicate that these T₄ld lanthanide boride complexes are spherically aromatic in nature with a universal La–Bₙ (d-p) σ and (d-p) δ coordination bonding pattern. The IR, Raman, and UV-Vis or photoelectron spectra of these novel metallo-borospherenes are computationally simulated to facilitate their spectral characterizations.

Keywords
First-principles theory · Metallo-Borospherenes · Tetrahedral structures · Bonding patterns · Spherical Aromaticity

Introduction
Boron as a prototypical electron-deficient element possesses a rich chemistry next only to carbon in the periodical table. It exhibits a strong propensity to form multi-center-two-electron (mc-2e) bonds in both bulk allotropes and polyhedral molecules [1, 2]. Persistent joint photoelectron spectroscopy (PES) and first-principles theory investigations in the past two decades have unveiled a rich landscape for size-selected boron clusters (Bₙ⁰⁻) from planar or quasi-planar structures (n = 3–38, 41, 42) to cage-like borospherenes (C₃/C₂ B₃₉⁻ and D₂d B₄₀⁻) which are all characterized with delocalized multi-center bonding [2–6]. Seashell-like borospherenes C₂ B₂₈⁻ and C₁ B₂₀⁻ were late observed in PES measurements as minor isomers competing with their quasi-planar global minimum (GM) counterparts [7, 8]. Endohedral M@B₄₀ (M = Ca, Sr) and exohedral M&B₄₀ (M = Be, Mg) metallo-borospherenes were predicted in theory shortly after the discovery of D₂d B₄₀⁻ [9]. Endohedral metallo-borospherenes D₂ Ta@B₂₂⁻ and D₂d U@B₄₀ were proposed to be superatom-like of 18-electron rule and 32-electron principles, respectively [10, 11]. Joint ion-mobility measurements and density functional theory (DFT) investigations indicated that boron cluster monocations (Bₙ¹⁺) possess double-ring tubular geometries in the size range between n = 16–25 [12]. Extensive GM searches showed that complicated structural competitions exist in medium-sized Bₙ clusters, with B₄₆ being the smallest core-shell boron cluster (B₄@B₄₂) and B₄₈, B₅₄, B₆₀, and B₆₂ being the first bilayer boron clusters predicted to date [13, 14]. Transition-metal-doping induces earlier planar→tubular→cage-like→core-shell structural transitions in boron clusters, resulting in unique structures and bonding in chemistry. Typical examples include the experimentally observed transition-metal-centered boron wheels M@Bₙ (Co@B₈⁻, Ru@B₉, and Ta@B₁₀⁻) and transition-metal-centered boron drums M@Bₙ⁻ (Mn@B₁₆⁻, Co@B₁₆⁻, Rh@B₁₈⁻, and Ta@B₂₀⁻) [15–20]. A family of di-La-doped inverse-sandwich-type mono-deck boron clusters La₃B₉⁻ (n = 7–9) [21, 22] and inverse triple-decker La₃B₁₄⁻ were observed in PES
experiments [23]. The first tri-La-doped spherical trihedral metallo-borospherene $D_{3h}$ La$_4$B$_{24}$ with three La atoms as integral parts of the cage surface was discovered very recently in a joint experimental and theoretical investigation [24]. Our group predicted the possibility of the smallest inverse sandwich bi-decker tubular molecular rotor $C_{2h}$ La$_2$B$_{30}$ (La$_2$B$_2@$B$_{18}$) [25] and the first core-shell spherical trihedral metallo-borospherenes $D_{3h}$ La$_3$B$_{20}$ ($La_3[B_2@B_{18}]$) which contains two equivalent eclipsed B$_3$ triangles on the top and bottom interconnected by three B$_2$ units on the waist and three deca-coordinate La atoms as integral parts of cage surface [26]. We also reported the smallest metallo-borospherene $D_{3h}$ Ta$_3$B$_{12}^-$ composed of two eclipsed B$_3$ triangles on the top and bottom interconnected by three B$_2$ units on the waist [27]. However, to the best of our knowledge, there have been no experimental or theoretical evidence reported on tetra-La-doped boron clusters to date. Tetra-metal-doped core-shell metallosilicon fullerenes $T_d$ M$_4@$Si$_{28}$ ($M = Al$ and Ga) in the structural motif of 4 + 28 have been predicted [28] to have the same tetrahedral symmetry as their carbon fullerene counterpart $T_d$ C$_{28}$ [29]. It is natural to ask at current stage what geometrical structures and bonding patterns of the tetra-La-doped boron clusters may have and if perfect tetrahedral metallo-borospherenes are favored over other geometries in both thermodynamics and dynamics.

Based on extensive GM searches and first-principles theory calculations, as an extension of the experimentally observed cage-like $D_{3h}$ La$_3$B$_{18}^-$ and theoretically predicted core-shell $D_{3h}$ La$_3$B$_{26}$ [25], we predict herein the perfect tetrahedral cage-like $T_d$ La$_4$B$_{24}$ (1) and core-shell $T_d$ La$_4$B$_{29}$ (2), $T_d$ La$_4$B$_{29}^+$ (3), and $T_d$ La$_4$B$_{29}^-$ (4) which possess four equivalent inter-connected B$_6$ triangles on the cage surface and four nona-coordinate La centers in four equivalent conjoined $η^9$-B$_9$ nonagonal ligands, presenting the first metallo-borospherene counterparts of the experimentally observed tetrahedral carbon fullerene $T_d$ C$_{28}$ [29]. More intriguingly, La$_4[B@B_4@B_{24}]^{0/-}$ (2/3/4) in the structural pattern of 1 + 4 + 28 possess a tetra-coordinate B center encapsulated in an inner tetrahedron (B')$_4$ and an outer tetrahedron La$_4$(B')$_{24}$. These high-symmetry lanthanide boride complexes turn out to be spherically aromatic in nature with a universal La–B$_9$ (p-d) $σ$ and (p-d) $δ$ coordination bonding pattern.

Methods

Extensive GM searches were performed on La$_4$B$_{24}$, La$_4$B$_{29}^+$ and La$_4$B$_{29}^-$ using the TGmin2 code [30] at DFT level, with the initial seeds being manually constructed based on the experimentally observed La$_3$B$_{18}^-$ [24] and theoretically predicted La$_3$B$_{19}$ and La$_3$B$_{20}^-$ [26]. Over 2000 trial structures were explored for each species in both singlet and triplet states at PBE/TZVP. The low-lying isomers were subsequently optimized at the PBE0 [31] and TPSSh [32] levels with the basis set of 6–311+G(d) [33] for B and Stuttgart relativistic small-core pseudopotential for La [34, 35] using the Gaussian 09 program suite [36], with the vibrational frequencies checked to make sure all the obtained structures are true minima on the potential surfaces. Low-lying isomers of the open-shell neutral La$_4$B$_{29}$ were acquired from the corresponding low-lying isomers of La$_4$B$_{29}^+$ and La$_4$B$_{29}^-$. Relative energies of the three lowest-lying isomers were further refined for La$_4$B$_{24}$ and La$_4$B$_{29}^-$ at the coupled cluster $CCSD(T)/6-$31G(d) level [37–39] implemented in MOLPRO [40] at PBE0 geometries. Chemical bonding analyses were performed for La$_4$B$_{24}$ (1) and La$_4[B@B_4@B_{24}]^{+}$ (3) using the adaptive natural density partitioning (AdNDP) approach [41] at the PBE0 level. Natural bonding orbital (NBO) analyses were achieved using the NBO 6.0 program [42]. Born–Oppenheimer molecular dynamics (BOMD) simulations were carried out on La$_4$B$_{24}$ (1), La$_4$B$_{29}$ (2), La$_4$B$_{29}^+$ (3), and La$_4$B$_{29}^-$ (4) for 30 ps at 300 K and 1000 K using the CP2K code [43].

Results and discussion

Structures and stabilities

With inspiration from the previously reported $D_{3h}$ La$_3$B$_{18}^-$ and $D_{3h}$ La$_3$B$_{20}^-$ [24, 26] which possess two equivalent eclipsed B$_3$ triangles interconnected by three B$_2$ units on the cage surface and three deca-coordinate La centers in three conjoined $η^9$-B$_{10}$ rings, we manually constructed the perfect tetrahedral cage-like $T_d$ La$_4$B$_{24}$ (1) with four equivalent inter-connected B$_6$ triangles on the cage surface and four nona-coordinate La centers in four equivalent conjoined $η^9$-B$_9$ nonagonal ligands, presenting the first metallo-borospherene counterparts of the experimentally observed tetrahedral carbon fullerene $T_d$ C$_{28}$ [29]. More intriguingly, La$_4[B@B_4@B_{24}]^{0/-}$ (2/3/4) in the structural pattern of 1 + 4 + 28 possess a tetra-coordinate B center encapsulated in an inner tetrahedron (B')$_4$ and an outer tetrahedron La$_4$(B')$_{24}$. These high-symmetry lanthanide boride complexes turn out to be spherically aromatic in nature with a universal La–B$_9$ (p-d) $σ$ and (p-d) $δ$ coordination bonding pattern.
carbon fullerene counterpart—the experimentally observed quintet \( T_d \) \( C_{28} \) \( ^5 \) \( A_1 \) \[29\]. Extensive molecular dynamic simulations indicate that \( \text{La}_4 \text{B}_{24} \) (1) is also highly dynamically stable, with the small calculated average root-mean-square-deviations of RMSD = 0.13 Å and maximum bond length deviations of MAXD = 0.43 Å at 1000 K, respectively (Fig. 2). Detailed NBO analyses show that the La centers in \( \text{La}_4 \text{B}_{24} \) (1) possess the natural atomic charge of \( q_{\text{La}} = +1.49 |e| \) and electronic configuration of La\{Xe\}\(4f^{10}6d^{1}6s^{0.09}\), indicating that La donates its \( 6s^{2} \) electron almost completely to the surrounding \( \text{B}_9 \) ligand in \( \text{La}_4 \text{B}_{24} \) (1) while accepting partial valence electron \( (\sim 0.32 |e|) \) from the boron ligand in its partially occupied 5d orbitals via \( p \rightarrow d \) back donations. Bond order analyses show that the La centers in \( \text{La}_4 \text{B}_{24} \) (1) possess the total Wiberg bond order of \( \text{WB}_{\text{La}} = 2.79 \) and average La–B bond order of \( \text{WB}_{\text{La-B}} = 0.26 \), evidencing the formation of effective La–B coordination interactions in the complex.

The high-symmetry tetrahedral \( T_d \) \( \text{La}_4[\text{B@B}_4 \text{@B}_{24}] \) (2) \( (^2 \)\( A_2 \)) was achieved by encapsulating a B-centered tetrahedral \( T_d \) \( \text{B@B}_4 \) core inside the cage-like \( \text{La}_4 \text{B}_{24} \) (1), forming a perfect tetrahedral core-shell lanthanide boride complex with a tetra-coordinate B at the cage center (Fig. 1). Surprisingly and intriguingly, extensive DFT calculations indicate that,

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**Fig. 1** Optimized structures of cage-like \( T_d \) \( \text{La}_4 \text{B}_{24} \) (1) and core-shell \( T_d \) \( \text{La}_4[\text{B@B}_4 \text{@B}_{24}] \) (2), \( T_d \) \( \text{La}_4[\text{B@B}_4 \text{@B}_{24}]^{+} \) (3), and \( T_d \) \( \text{La}_4[\text{B@B}_4 \text{@B}_{24}]^{-} \) (4), with the central B atom highlighted in blue and four apex B atoms of the tetrahedral \( T_d \) \( \text{B@B}_4 \) core highlighted in red in 2, 3, and 4.

**Fig. 2** Born-Oppenheimer molecular dynamics simulations of \( \text{La}_4 \text{B}_{24} \) (1) (a) and \( \text{La}_4[\text{B@B}_4 \text{@B}_{24}]^{-} \) (4) (b) at 1000 K. The root-mean-square-deviation (RMSD) and maximum bond length deviation (MAXD) values (on average) are indicated in Å.
with a singly occupied non-degenerate highest occupied \(\pi\)-orbital \((\alpha_3)\), the doublet \(\text{La}_4[@B@B@B_{24}]\) (2) well retains its identical tetrahedral \(T_d\) symmetry during full structural optimizations. As the most stable isomer obtained, it lies 0.79 eV lower than the second lowest-lying isomer \(C_1 \text{La}_4B_{29}\) (3 Å) (Fig. S2). The tetrahedral \(B@B_4\) core and \(\text{La}_4B_{24}\) (1) shell turn out to match both geometrically and electronically in \(\text{La}_4[@B@B@B_{24}]\) (2) which has the lowest vibrational frequency of \(\nu_{\text{min}} = 128.94 \text{ cm}^{-1}\) and \(\alpha\)-HOMO-LUMO gap of \(\Delta E_{\text{gap}} = 2.23 \text{ eV}\). Detaching one electron from or attaching one electron to \(\text{La}_4[@B@B@B_{24}]\) (2) results in the perfect singlet \(T_d\text{La}_4[@B@B@B_{24}]^+\) \((3, 1A_1)\) and \(T_d\text{La}_4[@B@B@B_{24}]^-\) \((4, 1A_1)\) which also appear to be the well-defined GMs of the systems lying 0.79 eV and 0.69 eV lower than the second lowest-lying core-shell \(C_1 \text{La}_4B_{29}^+\) and \(C_1 \text{La}_4B_{29}^-\) at PBE0, respectively (Fig. S3 and Fig. S4). \(\text{La}_4[@B@B@B_{24}]^\ddagger\) \((3/4)\) possess the large HOMO-LUMO gaps of \(\Delta E_{\text{gap}} = 2.84/2.21 \text{ eV}\) and lowest vibrational frequencies of \(\nu_{\text{min}} = 125.50/131.35 \text{ cm}^{-1}\). The \(\text{La}_4[@B@B@B_{24}]^{0/+/-}\) \((2/3/4)\) core-shell complex series in a \(1+4+28\) structural motif possess the B-B bond lengths of \(r_{\text{B-B}} = 1.65/1.64/1.66 \text{ Å}\) between the central B atom and inner tetrahedron \(B_4\), B-B distances of \(r_{\text{B-B}} = 1.73/1.73/1.73 \text{ Å}\) between the inner tetrahedron \(B_4\) and outer tetrahedron \(B_6(\text{d}-\text{p})\), and the \(B\)-B distances of \(r_{\text{B-B}} = 2.88/2.93/2.85 \text{ Å}\) between the B atom at the center and \(B\)-B atoms on the outer shell. They can thus be viewed as the first bi-shell metallo-borospherenes with the tetrahedral B center encapsulated in an inner tetrahedron \(B_4\) and an outer tetrahedron \(\text{La}_4B_6(\text{d}-\text{p})\). Similar to the previously reported endohedral metasilicon fullerenes \(T_d\text{M}_4@Si_{28} (M = \text{Al} \text{ and Ga})\) which follow the structural motif of \(4+28\) \([28]\), core-shell \(\text{La}_4[@B@B@B_{24}]^{0/+/-}\) \((2/3/4)\) in the structural motif of \(1+4+28\) possess the same tetrahedral symmetry as their carbon fullerene counterpart \(T_d\text{C}_{28}\) \([29]\). These core-shell complexes also appear to be highly dynamically stable, as exemplified in Fig. 2 for \(\text{La}_4[@B@B@B_{24}]^\ddagger\) \((4)\) which has the small calculated average RMSD = 0.13 Å and MAXD = 0.41 Å at 1000 K, respectively.

The behavior of the central B atom in these core-shell complexes appears to be especially interesting. Detailed NBO analyses indicate that the central B in \(\text{La}_4[@B@B@B_{24}]^{0/+/-}\) \((2/3/4)\) possesses the natural atomic charge of \(q_B = -1.00/\ -1.05/\ -1.00 \text{ [e]}\), \(\text{electronic configurations of B}[\text{He}]2s^{0.51}2p^{3.48}/[\text{He}]_{2s^{0.52}2p^{3.52}}/\text{B}[\text{He}]_{2s^{0.52}2p^{3.52}}\), and total Wiberg bond orders of \(\text{WB}_{13} = 3.71/3.71/3.71\), respectively. The central B atom thus carries approximately a unit negative charge of \(q_B = -1.0 \text{ [e]}\) in these complexes regardless of the charge states of the systems, resulting in a \(B^-\) mononanion at the cage center which is isovalent with a neutral C atom. The negatively charged tetra-coordinate \(B^-\) center in 2, 3, 4 is thus a boron analog of the tetrahedral C in \(T_d\text{CH}_4\), indicating the \(B^-\times C\) analogy \([44]\) in these B-centered core-shell complexes. The tetrahedral \(T_d\text{ B^-@B}_{4}\) unit in \(\text{La}_4[@B@B@B_{24}]^{0/+/-}\) \((2/3/4)\) appears to have the same symmetry as the well-known tetrahedral \(T_d\text{ BH}_4\) (which is isovalent with \(T_d\text{ CH}_4\) \([44]\)), in obvious contrast to the experimentally observed planar \(C_2\), \(B_2\) in gas phase \([2, 3]\) due to effective \(B(p)\text{B}(\pi)\) interactions between the \(B^-\text{B}_4\) core and \(T_d\text{ B}_{24}\) outer shell (as detailed below).

**Bonding analyses**

To better interpret the high stabilities of these \(T_d\) lanthanide boride complexes, we performed detailed AdNDP bonding analyses on the closed-shell \(\text{La}_4B_{24}\) (1) and \(\text{La}_4[@B@B@B_{24}]^\ddagger\) \((3)\) to recover both the localized and delocalized bonds of the systems. As shown in Fig. 3(a), \(\text{La}_4B_{24}\) (1) possesses 6 \(2c-2e\) B-B \(\sigma\) bonds with the occupation number of \(\sigma = 1.88 \text{ [e]}\) between the four interconnected \(B_6\) triangles on the cage surface and 16 \(3c-2e\) \(\pi\) bonds with \(\sigma = 1.91 \text{ [e]}\) on four equivalent \(B_6\) triangular motifs, forming the \(\sigma\) skeleton of the cage-like system. Over the \(\sigma\) skeleton, there exist 4 equivalent \(6c-2e\) \(\pi\) bonds with \(\sigma = 1.91\) over four quasi-planar \(B_6\) triangles at the corners. The remaining 16 delocalized bonds are mainly responsible for the \(La-B_9\) coordination interactions in the complex, including 12 equivalent \(5c-2e\) \(La-B_4\) \(\sigma\) bonds with \(\sigma = 1.72\) and 4 equivalent \(10c-2e\) \(La-B_9\) \(\delta\) bonds with \(\sigma = 1.62\) evenly distributed over four \(La-B_9\) nonagons on the cage surface. Such a bonding pattern renders spherical aromaticity to cage-like \(\text{La}_4B_{24}\) (1), as evidenced by the calculated negative nucleus-independent chemical shift (NICS) \([45]\) values of \(\text{NICS} = -31.69 \text{ ppm}\) at the cage center and \(\text{NICS} = -33.41 \text{ ppm}\) 1.0 Å above the cage center along the \(C_2\) molecular axes.

Figure 3(b) indicates that the core-shell \(\text{La}_4[@B@B@B_{24}]^\ddagger\) \((3)\) well inherits the main bonding elements of \(\text{La}_4B_{24}\) (1), with the 6 \(2c-2e\) B-B \(\sigma\) bonds, 16 \(3c-2e\) \(\sigma\) bonds, 12 \(5c-2e\) \(La-B_4\) \(\sigma\) bonds, and 4 \(10c-2e\) \(La-B_9\) \(\delta\) bonds remaining basically unchanged. The main difference occurs at the 4 \(2c-2e\) B-B \(\sigma\) bonds in the \(B_4\) core between the central B atom and \(B_4\) inner tetrahedron and 4 \(7c-2e\) \(B_6(\pi)\text{B}(\pi)\) \(\sigma\) interactions between the four \(B^+\) atoms in the inner shell and four capping \(B_6\) triangles in the outer shell in the first row and 3 \(29c-2e\) \(\pi\)-\(\pi\) \(\sigma\) bonds totally delocalized on the core-shell \(B_{29}\) framework \(([@B_4@B_{24}])\) in the fourth row. Interestingly, similar to \(\text{La}_4B_{24}\) (1), \(\text{La}_4[@B@B@B_{24}]^{0/+/-}\) \((2/3/4)\) possess the negative calculated NICS values of \(\text{NICS} = -33.92/\ -43.18/\ -28.19 \text{ ppm}\) 1.0 Å above the B center along the \(C_2\) molecular axes, respectively, indicating that these core-shell borospherenes are also spherically aromatic in nature. The 12 \(5c-2e\) \(La-B_4\) \(\sigma\) bonds and 4 \(10c-2e\) \(La-B_9\) \(\delta\) coordination bonds in \(\text{La}_4B_{24}\) (1) and \(\text{La}_4[@B@B@B_{24}]^\ddagger\) \((3)\) play a vital role in stabilizing these perfect tetrahedral lanthanide boride complexes.
The IR, Raman, and UV-Vis spectra of La₄B₂₄ (1) are computationally simulated in Fig. 4 to facilitate their future characterizations. La₄B₂₄ (1) possesses highly simplified IR and Raman spectra due to its high symmetry, including four sharp IR peaks at 215(t₂), 239(t₂), 810(t₂), and 1036 (t₂) cm⁻¹ and eight active Raman vibrations at 137 (a₁), 239(t₂), 391(a₁), 473(a₁), 1036(t₂), 1065(a₁), 1257(t₂), and 1267(a₁).
cm\(^{-1}\), respectively. Detailed vibrational analyses indicate that the symmetrical vibrations at 137 cm\(^{-1}\) (a\(_1\)) and 391 cm\(^{-1}\) (a\(_1\)) represent typical radial breathing modes (RBM)s of the cage-like complex which can be used to characterize single-walled hollow boron nanostructures [46]. The strong UV bands around 323, 341, 376, 436, and 459 nm originate from electronic transitions from deep inner shells of the neutral to its high-lying unoccupied molecular orbitals, while the weak broad bands around 490, 526, 625, and 772 nm mainly involve electronic excitations from the occupied frontier orbitals around the HOMO (t\(_2\)) of the neutral. As shown in Fig. 4(b), La\(_4\)[B@B\(_4\)@B\(_{24}\)]\(^{-}\) (4) exhibits similar IR and Raman spectral features to La\(_4\)B\(_{24}\) (1), with the strongest IR vibration at 258 cm\(^{-1}\) (t\(_2\)) and typical RBM vibrations at 153 cm\(^{-1}\) (a\(_1\)) and 448 cm\(^{-1}\) (a\(_1\)). The calculated PES spectrum of La\(_4\)[B@B\(_4\)@B\(_{24}\)]\(^{-}\) (4) exhibits major spectral features at 2.08, 3.51, 3.75, 4.31, and 5.18 eV which correspond to vertical electronic transitions from the ground state of the anion (\(^1\)A\(_g\)) to the ground state (\(^2\)A\(_2\)) and excited states (\(^2\)T\(_1\), \(^2\)T\(_2\), \(^2\)T\(_3\), \(^2\)T\(_2\)) of the neutral at the ground-state geometry of the anion, respectively.

Conclusions

Perfect tetrahedral cage-like La\(_4\)B\(_{24}\) (1) and core-shell La\(_4\)B\(_{29}\)\(^0/+/\) (2/3/4) with spherical aromaticity have been predicted in this work at first-principles theory level to be the first metallo-borospherenes reported to date possessing the same tetrahedral symmetry as their carbon fullerene counterpart \(T_d\) C\(_{28}\). The tetrahedral B@B\(_4\) core and tetrahedral La\(_4\)B\(_{24}\) (1) shell match both geometrically and electronically in the La\(_4\)B\(_{29}\)\(^0/+/\) (2/3/4) series. Such species could be synthesized and characterized in gas phases using a La-B binary target in PES experiments. [21–24] These high-symmetry lanthanide boride complexes and their chemically modified derivatives may serve as building blocks to form various nanoclusters and nanomaterials with novel electronic, magnetic, and optical properties.

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Availability of data and material All the data are available online.

Code availability N/A

Authors’ contributions Z. H. Wei and S. D. Li designed the project and X. Q. Lu and C. Y. Gao performed the calculations. All the authors participate in the discussion and preparation of the manuscript.

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Declarations

Conflict of interest The authors declare no conflicts of interests.

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