

# SCIENTIFIC REPORTS

OPEN

## From Quasi-Planar $B_{56}$ to Penta-Ring Tubular $Ca@B_{56}$ : Prediction of Metal-Stabilized $Ca@B_{56}$ as the Embryo of Metal-Doped Boron $\alpha$ -Nanotubes

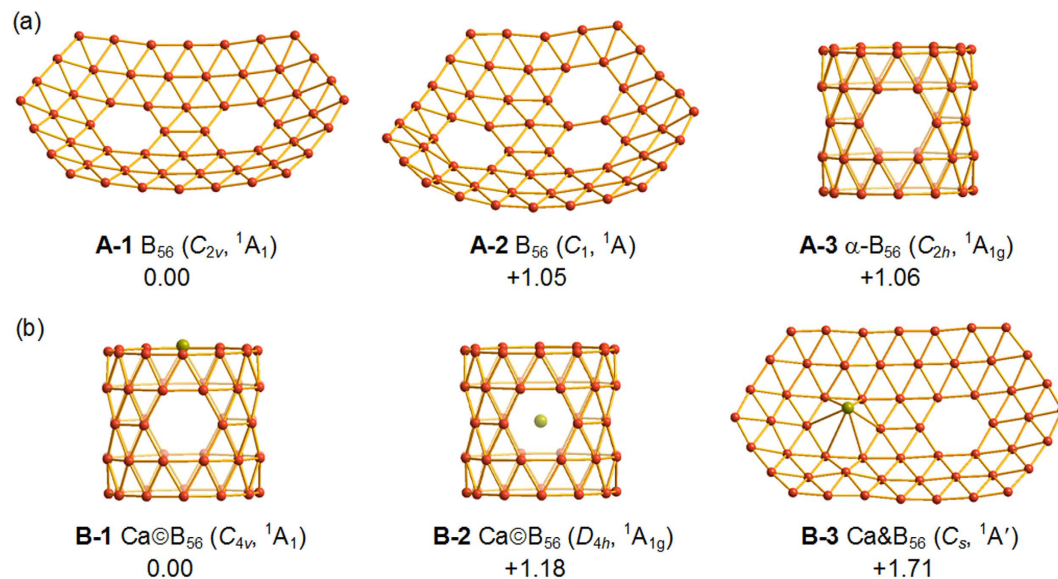
Received: 29 July 2016  
Accepted: 01 November 2016  
Published: 25 November 2016

Wen-Juan Tian<sup>1</sup>, Qiang Chen<sup>1,2</sup>, Xin-Xin Tian<sup>1</sup>, Yue-Wen Mu<sup>1</sup>, Hai-Gang Lu<sup>1</sup> & Si-Dian Li<sup>1</sup>

Motifs of planar metalloborophenes, cage-like metalloborospherenes, and metal-centered double-ring tubular boron species have been reported. Based on extensive first-principles theory calculations, we present herein the possibility of doping the quasi-planar  $C_{2v}B_{56}$  (A-1) with an alkaline-earth metal to produce the penta-ring tubular  $Ca@B_{56}$  (B-1) which is the most stable isomer of the system obtained and can be viewed as the embryo of metal-doped (4,0) boron  $\alpha$ -nanotube  $Ca@BNT_{(4,0)}$  (C-1).  $Ca@BNT_{(4,0)}$  (C-1) can be constructed by rolling up the most stable boron  $\alpha$ -sheet and is predicted to be metallic in nature. Detailed bonding analyses show that the highly stable planar  $C_{2v}B_{56}$  (A-1) is the boron analog of circumbiphenyl ( $C_{38}H_{16}$ ) in  $\pi$ -bonding, while the 3D aromatic  $C_{4v}Ca@B_{56}$  (B-1) possesses a perfect delocalized  $\pi$  system over the  $\sigma$ -skeleton on the tube surface. The IR and Raman spectra of  $C_{4v}Ca@B_{56}$  (B-1) and photoelectron spectrum of its monoanion  $C_{4v}Ca@B_{56}^-$  are computationally simulated to facilitate their spectroscopic characterizations.

It is well known that boron has a strong propensity to form multicenter-two-electron bonds (mc-2e bonds) to compensate for its electron deficiency in both polyhedral molecules and bulk allotropes. Multicenter bonding also appears to dominate the planar or quasi-planar structures of a wide range of gas-phase boron clusters  $B_n^{-/0}$  ( $n = 3-25, 27, 30, 35, 36$ ) characterized in a series of combined experimental and theoretical investigations in the past decade<sup>1-13</sup>. Both the quasi-planar  $C_{6v}B_{36}^{-/0}$ <sup>7,8</sup> with a perfect hexagonal hole at the center and the perfect planar  $C_{2v}Co@B_{18}^-$  with a hepta-coordinate Co were confirmed experimentally to be motifs of the atomically thin planar borophenes and metalloborophenes, respectively. In these flat species, periphery boron atoms are bonded with localized 2c-2e  $\sigma$  bonds along the boundary, while the inner and the periphery atoms are sewed together in blocks with delocalized mc-2e  $\sigma$  or  $\pi$  bonds. Multicenter bonding interactions go extremes from two-dimensional (2D) sheets to three-dimensional (3D) cages in the recently observed borospherenes (all-boron fullerenes)  $D_{2d}B_{40}^{-/0}$ <sup>14</sup>,  $C_3/C_2B_{39}^{-15}$ , and  $C_2B_{28}^{-/0}$ <sup>16</sup> in which all the valence electrons are distributed in delocalized mc-2e  $\sigma$  or  $\pi$  bonds ( $m \geq 3$ ). Both endohedral  $M@B_{40}$  ( $M = Ca, Sr$ ) and exohedral  $M@B_{40}$  ( $M = Be, Mg$ ) metalloborospherenes were predicted to be stable species<sup>17</sup>. Two cage-like cations  $C_1B_{41}^+$  and  $C_2B_{42}^{2+}$  predicted at density functional theory (DFT) have also been presented to the  $B_n^q$  borospherene family ( $q = n-40$ ) which are all composed of twelve interwoven boron double chains (BDCs) with six hexagonal or heptagonal faces<sup>18</sup>. Encapsulations of alkaline earth or transition metals have proven to be an effective approach to stabilize borospherene anions like  $T_hB_{36}^{4-}$  in  $Li_2[Ca@B_{36}]^{19}$ ,  $C_5B_{37}^{3-}$  in  $Ca@B_{37}^{-20}$ ,  $C_5B_{38}^{2-}$  in  $Ca@B_{38}^{21}$  and  $M@B_{38}$  ( $M = Sc, Y, Ti$ )<sup>21,22</sup>, and  $C_3/C_2B_{39}^-$  in  $Ca@B_{39}^{+23}$ . The discovery of the first double-ring (DR) tubular  $B_{20}$  and the experimental confirmation of the double-ring (DR) tubular  $B_n^+$  monocations ( $n = 16-25$ )<sup>24</sup>, on the other hand, unveils another important domain in the structural evolution of boron clusters. The recent experimental observation of the metal-centered DR tubular  $D_{8d}Co@B_{16}^-$  with the coordination of 16 further indicate that doping boron clusters with a transition

<sup>1</sup>Nanocluster Laboratory, Institute of Molecular Science, Shanxi University, Taiyuan 030006, China. <sup>2</sup>Institute of Materials Science and Department of Chemistry, Xinzhou Teachers' University, Xinzhou 034000, China. Correspondence and requests for materials should be addressed to Y.-W.M. (email: ywmu@sxu.edu.cn) or H.-G.L. (email: luhg@sxu.edu.cn) or S.-D.L. (email: lisidian@sxu.edu.cn)



**Figure 1.** Optimized structures of the three lowest-lying isomers of  $B_{56}$  (a) and  $CaB_{56}$  (b), with their relative energies indicated in eV at PBE0/6-311+G(d) level.

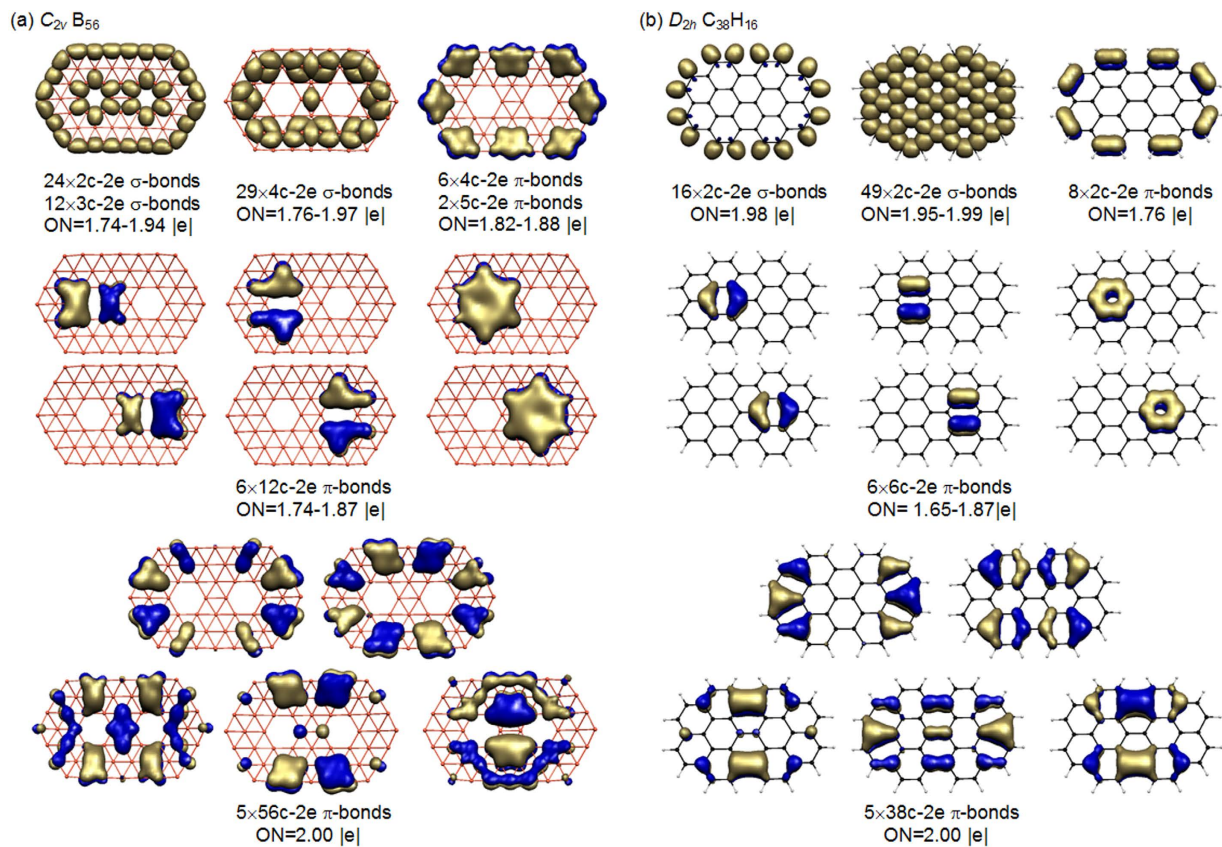
metal makes an earlier structural transition from 2D planar to 3D tubular in boron clusters<sup>25</sup>. Triple-ring (TR) tubular  $B_{3n}$  ( $n = 8-32$ ) have also been predicted to be competitive isomers at DFT<sup>26</sup>. Very recently, a penta-ring (PR) tubular  $\alpha$ - $B_{84}$  with six evenly distributed hexagonal holes in the middle was predicted to be the second lowest-lying isomer of the system at DFT<sup>27</sup>. However, to the best of our knowledge, there have been no PR tubular boron clusters or their metal complexes as the lowest-lying isomers of the systems reported to date. Detailed investigations on the geometrical and electronic structures of multi-ring tubular clusters and their metal-centered complexes may provide key information to understand the geometrical structures and growth mechanisms of the experimentally observed single-walled and multi-walled boron nanotubes (BNTs)<sup>28,29</sup> and the atomically thin borophenes with or without vacancies deposited on Ag(111) substrates<sup>30,31</sup>.

Based upon extensive first-principles theory calculations, we present herein the possibility of doping the previously predicted quasi-planar  $B_{56}$  (A-1)<sup>27</sup> with an alkaline earth metal to produce the charge-transfer PR tubular complex  $Ca\textcircled{B}_{56}$  (B-1) which is the most stable isomer of the system obtained and can be viewed as the embryo of metal-doped boron  $\alpha$ -nanotube  $Ca\textcircled{BNT}_{(4,0)}$  (C-1) in a bottom-up approach.  $Ca\textcircled{BNT}_{(4,0)}$  (C-1) can be constructed by rolling up the most stable boron  $\alpha$ -sheet<sup>32,33</sup> and is predicted to be metallic in nature. Detailed molecular orbital analyses show that the quasi-planar  $C_{2v}$   $B_{56}$  (A-1) is analogous to circumbiphenyl ( $C_{38}H_{16}$ ) in  $\pi$  bonding, while the PR tubular  $C_{4v}$   $Ca^{2+}\textcircled{B}_{56}^{2-}$  (B-1) possesses a perfect delocalized  $\pi$  system over a  $\sigma$ -skeleton on the tube surface to render tubular aromaticity to the system. The IR, Raman, and photoelectron spectra of the concerned species are simulated to facilitate their experimental characterizations.

## Results and Discussions

We start from the bare  $B_{56}$  which may serve as effective ligands to coordinate metal dopants. As shown in Fig. 1(a) and Fig. S1(a), the previously predicted quasi-planar  $C_{2v}$   $B_{56}$  (A-1) with two equivalent hexagonal holes<sup>27</sup> appears to be 1.05 eV and 1.06 eV more stable than the quasi-planar  $C_1$   $B_{56}$  (A-2) with three hexagonal holes around the center and the PR tubular  $C_{2h}$   $\alpha$ - $B_{56}$  (A-3) with four equivalent hexagonal holes in the middle at PBE0 level, respectively. Other low-lying isomers lie at least 1.19 eV above  $B_{56}$  (A-1), with the much concerned cage-like borospherene  $C_2$   $B_{56}$  (A-7) composed of eighteen interwoven BDCs<sup>14,15,19-21,23</sup> and the irregular cage-like  $C_1$   $B_{56}$  (A-9) obtained using first-principles simulated annealing<sup>34</sup> being 1.78 eV and 2.64 eV less stable, respectively. With two extra electrons, a quasi-planar  $C_{2v}$   $B_{56}^{2-}$  similar to  $B_{56}$  (A-1) appears to be 1.07 eV more stable than the PR tubular  $D_{4h}$   $\alpha$ - $B_{56}^{2-}$  similar to  $\alpha$ - $B_{56}$  (A-3) at PBE0.

With one doping Ca atom added in to compensate for the electron deficiency of the system, surprisingly, a dramatic structural transition occurs from the 2D quasi-planar  $C_{2v}$   $B_{56}$  (A-1) to 3D PR tubular  $C_{4v}$   $Ca\textcircled{B}_{56}$  (B-1) which has a Ca cap at one end of the tube along the four-fold molecular axis, as demonstrated in Fig. 1(b) and Fig. S1(b).  $Ca\textcircled{B}_{56}$  (B-1) contains an almost perfect PR tubular  $C_{4v}$   $\alpha$ - $B_{56}$  ligand similar to  $\alpha$ - $B_{56}$  (A-3) which can be constructed by rolling up the most stable boron  $\alpha$ -sheet<sup>32,33</sup>. From another perspective of view,  $Ca\textcircled{B}_{56}$  (B-1) can be viewed as a PR tube composed of interwoven BDCs with four hexagonal holes evenly distributed in the middle, in a structural pattern similar to that of the  $B_n^q$  borospherene family ( $q = n-40$ ,  $n = 36-42$ )<sup>14,15,19-21,23</sup>.  $C_{4v}$   $Ca\textcircled{B}_{56}$  (B-1) turns out to lie 1.18 eV and 1.71 eV lower than the Ca-centered PR tubular  $D_{4h}$   $Ca\textcircled{B}_{56}$  (B-2) based on  $\alpha$ - $B_{56}$  (A-3) and the face-capped quasi-planar  $C_s$   $Ca\&B_{56}$  (B-3) based on  $C_{2v}$   $B_{56}$  (A-1), respectively. Other low-lying planar, tubular, or cage-like isomers appear to be at least 1.82 eV less stable than  $Ca\textcircled{B}_{56}$  (B-1), with the endohedral metalloborospherenes  $S_4$   $Ca\textcircled{B}_{56}$  (B-6) based on  $B_{56}$  (A-7) and  $C_1$   $Ca\textcircled{B}_{56}$  (B-13) based on  $B_{56}$  (A-9) lying 1.87 eV and 2.29 eV higher, respectively. These large relative energies provide strong evidence that  $Ca\textcircled{B}_{56}$



**Figure 2.** AdNDP bonding patterns of  $C_{2v}$   $B_{56}$  (**1**) (a) compared with that of the  $D_{2h}$  circumbiphenyl  $C_{38}H_{16}$  (**b**), with the occupation numbers (ON) indicated.

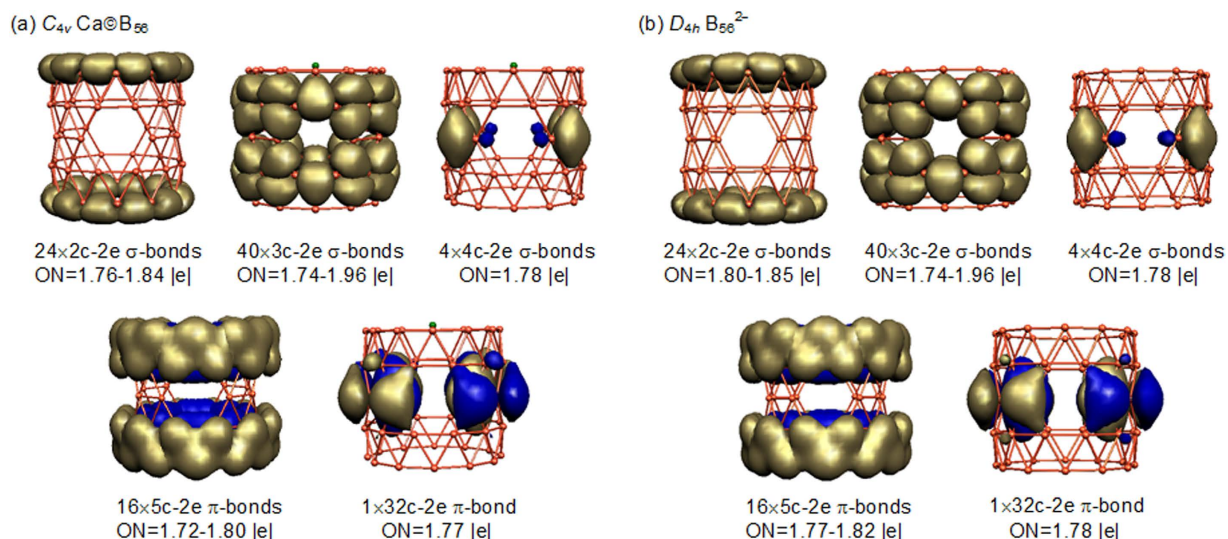
(**B-1**) is the first PR tubular species as the most stable isomer of the system obtained to date. We notice that  $C_{4v}$   $Ca@B_{56}$  (**B-1**) possesses two small degenerate imaginary vibrational frequencies at  $38.5i \text{ cm}^{-1}$  at PBE0 ( $e$  modes) which lead to the slightly distorted PR tubular  $C_s$   $Ca@B_{56}$  (**B-4**) when fully relaxed. However, the energy difference between  $C_{4v}$   $Ca@B_{56}$  (**B-1**) and  $C_s$   $Ca@B_{56}$  (**B-4**) turns out to be only 0.01 eV with zero-point corrections included, strongly suggesting that they correspond to the same tubular isomer possible to exist in experiments, given the accuracy of the DFT-PBE0 method employed.  $Ca@B_{56}$  (**B-1**) is thus the vibrationally averaged structure of PR tubular  $CaB_{56}$ , with the Ca atom slightly off-centered circling around the molecular axis of the PR tube on the top.

Such a structural transition from 2D planar to 3D PR tubular also occurs to  $SrB_{56}$  at PBE0 (see Fig. S2, the Stuttgart relativistic small-core pseudopotential and valence basis set was used for  $Sr^{35,36}$ ). Natural bonding orbital (NBO) analyses indicate that the PR tubular  $C_{4v}$   $Ca@B_{56}$  (**B-1**) and  $C_{4v}$   $Sr@B_{56}$  possess the natural atomic charges of  $q_{Ca} = +1.83|e|$  and  $q_{Sr} = +1.85|e|$  and the corresponding electronic configurations of  $Ca[Ar]4s^{0.07}3d^{0.09}$  and  $Sr[Kr]5s^{0.06}4d^{0.07}$ , respectively. They are therefore typical charge-transfer complexes  $C_{4v}$   $Ca^{2+}@B_{56}^{2-}$  (**B-1**) and  $C_{4v}$   $Sr^{2+}@B_{56}^{2-}$  in nature in which the alkaline earth metal donates two  $ns^2$  valence electrons to the PR tubular  $\alpha$ - $B_{56}$  acceptor. Such complexes are mainly stabilized by effective electrostatic interactions between the  $M^{2+}$  dication ( $M = Ca, Sr$ ) and the PR tubular  $\alpha$ - $B_{56}^{2-}$  ligand. Weak  $\pi \rightarrow d$  back donations from the  $\alpha$ - $B_{56}^{2-}$  ligand to the  $M^{2+}$  metal center may also contribute to stabilize the complexes, as suggested by the electronic configurations mentioned above, similar to the situation in  $M@B_{40}$  ( $M = Ca, Sr$ )<sup>17</sup>.

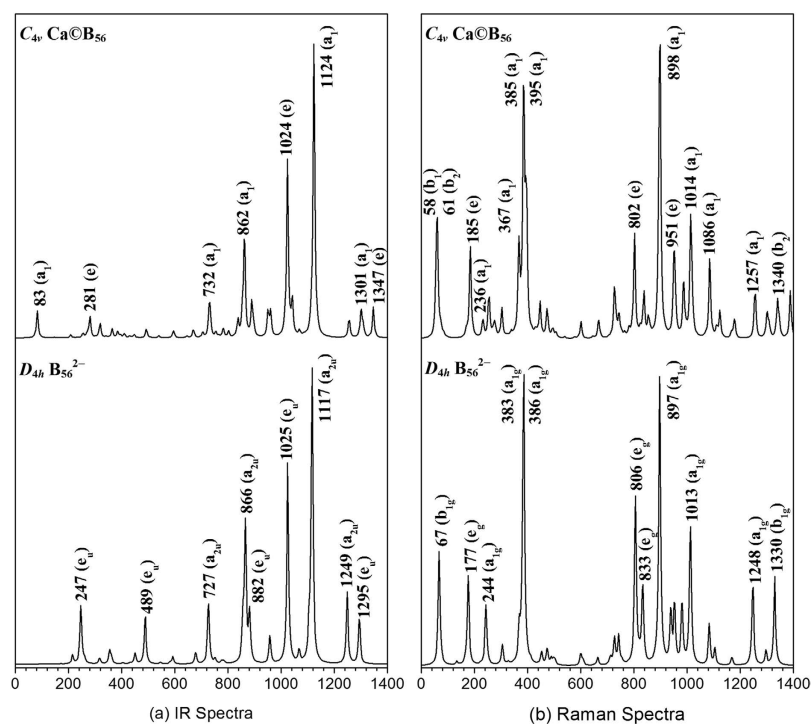
Extended molecular dynamics simulations using the CP2K program<sup>37</sup> indicate that  $Ca@B_{56}$  (**B-1**) is dynamically stable at both 600 K and 800 K, with the root-mean-square-deviations of RMSD = 0.18 Å and 0.18 Å and the maximum bond length deviations of MAXD = 1.10 Å and 1.13 Å, respectively (Fig. S3). We notice that, although the tubular  $\alpha$ - $B_{56}$  ligand experiences more or less structural deformations during MD simulations, the Ca cap in  $Ca@B_{56}$  (**B-1**) keeps almost still at the center of the top  $B_{12}$  ring in the simulation processes. MD simulations indicate that  $Ca@B_{56}$  (**B-1**) remains dynamically stable even at 1000 K, with RMSD = 0.19 Å and MAXD = 1.14 Å, respectively, further indicating its high dynamical stability.

The high stability of planar  $C_{2v}$   $B_{56}$  (**A-1**) originates from its electronic structure and bonding pattern. As analyzed in Fig. 2 using the adaptive natural density partitioning (AdNDP) approach<sup>38</sup>,  $C_{2v}$   $B_{56}$  (**A-1**) possesses 24  $2c-2e$  localized  $\sigma$  bonds between neighboring periphery B atoms along the boundary, 12  $3c-2e$  delocalized  $\sigma$  bonds on 12  $B_3$  triangles around the two hexagonal holes, and 29  $4c-2e$  delocalized  $\sigma$  bonds on 29 symmetrically distributed  $B_4$  rhombuses. The remaining 19  $\pi$  bonds can be classified into four sets, with one set with 6  $4c-2e$   $\pi$  bonds and 2  $5c-2e$   $\pi$  bonds along the periphery, two sets with 3  $12c-2e$   $\pi$  bonds over the hexagonal hole on the right and 3  $12c-2e$   $\pi$  bonds over the hexagonal hole on the left, and one set with 5  $56c-2e$   $\pi$  bonds over the whole molecular surface, in the overall symmetry of  $C_{2v}$ .  $C_{2v}$   $B_{56}$  (**A-1**) thus contains two local  $\pi$ -aromatic systems





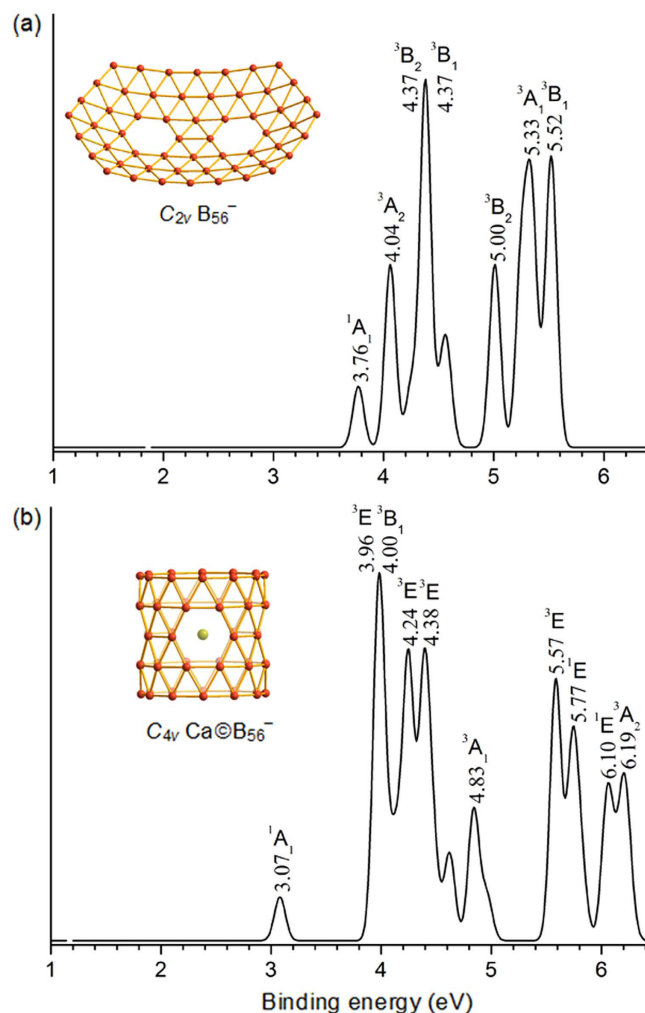
**Figure 3.** AdNDP bonding patterns of  $C_{4v}$  Ca@B<sub>56</sub> (a) compared with that of  $D_{4h}$  B<sub>56</sub><sup>2-</sup> (b) with the occupation numbers indicated.



**Figure 4.** Simulated IR (a) and Raman (b) spectra of  $C_{4v}$  Ca@B<sub>56</sub> (B-1) compared with that of the bare PR tubular  $D_{4h}$  B<sub>56</sub><sup>2-</sup>.

around the two hexagonal holes and one global  $\pi$ -aromatic system over the whole molecular plane which have a one-to-one correspondence with the aromatic  $\pi$ -systems of circumbiphenyl ( $C_{38}H_{16}$ ) (see Fig. 2). It is therefore the boron analog of  $D_{2h}$   $C_{38}H_{16}$ , the biggest boron analog of aromatic polycyclic hydrocarbon reported to date<sup>1-16</sup>.

The bonding pattern of PR tubular Ca@B<sub>56</sub> (B-1) is more unique and intriguing. As shown in Fig. 3, it has 24 2c-2e localized  $\sigma$  bonds between neighboring periphery boron atoms on the top and bottom of the tube with the occupation numbers of ON = 1.76–1.84 |e|, 40 3c-2e delocalized  $\sigma$  bonds on the 40 inner B<sub>3</sub> triangles with ON = 1.74–1.96 |e|, and 4 4c-2e delocalized  $\sigma$  bonds in the middle on the four uncovered B<sub>4</sub> rhombuses between neighboring hexagonal holes with ON = 1.78 |e|. The  $\sigma$ -skeleton on the tube surface thus contains 68  $\sigma$  bonds in total. The remaining 34 valence electrons form a perfectly delocalized  $\pi$  system over the delocalized  $\sigma$ -skeleton, with 16 5c-2e  $\pi$  bonds evenly distributed over two B<sub>24</sub> DR tubular subunits at the two ends of the tube with



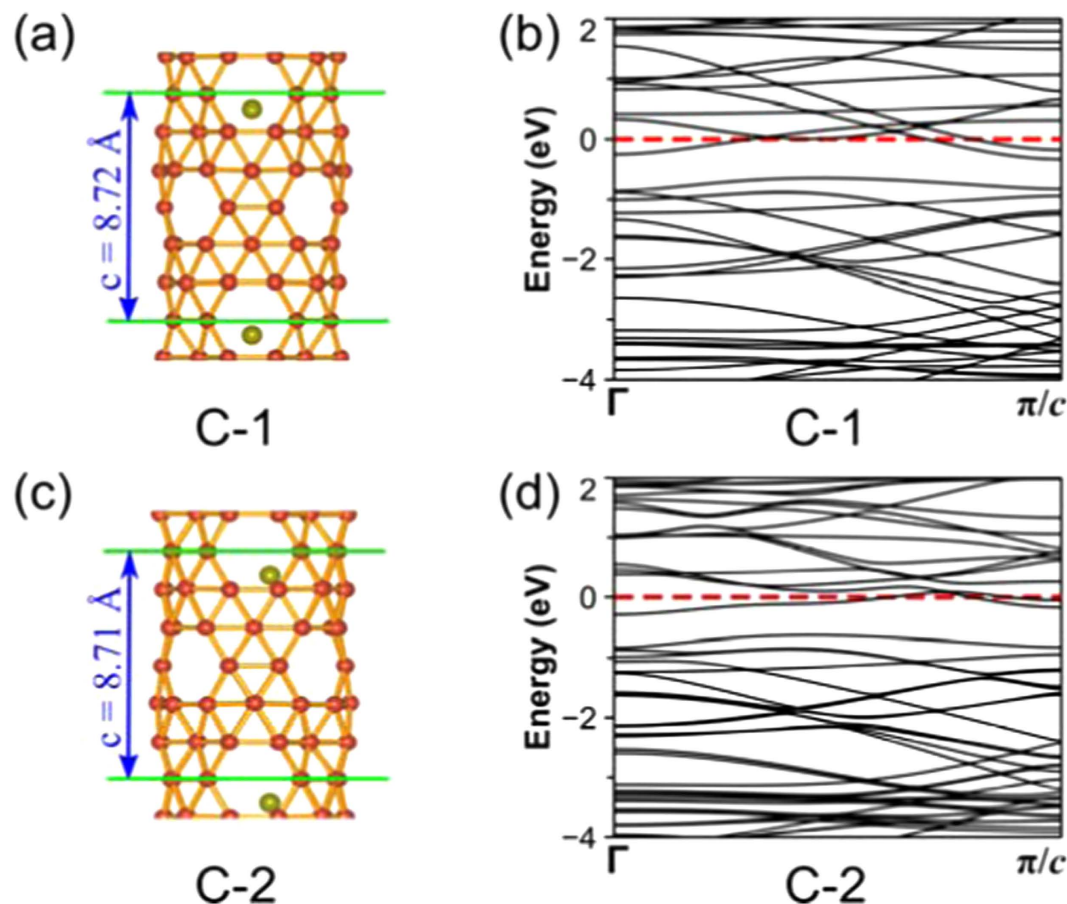
**Figure 5.** Simulated PES spectra of  $C_{2v} B_{56}^-$  (a) and  $C_{4v} Ca@B_{56}^-$  (b) at PBE0.

ON = 1.72–1.80 |e| and 1  $3c-2e$   $\pi$  bond over the four evenly distributed hexagonal holes between the two subunits with ON = 1.77 |e|, in the overall symmetry of  $C_{4v}$ . As shown in Fig. 3, the bared PR tubular  $D_{4h}$   $\alpha-B_{56}^{2-}$  dianion possesses the same  $\sigma$  and  $\pi$  bonding patterns as  $C_{4v} Ca@B_{56}^-$  (B-1), further supporting the charge transfer of two 4s electrons from Ca atom to the tubular  $\alpha-B_{56}$  ligand. The AdNDP bonding patterns of  $C_{4v} Ca@B_{56}^-$  (B-1) and  $D_{4h}$   $\alpha-B_{56}^{2-}$  with ON  $\geq 1.72$  |e| match the chemical intuitions for tubular boron clusters which can be constructed by rolling up the  $\alpha$ -sheet<sup>32,33</sup>. Such bonding patterns render 3D tubular aromaticities to the systems, as evidenced by the huge negative NICS values of  $-44.6$  ppm and  $-46.0$  ppm at the tube centers calculated for  $C_{4v} Ca@B_{56}^-$  (B-1) and  $D_{4h}$   $\alpha-B_{56}^{2-}$ , respectively.

The IR and Raman spectra of  $C_{4v} Ca@B_{56}^-$  (B-1) are computationally simulated and compared with that of the perfect PR tubular  $D_{4h}$   $\alpha-B_{56}^{2-}$  in Fig. 4 to facilitate its future spectroscopic characterization. As expected, the major IR peaks at  $1249\text{ cm}^{-1}$  ( $a_{2u}$  mode),  $1117\text{ cm}^{-1}$  ( $a_{2u}$ ),  $1025\text{ cm}^{-1}$  ( $e_u$ ), and  $866\text{ cm}^{-1}$  ( $a_{2u}$ ) in  $D_{4h}$   $\alpha-B_{56}^{2-}$  are all basically maintained in  $C_{4v} Ca@B_{56}^-$  (B-1). The major Raman features at  $1248\text{ cm}^{-1}$  ( $a_{1g}$ ),  $1013\text{ cm}^{-1}$  ( $a_{1g}$ ),  $897\text{ cm}^{-1}$  ( $a_{1g}$ ),  $806\text{ cm}^{-1}$  ( $e_g$ ), and  $386\text{ cm}^{-1}$  ( $a_{1g}$ ) in  $D_{4h}$   $\alpha-B_{56}^{2-}$  also appear in  $C_{4v} Ca@B_{56}^-$  (B-1). The breathing modes at  $236\text{ cm}^{-1}$  ( $a_1$ ) in  $C_{4v} Ca@B_{56}^-$  (B-1) and  $244\text{ cm}^{-1}$  ( $a_{1g}$ ) in  $D_{4h}$   $\alpha-B_{56}^{2-}$  belong to typical “radial breathing modes” (RBMs) of the tubular species which may help characterize metal-centered boron  $\alpha$ -nanotubes in future experiments. A strong RBM band observed at  $210\text{ cm}^{-1}$  was used to identify the hollow structures of the single-walled boron nanotubes<sup>28</sup>.

Combination of the PES spectra and first-principles theory calculations has proven to be the most powerful approach to characterize novel boron clusters over the past decade<sup>1–16,25</sup>. We calculate the vertical excitation energies and simulate the PES spectra of the corresponding monoanions of  $C_{2v} B_{56}^-$  (A-1) and  $C_{4v} Ca@B_{56}^-$  (B-1) at PBE0 level in Fig. 5. As shown in Fig. 5(a), quasi-planar  $C_{2v} B_{56}^-$ , the monoanion of  $C_{2v} B_{56}^-$  (A-1), possesses a high first vertical detachment energy of VDE =  $3.76\text{ eV}$  and a simulated PES spectrum similar to that of the observed quasi-planar  $C_s B_{40}^-$  which has the first VDE of  $3.60\text{ eV}$ <sup>14</sup>. PR tubular  $C_{4v} Ca@B_{56}^-$ , the monoanion of  $C_{4v} Ca@B_{56}^-$  (B-1), appears to possess a PES spectrum with a low VDE of  $3.07\text{ eV}$  and a large energy gap of  $0.89\text{ eV}$  (Fig. 6(b)), in line with the large HOMO-LUMO energy gap of  $2.00\text{ eV}$  calculated for tubular  $Ca@B_{56}^-$  (B-1) at PBE0.

Finally, using  $C_{4v} Ca@B_{56}^-$  (B-1) as an embryo at the center of the unit cell, we construct the metal-doped (4,0) boron  $\alpha$ -nanotube  $Ca@BNT_{(4,0)}$  (C-1) in a bottom-up approach which has a  $P_4$  symmetry as shown in Fig. 6(a).



**Figure 6.** Optimized geometries (a and c) and band structures (b and d) of  $\text{Ca@BNT}_{(4,0)}$  with  $P_4$  ( $C_4$ ) symmetry and  $\text{Ca@BNT}_{(4,0)}$  with  $P_1$  ( $C_1$ ) symmetry, with the lattice parameters  $c$  in  $z$  direction indicated.

A similar approach was used to predict the nanotubes of silicon<sup>39</sup>.  $\text{Ca@BNT}_{(4,0)}$  (C-1) turns out to possess the optimized diameter of 6.55 Å and the lattice parameter of  $c = 8.72$  Å in  $z$  direction (Fig. 6(a)). Interestingly, as indicated in its calculated band structures in Fig. 6(b), with several bands crossing the Fermi level,  $\text{Ca@BNT}_{(4,0)}$  (C-1) is predicted to be typically metallic in nature, in strong contrast to the bare  $\alpha$ -boron nanotube  $\text{BNT}_{(4,0)}$  which is a semiconductor with the band gap of 0.69 eV at PBE level (Fig. S4) (0.75 eV at GGA<sup>33</sup>), indicating that the transport properties of boron nanotubes can be dramatically changed by metal-doping. It is noticed that the slightly off-centered Ca-doped boron  $\alpha$ -nanotube  $\text{Ca@BNT}_{(4,0)}$  (C-2) with  $P_1$  symmetry (Fig. 6(c)) possesses a total energy slightly lower than  $\text{Ca@BNT}_{(4,0)}$  (C-1) (by 0.22 eV per unit cell). However, the two metallic Ca-doped boron  $\alpha$ -nanotube with slightly different geometries (Fig. 6(a and c)) possess very similar band structures (Fig. 6(b and d)), indicating that minor changes in positions of the metal donors cause no obvious changes in both the geometries and conductivities of metal-doped boron  $\alpha$ -nanotubes.

In summary, we have performed in this work an extensive first-principles theory investigation on the possibility of doping the quasi-planar  $C_{2v}$   $B_{56}$  (A-1) with an alkaline-earth metal to produce the 3D aromatic PR tubular  $\text{Ca@B}_{56}$  (B-1) which is the most stable isomer obtained and can be viewed as the embryo of the metal-doped boron  $\alpha$ -nanotube  $\text{Ca@BNT}_{(4,0)}$  (C-1). The high stability of the 3D aromatic  $C_{4v}$   $\text{Ca@B}_{56}$  (B-1) originates from its unique bonding pattern which possesses a perfect delocalized  $\pi$  system over a  $\sigma$ -skeleton on the tube surface. Metal dopants encapsulated in cage-like borospherenes to form metalloborospherenes<sup>17,19–23</sup>, inserted in planar borophenes to form metalloborophenes<sup>9</sup>, or wrapped up in boron nanotubes to form metal-doped boron nanotubes may effectively enhance the chemical stabilities and tune the transport properties of the boron nanostructures. Metal-stabilized boron nanostructures are expected to be complementary with the corresponding carbon nanomaterials in applications and warrant further theoretical and experimental investigations.

**Theoretical procedures.** Initial structures were constructed for  $\text{CaB}_{56}$  based on the previously reported lowest-lying planar or cage-like isomers of  $B_{56}$ <sup>27,34</sup>. Cage-like borospherene structures composed of interwoven BDCs were also built for  $B_{56}$  according to the structural pattern of borospherenes<sup>14,15,19–21,23</sup>. In particular, a PR tubular  $\alpha$ - $B_{56}$  (A-2) with four hexagonal holes evenly distributed in the middle was constructed by rolling up the most stable boron  $\alpha$ -sheet<sup>32,33</sup>. Low-lying isomers thus obtained were then fully optimized with frequencies checked at the hybrid DFT-PBE0<sup>40</sup> level with the basis set of 6–311+G(d)<sup>41</sup> implemented in Gaussian 09 suite<sup>42</sup>. Minima Hopping<sup>43</sup> searches with over 500 stationary points probed produced no isomers with lower energies

than  $\text{Ca@B}_{56}$  (**B-1**) (see Fig.1 and S1(b)). The bonding patterns of the quasi-planar  $\text{C}_{2v}\text{B}_{56}$  (**A-1**) (Fig. 2) and PR tubular  $\text{C}_{4v}\text{Ca@B}_{56}$  (**B-1**) (Fig. 3) were analyzed using the AdNDP method which is an extension of the Lewis valence bond theory to include multicenter mc-2e interactions ( $m \geq 3$ )<sup>38</sup> and has been successfully applied to various systems<sup>8–21,23,25</sup>. The photoelectron spectroscopy (PES) of the quasi-planar  $\text{C}_{2v}\text{B}_{56}^-$  and PR tubular  $\text{C}_{4v}\text{Ca@B}_{56}^-$  were simulated using the time-dependent DFT (TD-DFT-PBE0) approach<sup>44</sup>. The metal-centered  $\alpha$ -boron nanotube  $\text{Ca@BNT}_{(4,0)}$  (**C-1**) constructed by rolling up the most stable boron  $\alpha$ -sheet<sup>32,33</sup> was optimized using Vienna *ab initio* simulation package (VASP)<sup>45,46</sup> at Perdew–Burke–Ernzerhof (PBE)<sup>47</sup> level with the projector augmented wave (PAW)<sup>48,49</sup> pseudopotential method. The nucleus-independent chemical shift (NICS)<sup>50</sup> values at the tube centers of  $\text{Ca@B}_{56}$  (**B-1**) and  $D_{4h}\text{B}_{56}^{2-}$  were calculated to assess their tubular aromaticities.

## References

- Zhai, H.-J., Alexandrova, A. N., Birch, K. A., Boldyrev, A. I. & Wang, L.-S. Hepta- and octacoordinate boron in molecular wheels of eight- and nine-atom boron clusters: Observation and confirmation. *Angew. Chem. Int. Ed.* **42**, 6004–6008 (2003).
- Zhai, H.-J., Kiran, B., Li, J. & Wang, L.-S. Hydrocarbon analogues of boron clusters-planarity, aromaticity and antiaromaticity. *Nat. Mater.* **2**, 827–833 (2003).
- Kiran, B. *et al.* Planar-to-tubular structural transition in boron clusters:  $\text{B}_{20}$  as the embryo of single-walled boron nanotubes. *Proc. Natl. Acad. Sci. USA* **102**, 961–964 (2005).
- Huang, W. *et al.* A concentric planar doubly  $\pi$ -aromatic  $\text{B}_{19}^-$  cluster. *Nat. Chem.* **2**, 202–206 (2010).
- Li, W.-L., Zhao, Y.-F., Hu, H.-S., Li, J. & Wang, L.-S.  $[\text{B}_{30}]^-$ : a quasi-planar chiral boron cluster. *Angew. Chem. Int. Ed.* **53**, 5540–5545 (2014).
- Li, W.-L. *et al.* The  $\text{B}_{35}$  cluster with a double-hexagonal vacancy: a new and more flexible structural motif for borophene. *J. Am. Chem. Soc.* **136**, 12257–12260 (2014).
- Piazza, Z. A. *et al.* Planar hexagonal  $\text{B}_{36}$  as a potential basis for extended single-atom layer boron sheets. *Nat. Commun.* **5**, 3113 (2014).
- Chen, Q. *et al.* Quasi-planar aromatic  $\text{B}_{36}$  and  $\text{B}_{36}^-$  clusters: all-boron analogues of coronene. *Phys. Chem. Chem. Phys.* **16**, 18282–18287 (2014).
- Li, W.-L. *et al.* The Planar  $\text{CoB}_{18}^-$  Cluster as a Motif for Metallo-Borophenes. *Angew. Chem. Int. Ed.* **55**, 7358–7363 (2016).
- Alexandrova, A. N., Boldyrev, A. I., Zhai, H.-J. & Wang, L.-S. All-boron aromatic clusters as potential new inorganic ligands and building blocks in chemistry. *Coord. Chem. Rev.* **250**, 2811–2866 (2006).
- Romanescu, C., Galeev, T. R., Li, W.-L., Boldyrev, A. I. & Wang, L.-S. Transition-Metal-Centered Monocyclic Boron Wheel Clusters ( $\text{M@B}_n$ ): A New Class of Aromatic Borometallic Compounds. *Acc. Chem. Res.* **46**, 350–358 (2013).
- Sergeeva, A. P. *et al.* Understanding Boron through Size-Selected Clusters: Structure, Chemical Bonding, and Fluxionality. *Acc. Chem. Res.* **47**, 1349–1358 (2014).
- Wang, L.-S. Photoelectron spectroscopy of size-selected boron clusters: from planar structures to borophenes and borospherenes. *Int. Rev. Phys. Chem.* **35**, 69–142 (2016).
- Zhai, H.-J. *et al.* Observation of an all-boron fullerene. *Nat. Chem.* **6**, 727–731 (2014).
- Chen, Q. *et al.* Experimental and theoretical evidence of an axially chiral borospherene. *ACS Nano* **9**, 754–760 (2015).
- Wang, Y. J. *et al.* Observation and characterization of the smallest borospherene,  $\text{B}_{28}^-$  and  $\text{B}_{28}$ . *J. Chem. Phys.* **144**, 064307 (2016).
- Bai, H., Chen, Q., Zhai, H.-J. & Li, S.-D. Endohedral and exohedral metalloborospherenes:  $\text{M@B}_{40}$  ( $\text{M}=\text{Ca}, \text{Sr}$ ) and  $\text{M@B}_{40}$  ( $\text{M}=\text{Be}, \text{Mg}$ ). *Angew. Chem. Int. Ed.* **54**, 941–945 (2015).
- Chen, Q. *et al.* Cage-like  $\text{B}_{41}^+$  and  $\text{B}_{42}^{2+}$ : New chiral members of the borospherene family. *Angew. Chem. Int. Ed.* **54**, 941–945 (2015).
- Tian, W.-J. *et al.* Saturn-like charge-transfer complexes  $\text{Li}_4\text{@B}_{36}$ ,  $\text{Li}_5\text{@B}_{36}^+$ , and  $\text{Li}_6\text{@B}_{36}^{2+}$ : exohedral metalloborospherenes with a perfect cage-like  $\text{B}_{36}^{4-}$  core. *Phys. Chem. Chem. Phys.* **18**, 9922–9926 (2016).
- Chen, Q. *et al.* Endohedral charge-transfer complex  $\text{Ca@B}_{37}^-$ : stabilization of a  $\text{B}_{37}^{3-}$  borospherene trianion by metal-encapsulation. *Phys. Chem. Chem. Phys.* **18**, 14186–14190 (2016).
- Chen, Q. *et al.* Endohedral  $\text{Ca@B}_{38}$ : stabilization of a  $\text{B}_{38}^{2-}$  borospherene dianion by metal encapsulation. *Phys. Chem. Chem. Phys.* **18**, 11610–11615 (2016).
- Lu, Q.-L., Luo, Q.-Q., Li, Y.-D. & Huang, S.-G. DFT study on endohedral and exohedral  $\text{B}_{38}$  fullerenes:  $\text{M@B}_{38}$  ( $\text{M}=\text{Sc}, \text{Y}, \text{Ti}$ ) and  $\text{M@B}_{38}$  ( $\text{M}=\text{Nb}, \text{Fe}, \text{Co}, \text{Ni}$ ). *Phys. Chem. Chem. Phys.* **17**, 20897–20902 (2015).
- Chen, Q. *et al.* Endohedral  $\text{C}_3\text{Ca@B}_{39}^+$  and  $\text{C}_2\text{Ca@B}_{39}^+$ : axially chiral metalloborospherenes based on  $\text{B}_{39}^-$ . *Phys. Chem. Chem. Phys.* **17**, 19690–19694 (2015).
- Oger, E. *et al.* Boron cluster cations: transition from planar to cylindrical structures. *Angew. Chem. Int. Ed.* **46**, 8503–8506 (2007).
- Popov, I. A., Jian, T., Lopez, G. V., Boldyrev, A. I. & Wang, L.-S. Cobalt-centred boron molecular drums with the highest coordination number in the  $\text{CoB}_{16}^-$  cluster. *Nat. Commun.* **6**, 8654 (2015).
- Tian, F.-Y. & Wang, Y.-X. The competition of double-, four-, and three-ring tubular  $\text{B}_{3n}$  ( $n=8-32$ ) nanoclusters. *J. Chem. Phys.* **129**, 024903 (2008).
- Rahane, A. B. & Kumar, V.  $\text{B}_{84}$ : a quasi-planar boron cluster stabilized with hexagonal holes. *Nanoscale* **7**, 4055–4062 (2015).
- Ciuparu, D., Klie, R. F., Zhu, Y. & Pfefferle, L. Synthesis of Pure Boron Single-Wall Nanotubes. *J. Phys. Chem. B* **108**, 3967–3969 (2004).
- Liu, F. *et al.* Metal-like single crystalline boron nanotubes: synthesis and *in situ* study on electric transport and field emission properties. *J. Mater. Chem.* **20**, 2197–2205 (2010).
- Mannix, A. J. *et al.* Synthesis of borophenes: anisotropic, two-dimensional boron polymorphs. *Science* **350**, 1513–1516 (2015).
- Feng, B.-J. *et al.* Experimental realization of two-dimensional boron sheets. *Nat. Chem.* **8**, 563–568 (2016).
- Tang, H. & Ismail-Beigi, S. Novel Precursors for Boron Nanotubes: The Competition of Two-Center and Three-Center Bonding in Boron Sheets. *Phys. Rev. Lett.* **99**, 115501 (2007).
- Yang, X.-B., Ding, Y. & Ni, J. *Ab initio* prediction of stable boron sheets and boron nanotubes: Structure, stability, and electronic properties. *Phys. Rev. B* **77**, 041402 (2008).
- Wang, L., Zhao, J.-J., Li, F.-Y. & Chen, Z.-F. Boron fullerenes with 32–56 atoms: Irregular cage configurations and electronic properties. *Chem. Phys. Lett.* **501**, 16–19 (2010).
- Feller, D. The role of databases in support of computational chemistry calculations. *J. Comput. Chem.* **17**, 1571–1586 (1996).
- Schuchardt, K. L. *et al.* Basis Set Exchange: A Community Database for Computational Sciences. *J. Chem. Inf. Model.* **47**, 1045–1052 (2007).
- VandeVondele, J. *et al.* Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Comput. Phys. Commun.* **167**, 103–128 (2005).
- Zubarev, D. Y. & Boldyrev, A. I. Developing paradigms of chemical bonding: adaptive natural density partitioning. *Phys. Chem. Chem. Phys.* **10**, 5207–5217 (2008).
- Singh, A. K., Kumar, V., Briere, T. M. & Kawazoe, Y. Cluster assembled metal encapsulated thin nanotubes of silicon. *Nano Lett.* **2**, 1243–1248 (2002).



40. Adamo, C. & Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **110**, 6158–6170 (1999).
41. Krishnan, R., Binkley, J. S., Seeger, R. & Pople, J. A. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **72**, 650–654 (1980).
42. M. J. Frisch, *et al.* Gaussian 09, Revision D.01, Gaussian Inc., Wallingford, CT (2009).
43. Goedecker, S., Hellmann, W. & Lenosky, T. Global minimum determination of the Born-Oppenheimer surface within density functional theory. *Phys. Rev. Lett.* **95**, 055501 (2005).
44. Bauernschmitt, R. & Ahlrichs, R. Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory. *Chem. Phys. Lett.* **256**, 454–464 (1996).
45. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
46. Kresse, G. & Hafner, J. Norm-conserving and ultrasoft pseudopotentials for first-row and transition elements. *J. Phys. Condens. Matter* **6**, 8245–8257 (1994).
47. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
48. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953–17979 (1994).
49. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758–1775 (1999).
50. Schleyer, P. v. R., Maerker, C., Dransfeld, A., Jiao, H.-J. & Hommes, N. J. R. v. E. Nucleus-Independent Chemical Shifts: A Simple and Efficient Aromaticity Probe. *J. Am. Chem. Soc.* **118**, 6317–6318 (1996).

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21373130, 11504213, and 21473106).

## Author Contributions

S.-D. Li, Y.-W. Mu, and H.-G. Lu conceived and designed the work. W.-J. Tian, Q. Chen, and X.-X. Tian performed the calculations and analyzed the results. All the authors analyzed the data, discussed the results and made comments on the manuscript.

## Additional Information

**Supplementary information** accompanies this paper at <http://www.nature.com/srep>

**Competing financial interests:** The authors declare no competing financial interests.

**How to cite this article:** Tian, W.-J. *et al.* From Quasi-Planar B<sub>56</sub> to Penta-Ring Tubular Ca@B<sub>56</sub>: Prediction of Metal-Stabilized Ca@B<sub>56</sub> as the Embryo of Metal-Doped Boron  $\alpha$ -Nanotubes. *Sci. Rep.* **6**, 37893; doi: 10.1038/srep37893 (2016).

**Publisher's note:** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>

© The Author(s) 2016