Endohedral Ca@B_{38}: stabilization of a B_{38}^{2-} borospherene dianion by metal-encapsulation†

Qiang Chen,ab Hai-Ru Li,b Chang-Qing Miao,a Ying-Jin Wang,ab Hai-Gang Lu,b Yue-Wen Mu,b Guang-Ming Ren,a# Hua-Jin Zhai,a#b and Si-Dian Li*b

Based on extensive global-minimum searches and first-principles electronic structure calculations, we present the viability of an endohedral metalloborospherene C, Ca@B_{38} (1) which contains a C, B_{38}^{−2} (2) dianion composed of interwoven boron double chains with a σπ double delocalization bonding pattern, extending the B_{n}^{+} (n = −40) borospherene family from n = 39−42 to n = 38. Transition metal endohedral complexes M@B_{38} (M = Sc, Y, Ti) (3, 5, 7) based on C, B_{38}^{−2} (2) are also predicted.

As an electron-deficient element, boron has a strong propensity to form polyhedral structures with multicenter chemical bonding. However, gas-phase B_{n}^{−} clusters have proved to be planar or quasi-planar in a wide range of sizes (n = 3−25, 27, 30, 35, 36),1−10 in stark contrast to bulk boron. The possibility of all-boron fullerene was not considered prior to the 2007 proposal of B_{60} fullerene,11 which is constructed from C_{60} by capping the 20 surface hexagons. Subsequent computational investigations, however, showed that B_{60} strongly favors the core-shell-type structures.12,13 The first all-boron fullerenes D_{2}B_{60} and B_{60}, referred to as borospherenes in literature, were discovered in 2014 by Zhai et al. in a combined experimental and theoretical study.14 The first axially chiral borospherenes C/C, B_{38}^{−2} were observed by Chen et al. in 2015.15 Two cationic chiral members C, B_{38}^{−2}1 and C, B_{38}^{−2}2 were recently introduced to the borospherene family by Chen et al. on the basis of global minimum (GM) structural searches.16 The borospherenes B_{39} (2), B_{60} (2), and B_{62}2 reported so far form a n-isolvent B_{n} series in different charge states (n = −40). They are all composed of twelve interwoven boron double-chains (BDCs) with six hexagonal or heptagonal faces, that is, n_{6} + n_{7} = 6 with (n_{6}, n_{7}) = (3, 3), (2, 4), (1, 5), and (0, 6) for n=39, 40, 41, and 42, respectively. Such “cubic-box-like” borospherenes can be viewed as boron analogues of cubane (C_{n}H_{n}).14−16 These borospherenes possess a universal bonding pattern of σπ double delocalization, with 12 multicenter two-electron (mc-2e) π-bonds over a σ-skeleton with (n + 8) three-center two-electron (3c-2e) σ-bonds.14−16

The observations of D_{2}B_{60} and C/C, B_{38}^{−2} lead to a surge of research activities in borospherene chemistry, which is expected to parallel that of the fullerenes. Endohedral metalloborospherenes M@B_{60} (M = Ca, Sr) were firstly predicted by Bai et al. at the density functional theory (DFT) level.17 A computational study on the electronic structure and electronic spectra of D_{2}B_{60},18 a topological analysis of D_{2}B_{60},19 a theoretical study on endohedral M@B_{60} (M = Sc, Y, La),20 a molecular dynamics study on D_{2}B_{60} “nanobubble” at high temperatures (1000 and 1200 K),21 a theoretical prediction of the hydrogen-storage capacity of B_{60},22 and a computational design of Au-B_{60}-Au rectifier and photodetector23 quickly followed. Very recently, Chen et al. predicted the first axially chiral endohedral Ca@B_{38} monocation, in which the B_{38} cage serves as a superhalogen.24 Borospherenes (B_{38}, B_{60}, B_{62}1, and B_{62}2) possess the suitable cavities with a diameter of about 6.0 Å, which can host various kinds of alkaline earth and transition metals to form stable endohedral metalloborospherenes, similar to the well-known endohedral metallofullerenes: M@C_{60} (M = La, Ca) and M@C_{70} (M = Ca, Sr, Sm, Yb).25−32 Borospherenes are also capable of forming stable exohedral metalloborospherenes on the surface heptagons, such as the recently predicted M&B_{60} (M = Be, Mg).17 Concerning smaller fullerene-like boron clusters, a high-symmetry D_{2}B_{68} cage was recently predicted to be the lowest-lying isomer at the DFT level.13,33 Based on D_{2}B_{80}, a series of endohedral complexes M@B_{80} (M = Sc, Y, Ti) were subsequently proposed by encapsulating a transition metal atom inside the D_{2}B_{80} cage.34 But the D_{2}B_{80} cage possesses four hexagon holes, as well as two capped hexagons. This structural pattern is basically different from the B_{60} borospherene series (Ba_{9}, Ba_{10}, Ba_{14}, and Ba_{24}) which are composed of interwoven BDCs with six hexagon/heptagon holes (but without capped hexagons).14,15 Moreover, endohedral M@B_{80} (M = Ca, Sr) and M@B_{80} (M = Sc, Y, Ti) clusters involve electron donation from the metal centers to the high-lying LUMOs of D_{2}B_{60} and D_{2}B_{80} cages which have huge HOMO−LUMO gaps.14,33 Such orbital occupations should destabilize the endohedral systems thermodynamically. On the other hand, for neutral B_{n} cages with n < 40 which lack the necessary valence electrons to match the σπ double delocalization bonding pattern for stable borospherenes,
metal encapsulation is anticipated to help stabilize the systems. The current work represents an exploration in this direction.

Based on extensive GM searches and first-principles calculations, we present herein the possibility of the neutral endohedral Ca@B₁₈ (1) which is composed of twelve interwoven BDCs with a σ+τ double delocalization bonding pattern. Ca@B₁₈ (1) is a charge-transfer complex Ca²⁺@B₁₂⁻ which contains a Ca₂⁺B₁₂⁻ (2) borospherene dianion effectively stabilized by a Ca²⁺ cation encapsulated inside. The infrared (IR) and Raman spectra of 1, as well as the photoelectron spectra of two C₄, Ca@B₁₈ monoanions corresponding to the two lowest-lying isomers of Ca@B₁₈ are simulated, which should facilitate their forthcoming experimental characterizations. Transition metal endohedral C₄, M@B₁₈ (M = Sc, Y, and Ti) based on C₄, B₁₂⁻ (2) are also predicted which turn out to be far more stable than the recently proposed C₄, Mn@B₁₈ endohedral clusters⁴⁵ based on D₂₃h B₁₈.⁴³-⁴⁴

Considering the fact that high-symmetry cage-like D₃h B₁₈ has been predicted to be the lowest-energy isomer of B₁₈ at PBE0, it is reasonable to anticipate that the endohedral D₃h Ca@B₁₈ cluster be energetically favorable for Ca@B₁₈. However, as clearly indicated in Fig. S1 in the ESI, our MH global searches, with more than 2,800 stationary points being probed on the potential energy surface, show that a dramatic structural change occurs from B₁₈ to CaB₁₈: the endohedral C₄, Ca@B₁₈ (1, 1A) turns out to be the GM of Ca@B₁₈ complex, which possesses a C₄, B₁₂ cage composed of twelve interwoven BDCs with four hexagonal and two heptagonal faces, that is, (n₃, n₄) = (4, 2). In contrast, the endohedral D₃h Ca@B₁₈ based on the D₃h Ca@B₁₈ Cage motif is much less stable (by 1.47 eV; Fig. S1 in the ESI) than the GM, mainly due to the fact that it involves an electron transfer from the Ca center to the high-lying LUMO (2.25 eV above the HOMO) of the D₃h B₁₈ cage.⁴³

![Fig. 1 Optimized structure of C₄, Ca@B₁₈ (1) compared with that of C₄, B₁₂⁻ (2) at PBE0/6-311+G(d) level. The eight almost perfectly planar, close-packed B₈ triangles at the corners of the cubic-box are shaded in grey.](image1)

Global structural searches were performed for Ca@B₁₈ using the Minima Hopping (MH) algorithm¹³,³⁶ at DFT, in combination with manual structural constructions based on typical planar, cage-like, and tubular isomers of B₁₂.³³,³⁴,³⁷ Low-lying isomers were then fully optimized with frequencies checked and their relative energies evaluated at the hybrid DFT-PBE0²⁸ level with the 6-311+G(d) basis set²⁸ as implemented in the Gaussian 09 suite.⁴⁰ The Stuttgart relativistic small-core pseudopotential and valence basis sets⁴¹ were used for Sr and Y. Relative stabilities of the low-lying isomers within 0.5 eV were further refined using the coupled cluster method with triple excitations (CCSD(T))¹⁴-¹⁵ implemented in MOLPRO⁴⁰ with the 6-311G(d) basis set at PBE₀ geometries. Molecular dynamics (MD) simulations were performed for the two lowest-lying isomers of Ca@B₁₈ at 200, 300, and 500 K for 30 ps using the CP2K suite.⁴⁷ The optimized endohedral C₄, Ca@B₁₈ (1) is depicted in Fig. 1, compared with that of the B₁₂⁻ (2) dianion. Alternative isomeric structures are summarized in Fig. S1 for Ca@B₁₈ in the Electronic Supplementary Information (ESI). Figure 2 shows the configuration energy spectrum of Ca@B₁₈ at PBE0. Figure 3 presents the bonding patterns of the two lowest-lying isomers of Ca@B₁₈ using the adaptive natural density partitioning (AdNDP) method,⁴⁸ which includes the mc-2e bonding elements. Figure 4 depicts the simulated photoelectron spectra of two C₄, Ca@B₁₈ monoanions which correspond to the two lowest-lying isomers of Ca@B₁₈ (Fig. 2), using the time-dependent DFT (TD-PBE0) approach.⁴⁹ Fig. 5 shows the optimized structures of endohedral C₄, M@B₁₈ (M = Sc, Y, and Ti) (3, 5, 7), compared with their C₄, Mn@B₁₈ counterparts (4, 6, 8).

![Fig. 2 Configurational energy spectrum of Ca@B₁₈ at PBE0/6-311+G(d), with the relative energies indicated in eV. The red and blue bars denote cage-like structures and triple-ring tubes, respectively.](image2)
below, 1 is a charge-transfer complex in nature, Ca\textsuperscript{2+}@B\textsubscript{12}\textsuperscript{2−}, which follows the universal bonding pattern of σπ double delocalization for stable borophosphorus. Here the B\textsubscript{12}\textsuperscript{2−} dianion cage is effectively stabilized by the Ca\textsuperscript{2+} cation encapsulated inside, mainly via electrostatic effect. Ca\textsubscript{2}B\textsubscript{12} (1) represents the first neutral endohedral metalloborospherene with a C\textsubscript{60} buckyshell (2).

The second lowest-lying isomer C\textsubscript{1}, Ca@B\textsubscript{12} (\textsuperscript{A}A), which contains three hexagons and three heptagons (\textit{n}\textsubscript{H}, \textit{n}\textsubscript{H}) (3, 3), lies very close in energy to the GM by 0.08 eV at PBE0 (Fig. 2). It possesses a C\textsubscript{1} B\textsubscript{12} cage that can be achieved by replacing one B\textsubscript{1} heptagon on D\textsubscript{2h} B\textsubscript{12} with a B\textsubscript{2} hexagon and removing one B atom from a BDC to form a tetracoordinate B defect site between two neighboring hexagons on the mirror surface, similar to the experimentally observed C\textsubscript{2} B\textsubscript{12} \textsuperscript{−}.\textsuperscript{15} At the more accurate CCSD(T) level, the relative energy between these two isomers is only 0.03 eV, indicating that they are practically isoenergetic isomers and may coexist in experiments.

The third lowest-lying isomer C\textsubscript{1}, Ca@B\textsubscript{12} (\textsuperscript{A}A) is 0.16 eV above the GM at PBE0. It also contains three hexagons and three heptagons, that is, (\textit{n}\textsubscript{H}, \textit{n}\textsubscript{H}) (3, 3), which can be obtained from the experimentally observed C\textsubscript{1} B\textsubscript{12} \textsuperscript{−} \textsuperscript{−} by removing one B atom from a BDC between two neighboring heptagons to form a tetracoordinate B site. The fourth isomer C\textsubscript{1}, Ca@B\textsubscript{12} (\textsuperscript{A}A) lies 0.23 eV higher than the GM, with two neighboring hexagons and four heptagons (\textit{n}\textsubscript{H}, \textit{n}\textsubscript{H}) (2, 4). It can be achieved by replacing one hexagon from C\textsubscript{1} B\textsubscript{12} \textsuperscript{−} \textsuperscript{−} with a heptagon, with one heptagon on the mirror surface possessing two tetracoordinate B sites on opposite sides. The fifth isomer C\textsubscript{1}, Ca@B\textsubscript{12} (\textsuperscript{A}A) lies 0.41 eV above the GM. It also possesses two hexagons and four heptagons (\textit{n}\textsubscript{H}, \textit{n}\textsubscript{H}) (2, 4), with two tetracoordinate B sites at the two ends of the C\textsubscript{2} atom. The sixth isomer C\textsubscript{1}, Ca@B\textsubscript{12} (\textsuperscript{A}A) with a relative energy of 0.49 eV is the first exohedral isomer, with the Ca atom capping a B\textsubscript{1} ring. The seventh isomer C\textsubscript{1}, Ca@B\textsubscript{12} (\textsuperscript{A}A) is a capped triple-ring tube, being 0.50 eV higher than the GM. At the more reliable CCSD(T) level, the third to seventh isomers are 0.06, 0.09, 0.18, 0.22, and 0.40 eV higher than the GM, respectively, well supporting the energetics at PBE0. The first quasi-planar C\textsubscript{1}, Ca@B\textsubscript{12} (\textsuperscript{A}A) with a Ca-capped B\textsubscript{12} octagon lies 1.36 eV higher than the GM at PBE0 (Fig. 51 in the ESI\textsuperscript{t}). Note that the five lowest-lying isomers of C\textsubscript{2}B\textsubscript{12} all possess endohedral geometries which are the most possible candidates to be synthesized in experiments. Preliminary investigations at PBE0 also indicate that both endohedral C\textsubscript{1}, Mg@B\textsubscript{12} and C\textsubscript{1}, Sr@B\textsubscript{12} based on C\textsubscript{1} B\textsubscript{12} \textsuperscript{−} (2) are true minima of the systems, with the former favoring an exohedral C\textsubscript{1}, Mg@B\textsubscript{12} (similar to the sixth isomer of C\textsubscript{2}B\textsubscript{12} in Fig. 2) by 0.75 eV and the latter favoring a capped triple-ring tubular C\textsubscript{1}, Sr@B\textsubscript{12} (similar to the seventh isomer of C\textsubscript{2}B\textsubscript{12}) by 0.12 eV, respectively due to size effect in the alkaline earth metal series.\textsuperscript{17}

The stabilities of the two lowest-lying CaB\textsubscript{12} isomers are further explored using the MD simulations. As shown in Fig. S2 in the ESI\textsuperscript{t}, Ca@B\textsubscript{12} (1) is dynamically stable at 200, 300, and 500 K, with the root-mean-square-deviations of RMSD = 0.06, 0.07, and 0.10 Å and maximum bond length deviations of MAXD = 0.20, 0.24, and 0.36 Å (on average), respectively (Fig. S2a). The second C\textsubscript{2} isomer is also stable at both 200 and 300 K with RMSD = 0.06 and 0.08 Å and MAXD = 0.22 and 0.27 Å, respectively. However, it starts to fluctuate between two equivalent C\textsubscript{2} isomers at 500 K with RMSD = 0.13 Å and MAXD = 0.56 Å (Fig. S2b). Interestingly, the two C\textsubscript{2} isomers are interlinked via a C\textsubscript{2} intermediate structure in a concerted mechanism, which contains a tetracoordinate B site between two neighboring heptagons on C\textsubscript{2} axis (Fig. S2c). Further simulations indicate that Ca@B\textsubscript{12} (1) also "hops" at 700 K between the three lowest-lying isomers of CaB\textsubscript{12} (Fig. 2). The MD behaviors reflect the glassy nature of nanoboron at high temperatures.\textsuperscript{15,16,21,24}

Endohedral metalloborospherenes C\textsubscript{1}, Ca@B\textsubscript{12} (1) and the second lowest-lying C\textsubscript{1}, Ca@B\textsubscript{12} possess unique electronic structures and bonding patterns. Indeed, they have the large HOMO–LUMO gaps of 2.70 eV and 2.58 eV at PBE0 (Fig. 53), respectively, comparable with the corresponding values of 2.89, 2.73, and 3.13 eV obtained for C\textsubscript{1} B\textsubscript{12} \textsuperscript{−} , C\textsubscript{2} B\textsubscript{12} \textsuperscript{−} , and D\textsubscript{2h} B\textsubscript{12} at the same level.\textsuperscript{24,15} Natural bonding orbital (NBO) analyses show that the Ca centers in these complexes carry the positive charges of +1.69 [e] and 1.71 [e], respectively, with the electronic configurations of [Ar]4s\textsuperscript{13}2p\textsuperscript{12}3d\textsuperscript{17} and [Ar]4s\textsuperscript{12}2p\textsuperscript{12}3d\textsuperscript{16}. These results clearly indicate that the Ca center in these complexes donates two 4s\textsuperscript{2} electrons to the C\textsubscript{1} B\textsubscript{12} cage which behaves like a superoxyn (similar to B\textsubscript{12} which serves as a superhalogen in CaB\textsubscript{12} \textsuperscript{−} \textsuperscript{−}). These charge-transfer complexes mainly exhibit ionic interactions between the Ca\textsuperscript{2+} dication center and the B\textsubscript{12}−- dianion shell. Weak back donations from the π orbitals of B\textsubscript{12}− (as analyzed below) to the empty 4d orbitals of Ca may also contribute to the stabilization of the complexes. The calculated formation energies of ΔE\textsubscript{f} = −127.7 and ΔE\textsubscript{f} = −131.9 kcal/mol with respect to B\textsubscript{12}(C\textsubscript{2}) + Ca = Ca@B\textsubscript{12}(C\textsubscript{2}) and the vertical ionization potentials of 7.35 and 7.16 eV further demonstrate the thermodynamic stability of these neutral complexes.

The AdNDP bonding patterns of (a) the global minimum CaB\textsubscript{12} (1) and (b) the second lowest-lying isomer CaB\textsubscript{12}, with the occupation numbers (ONS) indicated. Both structures are rotated with respect to the original orientations in Fig. 1 and Fig. 2 to make their mirror planes perpendicular to the paper surface.
bonding pattern of σπ double delocalization for borospherenses. The second lowest-lying endohedral isomer C_{1} Ca@B_{38} also features a similar bonding pattern, with 45 3c-2e σ bonds on B_{3} triangles and one 5c-2e σ bond at the tetrahedron B site, as well as 12 5c-2e or 6c-2e π bonds (Fig. 3b). There exist no localized bonds in these complexes.

Note that a neutral C_{1} B_{38} cage lacks two valence electrons to satisfy the σπ double delocalization bonding requirement of a borospherene; the Ca center in 1 donates exactly two 4s^2 electrons to compensate for this electron deficiency. The optimized C_{1} B_{38}^2{−} dianion (2) is a true minimum with the smallest vibrational frequency of 160 cm⁻¹ and the HOMO–LUMO energy gap of 2.54 eV. It possesses exactly the same σπ double delocalization bonding pattern as C_{1} CaB_{38} (1) (Fig. 3a). It is also a 3D aromatic with the highly negative nucleus-independent chemical shift (NICS) of −37 ppm at the cage center, comparable to the corresponding value of NICS=−42 ppm of D_{2d} B_{38}. However, C_{1} B_{38}^2{−} (2) is not the GM of the dianion due to strong intramolecular Coulomb repulsion in the cage structure. The Ca center in 1 serves as a dication that neutralizes the negative charge the B_{38}^2{−} dianion cage carries, rendering high stability to 1 as the GM of the complex. Similar analyses apply to the second lowest-lying isomer of CaB_{38} in Fig. 2.

![Fig. 4](image_url) Simulated photoelectron spectra of (a) C_{1} Ca@B_{38}^− (1) and (b) C_{1} Ca@B_{38} which correspond to the global minimum and the second lowest-lying isomer of CaB_{38} shown in Fig. 2, respectively.

Anion photoelectron spectroscopy in combination with first-principles calculations has been a powerful approach in characterizing nanoclusters in the gas phase. We simulate the photoelectron spectra of the two C_{1} Ca@B_{38} monocations which correspond to the two lowest-lying isomers of CaB_{38} at PBE0 (Fig. 4) to aid their future experimental characterizations. Remarkably, the two isomers possess similar photoelectron spectra with the experimentally observed D_{2d} B_{38}^−. The calculated first adiabatic and vertical detachment energies (A/D/VDE) of the two C_{1} Ca@B_{38} isomers are 2.44/2.55 and 2.52/2.62 eV, respectively. Their calculated energy gaps amount to 1.32 and 1.35 eV. The sizable energy gaps of the two C_{1} Ca@B_{38} monocations are consistent with the electronic stability of their neutrals which have large HOMO-LUMO gaps as presented above (Fig. 53). In fact, C_{1} Ca@B_{38} (1) and the second lowest-lying C_{1} Ca@B_{38} are both n-isovalent with the observed D_{2d} B_{38} borospherene. These neutral metalloborospherenses and their monoanions invite forthcoming experimental explorations.

Vibrational spectroscopy has also proved to be an effective approach for experimental studies of nanoclusters. We calculate the vibrational frequencies and simulate the IR and Raman spectra of Ca@B_{38} (1) at PBE0 (Fig. S4 in the ESI†), which are compared with those of B_{38}^− (2). The three major IR peaks at 1220 (α′), 811 (α′), and 416 (α′) in 2 are basically maintained in 1, with small blue shifts (Fig. S4a). The main Raman features of 2 are also inherited in 1 (Fig. S4b). The two a ′ breathing modes at 254 cm⁻¹ and 454 cm⁻¹ belong to “radial breathing modes” (RBMs) of B_{38}^− (2) cage. RBMs have been used to identify the hollow structures of the single-walled boron nanotubes.52

![Fig. 5](image_url) Optimized endohedral C_{1} M@B_{38} (M = Sc, Y, Ti) (3, 5, and 7) compared with the recently proposed C_{3} M@B_{38} (M = Sc, Y, Ti) (4, 6, and 8), with their relative energies indicated in eV at PBE0 level. High symmetry structures are depicted for comparison and clarity.

Lastly, we briefly the results obtained for the series of transition metal doped endohedral complexes: M@B_{38} (M = Sc, Y, Ti). As shown in Fig. 5, the endohedral C_{3} Sc@B_{38} (3), C_{3} Y@B_{38} (5), and C_{3} Ti@B_{38} (7) based on the C_{3} B_{38}^2{−} motif are 1.37, 1.63, and 0.73 eV more stable than the recently proposed C_{3} Sc@B_{38} (4), C_{3} Y@B_{38} (6), and C_{3} Ti@B_{38} (8) based on the D_{2d} B_{38} cage at PBE0 level, respectively. Such huge energy differences are well in agreement with the calculated encapsulation energies of -163.5, -114.5, -127.8, -127.8, -186.9, and -152.7 kcal/mol for 3, 4, 5, 6, 7, and 8, respectively, and strongly suggest that 3, 5, and 7 be far more viable in experiments than 4, 6, and 8. NBO analyses show that the metal centers in 3, 4, 5, 6, 7, and 8 possess the natural atomic charges of +1.09, +0.80, +1.07, +1.15, +0.88, and +0.50 [e], respectively, indicating that the transition metal centers donate valence electrons to the cage-like B_{38} ligands, in line with the fact that boron has a higher electronegativity (2.04 in Pauling scale) than all the transition metals Sc (1.36), Y (1.22), and Ti (1.54) concerned in this work. The high stabilities of 3, 5, and 7 over 4, 6, and 8 can be understood based on the fact that the cage-like C_{3} B_{38} ligand requires extra electrons from the metal center to satisfy the bonding pattern of a stable borospherene while D_{2d} B_{38} possesses a stable closed-shell electronic configuration with a huge HOMO–LUMO gap of 2.25 eV. There exist also obvious π→d back donations from the B_{38} ligands to the transition metal centers in these complexes, as demonstrated by the electron configurations of Sc [Ar]4s^23d^17s, Y [Kr]5s^23d^1, and Ti [Ar]4s^23d^2, with the former three in 3, 5, and 7, respectively. We stress here that the current prediction of 3, 5, and 7 testifies to the idea of computational design of novel boron nanostructures on the basis of the structural principles and bonding patterns of boron clusters.

In conclusion, we have presented the viability of the endohedral metalloborospherene Ca@B_{38} (1) via extensive global structural searches, first-principles calculations, and bonding analyses. Ca@B_{38} (1) contains a B_{38}^2− (2) borospherene shell, which is stabilized by the
encapsulation of a Ca\(^{2+}\) center, forming the charge-transfer complex Ca\(^{2+}\@\text{Ba}\text{S}_\text{2}\). The complex is composed of twelve interwoven BOCs with six hexagonal/heptagonal faces and satisfy the bonding pattern of \(\sigma\pi\) double delocalization for borophenes. Similar transition-metal-doped endohedral metallaborophosphorus \(\text{C}_6\@\text{B}_{32}\) (3, 5, 7) are also predicted computationally, which turn out to be far more stable than the previously proposed \(\text{C}_6\@\text{B}_{32}\) clusters (4, 6, 8). The results achieved in this work suggest vast opportunities for rational design of novel boron nanostructures using the structural and bonding patterns of borophenes.

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Notes and references

We present the viability of an endohedral C$_7$Ca@B$_{38}$ which contains a C$_7$B$_{38}^{2-}$ borospherene cage composed of interwoven boron double chains with a σ+π double delocalization bonding pattern, extending the B$_n^q$ (q = n−40) borospherene family from n = 39–42 to n = 38.