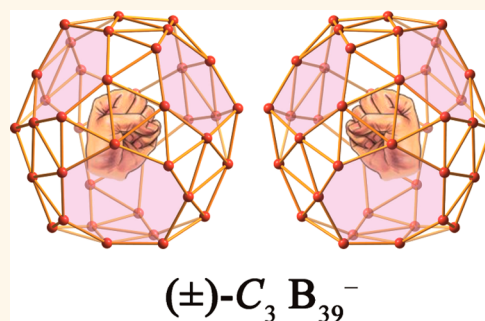


# Experimental and Theoretical Evidence of an Axially Chiral Borospherene

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**ABSTRACT** Chirality plays an important role in chemistry, biology, and materials science. The recent discovery of the  $B_{40}^{-/0}$  borospherenes marks the onset of a class of boron-based nanostructures. Here we report the observation of axially chiral borospherene in the  $B_{39}^-$  nanocluster on the bases of photoelectron spectroscopy, global minimum searches, and electronic structure calculations. Extensive structural searches in combination with density functional and CCSD(T) calculations show that  $B_{39}^-$  has a  $C_3$  cage global minimum with a close-lying  $C_2$  cage isomer. Both the  $C_3$  and  $C_2$   $B_{39}^-$  cages are chiral with degenerate enantiomers. The  $C_3$  global minimum consists of three hexagons and three heptagons around the vertical  $C_3$  axis. The  $C_2$  isomer is built on two hexagons on the top and at the bottom of the cage with four heptagons around the waist. Both the  $C_3$  and  $C_2$  axially chiral isomers of  $B_{39}^-$  are present in the experiment and contribute to the observed photoelectron spectrum. The chiral borospherenes also exhibit three-dimensional aromaticity, featuring  $\sigma$  and  $\pi$  double delocalization for all valence electrons. Molecular dynamics simulations reveal that these chiral  $B_{39}^-$  cages are structurally fluxional above room temperature, compared to the highly robust  $D_{2d} B_{40}$  borospherene. The current findings add chiral members to the borospherene family and indicate the structural diversity of boron-based nanomaterials.



**KEYWORDS:** borospherene · all-boron fullerene · axial chirality · photoelectron spectroscopy · global minimum searches ·  $\sigma$  and  $\pi$  double delocalization

Shortly after the discovery of the bulk synthesis of fullerenes,<sup>1</sup> the first axially chiral fullerene ( $D_2 C_{76}$ ) was characterized experimentally.<sup>2</sup> As the lighter neighbor of carbon in the periodic table, boron is electron-deficient and its chemical bonding is dominated by multicenter bonds, resulting in the formation of polyhedral molecules and unusual crystal allotropes.<sup>3,4</sup> Since the first proposal of a possible  $B_{80}$  cage, built from a  $C_{60}$ -like  $B_{60}$  by filling each of the 20 hexagons with a B atom,<sup>5</sup> the pursuit of boron cages has attracted significant computational activity in the past several years.<sup>6–14</sup> However, subsequent calculations found that the putative  $B_{80}$  cage is not the global minimum, and the most favorable  $B_{80}$  structure is likely a core–shell type three-dimensional structure.<sup>12,14–17</sup> On the other hand, size-selected boron nanoclusters ( $B_n^-$  and  $B_n$ ) have been shown in the past decade by systematic experimental and theoretical studies to be planar

or quasi-planar over a wide size range ( $n = 3–25, 30, 35, 36$ ),<sup>18–29</sup> including the quasi-planar chiral  $B_{30}^-$  observed recently.<sup>26</sup> This leaves a relatively small size regime ( $\sim 37–70$  atoms) for the possibility of all-boron cages. Very recently, we reported the first experimental and theoretical evidence for the existence of an all-boron fullerene at  $B_{40}$ .<sup>30</sup> Both  $B_{40}$  and its anion were found to have similar cage structures with  $D_{2d}$  symmetry. A name, borospherene, was suggested for the all-boron fullerene. The  $B_{40}$  borospherene is a slightly elongated cage, composed of interwoven double chains with two hexagons, one at the top and one at the bottom of the cage, and four heptagons on the waist.

In this contribution, we report a joint photoelectron spectroscopic and theoretical investigation on the  $B_{39}^-$  cluster, which is found to have an axially chiral  $C_3$  global minimum with a low-lying  $C_2$  axially chiral isomer. The  $B_{39}^-$  cluster represents the first borospherene with axial chirality as its

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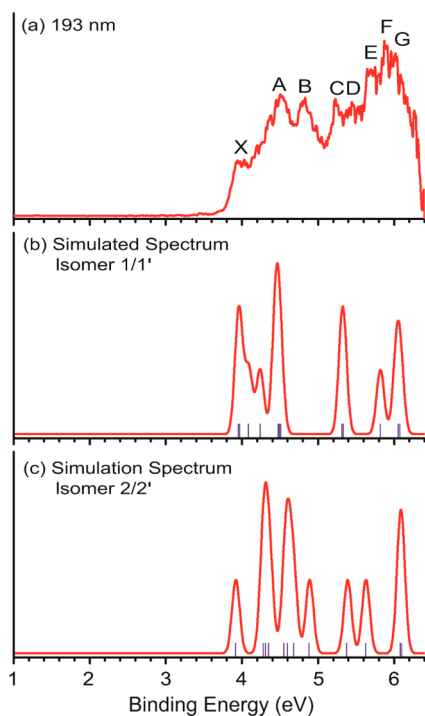
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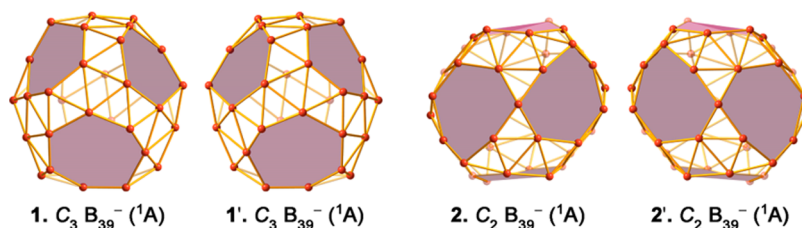
global minimum, suggesting that a new class of chiral borospherene-based nanostructures may exist. Chirality is important in chemistry, materials science, and biology. The observation of the axially chiral boron cage indicates the structural diversity of borospherenes, suggesting that much remains to be explored in low-dimensional boron nanomaterials.

## RESULTS

**Photoelectron Spectrum.** The  $B_{39}^-$  cluster was produced *via* laser vaporization of a  $^{10}\text{B}$ -enriched boron target and characterized using photoelectron spectroscopy (PES) (Figure 1a).<sup>31</sup> The leading PES band (X) has a vertical detachment energy (VDE) of 4.00(5) eV. Its well-defined onset allows the determination of an adiabatic detachment energy (ADE) of 3.84(5) eV, which represents the electron affinity (EA) of neutral  $B_{39}$ . The relatively large EA suggests that the  $B_{39}^-$  anion has a closed-shell electronic structure, and neutral  $B_{39}$  is



**Figure 1.** Photoelectron spectrum of  $B_{39}^-$  at 193 nm (a), compared with the simulated spectra at PBE0 based on the  $C_3$   $B_{39}^-$  global minimum (b) and the low-lying  $C_2$   $B_{39}^-$  isomer (c). The vertical bars in (b) and (c) show the calculated VDEs.

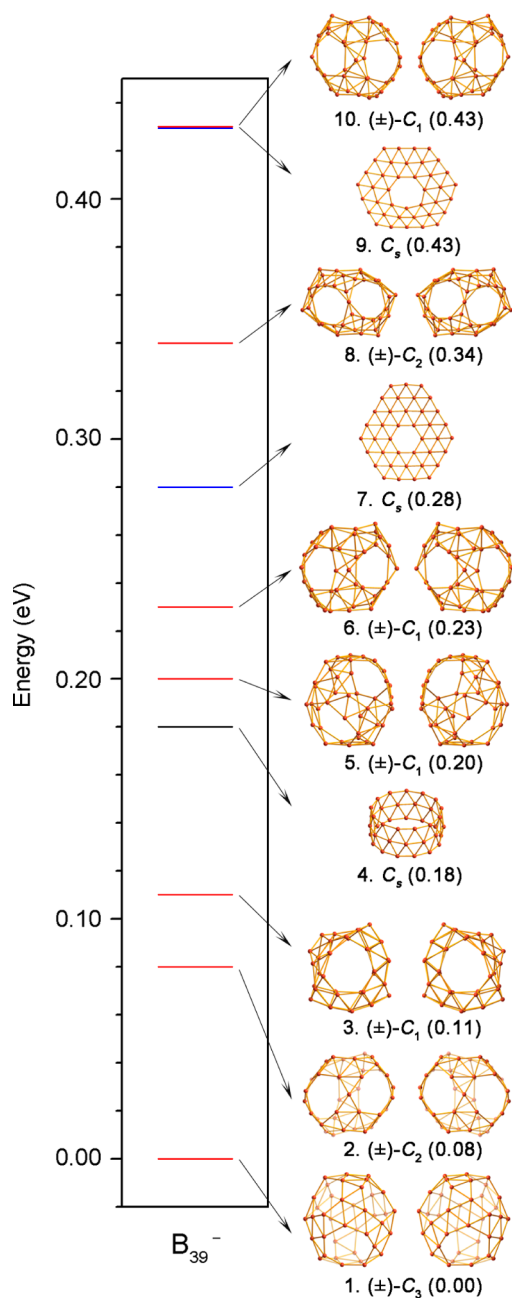


**Figure 2.** Optimized structures of the global minimum  $C_3$  and close-lying  $C_2$  isomers of  $B_{39}^-$ . The two enantiomers of the axially chiral structures are shown in each case. The hexagons and heptagons on the cage surface are shaded.

thus a superhalogen species. The next PES band (A) is observed at a VDE of 4.52 eV. Continuous electron signals exist in between bands X and A, suggesting additional, unresolved electronic transitions or possible contributions from coexisting isomers. Beyond band A, several well-defined bands are observed: B (4.82 eV), C (5.23 eV), D (5.45 eV), E (5.70 eV), F (5.88 eV), and G (6.00 eV). Overall, the PES pattern is rather congested and complicated, hinting that multiple isomers may be present in the  $B_{39}^-$  cluster beam.

**Structural Searches.** Global minimum searches for  $B_{39}^-$  were carried out using the Minima Hopping (MH) algorithm<sup>32,33</sup> at the density functional theory (DFT) level. Independent global minimum searches were also performed using the Basin Hopping (BH) method.<sup>27</sup> Low-lying structures were then fully optimized and their relative energies evaluated at both the DFT-PBE0<sup>34</sup> and CAM-B3LYP<sup>35</sup> levels with the 6-311+G\* basis set.<sup>36</sup> Isomers within 1.5 eV at the PBE0 level are summarized in Figure S1 for  $B_{39}^-$  and Figure S2 for  $B_{39}$  in the Supporting Information. To obtain more accurate relative energies, single-point CCSD(T) calculations<sup>37–39</sup> with the optimized PBE0 geometries and the 6-311G\* basis set were performed for the 12 lowest-lying isomers of  $B_{39}^-$ .

Figure 2 shows the global minimum  $C_3$  structure of  $B_{39}^-$  at CCSD(T) level and the second lowest-lying  $C_2$  isomer, which is only 0.08 eV above the  $C_3$  isomer. The configurational energy spectrum of  $B_{39}^-$  is illustrated in Figure 3 at the single-point CCSD(T)//PBE0/6-311G\* level. Interestingly, both  $C_3$  and  $C_2$  isomers are cages and are axially chiral. The degenerate global minima  $C_3(1)$  and  $C_3(1')$  form a pair of axially chiral enantiomers with respect to the  $C_3$  symmetry axis; the  $C_2(2)$  and  $C_2(2')$  isomers also form a pair of axially chiral enantiomers about the  $C_2$  symmetry axis. Among the first 12 most stable isomers at the CCSD(T) level, there are five additional cage isomers:  $C_1(3)$ ,  $C_1(5)$ ,  $C_1(6)$ ,  $C_2(8)$ , and  $C_1(10)$ , which are also chiral in nature (Figures 3 and S1). The first noncage isomer has a slightly distorted tubular structure (**4**,  $C_s$ ).<sup>20,40</sup> The first quasi-planar isomer (**7**,  $C_s$ ) is 0.28 eV above the global minimum at CCSD(T) and it is related to the recently observed hexagonal  $B_{36}^-$  cluster by attaching three B atoms along one edge.<sup>27</sup> Another quasi-planar isomer (**9**,  $C_s$ ) has a central heptagonal hole.



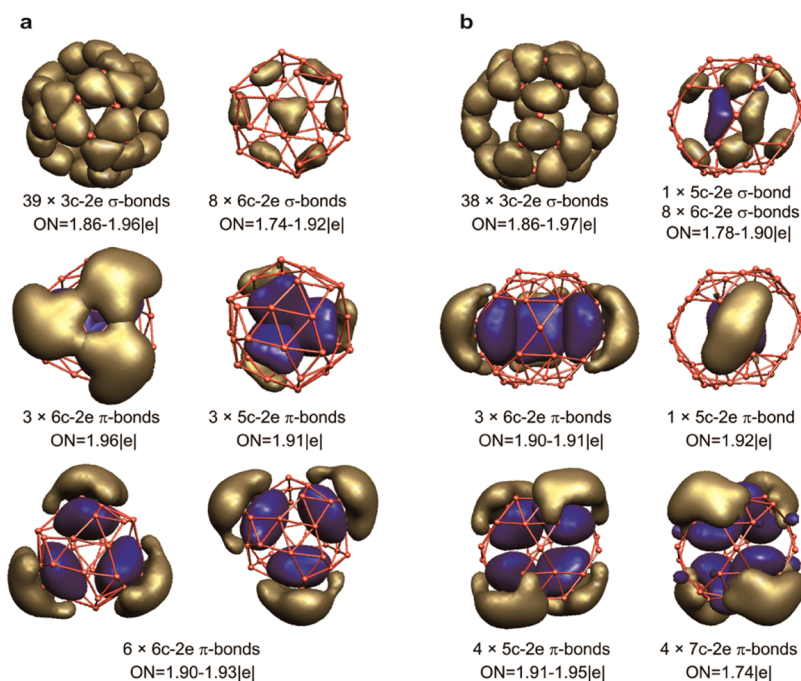
**Figure 3.** Configurational energy spectrum of  $B_{39}^-$  at the single-point CCSD(T)//PBE0/6-311G\* level. The energy of the global minimum is taken to be zero, and the relative energies are in eV. Cage-like enantiomer pairs are degenerate in energy. The red, black, and blue bars denote fullerene-like cages, triple-ring tubes, and quasi-planar structures, respectively.

The potential energy surface of  $B_{39}^-$  is highly complicated with numerous close-lying local minima (Figures 3 and S1). At the PBE0 level, cage isomers **1**, **2**, and **3** are within 0.2 eV, whereas the tubular isomer **4** and planar isomer **7** are slightly lower in energy than **1** by 0.19 and 0.24 eV, respectively. However, at the CAM-B3LYP level, which includes the long-range correction using the Coulomb attenuating method,<sup>35</sup> the cage isomer **1** becomes the global minimum, but only 0.01 eV below isomer **7**. The CAM-B3LYP results are

reinforced by the more accurate CCSD(T) data. At our highest level of CCSD(T)//PBE0/6-311G\*, isomer **1** remains the lowest in energy, closely followed by **2** at 0.08 eV higher. Isomers **3**–**6** are within 0.23 eV, whereas **7** is 0.28 eV higher in energy (Figure 3). On the basis of the energetics at CCSD(T), isomers **1**, **2**, and to a less extent, isomer **3**, may coexist experimentally and contribute to the observed PES spectrum. Note that  $B_{39}^-$  is the first case in boron anion clusters with a cage global minimum; the recently observed  $D_{2d} B_{40}^-$  borospherene is slightly higher than the planar global minimum, even though the neutral  $B_{40}$  borospherene is overwhelmingly the global minimum.<sup>30</sup> For neutral  $B_{39}$ , we only did PBE0 calculations (Figure S2). We found that the competition among cage, tubular, and quasi-planar structures remains, except that the triple-ring tubular isomer seems to be slightly more favored than in the anion case. The computational data also indicates that PBE0 biases toward quasi-planar or tubular structures, whereas CAM-B3LYP and the more reliable CCSD(T) favor cages.

**Comparison between Experiment and Theory.** To compare with the experimental data, we calculated the VDEs and simulated the PES spectra for the top 12 isomers, using the time-dependent DFT (TD-DFT) method.<sup>41</sup> Those from the two lowest energy isomers are compared with the experiment in Figure 1. The degenerate enantiomers of  $C_3$ (**1**) and  $C_2$ (**2**) should each produce the same PES spectra. The observed PES features X, A, C, F, and G are well reproduced by the simulated spectrum of the global minimum  $C_3$ (**1**) isomer (Figure 1b). The unresolved signals between bands X and A seem also to correspond to transitions of the  $C_3$  isomer. However, the simulated spectrum of the  $C_3$  isomer cannot explain all the observed PES bands, in particular, band B and the spectral region of D and E, which appear to come from the  $C_2$ (**2**) isomer (Figure 1c). Clearly, neither of the isomers alone can explain the observed spectrum. The combination of the two yields reasonable agreement with the experiment, providing credence for the coexistence of both the  $C_3$  and  $C_2$  isomers.

The simulated PES spectra for other low-lying cage isomers, **3**, **5**, **6**, **8**, and **10**, the tubular isomer **4**, and quasi-planar isomers **7**, **9**, **11**, and **13** are given in Figure S3. Because all these isomers are closed shell, they all give relatively high VDEs spanning the energy range of the experimental spectrum, except the isomer  $C_2$ (**8**), which has relatively low VDEs and can be ruled out. The situation of  $B_{39}^-$  is very different from  $B_{36}^-$  and  $B_{40}^-$ , where the neutral clusters are closed shell with large HOMO–LUMO gaps. The large energy gaps of  $B_{36}$  and  $B_{40}$  give rise to unusually low EAs for the neutral clusters. These spectral characteristics become defining features to unequivocally confirm the identified structures for the planar hexagonal  $B_{36}^{-/0}$  cluster and the  $B_{40}^{-/0}$  cage. For the complicated and congested spectrum of  $B_{39}^-$ , it is difficult to rule out safely any of the higher energy isomers based on the



**Figure 4.** AdNDP bonding pattern for (a) the global minimum  $C_3 B_{39}^-$  and (b) the close-lying isomer  $C_2 B_{39}^-$ . The occupation numbers (ONs) are indicated.

comparison of the simulated and experimental data alone. However, previous investigations on a wide range of planar and cage-like boron clusters<sup>18–30</sup> show that the CCSD(T) level of theory gives reliable energetics information and should give sufficient credence for the identified  $C_3(\mathbf{1})$  and  $C_2(\mathbf{2})$  cage structures for  $B_{39}^-$ .

It is interesting to note that isomer **3** is the closest cage-like isomer with respect to  $C_3(\mathbf{1})$  and  $C_2(\mathbf{2})$ . It also predicts the correct first VDE. However, its predicted transition at  $\sim 5.1$  eV is in between the well-separated experimental bands B and C, suggesting that the population of **3** should be small, if any, in the cluster beam of  $B_{39}^-$ . The contributions from other low-lying isomers beyond isomer **3** should be negligible in terms of the energetics at the CCSD(T) level (Figure 3). Thus, despite the congestion of the observed PES spectrum of  $B_{39}^-$  (Figure 1a) and its complicated potential energy surface (Figure 3), the current combined experimental and computational data suggests that the chiral  $C_3$  and  $C_2$  isomers should be the correct assignment.

## DISCUSSION

**Axially Chiral Borospherene.** The structure and bonding of the chiral  $C_3(\mathbf{1})$  and  $C_2(\mathbf{2}) B_{39}^-$  can be compared with those of the  $B_{40}$  borospherene. Structurally, the  $C_3(\mathbf{1}) B_{39}^-$  can be constructed from the  $B_{40}$  cage by replacing a  $B_7$  heptagon with a  $B_6$  hexagon, followed by a structural rearrangement. In fact, the  $C_3(\mathbf{1}) B_{39}^-$  was obtained automatically during the MH searches, starting from an initial structure constructed from  $B_{40}$  by replacing a heptagon on its waist with a hexagon. Moreover, the  $C_2(\mathbf{2}) B_{39}^-$  can be obtained from  $B_{40}$  by removal of one B

atom on the waist, so that one of the boron double chain on the waist is incomplete with a “defect” site.

The  $C_3(\mathbf{1}) B_{39}^-$  cage contains three hexagons on the top, three heptagons at the bottom, and 47 triangles along the interwoven double chains around the vertical  $C_3$  chiral axis, following Euler’s rule:  $E$  (90 edges) =  $F$  (47 triangular + 3 hexagonal + 3 heptagonal faces) +  $V$  (39 vertices) – 2. Electronically, the  $C_3(\mathbf{1}) B_{39}^-$  is closed-shell with a large HOMO–LUMO gap of 2.89 eV at PBE0 (Figure S4), which is close to the corresponding value of 3.13 eV obtained for the  $B_{40}$  borospherene at the same level.<sup>30</sup>

Similarly, the  $C_2(\mathbf{2}) B_{39}^-$  cage possesses a hexagon on the top and one at the bottom and four heptagons on the waist, consisting of 46 boron triangles also with a sizable HOMO–LUMO gap of 2.73 eV (Figure S4). The  $C_2(\mathbf{2})$  cage also conforms to Euler’s rule:  $E$  (89 edges) =  $F$  (46 triangular + 2 hexagonal + 4 heptagonal faces) +  $V$  (39 vertices) – 2.

**Chemical Bonding:  $\sigma$  Plus  $\pi$  Double Delocalization.** The chemical bonding of the  $C_3$  and  $C_2 B_{39}^-$  cages is analyzed using the adaptive natural density partitioning (AdNDP) method (Figure 4).<sup>42</sup> The  $C_3$  cage possesses 39 3c–2e and 8 6c–2e  $\sigma$  bonds (Figure 4a). For the 6c–2e  $\sigma$  bonds, the central  $B_3$  triangles make major contributions. Thus, all 47  $\sigma$  bonds are practically 3c–2e  $\sigma$  bonds, covering the cage surface uniformly with one  $\sigma$  bond for each  $B_3$  triangle. The remaining 12 bonds form the delocalized  $\pi$  framework. The three 6c–2e and three 5c–2e  $\pi$  bonds are associated with the top and bottom  $B_6$  triangles perpendicular to the  $C_3$  symmetry axis, respectively. The six 6c–2e  $\pi$  bonds on the waist cover

the zigzag double chain between the top and bottom  $B_6$  triangles. Thus, all the 118 valence electrons in the  $C_3$  isomer are evenly delocalized over the cage surface in both the  $\sigma$  and  $\pi$  frameworks, which effectively compensates for boron's intrinsic electron deficiency. This bonding pattern is similar to that in the  $D_{2d}B_{40}$ ,<sup>30</sup> and it appears to be critical for the high stability of borospherenes.

Because of the less symmetric  $C_2$  cage, an unusual  $5c-2e$   $\sigma$  bond is found (Figure 4b). It can be approximately viewed as a B 2p lone-pair. Indeed, the B atom at the "defect" site carries a negative natural charge of  $-0.60 |e|$ , unlike other B atoms in the cluster that are practically neutral. Other than that, the bonding pattern in the  $C_2 B_{39}^-$  is similar to that in the  $C_3$  isomer. The 12 delocalized  $\pi$  bonds found in  $D_{2d}B_{40}$  are characteristic of borospherenes, and they are well maintained in both the  $C_3$  and  $C_2$  cages of  $B_{39}^-$ .

The bonding pattern of  $\sigma$  plus  $\pi$  double delocalization renders 3D aromaticity to the  $B_{39}^-$  borospherenes. Nucleus independent chemical shift (NICS)<sup>43</sup> calculations show that both the  $C_3$  and  $C_2 B_{39}^-$  isomers have highly negative NICS values,  $-38$  and  $-39$  ppm, respectively, at the cage centers, which are comparable to the corresponding value of  $-42$  ppm calculated for the  $B_{40}$  cage at the same theoretical level.<sup>30</sup>

The  $C_3/C_2 B_{39}^-$  borospherenes can be further stabilized by binding with an alkali counterion to form a neutral, charge-transfer complex,  $M^+B_{39}^-$ . Figure S4 shows the cases of two  $C_1 Li^+B_{39}^-$  species, in which  $Li^+$  caps a heptagon face. The cage-like  $Li^+B_{39}^-$  complexes are also chiral with HOMO–LUMO gaps comparable to those of the parent  $B_{39}^-$  cluster and neutral  $D_{2d}B_{40}$ .

**Cube-Like Cages and Analogy to Cubane ( $C_8H_8$ ).** The chemical bonding of the  $B_{40}$  and  $B_{39}^-$  borospherenes can be further understood by comparing with that of the cubane ( $C_8H_8$ ), similar to the analogy between the bonding of planar boron clusters and that of polycyclic aromatic hydrocarbons.<sup>18,19,22–29</sup> The  $D_{2d}B_{40}$  and the two chiral isomers,  $C_3$  and  $C_2$ , of  $B_{39}^-$  can be viewed to possess cube-like cage structures with the six hexagonal or heptagonal holes as the faces and the eight  $B_6$  triangles as the corners of the cube (Figure S5). As deduced from the AdNDP analyses, each  $B_6$  triangle effectively contributes 3 electrons to the  $\pi$  framework, facilitating the global bonding of the  $B_6$  triangle to its three neighboring  $B_6$  units. The 12 delocalized  $\pi$  bonds over the  $\sigma$  skeleton in borospherenes resemble the 12 C–C bonds in cubane.

**Molecular Dynamics of  $B_{39}^-$ : A "Glassy" Form of Nanoboron?** To further explore the stability of the  $B_{39}^-$  chiral borospherenes, we carried out molecular dynamics (MD) simulations at the DFT level.<sup>44</sup> At 200 K, the  $C_3$  isomer is

dynamically stable during the 30 ps MD simulations (Figure S6). At 300 K and especially at 500 K, however, the  $B_{39}^-$  cluster starts to "hop" between different cage structures *via* concerted mechanisms with low energy barriers. The transformations involve synergetic bond breakage and formation, mainly between the  $C_3$  and  $C_2$  isomers, with small contributions from other low-lying cage-like isomers. Note that in the MD simulations, the  $C_2$ (**2**) isomer seems to be dynamically more stable than the global minimum  $C_3$ (**1**) isomer. This observation suggests that the relative population of  $C_3$  *versus*  $C_2$  isomers may vary, depending on experimental conditions.

The dynamical behavior of the cube-like  $B_{39}^-$  indicates that it is structurally fluxional above room temperature and may be viewed as a "glassy" form of nanoboron, much like a Rubik's cube with various permutations, hinting that the  $B_{39}^-$  cluster probably has a significantly lower melting point than bulk boron (2349 K). It should be pointed out that this behavior is size-dependent, because certain boron cages are more robust than others. For example, the  $B_{40}$  borospherene is dynamically stable even at 1000 K.<sup>30</sup> As already mentioned above, the  $C_3$  and  $C_2$  borospherenes, and other cage-like structures in Figure 3 as well, are composed of interwoven boron double chain nanoribbons. Such nanoribbons also make two-dimensional boron sheet or even a nanotube.<sup>45</sup> The current results show again the robustness of boron double chain nanoribbons in low-dimensional boron nanostructures. The chiral  $C_3$  and  $C_2 B_{39}^-$  borospherenes may serve as valuable models for mechanistic understanding of the nucleation and growth of chiral boron nanotubes. Indeed, the "defect" site in  $C_2 B_{39}^-$  and the unique dynamic behaviors of  $C_3$  and  $C_2 B_{39}^-$  should better facilitate the growth of chiral boron nanotubes.

## CONCLUSIONS

In conclusion, we have observed the first axially chiral  $B_{39}^-$  borospherene, which are found to have two close-lying, chiral isomers with  $C_3$  and  $C_2$  symmetries. Both isomers are shown to be present experimentally and contribute to the observed photoelectron spectrum of  $B_{39}^-$ . These axially chiral borospherenes possess 3D aromaticity and are characterized with  $\sigma$  plus  $\pi$  double delocalization in chemical bonding, similar to the  $B_{40}$  borospherene. The chiral cages are shown to be dynamically fluxional above room temperature. The current findings introduce chiral members to the borospherene family and indicate the structural diversity of the borospherene-based nanostructures.

Briefly, the  $B_{39}^-$  clusters were produced using a  $^{10}B$ -enriched boron disk target in the presence of a helium carrier gas seeded with 5% argon and were mass selected using a time-of-flight mass spectrometer. The  $B_{39}^-$  cluster was selected and photodetached

## METHODS SECTION

**Photoelectron Spectroscopy.** The experiment was done using a magnetic-bottle-type photoelectron spectroscopy apparatus,<sup>31</sup> equipped with a laser vaporization supersonic cluster source.

by a 193 nm photon beam from an ArF excimer laser. Photoelectron spectrum was obtained using a 3.5 m long electron flight tube and was calibrated using the known spectrum of Au<sup>-</sup>. The energy resolution of the magnetic-bottle electron analyzer was  $\Delta E/E \approx 2.5\%$ , that is,  $\sim 25$  meV for 1 eV kinetic energy electrons.

**Computational Methods.** The MH algorithm<sup>32,33</sup> and TGmin program<sup>27</sup> were employed independently to search for the global minimum of B<sub>39</sub><sup>-</sup>. MH is based on the principle of exploring the configurational space as fast as possible and of avoiding revisiting known parts of this space, which proves to be an efficient global minimum search algorithm for the potential energy surface of complex molecular systems. The MH calculations were carried out using the BIGDFT electronic structure code,<sup>46</sup> which is based on a systematic wavelet basis in combination with pseudopotentials and the standard local-density approximation (LDA)<sup>47</sup> and Perdew–Burke–Ernzerhof (PBE)<sup>48</sup> exchange-correlation functionals. Initial structures are primarily based on those of the recently studied B<sub>40</sub> cluster<sup>30</sup> by removing one B atom, further aided by manual structural constructions. About 5000 isomers were found from 8 independent MH searches, which include the low-lying C<sub>3</sub> and C<sub>2</sub> cage-like structures and their enantiomers.

To confirm the results of the MH searches, TGmin searches were also conducted. This involves the improved BH algorithm, which was carried out using the DFT formalism with the PBE exchange-correlation functional and the Goedecker–Teter–Hutter (GTH) pseudopotential<sup>47</sup> with the associated double- $z$  valence plus polarization (DZVP) basis set<sup>49</sup> using the CP2K program.<sup>44</sup> TGmin is a highly parallelized global optimization program. Starting from a given initial seed structure, it automatically generates displaced structures and input files for geometry optimization. Multiple geometry optimization jobs are submitted to the batch system on the computing platform. To identify duplicated structures, structural similarity comparison is carried out not only after the geometry optimization, but also during the geometry optimization. This kind of on-the-fly comparison notably reduced the CPU time for geometry optimization, thus increasing the efficiency of the global minimum search. More than 4600 isomers were produced via TGmin and no isomer is more stable than the C<sub>3</sub> structure and its enantiomer.

All low-lying isomers obtained from MH and TGmin searches were reoptimized at the PBE0/6-311+G\*<sup>34,36</sup> and CAM-B3LYP/6-311+G\*<sup>35,36</sup> levels using the Gaussian 09 program<sup>50</sup> and each reported isomer was ensured to be true minimum through frequency calculations. For more accurate relative energies, the optimized structures at PBE0 level were further evaluated via single-point CCSD(T)//PBE0/6-31G\*<sup>37–39,51</sup> and CCSD(T)//PBE0/6-311G\* calculations using the Molpro package.<sup>52</sup> For the neutral B<sub>39</sub> clusters, structures corresponding to the low-lying isomers of B<sub>39</sub><sup>-</sup> within 1 eV relative to the C<sub>3</sub> structure at PBE0/6-311+G\* were calculated using the same method. The VDEs of low-lying anion isomers were calculated using the TD-DFT method.<sup>41</sup> Chemical bonding analyses were performed using AdNDP<sup>42</sup> and visualized using Molekel.<sup>53</sup> Molecular dynamics simulations were performed using the software suite CP2K.<sup>44</sup>

**Conflict of Interest:** The authors declare no competing financial interest.

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**Supporting Information Available:** Alternative optimized structures for B<sub>39</sub><sup>-</sup> and B<sub>39</sub>, simulated photoelectron spectra of alternative low-lying isomers, comparison of the HOMO–LUMO gaps of B<sub>39</sub><sup>-</sup> and Li<sup>+</sup>B<sub>39</sub><sup>-</sup> with that of B<sub>40</sub>, comparison of the structures of B<sub>39</sub><sup>-</sup> and B<sub>40</sub> with cubane C<sub>8</sub>H<sub>8</sub>, molecular dynamics simulations, and the coordinates of the two lowest-lying chiral structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## REFERENCES AND NOTES

- Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K. D.; Huffman, D. R. Solid C<sub>60</sub>: A New Form of Carbon. *Nature* **1990**, *347*, 354–358.
- Ettl, R.; Chao, I.; Diederich, F.; Whetten, R. L. Isolation of C<sub>76</sub>, a Chiral (D<sub>2</sub>) Allotrope of Carbon. *Nature* **1991**, *353*, 149–153.
- Lipscomb, W. N. The Boranes and Their Relatives. *Science* **1977**, *196*, 1047–1055.
- Albert, B.; Hillebrecht, H. Boron: Elementary Challenge for Experimenters and Theoreticians. *Angew. Chem., Int. Ed.* **2009**, *48*, 8640–8668.
- Szwacki, N. G.; Sadrzadeh, A.; Yakobson, B. I. B<sub>80</sub> Fullerene: An *Ab Initio* Prediction of Geometry, Stability, and Electronic Structure. *Phys. Rev. Lett.* **2007**, *98*, 166804. Erratum: *Phys. Rev. Lett.* **2008**, *100*, 159901.
- Sheng, X. L.; Yan, Q. B.; Zheng, Q. R.; Su, G. Boron Fullerenes B<sub>32+8k</sub> with Four-Membered Rings and B<sub>32</sub> Solid Phases: Geometrical Structures and Electronic Properties. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9696–9702.
- 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.* **2010**, *501*, 16–19.
- Zhao, J. J.; Wang, L.; Li, F. Y.; Chen, Z. F. B<sub>80</sub> and Other Medium-Sized Boron Clusters: Core-Shell Structures, Not Hollow Cages. *J. Phys. Chem. A* **2010**, *114*, 9969–9972.
- Zope, R. R.; Baruah, T. Snub Boron Nanostructures: Chiral Fullerenes, Nanotubes and Planar Sheet. *Chem. Phys. Lett.* **2011**, *501*, 193–196.
- Özdoğan, C.; Mukhopadhyay, S.; Hayami, W.; Guvenc, Z. B.; Pandey, R.; Boustani, I. The Unusually Stable B<sub>100</sub> Fullerene, Structural Transitions in Boron Nanostructures, and a Comparative Study of  $\alpha$ - and  $\gamma$ -Boron and Sheets. *J. Phys. Chem. C* **2010**, *114*, 4362–4375.
- Quarles, K. D.; Kah, C. B.; Gunasinghe, R. N.; Musin, R. N.; Wang, X. Q. Filled Pentagons and Electron Counting Rule for Boron Fullerenes. *J. Chem. Theory Comput.* **2011**, *7*, 2017–2020.
- De, S.; Willand, A.; Amsler, M.; Pochet, P.; Genovese, L.; Goedecker, S. Energy Landscape of Fullerene Materials: A Comparison of Boron to Boron Nitride and Carbon. *Phys. Rev. Lett.* **2011**, *106*, 225502.
- Polad, S.; Ozay, M. A New Hole Density as a Stability Measure for Boron Fullerenes. *Phys. Chem. Chem. Phys.* **2013**, *15*, 19819–19824.
- Lv, J.; Wang, Y. C.; Zhu, L.; Ma, Y. M. B<sub>38</sub>: An All-Boron Fullerene Analogue. *Nanoscale* **2014**, *6*, 11692–11696.
- Prasad, D. L. V. K.; Jemmis, E. D. Stuffing Improves the Stability of Fullerene-like Boron Clusters. *Phys. Rev. Lett.* **2008**, *100*, 165504.
- Shang, B.; Yuan, L. F.; Zeng, X. C.; Yang, J. L. *Ab Initio* Prediction of Amorphous B<sub>84</sub>. *J. Phys. Chem. A* **2010**, *114*, 2245–2249.
- Li, F. Y.; Jin, P.; Jiang, D. E.; Wang, L.; Zhang, S. B.; Zhao, J. J.; Chen, Z. F. B<sub>80</sub> and B<sub>101–103</sub> Clusters: Remarkable Stability of the Core-Shell Structures Established by Validated Density Functionals. *J. Chem. Phys.* **2012**, *136*, 074302.
- 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.* **2003**, *42*, 6004–6008.
- Zhai, H. J.; Kiran, B.; Li, J.; Wang, L. S. Hydrocarbon Analogues of Boron Clusters—Planarity, Aromaticity and Antiaromaticity. *Nat. Mater.* **2003**, *2*, 827–833.
- Kiran, B.; Bulusu, S.; Zhai, H. J.; Yoo, S.; Zeng, X. C.; Wang, L. S. Planar-to-Tubular Structural Transition in Boron Clusters: B<sub>20</sub> as the Embryo of Single-Walled Boron Nanotubes. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102*, 961–964.
- Oger, E.; Crawford, N. R. M.; Kelting, R.; Weis, P.; Kappes, M. M.; Ahlrichs, R. Boron Cluster Cations: Transition from Planar to Cylindrical Structures. *Angew. Chem., Int. Ed.* **2007**, *46*, 8503–8506.
- Sergeeva, A. P.; Zubarev, D. Yu.; Zhai, H. J.; Boldyrev, A. I.; Wang, L. S. A Photoelectron Spectroscopic and Theoretical

- Study of  $B_{16}^-$  and  $B_{16}^{2-}$ : An All-Boron Naphthalene. *J. Am. Chem. Soc.* **2008**, *130*, 7244–7246.
23. Huang, W.; Sergeeva, A. P.; Zhai, H. J.; Averkiev, B. B.; Wang, L. S.; Boldyrev, A. I. A Concentric Planar Doubly  $\pi$ -Aromatic  $B_{19}^-$  Cluster. *Nat. Chem.* **2010**, *2*, 202–206.
  24. Sergeeva, A. P.; Piazza, Z. A.; Romanescu, C.; Li, W. L.; Boldyrev, A. I.; Wang, L. S.  $B_{22}^-$  and  $B_{23}^-$ : All-Boron Analogues of Anthracene and Phenanthrene. *J. Am. Chem. Soc.* **2012**, *34*, 18065–18073.
  25. Popov, I. A.; Piazza, Z. A.; Li, W. L.; Wang, L. S.; Boldyrev, A. I. A Combined Photoelectron Spectroscopy and *Ab Initio* Study of the Quasi-Planar  $B_{24}^-$  Cluster. *J. Chem. Phys.* **2013**, *139*, 144307.
  26. Li, W. L.; Zhao, Y. F.; Hu, H. S.; Li, J.; Wang, L. S.  $[B_{30}]^-$ : A Quasipolar Chiral Boron Cluster. *Angew. Chem., Int. Ed.* **2014**, *53*, 5540–5545.
  27. Piazza, Z. A.; Hu, H. S.; Li, W. L.; Zhao, Y. F.; Li, J.; Wang, L. S. Planar Hexagonal  $B_{36}$  as a Potential Basis for Extended Single-Atom Layer Boron Sheets. *Nat. Commun.* **2014**, *5*, 3113.
  28. Sergeeva, A. P.; Popov, I. A.; Piazza, Z. A.; Li, W. L.; Romanescu, C.; Wang, L. S.; Boldyrev, A. I. Understanding Boron Through Size-Selected Clusters: Structure, Chemical Bonding, and Fluxionality. *Acc. Chem. Res.* **2014**, *47*, 1349–1358.
  29. Li, W. L.; Chen, Q.; Tian, W. J.; Bai, H.; Zhao, Y. F.; Hu, H. S.; Li, J.; Zhai, H. J.; Li, S. D.; Wang, L. S. The  $B_{35}$  Cluster with a Double-Hexagonal Vacancy: A New and More Flexible Structural Motif for Borophene. *J. Am. Chem. Soc.* **2014**, *136*, 12257–12260.
  30. Zhai, H. J.; Zhao, Y. F.; Li, W. L.; Chen, Q.; Bai, H.; Hu, H. S.; Piazza, Z. A.; Tian, W. J.; Lu, H. G.; Wu, Y. B.; Mu, Y. W.; Wei, G. F.; Liu, Z. P.; Li, J.; Li, S. D.; Wang, L. S. Observation of an All-Boron Fullerene. *Nat. Chem.* **2014**, *6*, 727–731.
  31. Wang, L. S.; Cheng, H. S.; Fan, J. Photoelectron Spectroscopy of Size-Selected Transition Metal Clusters:  $Fe_n^-$ ,  $n = 3–24$ . *J. Chem. Phys.* **1995**, *102*, 9480–9493.
  32. Goedecker, S. Minima Hopping: An Efficient Search Method for the Global Minimum of the Potential Energy Surface of Complex Molecular Systems. *J. Chem. Phys.* **2004**, *120*, 9911–9917.
  33. Goedecker, S.; Hellmann, W.; Lenosky, T. Global Minimum Determination of the Born-Oppenheimer Surface within Density Functional Theory. *Phys. Rev. Lett.* **2005**, *95*, 055501.
  34. Adamo, C.; Barone, V. Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0 Model. *J. Chem. Phys.* **1999**, *110*, 6158–6170.
  35. Yanai, T.; Tew, D.; Handy, N. C. A New Hybrid Exchange-Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57.
  36. 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.* **1980**, *72*, 650–654.
  37. Čížek, J. On the Use of the Cluster Expansion and the Technique of Diagrams in Calculations of Correlation Effects in Atoms and Molecules. *Adv. Chem. Phys.* **1969**, *14*, 35–89.
  38. Purvis, G. D., III; Bartlett, R. J. A Full Coupled-Cluster Singles and Doubles Model: The Inclusion of Disconnected Triples. *J. Chem. Phys.* **1982**, *76*, 1910–1918.
  39. Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. A Fifth-Order Perturbation Comparison of Electron Correlation Theories. *Chem. Phys. Lett.* **1989**, *157*, 479–483.
  40. Tian, F. Y.; Wang, Y. X. The Competition of Double-, Four-, and Three-Ring Tubular  $B_{3n}$  ( $n = 8–32$ ) Nanoclusters. *J. Chem. Phys.* **2008**, *129*, 024903.
  41. Bauernschmitt, R.; Ahlrichs, R. Treatment of Electronic Excitations within the Adiabatic Approximation of Time Dependent Density Functional Theory. *Chem. Phys. Lett.* **1996**, *256*, 454–464.
  42. Zubarev, D. Yu.; Boldyrev, A. I. Developing Paradigms of Chemical Bonding: Adaptive Natural Density Partitioning. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5207–5217.
  43. Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. v. E. Nucleus-Independent Chemical Shifts: A Simple and Efficient Aromaticity Probe. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.
  44. VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. QUICKSTEP: Fast and Accurate Density Functional Calculations Using a Mixed Gaussian and Plane Waves Approach. *Comput. Phys. Commun.* **2005**, *167*, 103–128.
  45. Singh, A. K.; Sadrzadeh, A.; Yakobson, B. I. Probing Properties of Boron  $\alpha$ -Tubes by *Ab Initio* Calculations. *Nano Lett.* **2008**, *8*, 1314–1317.
  46. Genovese, L.; Neelov, A.; Goedecker, S.; Deutsch, T.; Ghasemi, S. A.; Willand, A.; Caliste, D.; Zilberberg, O.; Rayson, M.; Bergman, A.; Schneider, R. Daubechies Wavelets as a Basis Set for Density Functional Pseudopotential Calculations. *J. Chem. Phys.* **2008**, *129*, 014109.
  47. Goedecker, S.; Teter, M.; Hutter, J. Separable Dual-Space Gaussian Pseudopotentials. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 1703–1710.
  48. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
  49. VandeVondele, J.; Hutter, J. Gaussian Basis Sets for Accurate Calculations on Molecular Systems in Gas and Condensed Phases. *J. Chem. Phys.* **2007**, *127*, 114105.
  50. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; *et al.* *Gaussian 09*, Revision B.01; Gaussian Inc., Wallingford, CT, 2010.
  51. Dill, J. D.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XV. Extended Gaussian-Type Basis Sets for Lithium, Beryllium, and Boron. *J. Chem. Phys.* **1975**, *62*, 2921–2922.
  52. Werner, H. J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Lindh, R.; Mitrushenkov, A.; Rauhut, G.; *et al.* *MOLPRO*, version 2012.1.
  53. Varetto, U. *Molekel 5.4.0.8*; Swiss National Supercomputing Center: Manno, Switzerland, 2009.