

# Cage-Like $\text{La}_4\text{B}_{24}$ and Core-Shell $\text{La}_4\text{B}_{29}^{0+/-}$ : Perfect Spherically Aromatic Tetrahedral Metallo-Borospherenes

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## Research Article

**Keywords:** First-Principles Theory, Metallo-Borospherenes, Tetrahedral Structures, Bonding Patterns, Spherical Aromaticity

**Posted Date:** February 9th, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-161832/v1>

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**Version of Record:** A version of this preprint was published at Journal of Molecular Modeling on April 21st, 2021. See the published version at <https://doi.org/10.1007/s00894-021-04739-8>.

## 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  $T_d$  La<sub>4</sub>B<sub>24</sub> (**1**) and core-shell  $T_d$  La<sub>4</sub>B<sub>29</sub> (**2**),  $T_d$  La<sub>4</sub>B<sub>29</sub><sup>+</sup> (**3**), and  $T_d$  La<sub>4</sub>B<sub>29</sub><sup>-</sup> (**4**) which all possess the same geometrical symmetry as their carbon fullerene counterpart  $T_d$  C<sub>28</sub>, with four equivalent interconnected B<sub>6</sub> triangles on the cage surface and four nona-coordinate La centers in four conjoined η<sup>9</sup>-B<sub>9</sub> rings. In these tetra-La-doped boron complexes, La<sub>4</sub>[B@B<sub>4</sub>@B<sub>24</sub>]<sup>0/+/-</sup> (**2/3/4**) in the structural motif of 1+4+28 contain a B-centered tetrahedral T<sub>d</sub> B@B<sub>4</sub> core in a La-decorated tetrahedral La<sub>4</sub>B<sub>24</sub> shell, with the negatively charged tetra-coordinate B<sup>-</sup> at the center being the boron analog of tetrahedral C in T<sub>d</sub> CH<sub>4</sub> (B<sup>-</sup> ~C). Detailed orbital and bonding analyses indicate that these T<sub>d</sub> lanthanide boride complexes are spherically aromatic in nature with a universal La–B<sub>9</sub> (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.

## 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 (B<sub>n</sub><sup>-/0</sup>) from planar or quasi-planar structures (n = 3–38, 41, 42) to cage-like borospherenes (C<sub>3</sub>/C<sub>2</sub> B<sub>39</sub><sup>-</sup> and D<sub>2d</sub> B<sub>40</sub><sup>-/0</sup>) which are all characterized with delocalized multi-center bonding [2–6]. Seashell-like borospherenes C<sub>2</sub> B<sub>28</sub><sup>-</sup> and C<sub>s</sub> B<sub>29</sub><sup>-</sup> were late observed in PES measurements as minor isomers competing with their quasi-planar global minimum (GM) counterparts [7, 8]. Endohedral M@B<sub>40</sub> (M = Ca, Sr) and exohedral M&B<sub>40</sub> (M = Be, Mg) metallo-borospherenes were predicted in theory shortly after the discovery of D<sub>2d</sub> B<sub>40</sub><sup>-/0</sup> [9]. Endohedral metallo-borospherenes D<sub>2</sub> Ta@B<sub>22</sub><sup>-</sup> and D<sub>2d</sub> U@B<sub>40</sub> were proposed to be superatoms matching the 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 (B<sub>n</sub><sup>+</sup>) 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 B<sub>n</sub> clusters, with B<sub>46</sub> being the smallest core-shell boron cluster (B<sub>4</sub>@B<sub>42</sub>) and B<sub>48</sub>, B<sub>54</sub>, B<sub>60</sub>, and B<sub>62</sub> 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@B<sub>n</sub> (Co@B<sub>8</sub><sup>-</sup>, Ru@B<sub>9</sub><sup>-</sup>, and Ta@B<sub>10</sub><sup>-</sup>) and transition-metal-centered boron drums M@B<sub>n</sub><sup>-</sup> (Mn@B<sub>16</sub><sup>-</sup>, Co@B<sub>16</sub><sup>-</sup>, Rh@B<sub>18</sub><sup>-</sup>, and Ta@B<sub>20</sub><sup>-</sup>) [15–

20]. A family of di-La-doped inverse-sandwich-type mono-deck boron clusters  $\text{La}_2\text{B}_n^-$  ( $n = 7-9$ ) [21, 22] and inverse triple-decker  $\text{La}_3\text{B}_{14}^-$  were observed in PES experiments [23]. The first tri-La-doped spherical trihedral metallo - borospherene  $D_{3h}$   $\text{La}_3\text{B}_{18}^-$  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  $C_{2h}$   $\text{La}_2\text{B}_{20}^-$  ( $\text{La}_2[\text{B}_2@\text{B}_{18}]$ ) [25] and the first core-shell spherical trihedral metallo-borospherenes  $D_{3h}$   $\text{La}_3\text{B}_{20}^-$  ( $\text{La}_3[\text{B}_2@\text{B}_{18}]^-$ ) which contains two equivalent eclipsed  $\text{B}_6$  triangles on the top and bottom interconnected by three  $\text{B}_2$  units on the waist and three deca-coordinate La atoms as integral parts of cage surface [26]. We also reported the smallest metallo-borospherene  $D_{3h}$   $\text{Ta}_3\text{B}_{12}^-$  composed of two eclipsed  $\text{B}_3$  triangles on the top and bottom interconnected by three  $\text{B}_2$  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  $T_d \text{M}_4@\text{Si}_{28}$  ( $\text{M} = \text{Al}$  and  $\text{Ga}$ ) in the structural motif of  $4 + 28$  have been predicted [28] to have the same tetrahedral symmetry as their carbon fullerene counterpart  $T_d \text{C}_{28}$  [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  $D_{3h}$   $\text{La}_3\text{B}_{18}^-$  [24] and theoretically predicted core-shell  $D_{3h}$   $\text{La}_3\text{B}_{20}^-$  [25], we predict herein the perfect tetrahedral cage-like  $T_d \text{La}_4\text{B}_{24}$  (1) and core-shell  $T_d \text{La}_4\text{B}_{29}$  (2),  $T_d \text{La}_4\text{B}_{29}^+$  (3), and  $T_d \text{La}_4\text{B}_{29}^-$  (4) which possess four equivalent inter-connected  $\text{B}_6$  triangles on the cage surface and four nona-coordinate La centers in four equivalent conjoined  $\eta^9\text{-B}_9$  nonagonal ligands, presenting the first metallo-borospherene counterparts of the experimentally observed tetrahedral carbon fullerene  $T_d \text{C}_{28}$  [29]. More intriguingly,  $\text{La}_4[\text{B}@\text{B}_{24}]^{0/+/-}$  (2/3/4) in the structural pattern of  $1 + 4 + 28$  possess a tetra-coordinate B center encapsulated in an inner tetrahedron  $(\text{B}^\circ)_4$  and an outer tetrahedron  $\text{La}_4(\text{B}^\circ)_{24}$ . These high-symmetry lanthanide boride complexes turn out to be spherically aromatic in nature with a universal La-B<sub>9</sub> (p-d)  $\sigma$  and (p-d)  $\delta$  coordination bonding pattern.

## Methods

Extensive GM searches were performed on  $\text{La}_4\text{B}_{24}$ ,  $\text{La}_4\text{B}_{29}^+$  and  $\text{La}_4\text{B}_{29}^-$  using the TGmin2 code [30] at DFT level, with the initial seeds being manually constructed based on the experimentally observed  $\text{La}_3\text{B}_{18}^-$  [24] and theoretically predicted  $\text{La}_3\text{B}_{19}^-$  and  $\text{La}_3\text{B}_{20}^-$  [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  $\text{La}_4\text{B}_{29}$  were acquired from

the corresponding low-lying isomers of  $\text{La}_4\text{B}_{29}^+$  and  $\text{La}_4\text{B}_{29}^-$ . Relative energies of the three lowest-lying isomers were further refined for  $\text{La}_4\text{B}_{24}$  and  $\text{La}_4\text{B}_{29}^+$  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  $\text{La}_4\text{B}_{24}$  (**1**) and  $\text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]^+$  (**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  $\text{La}_4\text{B}_{24}$  (**1**),  $\text{La}_4\text{B}_{29}$  (**2**),  $\text{La}_4\text{B}_{29}^+$  (**3**), and  $\text{La}_4\text{B}_{29}^-$  (**4**) for 30 ps at 300 K and 1000K using the CP2K code [43].

## Results And Discussion

### Structures and Stabilities

With inspiration from the previously reported  $D_{3h}\text{La}_3\text{B}_{18}^-$  and  $D_{3h}\text{La}_3\text{B}_{20}^-$  [24, 26] which possess two equivalent eclipsed  $\text{B}_6$  triangles interconnected by three  $\text{B}_2$  units on the cage surface and three deca-coordinate La centers in three conjoined  $\eta^{10}\text{-B}_{10}$  rings, we manually constructed the perfect tetrahedral cage-like  $T_d\text{La}_4\text{B}_{24}$  (**1**) with four equivalent interconnected  $\text{B}_6$  triangles on the cage surface and four nona-coordinate La centers in four conjoined  $\eta^9\text{-B}_9$  rings (Fig. 1) Encouragingly, extensive GM searches show that, being overwhelmingly more stable than other low-lying isomers,  $\text{La}_4\text{B}_{24}$  (**1**,  ${}^1\text{A}_1$ ) is the well-defined GM of the neutral (Fig. S1) with the lowest vibrational frequency of  $\nu_{\min} = 119.87 \text{ cm}^{-1}$  at PBE0. It is 0.79 eV more stable than the second lowest-lying isomer  $C_s\text{La}_4\text{B}_{24}$  with a  $\text{B}_2$  core and 1.23 eV more stable than the third lowest-lying isomer  $C_s\text{La}_4\text{B}_{24}$  with a  $\text{B}_3$  core at CCSD(T) level, respectively (Fig. S1). The triplet cage-like  $C_1\text{La}_4\text{B}_{24}$  ( ${}^3\text{A}$ ) slightly distorted due to Jahn-Teller effect appears to be much less stable than the  $T_d$  GM (by 1.28 eV) at PBE0 (Fig. S1).  $\text{La}_4\text{B}_{24}$  (**1**) possesses the B-B bond length of  $r_{\text{B}-\text{B}} = 1.57 \text{ \AA}$  between the interconnected  $\text{B}_6$  triangles, B-B bond length of  $r'_{\text{B}-\text{B}} = 1.66 \text{ \AA}$  within the central  $\text{B}_3$  triangles in  $\text{B}_6$  triangular motifs, and average La–B coordination bond length of  $r_{\text{La}-\text{B}} = 2.75 \text{ \AA}$  between La atoms and their  $\eta^9\text{-B}_9$  ligands. The large calculated HOMO–LUMO gap of  $\Delta E_{\text{gap}} = 2.35 \text{ eV}$  at PBE0 well supports its high chemical stability. Cage-like  $\text{La}_4\text{B}_{24}$  (**1**) appears to be the first metallo-borospherene possessing the same tetrahedral symmetry as its carbon fullerene counterpart – the experimentally observed quintet  $T_d\text{C}_{28}$  ( ${}^5\text{A}_1$ ) [29]. Extensive molecular dynamics 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  $\text{RMSD} = 0.13 \text{ \AA}$  and maximum bond length deviations of  $\text{MAXD} = 0.43 \text{ \AA}$  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  $q_{\text{La}} = +1.49 \text{ |e|}$  and electronic configuration of  $\text{La}[\text{Xe}]4\text{f}^{0.16}5\text{d}^{1.32}6\text{s}^{0.09}$ , indicating that La donates its  $6\text{s}^2$  electron almost completely to the surrounding  $\text{B}_9$  ligand in  $\text{La}_4\text{B}_{24}$  (**1**) while accepting partial valence electron ( $\sim 0.32 \text{ |e|}$ ) from the boron ligand in its partially occupied 5d orbitals via p→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  $\text{WBI}_{\text{La}}=2.79$  and average La–B bond order of  $\text{WBI}_{\text{La--B}}=0.26$ , evidencing the formation of effective La–B coordination interactions in the complex.

The high-symmetry tetrahedral  $T_d \text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]$  (**2**) ( $^2\text{A}_2$ ) was achieved by encapsulating a B-centered tetrahedral  $T_d \text{B}@\text{B}_4$  core inside 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, with a singly occupied non-degenerate highest occupied  $\alpha$ -orbital ( $a_2$ ), the doublet  $\text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]$  (**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  $C_1 \text{La}_4\text{B}_{29}$  ( $^2\text{A}$ ) (Fig. S2). The tetrahedral  $\text{B}@\text{B}_4$  core and  $\text{La}_4\text{B}_{24}$  (**1**) shell turn out to match both geometrically and electronically in  $\text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]$  (**2**) which has the lowest vibrational frequency of  $\nu_{\min} = 128.94 \text{ cm}^{-1}$  and  $\alpha$ -HOMO-LUMO gap of  $\Delta E_{\text{gap}} = 2.23 \text{ eV}$ . Detaching one election from or attaching one electron to  $\text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]$  (**2**) results in the perfect singlet  $T_d \text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]^+$  (**3**,  $^1\text{A}_1$ ) and  $T_d \text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]^-$  (**4**,  $^1\text{A}_1$ ) 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  $C_s \text{La}_4\text{B}_{29}^+$  and  $C_1 \text{La}_4\text{B}_{29}^-$  at PBE0, respectively (Fig. S3 and Fig. S4).  $\text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]^{+/-}$  (**3/4**) possess the large HOMO-LUMO gaps of  $\Delta E_{\text{gap}} = 2.84/2.21 \text{ eV}$  and lowest vibrational frequencies of  $\nu_{\min} = 125.50/131.35 \text{ cm}^{-1}$ . The  $\text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]^{0+/-}$  (**2/3/4**) core-shell complex series in a  $1 + 4 + 28$  structural motif possess the B-B bond lengths of  $r_{\text{B-B}}=1.65/1.64/1.66 \text{ \AA}$  between the central B atom and inner tetrahedron ( $\text{B}^i$ )<sub>4</sub>, B-B distances of  $r_{\text{B-B}}=1.73/1.73/1.73 \text{ \AA}$  between the inner tetrahedron ( $\text{B}^i$ )<sub>4</sub> and outer tetrahedron ( $\text{B}^o$ )<sub>24</sub>, and the La–B distances of  $r_{\text{La--B}}=2.88/2.93/2.85 \text{ \AA}$  between the B atom at the center and La atoms on the outer shell. They can thus be viewed as the first bi-shell metallo-borospherenes with the B center encapsulated in an inner tetrahedron ( $\text{B}^i$ )<sub>4</sub> and an outer tetrahedron  $\text{La}_4(\text{B}^o)_{24}$ . Similar to the previously reported endohedral metallosilicon fullerenes  $T_d \text{M}_4@\text{Si}_{28}$  ( $\text{M} = \text{Al}$  and  $\text{Ga}$ ) which follow the structural motif of  $4 + 28$  [28], core-shell  $\text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]^{0+/-}$  (**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  $\text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]^-$  (**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  $\text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]^{0+/-}$  (**2/3/4**) possesses the natural atomic charge of  $q_B=-1.00/-1.05/-1.00 |e|$ , electronic configurations of  $\text{B}[\text{He}]2\text{s}^{0.51}2\text{p}^{3.48}/\text{B}[\text{He}]2\text{s}^{0.52}2\text{p}^{3.52}/\text{B}[\text{He}]2\text{s}^{0.52}2\text{p}^{3.52}$ , and total Wiberg bond orders of  $\text{WBI}_B = 3.71/3.71/3.71$ , respectively. The central B atom thus carries approximately a unitary negative charge of  $q_B \approx -1.0 |e|$  in these complexes regardless of the charge states of the systems, resulting in a  $\text{B}^-$  monoanion 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  $T_d$   $CH_4$ , indicating the  $B^- \sim C$  analogy [44] in these B-centered core-shell complexes.

## 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  $La_4B_{24}$  (**1**) and  $La_4[B@B_4@B_{24}]^+$  (**3**) to recover both the localized and delocalized bonds of the systems. As shown in Fig. 3(a),  $La_4B_{24}$  (**1**) possesses 6 2c-2e B-B  $\sigma$  bonds with the occupation number of  $ON = 1.88 |e|$  between the four inter-connected  $B_6$  triangles on the cage surface and 16 3c-2e  $\sigma$  bonds with  $ON = 1.91 |e|$  on four equivalent  $B_6$  triangular motifs, forming the  $\sigma$  skeleton of the cage-like system. As expected from chemical intuition, there exist 4 equivalent 6c-2e  $\pi$  bonds with  $ON = 1.91$  over the four interconnected  $B_6$  triangles. The remaining 16 delocalized bonds are mainly responsible for the  $La - B_9$  coordination interactions in the complex, including 12 equivalent 5c-2e  $La - B_4$  (d-p)  $\sigma$  bonds with  $ON = 1.72$  and 4 equivalent 10c-2e  $La - B_9$  (d-p)  $\delta$  bond with  $ON = 1.62$  evenly distributed over four  $La@B_9$  nonagons on the cage surface. Such a bonding pattern renders spherical aromaticity to cage-like  $La_4B_{24}$  (**1**), as evidenced by the calculated negative nucleus-independent chemical shift (NICS) [45] values of  $NICS = -31.69$  ppm at the cage center and  $NICS = -33.41$  ppm 1.0 Å above the cage center along the  $C_2$  molecular axes.

Figure 3(b) indicates that the core-shell  $La_4[B@B_4@B_{24}]^+$  (**3**) well inherits the main bonding elements of  $La_4B_{24}$  (**1**), with the 6 2c-2e B-B  $\sigma$  bonds, 16 3c-2e  $\sigma$  bonds, 12 5c-2e  $La - B_4$  (d-p)  $\sigma$  bonds, and 4 10c-2e  $La - B_9$  (d-p)  $\delta$  bonds remaining basically unchanged. The main difference occurs at the 4 2c-2e B-B  $\sigma$  bonds in the  $B@B_4$  core between the central B atom and  $(B^i)_4$  inner tetrahedron and 4 7c-2e  $B_6(\pi)$ -B(p)  $\sigma$  interactions between the four  $B^i$  atoms in the inner shell and four capping  $B_6$  triangles in the outer shell in the first row and 3 29c-2e  $\pi$ -p  $\sigma$  bonds totally delocalized on the core-shell  $B_{29}$  framework ( $[B@B_4@B_{24}]$ ) in the fourth row. Interestingly, similar to  $La_4B_{24}$  (**1**),  $La_4[B@B_4@B_{24}]^{0+/+/-}$  (**2/3/4**) possess the negative calculated NICS values of  $NICS = -33.92 / -43.18 / -28.19$  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  $La - B_4$  (d-p)  $\sigma$  and 4 10c-2e  $La - B_9$  (d-p)  $\delta$  coordination bonds in  $La_4B_{24}$  (**1**) and  $La_4[B@B_4@B_{24}]^+$  (**3**) play a vital role in stabilizing these perfect tetrahedral lanthanide boride complexes.

## IR, Raman, and UV-Vis/PES Spectral Simulations

The IR, Raman, and UV-Vis spectra of  $La_4B_{24}$  (**1**) and IR, Raman, and PES spectra of  $La_4[B@B_4@B_{24}]^-$  (**4**) are computationally simulated in Fig. 4 to facilitate their future characterizations.  $T_d$   $La_4B_{24}$  (**1**) possesses highly simplified IR and Raman spectra due to its high symmetry, including four sharp IR peaks at 215( $t_2$ ), 239( $t_2$ ), 810( $t_2$ ) and 1036 ( $t_2$ )  $cm^{-1}$  and eight active Raman vibrations at 137 ( $a_1$ ), 239( $t_2$ ), 391( $a_1$ ), 473( $a_1$ ), 1036( $t_2$ ), 1065( $a_1$ ), 1257( $t_2$ ) and 1267( $a_1$ )  $cm^{-1}$ , respectively. Detailed

vibrational analyses indicate that the symmetrical vibrations at  $137\text{ cm}^{-1}$  ( $a_1$ ) and  $391\text{ cm}^{-1}$  ( $a_1$ ) represent typical radial breathing modes (RBMs) 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),  $\text{La}_4[\text{B@B}_4@\text{B}_{24}]^-$  (**4**) exhibits similar IR and Raman spectral features to  $\text{La}_4\text{B}_{24}$  (**1**), with the strongest IR vibration at  $258\text{ cm}^{-1}$  ( $t_2$ ) and typical RBM vibrations at  $153\text{ cm}^{-1}$  ( $a_1$ ) and  $448\text{ cm}^{-1}$ . The calculated PES spectrum of  $\text{La}_4[\text{B@B}_4@\text{B}_{24}]^-$  (**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 ( $^1\text{A}_1$ ) to the ground state ( $^2\text{A}_2$ ) and excited states ( $^2\text{T}_1$ ,  $^2\text{T}_2$ ,  $^2\text{T}_2$ ,  $^2\text{T}_2$ ) of the neutral at the ground-state geometry of the anion, respectively.

## Conclusions

Perfect tetrahedral cage-like  $\text{La}_4\text{B}_{24}$  (**1**) and core-shell  $\text{La}_4\text{B}_{29}^{0/+//-}$  (**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  $T_d\text{C}_{28}$ . The tetrahedral  $\text{B@B}_4$  core and tetrahedral  $\text{La}_4\text{B}_{24}$  (**1**) shell match both geometrically and electronically in the  $\text{La}_4\text{B}_{29}^{0/+//-}$  (**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.

## Declarations

### Funding:

The work was supported by the National Natural Science Foundation of China (21720102006 and 21973057 to S.-D. Li).

### Conflicts of interest//Competing interests:

The authors declare no competing financial interests

### Availability of data and material:

All the data in this work are transparent

### Code availability:

N/A

## Authors' contributions:

S.-D. Li and Z.-H. Wei designed the project and X.-Q. Lu and C.-Y. Gao carried out the calculations. All authors discussed the results and made comments and edits to the manuscript.

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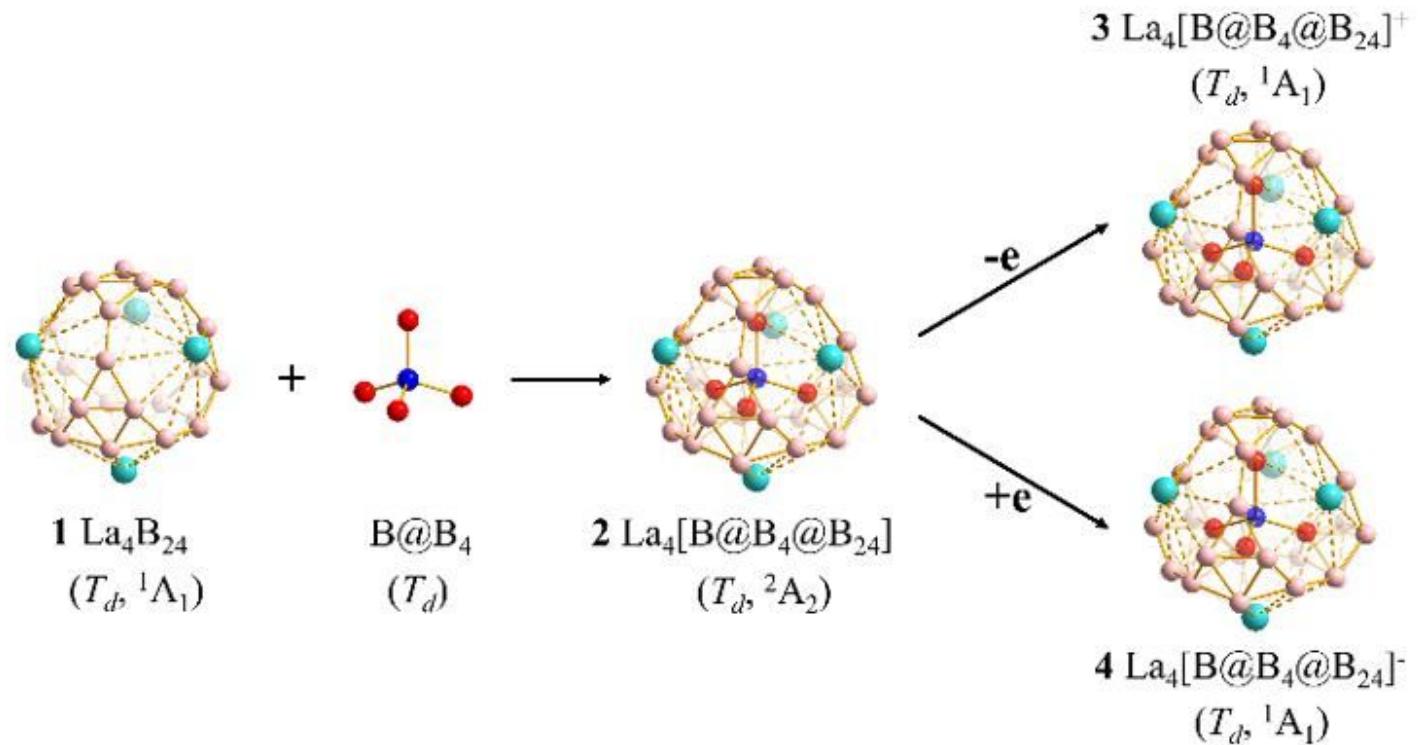
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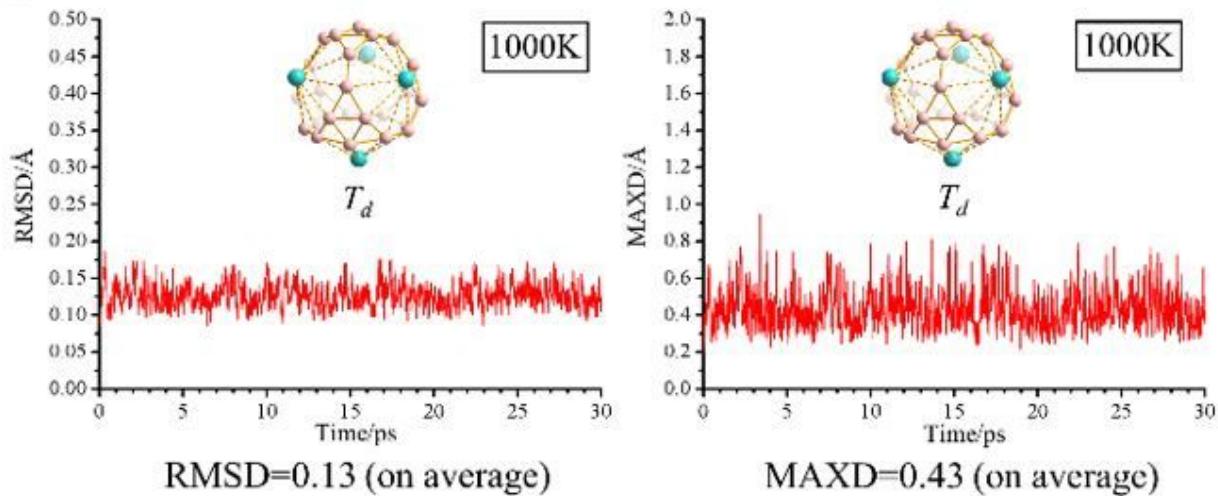
## Figures



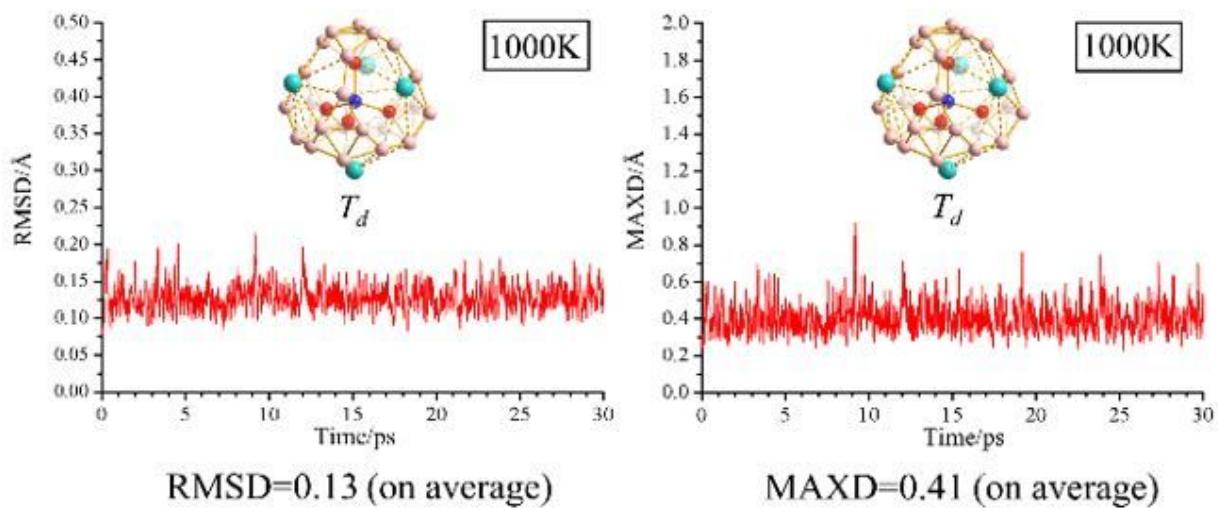
**Figure 1**

Optimized structures of cage-like Td La4B24 (1) and core-shell Td La4[B@B4@B24] (2), Td La4[B@B4@B24]+ (3), and Td La4[B@B4@B24]- (4), with the central B atom highlighted in blue and four apex B atoms of the tetrahedral Td B@B4 core highlighted in red in 2, 3, and 4.

(a)  $\text{La}_4\text{B}_{24}$  (**1**)



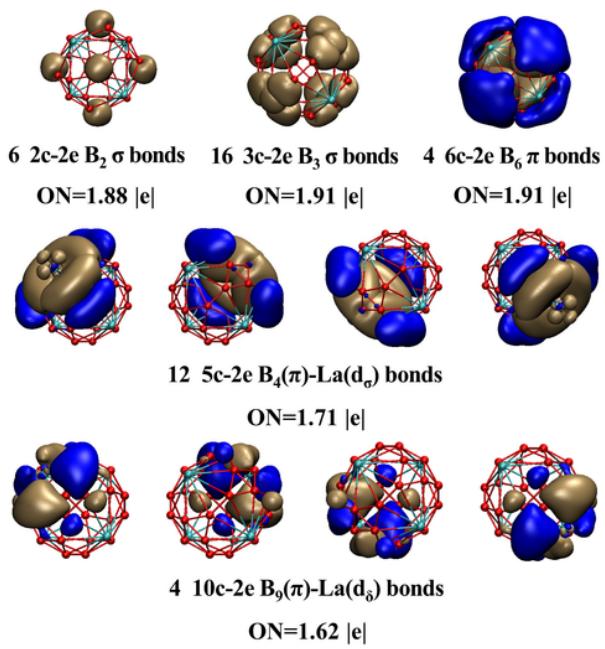
(b)  $\text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]^-$  (**4**)



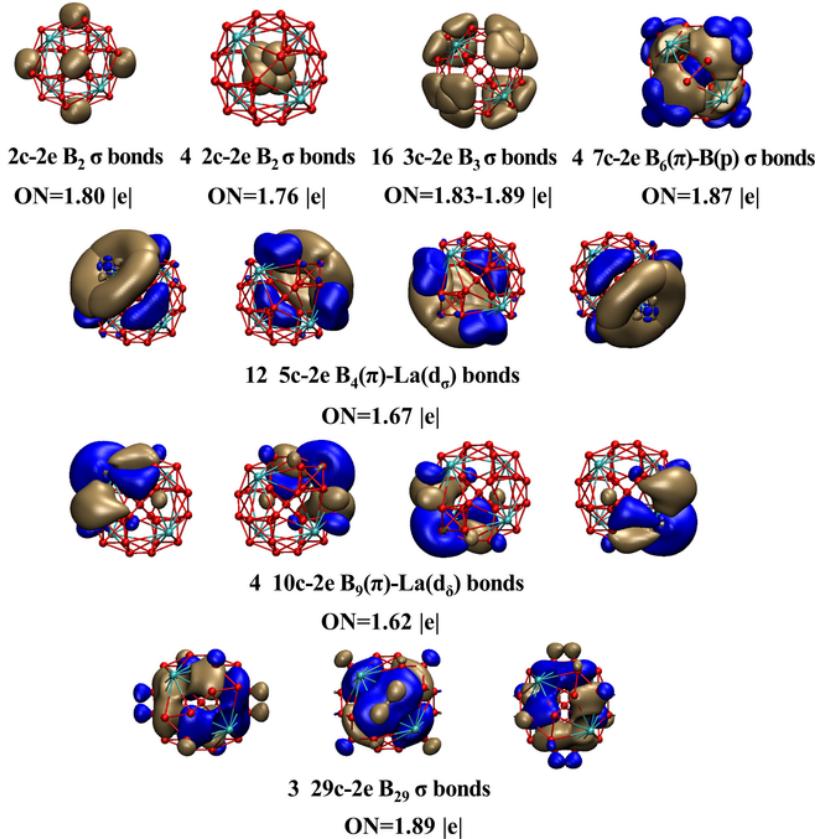
**Figure 2**

Born-Oppenheimer molecular dynamics simulations of  $\text{La}_4\text{B}_{24}$  (**1**) (a) and  $\text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]^-$  (**4**) (b) at 1000 K. The root-mean-square-deviation (RMSD) and maximum bond length deviation (MAXD) values (on average) are indicated in  $\text{\AA}$ .

(a)  $\text{La}_4\text{B}_{24}$  (**1**)

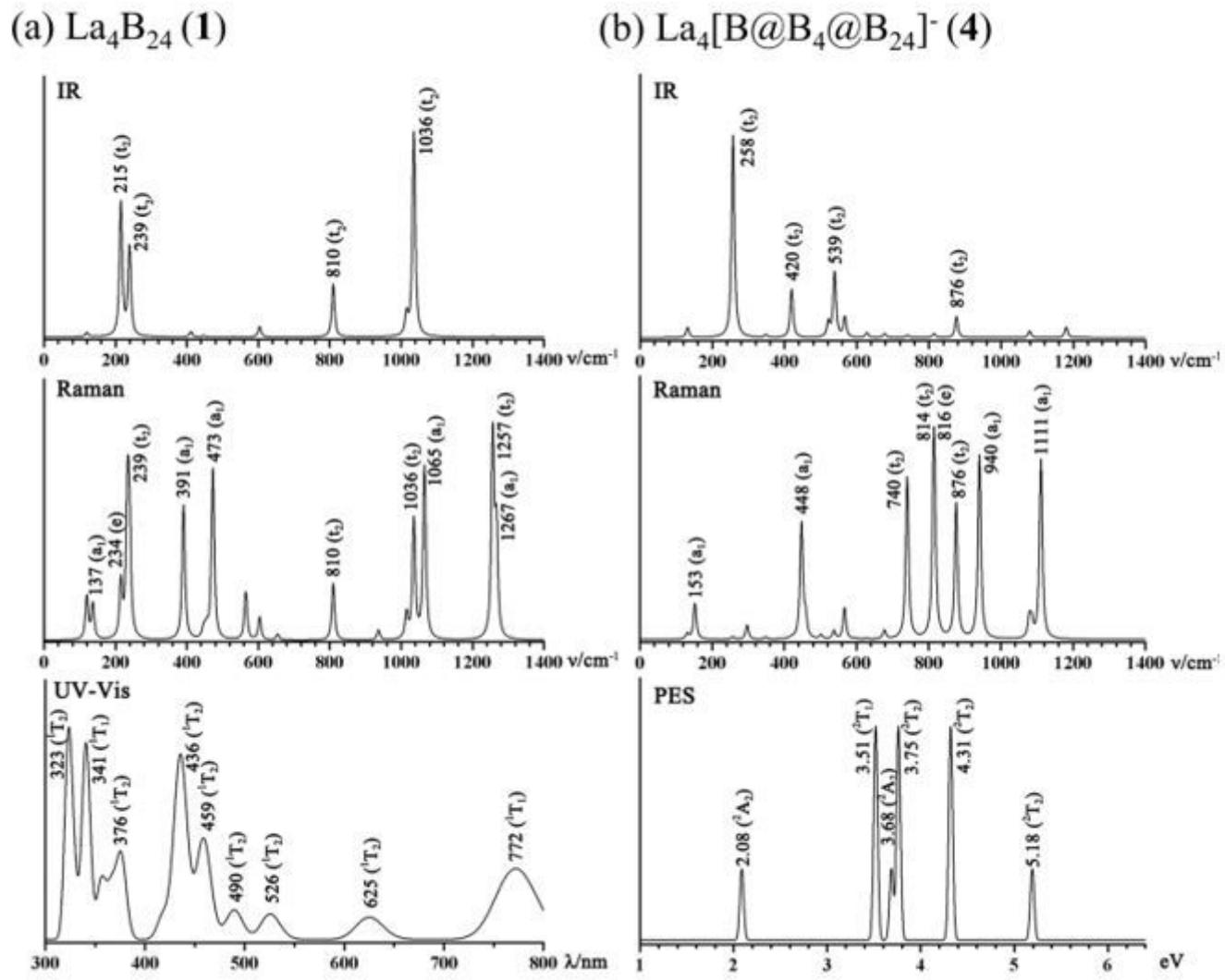


(b)  $\text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]^+$  (**3**)



**Figure 3**

AdNDP bonding patterns of the closed-shell  $\text{La}_4\text{B}_{24}$  (**1**) (a) and  $\text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]^+$  (**3**) (b), with the occupation numbers (ONs) indicated.



**Figure 4**

Simulated IR, Raman and UV-Vis spectra of  $\text{La}_4\text{B}_{24}$  (1) (a) and IR, Raman and PES spectra of  $\text{La}_4[\text{B}@\text{B}_4@\text{B}_{24}]^-$  (4) (b) at PBE0 level.

## Supplementary Files

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