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Endohedral C₃ Ca@B₃₉⁺ and C₂ Ca@B₃₉⁺: Axially Chiral Metalloborospherenes Based on B₃₉⁺

Qiang Chen, Ting Gao, Wen-Juan Tian, Hui Bai, Su-Yan Zhang, Hai-Ru Li, Chang-Qing Miao, Yue-Wen Mu, Hai-Gang Lu, Hua-Jin Zhai, and Si-Dian Li

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Using the newly discovered borospherenes C₃ B₆₀⁻ and C₂ B₆₀⁻ as molecular devices and based on extensive global-minimum searches and first-principles calculations, we present herein the possibility of the first axially chiral metalloborospherenes C₃ Ca@B₃₉⁺ (1, 1'-A) and C₂ Ca@B₃₉⁺ (2, 1'-A) which are the global minimum and the second lowest-lying isomer of CaB₆₀⁻, respectively. These metalloborospherenes species turn out to be charge-transfer complexes Ca²⁺@B₆₀⁻ in nature, with the Ca centre on the Cₛ or C₅ molecular axis donating one electron to the B₆₀ cage which behaves like a superhalogen. Molecular orbital analyses indicate that Cₛ/C₅ Ca@B₆₀⁻ possess the universal bonding pattern of σ plus π double delocalization, similar to their Cₛ/C₅ B₆₀⁻ parents. Molecular dynamics simulations show that both C₃ Ca@B₃₉⁺ (1) and C₂ Ca@B₃₉⁺ (2) are dynamically stable at 200 K, with the former starting to fluctuate structurally at 300 K and the latter at 400 K, again similar to Cₛ/C₅ B₆₀⁻. The infrared and Raman spectra of Cₛ/C₅ Ca@B₆₀⁻ (1/2) are simulated and compared with those of Cₛ/C₅ B₆₀⁻ to facilitate their forthcoming experimental characterizations.

The first endohedral metallofullerene, La@C₆₀, was discovered immediately after C₆₀ in 1985. Various endohedral metallofullerenes and non-metal-doped fullerene matrices were subsequently synthesized and isolated, including Cₛ Ca@C₆₀ with a calcium atom inside C₆₀ and the M@C₇₆ (M = Ca, Sr, Sm, Yb) with an alkaline earth or rare earth metal inside chiral C₇₆, which remarkably enrich the chemistry of carbon fullerenes. Boron, the lighter neighbor of carbon in the periodic table, is characterized with the multicenter chemical bonding, which compensates for boron’s electron deficiency in solids and polyhedral molecules. Small boron clusters Bₙ are known to be planar or quasi-planar with a wide range of sizes (n = 3–25, 30, 35, 36) in a series of combined experimental and theoretical investigations. The possibility of all-boron fullerenes was not considered before the celebrated I₃ B₆₀ buckyball was proposed in 2007, which was built based on the C₆₀ motif by capping all the twenty surface hexagons. However, B₆₀ was later found to favor the core-shell-type structures at various theoretical levels. Cage-like Dₘ₄ B₆₀, the first all-boron fullerenes referred as borospherenes in literature, were discovered in 2014 in a combined experimental and theoretical investigation, revealing the planar-to-cage-like structural transition in B₆₀ at around n = 40. The first axially chiral borospherenes C₃ B₁₉⁺ and C₂ B₁₉⁺, the global minimum and the second lowest-lying isomer of B₁₉⁺, respectively, were observed in 2015. Two cationic chiral members C₃ B₁₉⁺ and C₂ B₁₉⁺ were recently presented to the borospherene family based on extensive global-minimum searches and first-principles calculations. These borospherenes are all composed of twelve interwoven boron double-chains with six hexagonal/heptagonal faces and possess the universal bonding pattern of σ plus π double delocalization. B₉⁷⁺, B₉₅⁺, B₈₁⁺, and B₇₉⁺ thus form a π-isovalent Bₙ series in different charge states (n = 40–49), which all have 12 multicenter two-electron π-bonds (12 mc₂e π) over a σ-skeleton made of n + 8 delocalized three-center two-electron σ-bonds (n + 8 3c-2e σ). The observation of the Dₘ₄ B₆₀⁻ borospherenes leads to a quick surge of borospherene chemistry. The endohedral M@B₆₀ metalloborospherenes (M = Ca, Sr) were predicted to be viable species in a recent communication at the density functional theory (DFT) level. A theoretical study on the electronic structure and electronic spectra of Dₘ₄ B₆₀ was followed by a computational investigation on the endohedral M@B₆₀ (M = Sc, Y, La) quickly followed.
Using the C2/C3 B$_{39}$ borospherenes as molecular devices and based on extensive first-principles calculations, we present herein the viability of the first axially chiral metalloborospherenes C$_1$ Ca@B$_{39}$*(1, 1) and C$_2$ Ca@B$_{39}$*(2, 1), which are the global minimum (GM) and the second lowest-lying isomer of CaB$_{39}$, respectively. These endohedral metalloborospherenes, along with their degenerate enantiomers, turn out to be charge-transfer complexes Ca$^+@B_{39}$ in nature, in which the Ca centre donates one electron to the B$_{39}$ cage. Both C$_1$ Ca@B$_{39}$* (1) and C$_2$ Ca@B$_{39}$* (2) are found to be dynamically stable at 200 K and structurally fluctuate above 400 K. Chemical bonding analyses indicate that these metalloborospherenes inherit the bonding pattern of $\pi$ plus $\sigma$ double delocalization from their $\text{C}_2/\text{C}_3$ B$_{39}$ parents. These B$_{39}$-based metalloborospherenes differ from the previously reported M@B$_{39}$ (M = Ca, Sr)$^{26}$ in axial chirality. To facilitate their future experimental characterizations, the infrared (IR) and Raman spectra of C$_1$ Ca@B$_{39}$* (1) and C$_2$ Ca@B$_{39}$* (2) are predicted and compared with those of the C$_2$C$_2$ B$_{39}$ cages. Preliminary calculations indicate that, at DFT-PBE0 level, the endohedral Sr@B$_{39}$* competes with its triple-ring tubular counterpart in thermodynamics, Ca@B$_{39}$ and Sr@B$_{39}$ are true minima of the neutrals, while Be@B$_{39}$ and Mg@B$_{39}$ appear to be less stable than their exohedral rivals due to size effect$^{26}$.

The GM structural searches were performed for CaB$_{39}$* using the Minima Hopping (MH) algorithm$^{28,31}$ at the DFT level. A total of 2328 stationary points were scanned on the potential energy surface of the monocation, in combination with manual structural constructions based on the typical planar, cage-like, and tubular isomers of B$_{39}$.$^{24}$ Low-lying isomers were then fully optimized and their relative energies evaluated at both the hybrid DFT-PBE0$^{30}$ and CAM-B3LYP (which includes the long-range corrections using the Coulomb attenuating method)$^{31}$ levels with the 6-311+G(d) basis set$^{32}$ as implemented in Gaussian 09 suitable for Gaussian 09$^{33}$. The relative stabilities of the five lowest-lying isomers were further refined using the more accurate coupled cluster method with triple excitations (CCSD(T))$^{34,35}$ implemented in MOLPRO$^{36}$ with the 6-31G(d) basis set at the PBE0 geometries. Molecular dynamics (MD) simulations were performed for the monocations at 200, 300, and 400 K for 30 ps using the software suite CP2K.$^{40}$ The optimized endohedral C$_2$/C$_3$ Ca@B$_{39}$* (1/2) and their degenerate enantiomers C$_1$/C$_2$ Ca@B$_{39}$* (1'/2') are depicted in Fig. 1. More alternative isomers are summarized in Fig. S1 in the Supplementary Information. Fig. 2 shows the molecular orbital energy levels of C$_1$/C$_2$ Ca@B$_{39}$* (1/2) at DFT-PBE0. The bonding patterns of C$_2$/C$_3$ Ca@B$_{39}$* (1/2) are analyzed in Fig. 3 using the adaptive natural density partitioning (AdNDP) method which includes multicenter two-electron (mc-2e) interactions.$^{41}$ Fig. 4 shows the IR and Raman spectra of C$_1$/C$_2$ Ca@B$_{39}$* (1) and C$_1$/C$_2$ Ca@B$_{39}$* (2), as compared with those of C$_3$ B$_{39}$ and C$_2$ B$_{39}$, respectively. We mainly focus on the DFT-PBE0 results in the following discussion, which are generally well supported by the CAM-B3LYP data (Fig. S1).

Considering the fact that C$_1$ B$_{39}$ and C$_2$ B$_{39}$ borospherenes coexist in the gas phase,$^{24}$ we started our structural searches for CaB$_{39}$* from the initial structures of C$_1$ Ca@B$_{39}$ and C$_2$ Ca@B$_{39}$ which were manually constructed by locating a Ca atom on the two- or three-fold molecular axis inside the B$_{39}$ cage. Interestingly, both the C$_1$ B$_{39}$* and C$_2$ B$_{39}$* cages keep almost intact during the structural optimizations. More encouragingly, the optimized closed-shell C$_1$ Ca@B$_{39}$* (1, 1) and C$_2$ Ca@B$_{39}$* (2, 1) appear to be the global minimum and the second lowest-lying isomer of CaB$_{39}$*, respectively, with the former being 0.26 and 0.15 eV more stable than the latter at the DFT-PBE0 and CAM-B3LYP levels. The CCSD(T) level, C$_1$ Ca@B$_{39}$* (1) and C$_2$ Ca@B$_{39}$* (2) turn out to be almost isoenergetic with the minor relative energy of 0.03 eV, suggesting that the two close-lying isomers compete in thermodynamics and may coexist in experiments, similar to the situation of C$_1$/C$_2$ B$_{39}$.$^{24}$ The third and fourth lowest-lying C$_1$ Ca@B$_{39}$* (3) and C$_1$ Ca@B$_{39}$* (4) which are the positional isomers of C$_2$ Ca@B$_{39}$* (2) with two hexagons and four heptagons on the surface, lie 0.17 and 0.24 eV higher than C$_1$ Ca@B$_{39}$* (1) at CCSD(T), respectively. The fifth lowest-lying C$_1$ Ca@B$_{39}$* (5) with one pentagon, three hexagons, and three heptagons on the cage surface appears to be 0.45 eV higher than C$_1$ Ca@B$_{39}$* (1) at CCSD(T). The typical triple-ring tubular C$_1$ CaB$_{39}$* (6) with a Ca on the top, the exohedral C$_1$ Ca@B$_{39}$* (18) with a $n^1$-Ca face-capping a heptagon on the surface, and the quasi-planar C$_1$ CaB$_{39}$* (30) with a tri-coordinate Ca on one edge of the C$_1$ B$_{39}$* with a hexagon hole at the centre$^{24}$ turn out to be at least 0.60 eV less stable than C$_1$ Ca@B$_{39}$* (1) at DFT-PBE0 (Fig.S1). The Ca atom effectively stabilizes the endohedral configurations (1–5), making them energetically favourable with respect to other low-lying isomers.

Vibrational analyses show that C$_1$ Ca@B$_{39}$* (1) possesses the smallest vibrational frequency of $\nu_{\text{min}} = 144$ cm$^{-1}$ (a mode), in which the Ca centre vibrates vertically along the three-fold molecular axis. In contrast, C$_2$ Ca@B$_{39}$* (2) has a small imaginary vibrational frequency of $\nu_{\text{min}} = 18$ cm$^{-1}$ (b mode), which leads to a slightly distorted C$_2$ Ca@B$_{39}$* with $\nu_{\text{min}} = 18$ cm$^{-1}$ (a mode) when fully optimized. However, with zero-point corrections, C$_2$ Ca@B$_{39}$* turns out to be isoenergetic with the distorted C$_1$ Ca@B$_{39}$*.$^{42}$ They correspond practically to the same structure with the Ca centre lying 3.03 and 3.09 Å from the tetracoordinate B at the “defect” site on the front and the boron double chain on the back in C$_2$ B$_{39}$ (Fig. 1), respectively,$^{24}$ similar to the situation in C$_2$ Ca@B$_{40}$.$^{26}$ To the best of our knowledge, C$_1$/C$_2$ Ca@B$_{39}$* (1/2) are the first axially chiral metalloborospherenes reported to date, with the Ca centre lying exactly on the C$_1$ or C$_2$ molecular axis inside the B$_{39}$ cage. The observed borospherenes D$_{3d}$ B$_{39}$ and C$_2$/C$_3$ B$_{39}$ are about 1.0 Å smaller than C$_{60}$ in diameters,$^{27}$ making them more suitable to...
host a metal atom inside on the two- or three-fold molecular axis.26,28

The high stabilities of these metalloborospherenes originate from their electronic structure and bonding patterns. Natural bonding orbital analyses show that the Ca centre in C1 Ca@B39− (1) and C2 Ca@B39− (2) carries a positive charge of +1.58 and +1.60 |e|, respectively, with the corresponding electronic configurations of Ca [Ar]4s 2p 6 3d 10 4f 18 and Ca [Ar]4s 2p 6 3d 10 4f 18. These results clearly indicate that the Ca centre in CaB39− donates one electron to the B39 cage which behaves like a superhalogen.42 The charge-transfer Ca2+@B39− (1/2) complexes mainly show ionic interactions between the Ca2+ centre and B39− cage. C3/C4 Ca@B39− (1/2) may also benefit from weak back-donations from the delocalized π orbitals of B39− to Ca 3d atomic orbitals (see below). As indicated in Fig. 2, C1 Ca@B39− (1) and C2 Ca@B39− (2) possess the huge HOMO–LUMO gaps of 3.06 and 2.66 eV at DFT-PBE0, respectively, well comparable with the values of 2.89, 2.73, and 3.13 eV obtained for C3 B39−, C4 B39−, and D2d B48 at the same level.13,24 The calculated formation energies of C1 Ca@B39− (1) and C2 Ca@B39− (2) are −119.6 and −113.0 kcal/mol at DFT-PBE0 with respect to Ca2+ + B39− = CaB39− and −302.9 and −299.3 kcal/mol with respect to Ca2+ + B39− = CaB39−, respectively, further demonstrating the high thermodynamic stabilities of these monocation complexes.

![Image](image_url)

**Fig. 3** AdNDP bonding patterns of C1 Ca@B39− (1) (a) and C2 Ca@B39− (2) (b). The occupation numbers (ONs) are indicated.

AdNDP analyses unveil the bonding patterns of these Ca3+@B39− complexes. As shown in Fig. 3a, C3 Ca@B39− (1) possesses 39 3c-2e σ and 8 6c-2e σ bonds. As the central B3 triangle makes major contribution to the 6c-2e σ bonds, these σ interactions can be practically treated as 47 3c-2e σ bonds evenly distributed on the cage surface with one 3c-2e σ bond on each B3 triangle. Meanwhile, there exist 3 6c-2e π bonds on the top, 3 5c-2e π bonds at the bottom, and 6 6c-2e π bonds around the waist over the σ skeleton. All the 118 valence electrons in C1 Ca@B39− (1) are thus delocalized in either multicenter σ or π bonds, forming an effective σ plus π double delocalization, which compensates for the electron deficiency of the boron cage. The 12 delocalized π bonds over the C3 B39− cage may back-donate partial electron(s) to the empty Ca 3d atomic orbitals sprouting from inside, as reflected in the Ca electron configurations discussed above. The σ plus π double delocalization bonding pattern of C1 Ca@B39− (1) is actually the same as that of the bare C3 B39−.24 As shown in Fig. 3b, C1 Ca@B39− (2) also has the same bonding interaction as C2 B39−.24 Thus, as isovalent systems, C3/C4 Ca2+@B39− (1/2) inherit both the axial chirality and bonding pattern of their C1/C2 B39− parents.

It is known that both C1 B39− and C2 B39− are dynamically stable at 200 K and fluctuate between low-lying structures above 300 K (i.e. above 300 K, C1 B39− and C2 B39− clusters "hop" between different cage-like structures in concerted mechanisms with low energy barriers. Such structural transformations involve synergetic bond breakage and formation).24 Extensive MD simulations (Fig. S2) indicate that, when incorporated with a Ca atom inside, both C3 Ca@B39− (1) and C4 Ca@B39− (2) remain dynamically stable at 200 K, with the average root-mean-square-deviation (RMSD) of 0.07 and 0.07 Å and maximum bond length deviation (MAXD) of 0.28 and 0.27 Å, respectively. At 300 K, C1 Ca@B39− (2) maintains its structural integrity with RMXD = 0.08 Å and MAXD = 0.31 Å, while C2 Ca@B39− (1) starts to "hop" between C1 (1), C3 (3), and C2 (2) configurations in concerted mechanisms with RMXD = 0.19 Å and MAXD = 0.86 Å. Further MD simulations show that both C1 Ca@B39− (1) and C4 Ca@B39− (2) fluctuate structurally between low-lying structures at 400 K (Fig. S2), similar to C1/C2 B39−.24 Overall, C3/C4 Ca@B39− behave similar to C1/C2 B39− in molecular dynamics.

![Image](image_url)

**Fig. 4** Simulated IR (a) and Raman (b) spectra of C1 Ca@B39− (1) and C3 Ca@B39− (2) compared with those of their C1 B39− and C2 B39− parents.

The combination of infrared photodissociation (IR-PD) spectroscopy and first-principles calculations has proven to be an effective approach in characterizing novel cluster monocations.43,44 We calculate here the vibrational frequencies and simulate the IR spectra of C1/C2 Ca@B39− (1/2) in Fig. 4a, compared with those of C1/C2 B39− at DFT-PBE0. C1 Ca@B39− (1) appears to exhibit similar IR features with C3 B39−, with the three strongest IR peaks at 1233 cm−1 (e), 1261 cm−1 (a), and 1310 cm−1 (e) in the latter well remained in the former (Fig. 4a). All other IR active vibrations are very weak. The IR vibrations associated with the Ca centre appear to lie below 230 cm−1. The simulated Raman spectrum of C1 Ca@B39− is also similar.
to that of CrB$_{39}$ (Fig. 4b). As expected, both the predicted IR and Raman spectra of CrCa@B$_{39}$ (2) are similar with those of CrB$_{39}$ (Fig. 4).

In conclusion, we have presented at first-principles level the viability of the first axially chiral metalloborospherenes Cr/Cr Ca@B$_{39}$ (1/2), utilizing the experimentally known Cr/Cr B$_{39}$ as molecular devices. Bonding analyses reveal the universal σ plus π double delocalization of these Ca@B$_{39}$ complexes. Their IR and Raman spectra are predicted to be similar with those of their Cr/Cr B$_{39}$ parents. The axially chiral metalloborospherenes predicted in this work invite further theoretical and experimental investigations to form chiral borospherene-based nanomaterials.

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**Notes and references**

Axially chiral endohedral metalloborospherenes $C_{2}/C_{2} Ca@B_{39}^{-}$ are predicted via first-principles calculations using the newly discovered $C_{3}/C_{2} B_{35}$ as molecular devices. These metalloborospherenes turn out to be charge-transfer complexes $Ca^{2+}@B_{39}^{-}$ in nature with the universal bonding pattern of σ plus π double delocalization.