

# From planar boron clusters to borophenes and metalborophenes

Wan-Lu Li, Xin Chen, Tian Jian, Teng-Teng Chen, Jun Li and Lai-Sheng Wang

**Abstract** | Elemental boron and its compounds exhibit unusual structures and chemical bonding owing to the electron deficiency of boron. Joint photoelectron spectroscopy and theoretical studies over the past decade have revealed that boron clusters possess planar or quasi-planar (2D) structures up to relatively large sizes, laying the foundations for the discovery of boron-based nanostructures. The observation of the 2D  $B_{36}$  cluster provided the first experimental evidence that extended boron monolayers with hexagonal vacancies were potentially viable and led to the proposition of ‘borophenes’ — boron analogues of 2D carbon structures such as graphene. Metal-doping can expand the range of potential nanostructures based on boron. Recent studies have shown that the  $CoB_{18}^-$  and  $RhB_{18}^-$  clusters possess unprecedented 2D structures, in which the dopant metal atom is part of the 2D boron network. These doped 2D clusters suggest the possibilities of creating metal-doped borophenes with potentially tunable electronic, optical and magnetic properties. Here, we discuss the recent experimental and theoretical advances in 2D boron and doped boron clusters, as well as their implications for metalborophenes.

Boron exists in a large number of unusual chemical structures, both in its elemental form and its many chemical compounds<sup>1</sup>, as a direct consequence of its electron deficiency. The discoveries of exciting carbon nanostructures, such as fullerenes<sup>2</sup>, nanotubes<sup>3</sup> and graphenes<sup>4</sup>, suggested the attractive prospect that boron — carbon’s lighter neighbour — could form similar structures. Like carbon, boron can form exceptionally strong homonuclear covalent bonds, which are reflected in the super-hard character of almost all boron polymorphs<sup>5</sup>. Boron nanotubes made of triangular boron sheets were, in fact, proposed shortly after carbon nanotubes were discovered<sup>6,7</sup>. However, computational studies suggested that triangular planar boron lattices with hexagonal vacancies were more stable and more suitable to form the putative boron nanotubes<sup>8,9</sup>. The proposed  $B_{80}$  fullerene featured pentagonal vacancies<sup>10</sup>, which might explain why it is a much higher-energy isomer than the various low-symmetry structures of the core-shell type<sup>11–14</sup>. A systematic understanding of the

geometric structures and chemical bonding of size-selected boron clusters, and of their evolution as a function of size, is clearly an essential foundation for the discovery of new boron-based nanostructures. This, however, has proved to be a challenge that has required more than a decade of sustained joint experimental and theoretical investigation<sup>15–17</sup>.

Neutral clusters are generally more difficult to study because mass spectrometric techniques, necessary for cluster size selection, require charged particles. Small boron cluster cations were first produced and their fragmentation and chemical reactivity were studied in the late 1980s<sup>18–21</sup>, but no structural and spectroscopic information was available until 2002, when photoelectron spectroscopy (PES) was combined with quantum chemistry to investigate size-selected boron clusters<sup>22</sup>. Since then, PES in conjunction with high-level *ab initio* calculations has become an effective means to probe the electronic structure and chemical bonding of boron clusters<sup>22–39</sup>. Size-selected anionic boron

clusters are extremely interesting, as even fairly large clusters have been found to be planar or quasi-planar (2D)<sup>22–39</sup>. Although bulk boron is characterized by 3D polyhedral structural features<sup>5,40,41</sup>, early theoretical calculations suggested that the isolated  $B_{12}$  icosahedron — the dominant motif in bulk boron — was less stable than 2D structures<sup>42,43</sup>. The higher stability of 2D structures can be ascribed to the electron-deficient character of boron and its propensity to form multi-centred chemical bonds<sup>1</sup>. Chemical bonding analyses based on the adaptive natural density partitioning (AdNDP) method<sup>44</sup> revealed that all 2D boron clusters consist of an outer ring featuring strong two-centre, two-electron ( $2c-2e$ ) B–B bonds (in which two valence electrons are shared between two atoms) and one or more inner atoms interacting with the peripheral ring almost exclusively through delocalized  $\sigma$  and  $\pi$  bonding<sup>15–17,45</sup>. The electron delocalization has an important role in stabilizing the 2D structures, giving rise to concepts of  $\sigma$  and  $\pi$  aromaticity and antiaromaticity according to Hückel’s rule<sup>15–17,25,45–47</sup>. Recent investigations have shown that even larger anionic boron clusters, including those comprising over 30 atoms, preferentially adopt planar structures<sup>48–50</sup>. Even the minimum-energy structure of  $B_{40}^-$  — the largest experimentally characterized boron cluster — corresponds to a 2D arrangement of the atoms<sup>51</sup>, although 3D borospherene  $B_{40}^-$  is also an energetically accessible isomer. By contrast, for a neutral cluster of the same size,  $B_{40}$  borospherene is the most stable structure<sup>51</sup>.

Notably, the discovery of the planar hexagonal  $B_{36}$  cluster provided the first experimental evidence for the viability of monolayer boron, which was named borophene<sup>48</sup>. The  $B_{35}^-$  cluster with two adjacent hexagonal vacancies provided an even more flexible motif for borophenes<sup>49</sup>. The double hexagonal vacancies in  $B_{35}^-$  result in an asymmetric cluster, enabling borophenes with different hole densities and orientations to be constructed. Earlier experimental and theoretical characterizations of boron clusters were reviewed in 2006 (REF. 15), and a brief account addressing the structural fluxionality and chemical bonding appeared in 2014 (REF. 16). Recently,

a more comprehensive review that includes the progress made over the past decade on the characterization of size-selected boron clusters using PES and computational chemistry has been published<sup>17</sup>.

The structures and properties of boron clusters can be further tuned by doping with metal atoms, considerably expanding the plethora of possible boron-based nanostructures. A series of aromatic borometallic molecular wheels with a highly coordinated central transition metal atom, M, inside a monocyclic boron ring (designated as  $M@B_n^-$ ) has been produced and characterized for  $n=8-10$  (REFS 52–56). Very recently, larger doped boron clusters,  $CoB_{16}^-$  and  $MnB_{16}^-$ , have been observed to feature unprecedented tubular (or drum-like) structures<sup>57,58</sup>. A low-lying  $TaB_{20}^-$  drum isomer of perfect  $D_{10d}$  symmetry has also recently been found<sup>59</sup>. The discoveries of 2D  $CoB_{18}^-$  and  $RhB_{18}^-$  clusters, in which planar boron lattices are doped by the transition metal atoms, were surprising, opening up the possibility of metallo-borophenes<sup>60,61</sup>. In the meantime, properties of hypothesized metalloborophenes that contain other transition metals, such as iron and manganese, have also been studied computationally<sup>62–65</sup>. The recent syntheses and characterization of borophenes on silver substrates<sup>66,67</sup> make the idea of synthesizable metalloborophenes conceivable, opening the door to a new class of 2D materials with tunable chemical and physical properties. In this Perspective, we discuss the exciting advances in the studies of size-selected boron and doped boron clusters and, in particular, the findings of planar  $CoB_{18}^-$  and  $RhB_{18}^-$  and their implications for metalloborophenes.

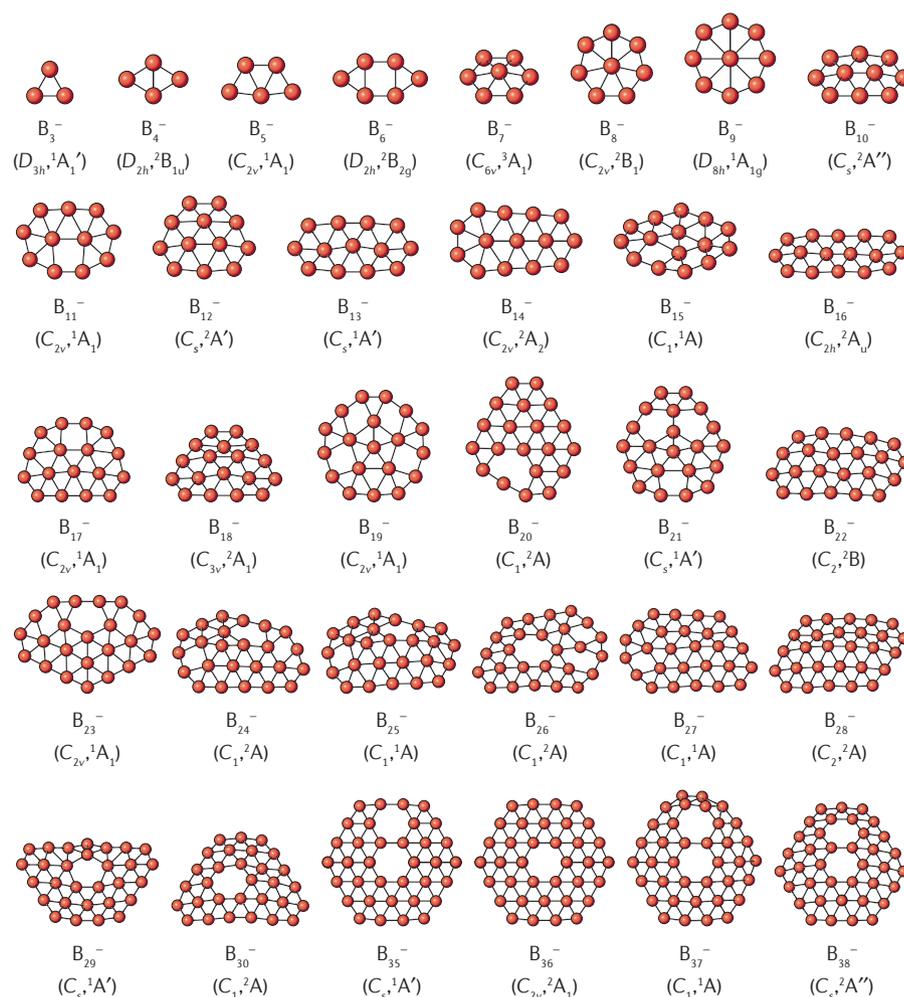
### Planar boron clusters

#### Medium-sized boron clusters

FIGURE 1 summarizes the global minimum structures of  $B_n^-$  for  $n=3-30$  and  $35-38$ , confirmed from careful comparison between PES and theoretical studies. These results represent a sustained and systematic joint experimental and theoretical effort, spanning more than a decade from the first study in 2002 (REF. 22) to the very recent resolution of the structures of  $B_{37}^-$  and  $B_{38}^-$  (REF. 50). The minimum-energy structures of the boron cluster monoanions are presented in FIG. 1, but, in some cases, energetically accessible isomers exist. When a low-energy isomer is energetically close to the minimum-energy isomer, the two may coexist at finite temperatures, and they can be observed experimentally in different ratios. For example, the majority of the most stable

structures are 2D, but in the cases of  $B_{28}^-$  and  $B_{29}^-$ , small amounts of 3D borospherene isomers have been observed to coexist with the 2D structures<sup>37,38,68</sup>. Note that some of the 2D structures shown in FIG. 1 are quasi-planar; for example, both  $B_7^-$  and  $B_{12}^-$  have bowl-shaped structures<sup>25,26</sup>. The distortion is due to the peripheral B–B bonds being stronger and shorter than the internal bonds, causing slight out-of-plane migration of the interior atoms. This explanation was confirmed by substituting a peripheral boron atom with a larger valence-isoelectronic atom, aluminium. The resulting  $AlB_6^-$  and  $AlB_{11}^-$  clusters were indeed found to be planar because the longer Al–B bonds expanded the size of the outer ring<sup>69</sup>.

Neutral boron clusters are considerably more challenging to study experimentally, owing to the difficulty in cluster size discrimination. Charged clusters can be conveniently detected and size-selected by mass spectrometry, whereas neutral clusters require more sophisticated experimental techniques. For example, IR spectra of  $B_{11}$ ,  $B_{16}$  and  $B_{17}$  were measured using an IR–UV double resonance approach, and these neutral clusters were all found to have structures similar to those of the most energetically stable corresponding anions<sup>70</sup>. Neutral spectroscopic information can also be obtained from PES of the corresponding anions. In particular, high-resolution PES of negatively charged clusters can



yield vibrational information about the corresponding neutral final states. Very recently, a high-resolution PES study of  $B_{11}^-$  and  $B_{12}^-$  using photoelectron imaging has resolved several vibrational modes for the corresponding neutral  $B_{11}$  and  $B_{12}$  clusters, confirming that their 2D structures are similar to the parent anions<sup>71</sup>.

The structures of a series of  $B_n^+$  cationic clusters for  $n = 12-25$  were investigated using ion mobility experiments in combination with density functional theory (DFT) calculations<sup>72</sup>. The structures of  $B_{12}^+$  and  $B_{15}^+$  were found to be similar to those of the corresponding anions (FIG. 1). Anionic  $B_{13}^-$  and  $B_{14}^-$  have elongated 2D structures (FIG. 1) because they are antiaromatic (each with eight  $\pi$  electrons) according to Hückel's rule<sup>25</sup>. However, the structures of  $B_{13}^+$  and  $B_{14}^+$  were found to be more circular, consistent with previous calculations<sup>73,74</sup>. A major departure of the structures of the cationic clusters from those of the 2D anions (FIG. 1) was reported for  $n = 16$ , beyond which ( $n = 16-25$ ) tubular structures were deduced<sup>72</sup>. Very recently, the IR spectrum of  $B_{13}^+$  has been reported<sup>75</sup>, confirming its circular structure and its structural dynamicity<sup>76</sup>.

### The structures of $B_{36}^-$ and $B_{35}^-$

Beyond  $n = 30$ , the  $B_{36}^-$  cluster gives a characteristic photoelectron spectrum displaying an unusually low electron binding energy<sup>17,48</sup>. The minimum-energy structure for  $B_{36}^-$  was found to have pseudo- $C_{6v}$  symmetry (only slightly distorted relative to  $C_{2v}$ ) with a central hexagonal vacancy (FIG. 1) not observed in other known structures previously, whereas neutral  $B_{36}$  was found to have  $C_{6v}$  symmetry.

**The hexagonal  $B_{36}$  cluster and the concept of borophene.** Boron cannot form graphene-like hexagonal layers because of its electron deficiency. Boron sheets consisting of  $B_3$  triangles, which are

obtained by incorporating a boron atom in the centre of the hexagon of a graphene-like boron structure, were originally used to form the hypothesized boron nanotubes<sup>6,7</sup>. However, such triangular lattices are too electron-rich, so that out-of-plane distortions occur, leading to rippled boron layers according to subsequent computational investigations<sup>77-80</sup>. Further theoretical studies suggested that a triangular lattice with periodic hexagonal vacancies would be truly planar and much more stable than a close-packed triangular lattice<sup>8,9</sup>. The hexagonal vacancy found in the  $B_{36}$  cluster<sup>48</sup> is reminiscent of the hexagonal vacancies in the predicted 2D boron sheets<sup>8,9</sup>. The proposed 2D boron structure based on the  $B_{36}$  cluster (shown in FIG. 2a) exhibits a hexagonal hole density of  $\eta = 1/27$  (one vacancy for every 27 triangular lattice sites)<sup>8</sup>. Therefore, the hexagonal  $B_{36}$  cluster can be considered as the repeated motif of an extended boron-monolayer with hexagonal vacancies, in analogy with the hexagonal  $C_6$  motif in graphene. The  $B_{36}$  cluster thus provides indirect experimental evidence for the viability of monolayer boron with hexagonal vacancies. The name 'borophene' was coined to designate this class of new boron nanostructures in analogy to graphene<sup>48</sup>.

### $B_{35}^-$ as a more flexible motif for borophenes.

The photoelectron spectrum of  $B_{35}^-$  was well resolved and displayed some similarity to that of  $B_{36}^-$ , suggesting that the minimum-energy structure of  $B_{35}^-$  might be related to the structure of  $B_{36}^-$  (REF. 49). Minimum-energy structure searches identified the most stable structure of  $B_{35}^-$  to be quasi-planar with a double-hexagonal vacancy (FIG. 1), which can be obtained by simply removing a boron atom from the interior plane of pseudo- $C_{6v}$   $B_{36}^-$ . The simulated photoelectron spectrum of  $B_{35}^-$  was in remarkable agreement with experiment,

providing firm confirmation of the stability of the quasi-planar structure found for  $B_{35}^-$ . It turned out that the hexagonal  $B_{35}$  cluster can be an even more flexible building block for constructing borophenes (shown schematically in FIG. 2b,c)<sup>49</sup>. Other arrangements of the  $B_{35}$  clusters are also possible, creating borophenes with different hole patterns and densities, many of which have been considered computationally<sup>81,82</sup>. The double hexagonal vacancy seems to be a common structural feature in large 2D boron clusters; it was also found in the recently reported  $B_{37}^-$  and  $B_{38}^-$  clusters<sup>50</sup> (FIG. 1), as well as in the low-energy 2D  $B_{40}^-$  isomer<sup>51</sup>.

### Experimental syntheses of borophenes on inert substrates.

Boron does not exist in any bulk allotropes with layered structures, so experimental production of borophenes would have to rely on nucleation and growth on chemically inert substrates; a vacuum environment or inert atmosphere would be required to avoid oxidation or other inadvertent reactions of the nascent borophenes. Hence, it is not surprising that the first considerations of the formation of borophenes were purely theoretical<sup>83-85</sup>. Initial studies of borophenes on silver or copper substrates predicted the  $\beta_{12}$  structure<sup>81</sup>, which consists of rows of hexagonal vacancies similar to the structure shown in FIG. 2c, to be the most stable<sup>85</sup>. In a recent major advance in the experimental synthesis, borophenes were grown on a Ag(111) surface and their structures characterized by using both scanning tunnelling microscopy and transmission electron microscopy<sup>66</sup>. Even with these high-resolution methods, the atomic structures were not fully resolved, but comparison between simulated images and experiment suggested that the synthesized borophenes have a corrugated triangular lattice. Subsequent experimental and theoretical investigations concluded that the synthesized borophenes on

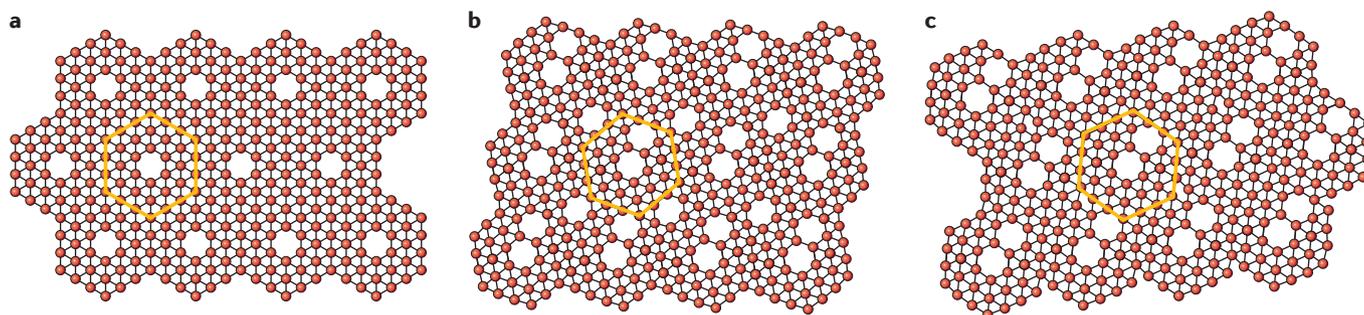


Figure 2 | **Borophenes.** Two-dimensional boron clusters with hexagonal vacancies can be viewed as motifs to produce borophenes with different hole densities and hole patterns. The yellow frame highlights the single unit structure that is periodically repeated in two dimensions. **a** | Borophene formed from  $B_{36}$  (REF. 48). **b** | Borophene formed from  $B_{35}$  (REF. 49). **c** | Borophene formed from  $B_{35}$  with a different hole pattern<sup>49</sup>.

Ag(111) are likely to have the  $\beta_{12}$  and  $\chi_3$  structures<sup>67,86,87</sup>, which both feature hexagonal vacancies<sup>81</sup>. These conclusions are in line with theoretical calculations, which suggest that borophenes with hexagonal vacancies are more stable than those presenting a close-packed and corrugated triangular lattice both in free-standing layers<sup>8,9,81,82</sup> and on silver substrates<sup>85–89</sup>. An interesting substrate-induced undulation of the  $\beta_{12}$  borophene on Ag(111) was recently predicted and observed experimentally<sup>87</sup>. The rippled configuration of the borophene atomic structure results from the surface morphology of the substrate and suggests potential for increased mechanical flexibility. Borophenes represent a new class of 2D materials with many interesting potential properties, such as graphene-like metallic character as Dirac fermion charge carriers, excellent elasticity with ideal mechanical strength<sup>88–92</sup> and relatively high-temperature superconductivity<sup>93–96</sup>.

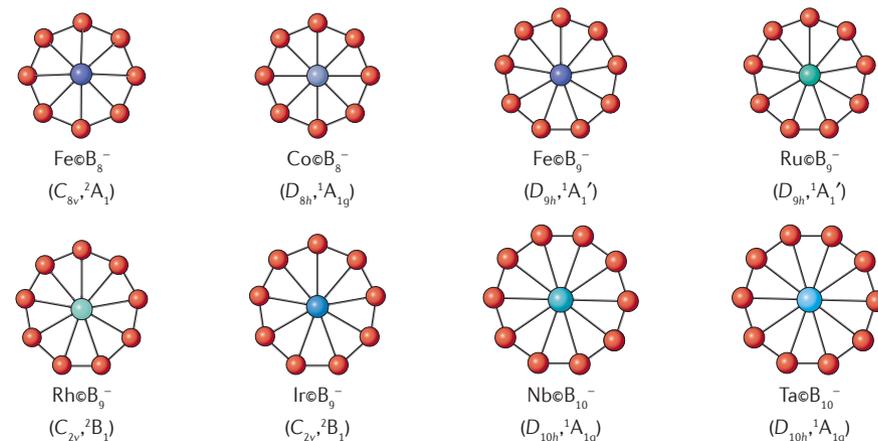
### Metal-doped boron clusters

Doping boron clusters with metal atoms provides a means to expand the potential nanostructures that can be constructed from boron. Unlike valence-perfect carbon, the electron deficiency of boron implies that its clusters would be much more susceptible to metal doping, potentially leading to new structures, bonding and tunable properties. Several metal-doped boron clusters have been characterized by joint PES and computational studies, from the metal-centred borometallic wheels ( $M\textcircled{B}_n^-$ ,  $n=8–10$ )<sup>52–56</sup> to sandwich-type clusters<sup>97–103</sup> and drum-type structures<sup>57–59</sup> (FIG. 3). In particular, the recent observation of the planar  $\text{CoB}_{18}^-$  and  $\text{RhB}_{18}^-$  clusters with the metal dopant as a part of the 2D boron network suggests the tangible possibility of metalloborophenes<sup>60,61</sup>.

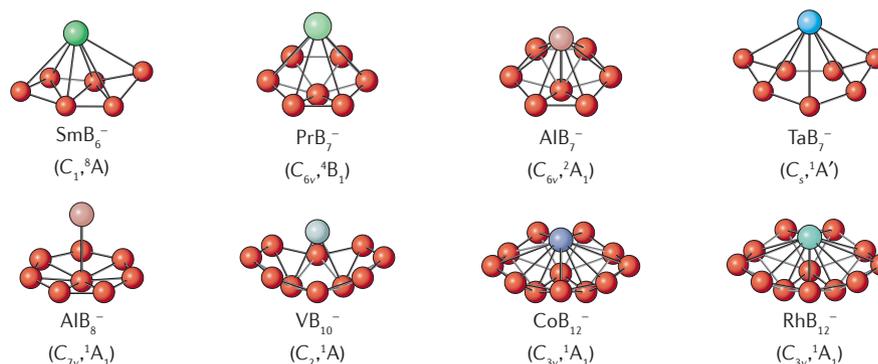
### Small metal-doped boron clusters $M\textcircled{B}_n^-$

Inspired by the highly symmetric doubly aromatic  $B_9^-$  boron wheel or  $B\textcircled{B}_8^-$ , which consists of a central boron atom in a  $B_8$  ring<sup>24</sup> (FIG. 1), a design principle was proposed in which the central boron atom would be replaced by a metal atom to create similar doubly aromatic borometallic clusters<sup>52,104</sup>. Initially, a series of highly stable transition metal-centred monocyclic boron rings  $M\textcircled{B}_n^-$  (with  $n=8–10$ ) were produced<sup>52–56</sup>, including the record 10-coordinated tantalum and niobium for 2D systems<sup>54</sup> (FIG. 3). Subsequently, larger  $\text{CoB}_{12}^-$  and  $\text{RhB}_{12}^-$  clusters were found to exist in half-sandwich-type structures with the quasi-planar  $B_{12}$  moiety coordinated to the

### Metal-centred monocyclic rings



### Half-sandwich structures



### Metal-centred tubular structures

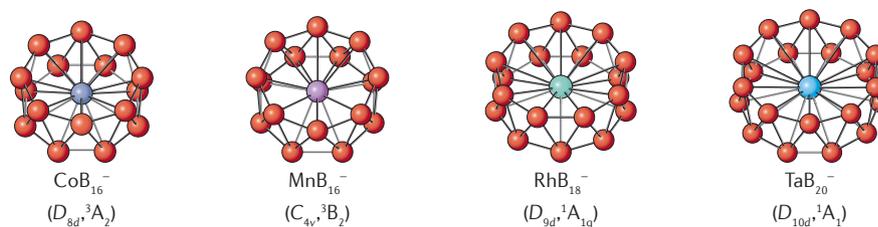


Figure 3 | **Metal-doped boron clusters.** Metal-centred monocyclic rings<sup>52–56</sup>, half-sandwich type structures<sup>97–103</sup> and metal-centred tubular structures<sup>57–59</sup> are three classes of metal-doped boron clusters that have been observed experimentally. For each structure, the point group symmetry and electronic state are reported.

metal atom<sup>100</sup> (FIG. 3). The  $\text{FeB}_{14}^-$  and  $\text{FeB}_{16}^-$  clusters were studied computationally and predicted to be arranged in drum-type structures<sup>105,106</sup>. The first doped drum-type boron clusters to be investigated jointly by PES and theoretical calculations were  $\text{CoB}_{16}^-$  and  $\text{MnB}_{16}^-$ , which were found to be characterized by two  $B_8$  moieties sandwiching the central metal atom<sup>57,58</sup> (FIG. 3). Very recently, another joint PES and theoretical study has shown that the  $\text{TaB}_{20}^-$  cluster possesses two close-lying isomers: a  $B_2$ -capped- $\text{TaB}_{18}^-$  drum-type structure and an unprecedented  $D_{10d}$ - $\text{TaB}_{20}^-$  drum structure with a record 20-coordinated tantalum atom<sup>59</sup> (FIG. 3).

The most surprising observation was the Co-doped  $B_{18}^-$  cluster,  $\text{CoB}_{18}^-$ , which was investigated by means of PES and *ab initio* calculations<sup>60</sup>. A drum-type structure similar to  $\text{CoB}_{16}^-$  was expected, but instead a perfect 2D structure was found, in which the cobalt atom became an integral part of the planar boron network. Subsequently, the  $\text{RhB}_{18}^-$  cluster was found to exist in two isoenergetic structures<sup>61</sup>: a drum isomer (FIG. 3) and a 2D structure similar to that of  $\text{CoB}_{18}^-$ . These relatively large 2D doped boron clusters with the metal dopants as a part of the 2D boron cluster are unprecedented. The analyses of their structures and bonding suggest that infinitely large boron monolayers decorated

with metal dopants, that is, metallo-borophenes, are potentially viable. These recent findings and their implications for metalloborophenes constitute the impetus for this Perspective and are the main focus in the following.

### Cobalt as an integral part of $\text{CoB}_{18}^-$

FIGURE 4a shows the 193 nm photoelectron spectrum of  $\text{CoB}_{18}^-$ , which revealed extremely high electron binding energies compared with  $\text{CoB}_{16}^-$ , suggesting that  $\text{CoB}_{18}^-$  is an electronically stable system. Searches for minimum-energy structures using the Tsinghua Global Minimum (TGMin) method, which is based on a basin-hopping algorithm<sup>107,108</sup>, in combination with high-level calculations found that the most stable structure of the  $\text{CoB}_{18}^-$  cluster is perfectly planar with  $C_{2v}$  symmetry (insert, FIG. 4b). Conversely, the putative drum-shaped structure (insert, FIG. 4c) was found to be a much

higher-energy isomer. The simulated spectrum for the planar structure (FIG. 4b) agrees well with the experimental spectrum, as opposed to those simulated for other low-energy isomers<sup>60</sup>, providing firm evidence that the identified 2D  $\text{CoB}_{18}^-$  isomer is the most stable.

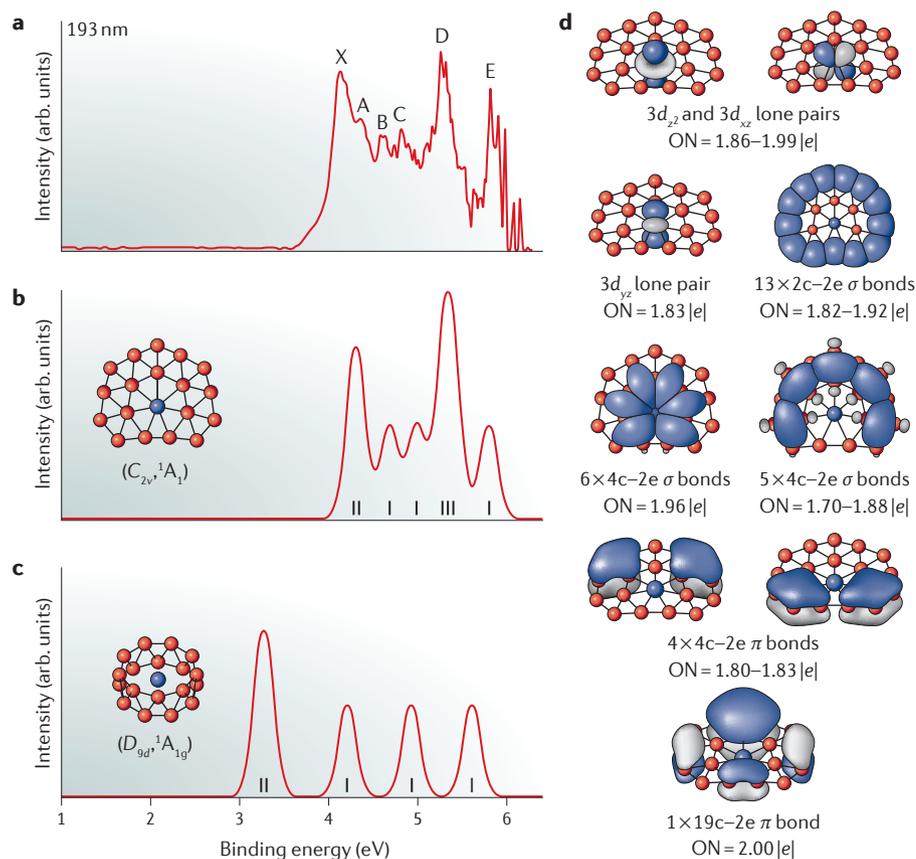
The cobalt atom in 2D  $\text{CoB}_{18}^-$  is bonded to seven boron atoms in its first coordination shell, different from the  $\text{Co}@B_8^-$  borometallic wheel<sup>52</sup> (FIG. 3). In  $\text{Co}@B_8^-$ , the peripheral B–B distances are relatively short and an eight-atom ring is necessary to accommodate the cobalt atom, which is bonded to the boron ring through delocalized covalent bonding<sup>52</sup>. In the planar  $\text{CoB}_{18}^-$  cluster, the interior B–B bonds around the cobalt atom are slightly longer; hence, a seven-atom ring creates enough room to accommodate cobalt. In fact, the cobalt atom in  $\text{CoB}_{18}^-$  is an integral part of the boron network with strong covalent interactions. The binding energy between the cobalt atom and the

$B_{18}$  host is calculated to be  $162 \text{ kcal mol}^{-1}$ , indicating the potential thermodynamic stability of  $\text{CoB}_{18}^-$ . Chemical bonding analyses using the AdNDP method<sup>44</sup> (FIG. 4d) indicate that the  $3d_{z^2}$ ,  $3d_{xz}$  and  $3d_{yz}$  orbitals of cobalt remain nearly doubly occupied as lone pairs (occupation number,  $\text{ON} = 1.83\text{--}1.99 |e|$ ); hence, there are only very weak  $\pi\text{--}\pi$  interactions between cobalt and boron. The cobalt atom interacts with the surrounding seven boron atoms mainly through the six  $4c\text{--}2e$  delocalized  $\sigma$  bonds ( $\text{ON} = 1.96 |e|$ ) (FIG. 4d). In addition to the thirteen localized  $2c\text{--}2e$  peripheral B–B bonds, there are five delocalized  $4c\text{--}2e$   $\sigma$  bonds, primarily describing bonding between the inner  $B_7$  ring and the periphery. Most interestingly, there are five delocalized  $\pi$  bonds with ten delocalized  $\pi$  electrons, which suggest unique Hückel aromaticity for the planar  $\text{CoB}_{18}^-$  cluster, similar to the bare 2D boron clusters<sup>15–17,47</sup>.

The oxidation state of the central transition metal atom in  $\text{CoB}_{18}^-$  also deserves comment, as it is relevant to the catalytic and magnetic properties of the system. The  $\text{CoB}_{18}^-$  cluster is closed shell and thus diamagnetic. Integration of the  $3d$  electrons remaining on the cobalt atom revealed a remarkably low oxidation state, cobalt(I), owing to the weak oxidizing ability or low electronegativity of boron. Conversely, the removal of an electron from the  $3d_{z^2}$  highest occupied molecular orbital results in a neutral, paramagnetic  $\text{CoB}_{18}$  cluster<sup>59</sup> and a higher oxidation state for cobalt, that is, cobalt(II). It is interesting to note that the low oxidation state of cobalt in  $\text{CoB}_{18}^-$  suggests that it would be readily oxidized, yet it exhibits a very high electron binding energy because of its closed-shell nature. The high electron binding energy may indicate possible chemical stability, which will be important for the putative metalloborophenes discussed below.

### Competition between 2D and 3D $\text{RhB}_{18}^-$

As shown above, the cobalt atom is clearly too small to form the  $D_{9d}$  drum for  $\text{CoB}_{18}^-$ . Rhodium is below cobalt in the periodic table and is slightly bigger. So, an interesting question arises: does  $\text{RhB}_{18}^-$  favour the  $D_{9d}$  drum or a 2D structure similar to  $\text{CoB}_{18}^-$ ? The photoelectron spectrum of  $\text{RhB}_{18}^-$  shows a weak feature at a low binding energy (FIG. 5a), suggesting the presence of more than one isomer<sup>61</sup>. Minimum-energy structure searches along with high-accuracy calculations resulted in two low-energy structures with total energies that differ by only  $6 \text{ kcal mol}^{-1}$  (REF. 61). Highly accurate

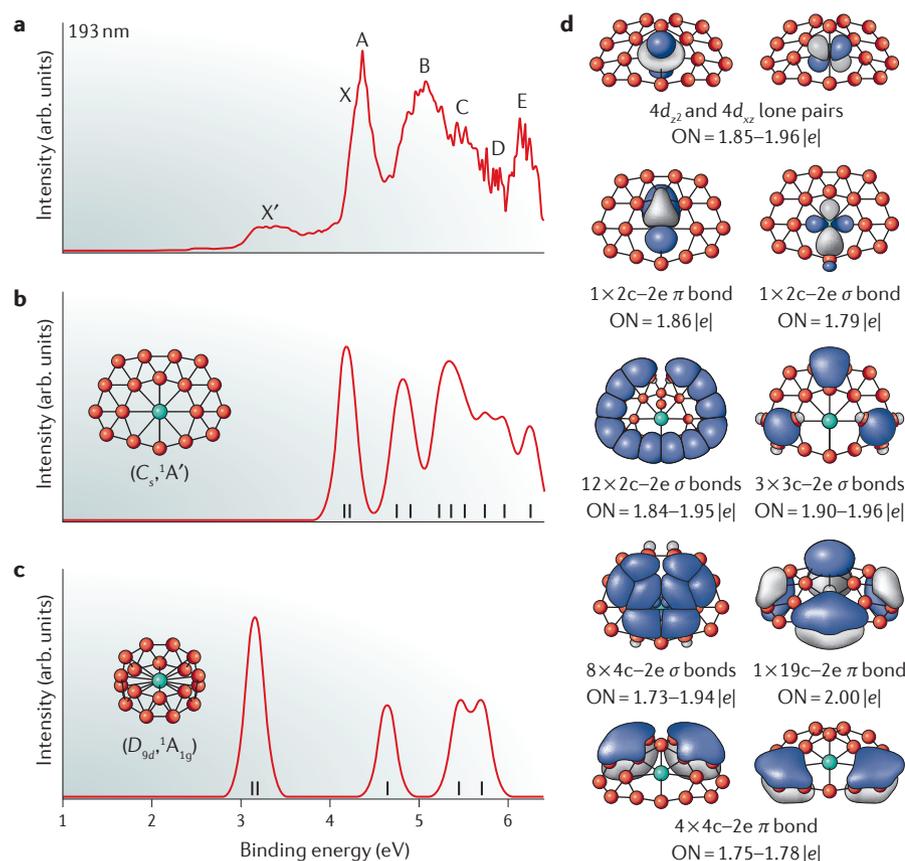


**Figure 4 | The  $\text{CoB}_{18}^-$  cluster.** **a** | Photoelectron spectrum of  $\text{CoB}_{18}^-$  measured at 193 nm (6.424 eV). The observed photodetachment bands are labelled with capital letters<sup>60</sup>. **b** | The simulated spectrum for the  $\text{CoB}_{18}^-$  minimum-energy structure corresponding to a closed shell ( $C_{2v}$ ) structure (shown in inset). The vertical bars are the computed detachment transitions<sup>60</sup>. **c** | The simulated spectrum of a higher-energy drum-like isomer ( $D_{9d}$ ) of  $\text{CoB}_{18}^-$  (shown in inset)<sup>60</sup>. **d** | Chemical bonding analyses for the global minimum  $C_{2v}$  structure of  $\text{CoB}_{18}^-$  using adaptive natural density partitioning<sup>44</sup>. Note that the five delocalized  $\pi$  bonds render  $\text{CoB}_{18}^-$  aromatic<sup>60</sup>. ON, occupation number. Adapted with permission from REF. 60, Wiley-VCH.

coupled cluster calculations (CCSD(T)) found the minimum-energy structure to be quasi-planar with  $C_s$  symmetry at finite temperatures (insert, FIG. 5b) and its simulated spectrum to agree well with the main PES features observed experimentally<sup>61</sup>. The  $D_{9d}$  drum structure (insert, FIG. 5c) was found to be a slightly higher-energy isomer at finite temperatures, and its simulated spectrum found to be consistent with the weak low-binding-energy signals detected experimentally<sup>61</sup>. The combined theoretical data for the two isomers are in good agreement with the experimental observations, providing considerable credence for the coexistence of the two isomers. As expected, the slightly larger rhodium atom does indeed stabilize the  $D_{9d}$  drum-like isomer relative to drum-like  $\text{CoB}_{18}^-$ , resulting in a smaller energy difference between the drum-like and 2D  $\text{RhB}_{18}^-$  isomers<sup>60</sup>. At 0 K and at the

CCSD(T) level of theory, the  $\text{CoB}_{18}^-$  2D isomer is 25 kcal mol<sup>-1</sup> more stable than the drum-like isomer, whereas drum-like  $\text{RhB}_{18}^-$  is 5.29 kcal mol<sup>-1</sup> more stable than the 2D isomer. However, at finite temperatures, the  $\text{RhB}_{18}^-$  2D isomer becomes more stable because of entropic effects and is indeed the main isomer observed experimentally. Two-dimensional  $\text{RhB}_{18}^-$  is slightly different from the perfectly planar  $\text{CoB}_{18}^-$  cluster. As was observed for the  $\text{Rh}\text{CoB}_9^-$  and  $\text{Co}\text{CoB}_8^-$  borometallic wheels<sup>53</sup> (FIG. 3), the larger rhodium atom in 2D  $\text{RhB}_{18}^-$  requires an eight-atom first-coordination shell, which is larger than the seven-atom one required by the cobalt atom in 2D  $\text{CoB}_{18}^-$ . However, even the eight-atom coordination shell is too small for rhodium in the 2D  $\text{RhB}_{18}^-$ . This is reflected by the out-of-plane dislocation of one of the boron atoms coordinated to rhodium, which gives rise to a penta-coordinated boron atom and the

overall convex shape of the 2D  $\text{RhB}_{18}^-$  cluster. Although the bonds in the  $\text{B}_{18}^-$  frameworks in  $\text{RhB}_{18}^-$  and  $\text{CoB}_{18}^-$  show some similarities — for example, both have ten  $\pi$  electrons with Hückel aromaticity (FIG. 5d) — the bonds between the central metal atom and the surrounding boron atoms exhibit some interesting differences. There is a fairly strong localized  $\pi$  bond between the rhodium atom and the buckled boron atom; there is also a localized Rh–B  $\sigma$  bond with the boron atom opposite the buckled atom, in addition to the delocalized  $\sigma$  bonds between rhodium and its first coordination shell. Overall, the rhodium atom displays quite strong covalent bonding with the surrounding eight boron atoms and, as occurs for cobalt in  $\text{CoB}_{18}^-$ , becomes an integral part of the 2D framework in planar  $\text{RhB}_{18}^-$ . Hence, despite the slight difference in bonding, both the cobalt and rhodium atoms become an integral part of the 2D boron network in their respective doped boron clusters.



**Figure 5 | The  $\text{RhB}_{18}^-$  cluster.** **a** | Photoelectron spectrum of  $\text{RhB}_{18}^-$  measured at 193 nm (6.424 eV). The observed photodetachment bands are labelled with capital letters<sup>61</sup>. **b** | Simulated spectrum for the  $\text{RhB}_{18}^-$  minimum-energy structure corresponding to a closed-shell ( $C_s$ ) structure (shown in inset). The vertical bars are the computed detachment transitions<sup>61</sup>. **c** | Simulated spectrum of a close-lying drum-like  $\text{RhB}_{18}^-$  isomer ( $D_{9d}$ ) (shown in inset). This isomer is present experimentally as a secondary species and is responsible for the weak detachment feature X' (REF. 61). **d** | Chemical bonding analyses for the global minimum 2D  $C_s$  structure of  $\text{RhB}_{18}^-$  using adaptive natural density partitioning<sup>44</sup>. Note that the five delocalized  $\pi$  bonds render  $\text{RhB}_{18}^-$  aromatic<sup>61</sup>. ON, occupation number. Adapted from REF. 61 under a Creative Commons license [CC BY 3.0](https://creativecommons.org/licenses/by/3.0/).

### 2D $\text{MB}_n$ clusters and metalloborophenes

The observation of large planar doped boron clusters, in which transition metal dopants become an integral part of the 2D boron network, suggests that infinitely large 2D boron monolayers doped with metals (that is, metalloborophenes) are potentially viable. Unlike graphene, borophenes exhibit remarkable structural diversity and flexibility with different patterns of hexagonal vacancies and densities in an otherwise planar triangular lattice (FIG. 2). The hexagonal vacancies are necessary to balance the electron distributions effectively, giving rise to the highly stable and planar boron monolayers<sup>8,9</sup>, as opposed to the electron-rich close-packed triangular lattice, which results in corrugations and out-of-plane distortions<sup>77–80</sup>. Appropriate metal doping into the borophene plane has similar effects to the hexagonal vacancies, potentially creating a new class of 2D materials with tunable catalytic, magnetic and optical properties. Perfectly planar  $\text{CoB}_{18}^-$  was the first experimentally confirmed cluster in which the cobalt atom was found to be covalently bonded to the boron network and may be viewed as the unitary structure for extended metalloborophenes.

FIGURE 6a presents a schematic of an extended 2D structure formed by using the planar  $\text{CoB}_{18}$  units. The  $\text{CoB}_{18}$  motif has a hepta-coordinated Co centre; thus, pentagonal-shaped vacancies inevitably appear in a periodic arrangement. In the current case, each pentagonal-shaped vacancy consists of nine atoms, two of

which are shared between two adjacent vacancies to form a nonagonal vacancy. The nonagonal-hole density of this putative metalloborophene is one nonagonal vacancy per  $\text{CoB}_{18}$  unit. However, the  $\text{RhB}_{18}$  quasi-planar cluster can serve as a better unit structure to construct a close-packed metalloborophene sheet without any vacancies over the plane, as illustrated in FIG. 6b. Although the eight Rh–B bonds in  $\text{RhB}_{18}$  are not equivalent, an idealized eight-coordinate network is viable to form a perfectly planar or quasi-planar structure without vacancies. FIGURE 6b shows a schematic structure (not optimized) of a possible metalloborophene based on  $\text{RhB}_{18}$ , in which the corrugation is due to the quasi-planarity of the 2D  $\text{RhB}_{18}$  units. It is conceivable that perfect planar building blocks will be discovered with suitable dopants. In general, planar structural units with hexagonal or octagonal symmetries are more suitable for assembling metalloborophenes without vacancies. Metal atoms with covalent radii smaller than cobalt may be candidates to form hexa-coordinated doped boron clusters, whereas metal atoms with covalent radii comparable to rhodium may be good candidates to form octa-coordinated doped boron clusters. With the available transition metal and lanthanide elements with different atomic sizes, electron configurations and oxidation states, it may be possible to discover metalloborophenes with tunable optical, catalytic and magnetic properties.

Iron-doped boron monolayers have recently been studied using DFT calculations<sup>62</sup>. Three stable iron-doped borophenes with decreasing stabilities were found, namely  $\alpha\text{-FeB}_6$ ,  $\beta\text{-FeB}_6$  and  $\gamma\text{-FeB}_6$ . The most stable form,  $\alpha\text{-FeB}_6$ , consists of octa-coordinated Fe ( $\text{Fe}@\text{B}_8$ ) with a slight corrugation of the boron plane, similar to the model shown in FIG. 6b. The second most stable form,  $\beta\text{-FeB}_6$ , can be viewed as an iron atom existing in each hexagonal vacancy of the  $\alpha$ -sheet<sup>8</sup>. The iron atoms are out-of-plane in the  $\beta\text{-FeB}_6$  structure, because the hexagonal hole is too small to include an iron atom. The least stable  $\gamma\text{-FeB}_6$  sheet is perfectly planar, consisting of a graphene-like boron layer with half of the hexagons filled with an iron atom. The  $\alpha\text{-FeB}_6$  monolayer is predicted to be metallic, whereas both the  $\beta\text{-FeB}_6$  and  $\gamma\text{-FeB}_6$  metalloborophenes are predicted to be semiconductors with considerable absorption in the visible spectral range. A more recent study<sup>63</sup> reports an  $\text{FeB}_2$  metalloborophene layer, which displays linear dispersion (that is, Dirac cones) near the Fermi level. The  $\text{FeB}_2$  layer consists of

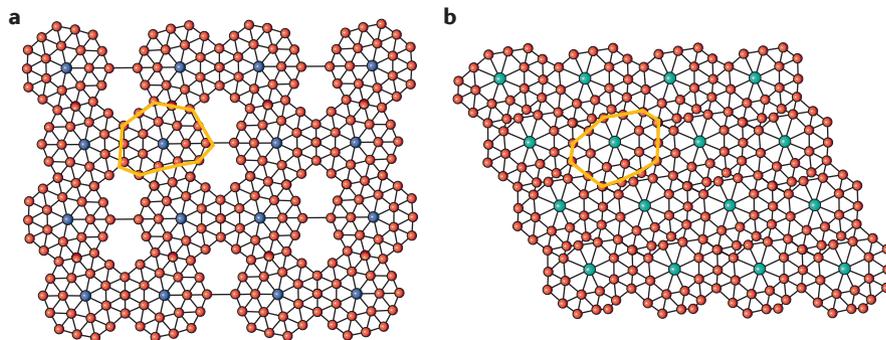


Figure 6 | **Metalloborophenes.** **a** | A schematic metalloborophene layer constructed from planar  $\text{CoB}_{18}$  units. **b** | A schematic metalloborophene layer constructed from quasi-planar  $\text{RhB}_{18}$  units. The yellow frame in each figure indicates the unit structure that is repeated in the two spatial dimensions. These are schematic (non-optimized) structures, showing the viability of metalloborophenes inspired by the 2D metal-doped boron clusters<sup>60,61</sup>.

a hexagonal boron layer with an iron atom coordinated above each hexagon out of the boron plane. Another recent theoretical study<sup>64</sup> found a new 2D  $\text{FeB}_6$  allotrope, *tri-FeB<sub>6</sub>*, which essentially consists of two  $\alpha$ -sheets sandwiching an iron layer located at each hexagonal vacancy. The *tri-FeB<sub>6</sub>* 2D layer is found to be much more stable than the monolayer metalloborophenes, as well as having greatly enhanced in-plane stiffness with unusual negative Poisson's ratio upon oxidation. These theoretical studies provide further evidence for the viability of metalloborophenes.

As there are no bulk metal borides containing layers of boron doped with metal atoms<sup>109</sup>, the putative metalloborophenes potentially represent a completely new class of 2D materials following borophenes. These new nanostructures may be synthesized through similar methods to those used for the syntheses of borophenes<sup>66,67</sup> by introducing a desired metal component during deposition on a chemically inert substrate.

### Concluding remarks and perspectives

Boron is known to be a 'rule breaker' because of its electron deficiency, resulting in chemical compounds with unusual stoichiometry and chemical bonding. Size-selected boron clusters are no exception. Through the extensive experimental and theoretical efforts of the past decade, we have discovered a remarkable structural diversity for boron clusters of different sizes. The structural scene becomes even more complicated when boron clusters are doped with metal atoms, owing to possible spin multiplicity and strong electron correlation effects. Comprehensive understanding of boron and/or metal-doped boron clusters requires state-of-the-art experimental approaches

and high-level theoretical calculations to explore the potential energy landscape and mechanisms of chemical bonding. Unlike bulk boron, the boron clusters that have been investigated experimentally are mostly found to exist in stable 2D structures, even up to fairly large cluster sizes. The discovery of the planar hexagonal  $\text{B}_{36}$  cluster was a breakthrough in the study of boron clusters, giving rise to the concept of borophene and its experimental viability. Subsequent syntheses of borophenes on silver substrates have provided macroscopic samples of this new form of 2D materials, which will stimulate intense investigations into their unusual chemical and physical properties<sup>110–113</sup>. The recent observations of transition metal-doped 2D boron clusters ( $\text{CoB}_{18}^-$  and  $\text{RhB}_{18}^-$ ) suggest the exciting possibility of metalloborophenes, which represent a new class of 2D materials with tunable chemical and physical properties. These findings have stimulated broad interest in boron clusters and nanostructures. With improving experimental sophistication and increasing computational power, it is expected that boron clusters with exotic structures and chemical bonds, or new boron-based nanostructures with tailored structures and properties, will be uncovered at an increasing pace.

Wan-Lu Li, Xin Chen and Jun Li are at the Department of Chemistry, and Key Laboratory of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China.

Tian Jian, Teng-Teng Chen and Lai-Sheng Wang are at the Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA.

Correspondence to J.L. and L.S.W.  
[junli@tsinghua.edu.cn](mailto:junli@tsinghua.edu.cn);  
[lai-sheng\\_wang@brown.edu](mailto:lai-sheng_wang@brown.edu)

doi:10.1038/s41570-017-0071-7  
 Published online 27 Sep 2017

- Lipscomb, W. N. The boranes and their relatives. *Science* **196**, 1047–1055 (1977).
- Kroto, H. W., Heath, J. R., O'Brian, S. C., Curl, R. F. & Smalley, R. E. C<sub>60</sub>: Buckminsterfullerene. *Nature* **318**, 162–163 (1985).
- Iijima, S. Helical microtubules of graphitic carbon. *Nature* **354**, 56–58 (1991).
- Geim, A. K. & Novoselov, K. S. The rise of graphene. *Nat. Mater.* **6**, 183–191 (2007).
- Oganov, A. R. *et al.* Ionic high-pressure form of elemental boron. *Nature* **457**, 863–867 (2009).
- Boustani, I. & Quandt, A. Nanotubes of bare boron clusters: *ab initio* and density functional study. *Europhys. Lett.* **39**, 527–532 (1997).
- Gindulyte, A., Lipscomb, W. N. & Massa, L. Proposed boron nanotubes. *Inorg. Chem.* **37**, 6544–6545 (1998).
- 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., 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).
- 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.* **98**, 166804 (2007).
- Prasad, D. L. V. K. & Jemmis, E. D. Stuffing improves the stability of fullerene-like boron clusters. *Phys. Rev. Lett.* **100**, 165504 (2008).
- Li, H. *et al.* Icosahedral B<sub>12</sub><sup>-</sup>-containing core-shell structures of B<sub>80</sub>. *Chem. Commun.* **46**, 3878–3880 (2010).
- De, S. *et al.* Energy landscape of fullerene materials: a comparison of boron to boron nitride and carbon. *Phys. Rev. Lett.* **106**, 225502 (2011).
- Li, F. Y. *et al.* B<sub>80</sub> and B<sub>101–105</sub> clusters: remarkable stability of the core-shell structures established by validated density functionals. *J. Chem. Phys.* **136**, 074302 (2012).
- 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).
- 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).
- Hanley, L., Whitten, J. L. & Anderson, S. L. Collision-induced dissociation and *ab initio* studies of boron cluster ions: determination of structures and stabilities. *J. Phys. Chem.* **92**, 5803–5812 (1988).
- Ruatta, S. A., Hanley, L. & Anderson, S. L. Dynamics of boron cluster ion reactions with deuterium: adduct formation and decay. *J. Chem. Phys.* **91**, 226–239 (1989).
- Hintz, P. A., Ruatta, S. A. & Anderson, S. L. Interaction of boron cluster ions with water: single collision dynamics and sequential etching. *J. Chem. Phys.* **92**, 292–303 (1990).
- Hintz, P. A., Sowa, M. B., Ruatta, S. A. & Anderson, S. L. Reactions of boron cluster ions (B<sub>n</sub><sup>+</sup>, n = 2–24) with N<sub>2</sub>O: NO versus NN bond activation as a function of size. *J. Chem. Phys.* **94**, 6446–6458 (1991).
- Zhai, H. J., Wang, L. S., Alexandrova, A. N. & Boldyrev, A. I. Electronic structure and chemical bonding of B<sub>5</sub><sup>-</sup> and B<sub>3</sub> by photoelectron spectroscopy and *ab initio* calculations. *J. Chem. Phys.* **117**, 7917–7924 (2002).
- Alexandrova, A. N. *et al.* Structure and bonding in B<sub>6</sub><sup>-</sup> and B<sub>6</sub><sup>0</sup>: planarity and antiaromaticity. *J. Phys. Chem. A* **107**, 1359–1369 (2003).
- 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).
- Alexandrova, A. N., Boldyrev, A. I., Zhai, H. J. & Wang, L. S. Electronic structure, isomerism, and chemical bonding in B<sub>7</sub><sup>-</sup> and B<sub>7</sub><sup>0</sup>. *J. Phys. Chem. A* **108**, 3509–3517 (2004).
- Kiran, B. *et al.* Planar-to-tubular structural transition in boron clusters: B<sub>30</sub> as the embryo of single-walled boron nanotubes. *Proc. Natl Acad. Sci. USA* **102**, 961–964 (2005).
- Sergeeva, A. P., Zubarev, D. Y., Zhai, H. J., Boldyrev, A. I. & Wang, L. S. A photoelectron spectroscopic and theoretical study of B<sub>16</sub><sup>-</sup> and B<sub>16</sub><sup>2-</sup>: an all-boron naphthalene. *J. Am. Chem. Soc.* **130**, 7244–7246 (2008).
- Huang, W. *et al.* A concentric planar doubly  $\pi$ -aromatic B<sub>19</sub><sup>-</sup> cluster. *Nat. Chem.* **2**, 202–206 (2010).
- Sergeeva, A. P., Averkiev, B. B., Zhai, H. J., Boldyrev, A. I. & Wang, L. S. All-boron analogues of aromatic hydrocarbons: B<sub>17</sub><sup>-</sup> and B<sub>18</sub><sup>-</sup>. *J. Chem. Phys.* **134**, 224304 (2011).
- Piazza, Z. A. *et al.* A photoelectron spectroscopy and *ab initio* study of B<sub>21</sub><sup>-</sup>: negatively charged boron clusters continue to be planar at 21. *J. Chem. Phys.* **136**, 104310 (2012).
- Sergeeva, A. P. *et al.* B<sub>22</sub><sup>-</sup> and B<sub>25</sub><sup>-</sup>: all-boron analogues of anthracene and phenanthrene. *J. Am. Chem. Soc.* **134**, 18065–18073 (2012).
- 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<sub>24</sub><sup>-</sup> cluster. *J. Chem. Phys.* **139**, 144307 (2013).
- Piazza, Z. A. *et al.* A photoelectron spectroscopy and *ab initio* study of the structures and chemical bonding of the B<sub>25</sub><sup>-</sup> cluster. *J. Chem. Phys.* **141**, 034303 (2014).
- Li, W. L., Zhao, Y. F., Hu, H. S., Li, J. & Wang, L. S. [B<sub>30</sub><sup>-</sup>]: a quasiplanar chiral boron cluster. *Angew. Chem. Int. Ed.* **53**, 5540–5545 (2014).
- Li, W. L., Pal, R., Piazza, Z. A., Zeng, X. C. & Wang, L. S. B<sub>27</sub><sup>-</sup>: appearance of the smallest planar boron cluster containing a hexagonal vacancy. *J. Chem. Phys.* **142**, 204305 (2015).
- Wang, Y. J. *et al.* Observation and characterization of the smallest borospherene, B<sub>28</sub><sup>-</sup> and B<sub>28</sub>. *J. Chem. Phys.* **144**, 064307 (2016).
- Li, H. R. *et al.* Competition between quasi-planar and cage-like structures in the B<sub>29</sub><sup>-</sup> cluster: photoelectron spectroscopy and *ab initio* calculations. *Phys. Chem. Chem. Phys.* **18**, 29147–29155 (2016).
- Luo, X. M. *et al.* B<sub>26</sub><sup>-</sup>: the smallest planar boron cluster with a hexagonal vacancy and a complicated potential landscape. *Chem. Phys. Lett.* **683**, 336–341 (2017).
- Hubert, H. *et al.* Icosahedral packing of B<sub>2</sub> icosahedra in boron suboxide (B<sub>6</sub>O). *Nature* **391**, 376–378 (1998).
- White, M. A., Cerqueira, A. B., Whiteman, C. A., Johnson, M. B. & Ogitsu, T. Determination of phase stability of elemental boron. *Angew. Chem. Int. Ed.* **54**, 3626–3629 (2015).
- Kawai, R. & Weare, J. H. Instability of the B<sub>12</sub> icosahedral cluster: rearrangement to a lower energy structure. *J. Chem. Phys.* **95**, 1151–1159 (1991).
- Boustani, I. Systematic *ab initio* investigation of bare boron clusters: determination of the geometry and electronic structures of B<sub>n</sub><sup>-</sup>, n = 2–14. *Phys. Rev. B* **55**, 16426–16438 (1997).
- Zubarev, D. Y. & Boldyrev, A. I. Developing paradigms of chemical bonding: adaptive natural density partitioning. *Phys. Chem. Chem. Phys.* **10**, 5207–5217 (2008).
- Zubarev, D. Y. & Boldyrev, A. I. Comprehensive analysis of chemical bonding in boron clusters. *J. Comput. Chem.* **28**, 251–268 (2007).
- Fowler, J. E. & Ugalde, J. M. The curiously stable B<sub>13</sub><sup>+</sup> cluster and its neutral and anionic counterparts: the advantage of planarity. *J. Phys. Chem. A* **104**, 397–403 (2000).
- Boldyrev, A. I. & Wang, L. S. Beyond organic chemistry: aromaticity in atomic clusters. *Phys. Chem. Chem. Phys.* **18**, 11589–11605 (2016).
- Piazza, Z. A. *et al.* Planar hexagonal B<sub>36</sub> as a potential basis for extended single-atom layer boron sheets. *Nat. Commun.* **5**, 3113 (2014).
- Li, W. L. *et al.* The B<sub>35</sub> cluster with a double-hexagonal vacancy: a new and more flexible structural motif for borophene. *J. Am. Chem. Soc.* **136**, 12257–12260 (2014).
- Chen, Q. *et al.* 2D B<sub>36</sub><sup>-</sup> and B<sub>37</sub><sup>-</sup> clusters with a double-hexagonal vacancy: molecular motifs for borophenes. *Nanoscale* **9**, 4550–4557 (2017).
- Zhai, H. J. *et al.* Observation of an all-boron fullerene. *Nat. Chem.* **6**, 727–731 (2014).
- Romanescu, C., Galeev, T. R., Li, W. L., Boldyrev, A. I. & Wang, L. S. Aromatic metal-centered monocyclic boron rings: Co@B<sub>9</sub><sup>-</sup> and Ru@B<sub>9</sub><sup>-</sup>. *Angew. Chem. Int. Ed.* **50**, 9334–9337 (2011).
- Li, W. L. *et al.* Transition-metal-centered nine-membered boron rings: M@B<sub>9</sub> and M@B<sub>9</sub><sup>-</sup> (M = Rh, Ir). *J. Am. Chem. Soc.* **134**, 165–168 (2012).
- Galeev, T. R., Romanescu, C., Li, W. L., Wang, L. S. & Boldyrev, A. I. Observation of the highest coordination number in planar species: decacoordinated Ta@B<sub>10</sub><sup>-</sup> and Nb@B<sub>10</sub><sup>-</sup> anions. *Angew. Chem. Int. Ed.* **51**, 2101–2105 (2012).
- Romanescu, C. *et al.* Experimental and computational evidence of octa- and nona-coordinated planar iron-doped boron clusters: Fe@B<sub>8</sub><sup>-</sup> and Fe@B<sub>9</sub><sup>-</sup>. *J. Organomet. Chem.* **721–722**, 148–154 (2012).
- Romanescu, C., Galeev, T. R., Li, W. L., Boldyrev, A. I. & Wang, L. S. Transition-metal-centered monocyclic boron wheel clusters (M@B<sub>n</sub>): a new class of aromatic borometallic compounds. *Acc. Chem. Res.* **46**, 350–358 (2013).
- 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 CoB<sub>16</sub><sup>-</sup> cluster. *Nat. Commun.* **6**, 8654 (2015).
- Jian, T. *et al.* Manganese-centered tubular boron cluster — MnB<sub>16</sub><sup>-</sup>: a new class of transition-metal molecules. *J. Chem. Phys.* **144**, 154310 (2016).
- Li, W. L. *et al.* Observation of a metal-centered B<sub>7</sub>-Ta@B<sub>18</sub><sup>-</sup> tubular molecular rotor and a perfect Ta@B<sub>20</sub><sup>-</sup> boron drum with the record coordination number of twenty. *Chem. Commun.* **53**, 1587–1590 (2017).
- Li, W. L. *et al.* The planar CoB<sub>18</sub><sup>-</sup> cluster as a motif for metallo-borophenes. *Angew. Chem. Int. Ed.* **55**, 7358–7363 (2016).
- Jian, T. *et al.* Competition between drum and quasi-planar structures in RhB<sub>18</sub><sup>-</sup>: motifs for metallo-boron nanotubes and metallo-borophenes. *Chem. Sci.* **7**, 7020–7027 (2016).
- Zhang, H., Li, Y., Hou, J., Tu, K. & Chen, Z. FeB<sub>6</sub> monolayers: the graphene-like material with hypercoordinate transition metal. *J. Am. Chem. Soc.* **138**, 5644–5651 (2016).
- Zhang, H., Li, Y., Hou, J., Du, A. & Chen, Z. Dirac state in the FeB<sub>2</sub> monolayer with graphene-like boron sheet. *Nano Lett.* **16**, 6124–6129 (2016).
- Li, J. *et al.* Global minimum of two-dimensional FeB<sub>6</sub> and an oxidation induced negative Poisson's ratio: a new stable allotrope. *J. Mater. Chem. C* **4**, 9613–9621 (2016).
- Li, J. *et al.* Voltage-gated spin-filtering properties and global minimum of planar MnB<sub>6</sub> and half-metallicity and room-temperature ferromagnetism of its oxide sheet. *J. Mater. Chem. C* **4**, 10866–10875 (2016).
- Mannix, A. J. *et al.* Synthesis of borophenes: anisotropic, two-dimensional boron polymorphs. *Science* **350**, 1513–1516 (2015).
- Feng, B. *et al.* Experimental realization of two-dimensional boron sheets. *Nat. Chem.* **8**, 563–568 (2016).
- Zhao, J. *et al.* B<sub>28</sub>: the smallest all-boron cage from an *ab initio* global search. *Nanoscale* **7**, 15086–15090 (2015).
- Romanescu, C., Sergeeva, A. P., Li, W. L., Boldyrev, A. I. & Wang, L. S. Planarization of B<sub>7</sub><sup>-</sup> and B<sub>12</sub><sup>-</sup> clusters by isoelectronic substitution: AlB<sub>6</sub><sup>-</sup> and AlB<sub>11</sub><sup>-</sup>. *J. Am. Chem. Soc.* **133**, 8646–8653 (2011).
- Romanescu, C., Harding, D. J., Fielicke, A. & Wang, L. S. Probing the structures of neutral boron clusters using infrared/vacuum ultraviolet two color ionization: B<sub>11</sub>, B<sub>6</sub>, and B<sub>7</sub>. *J. Chem. Phys.* **137**, 014317 (2012).
- Czekner, J., Cheung, L. F. & Wang, L. S. Probing the structures of neutral B<sub>11</sub> and B<sub>12</sub> using high resolution photoelectron imaging of B<sub>11</sub><sup>-</sup> and B<sub>12</sub><sup>-</sup>. *J. Phys. Chem. C* **121**, 10752–10759 (2017).
- Oger, E. *et al.* Boron cluster cations: transition from planar to cylindrical structures. *Angew. Chem. Int. Ed.* **46**, 8503–8506 (2007).
- Boustani, I. Systematic LSD investigation on cationic boron clusters: B<sub>n</sub><sup>+</sup> (n = 2–14). *Int. J. Quantum Chem.* **52**, 1081–1111 (1994).
- Ricca, A. & Bauschlicher, C. W. The structure and stability of B<sub>n</sub><sup>+</sup> clusters. *Chem. Phys. Lett.* **208**, 233–242 (1996).
- Fagiani, M. R. *et al.* Structure and fluxionality of B<sub>13</sub><sup>+</sup> probed by infrared photodissociation spectroscopy. *Angew. Chem. Int. Ed.* **56**, 501–504 (2017).
- Martinez-Guajardo, G. *et al.* Unraveling phenomenon of internal rotation in B<sub>13</sub><sup>+</sup> through chemical bonding analysis. *Chem. Commun.* **47**, 6242–6244 (2011).
- Boustani, I., Quandt, A., Hernández, E. & Rubio, A. New boron based nanostructured materials. *J. Chem. Phys.* **110**, 3176–3185 (1999).

78. Evans, M. H., Joannopoulos, J. D. & Pantelides, S. T. Electronic and mechanical properties of planar and tubular boron structures. *Phys. Rev. B* **72**, 045434 (2005).
79. Kunstmann, J. & Quandt, A. Broad boron sheets and boron nanotubes: an *ab initio* study of structural, electronic, and mechanical properties. *Phys. Rev. B* **74**, 035413 (2006).
80. Lau, K. C. & Pandey, R. Stability and electronic properties of atomistically-engineered 2D boron sheets. *J. Phys. Chem. C* **111**, 2906–2912 (2007).
81. Penev, E. S., Bhowmick, S., Sadzadeh, A. & Yakobson, B. I. Polymorphism of two-dimensional boron. *Nano Lett.* **12**, 2441–2445 (2012).
82. Wu, X. *et al.* Two-dimensional boron monolayer sheets. *ACS Nano* **6**, 7443–7453 (2012).
83. Liu, Y., Penev, E. S. & Yakobson, B. I. Probing the synthesis of two-dimensional boron by first-principles computations. *Angew. Chem. Int. Ed.* **52**, 3156–3159 (2013).
84. Liu, H., Gao, J. & Zhao, J. From boron cluster to two-dimensional boron sheet on Cu(111) surface: growth mechanism and hole formation. *Sci. Rep.* **3**, 3238 (2013).
85. Zhang, Z., Yang, Y., Gao, G. & Yakobson, B. I. Two-dimensional boron monolayers mediated by metal substrates. *Angew. Chem. Int. Ed.* **54**, 13022–13026 (2015).
86. Xu, S., Zhao, Y., Liao, J., Yang, X. & Xu, H. The nucleation and growth of borophene on the Ag(111) surface. *Nano Res.* **9**, 2616–2622 (2016).
87. Zhang, Z. *et al.* Substrate-induced nanoscale undulations of borophene on silver. *Nano Lett.* **16**, 6622–6627 (2016).
88. Mannix, A. J., Kiraly, B., Hersam, M. C. & Guisinger, N. P. Synthesis and chemistry of elemental 2D materials. *Nat. Rev. Chem.* **1**, 0014 (2017).
89. Shu, H., Li, F., Liang, P. & Chen, X. Unveiling the atomic structure and electronic properties of atomically thin boron sheets on an Ag(111) surface. *Nanoscale* **8**, 16284–16291 (2016).
90. Zabolotskiy, A. D. & Lozovik, Y. E. Strain-induced pseudomagnetic field in the Dirac semimetal borophene. *Phys. Rev. B* **94**, 165403 (2016).
91. Sun, H. Li, Q. & Wan, X. C. First-principles study of thermal properties of borophene. *Phys. Chem. Chem. Phys.* **18**, 14927–14932 (2016).
92. Zhang, Z., Yang, Y., Penev, E. S. & Yakobson, B. I. Elasticity, flexibility, and ideal strength of borophenes. *Adv. Funct. Mater.* **27**, 1605059 (2017).
93. Zhao, Y. Zeng, S. & Ni, J. Phonon-mediated superconductivity in borophenes. *Appl. Phys. Lett.* **108**, 242601 (2016).
94. Penev, E. S., Kutana, A. & Yakobson, B. I. Can two-dimensional boron superconduct? *Nano Lett.* **16**, 2522–2526 (2016).
95. Xiao, R. C. *et al.* Enhanced superconductivity by strain and carrier-doping in borophene: a first principles prediction. *Appl. Phys. Lett.* **109**, 122604 (2016).
96. Gao, M., Li, Q. Z., Yan, X. W. & Wang, J. Prediction of phonon-mediated superconductivity in borophene. *Phys. Rev. B* **95**, 024505 (2017).
97. Galeev, T. R., Romanescu, C., Li, W. L., Wang, L. S. & Boldyrev, A. I. Valence isoelectronic substitution in the  $B_8^-$  and  $B_9^-$  molecular wheels by an Al dopant atom: umbrella-like structures of  $AlB_7^-$  and  $AlB_8^-$ . *J. Chem. Phys.* **135**, 104301 (2011).
98. Li, W. L., Romanescu, C., Piazza, Z. A. & Wang, L. S. Geometrical requirements for transition-metal-centered aromatic boron wheels: the case of  $VB_{10}^-$ . *Phys. Chem. Chem. Phys.* **14**, 13663–13669 (2012).
99. Li, W. L. *et al.* On the way to the highest coordination number in the planar metal-centered aromatic  $Ta@B_{10}^-$  cluster: evolution of the structures of  $TaB_n^-$  ( $n = 3 - 8$ ). *J. Chem. Phys.* **139**, 104312 (2013).
100. Popov, I. A., Li, W. L., Piazza, Z. A., Boldyrev, A. I. & Wang, L. S. Complexes between planar boron clusters and transition metals: a photoelectron spectroscopy and *ab initio* study of  $CoB_{12}^-$  and  $RhB_{12}^-$ . *J. Phys. Chem. A* **118**, 8098–8105 (2014).
101. Li, W. L. *et al.* Hexagonal bipyramidal  $Ta_2B_8^{-10}$  clusters:  $B_6$  rings as structural motifs. *Angew. Chem. Int. Ed.* **53**, 1288–1292 (2014).
102. Robinson, P. J., Zhang, X., McQueen, T., Bowen, K. H. & Alexandrova, A. N.  $SmB_6^-$  cluster anion: covalency involving *f* orbitals. *J. Phys. Chem. A* **121**, 1849–1854 (2017).
103. Chen, T. T. *et al.*  $PrB_7^-$ : A praseodymium-doped boron cluster with a Pr(II) center coordinated by a doubly aromatic planar  $\eta^7-B_5^{5-}$  ligand. *Angew. Chem. Int. Ed.* **56**, 6916–6920 (2017).
104. Romanescu, C., Galeev, T. R., Li, W. L., Boldyrev, A. I. & Wang, L. S. Geometric and electronic factors in the rational design of transition-metal-centered boron molecular wheels. *J. Chem. Phys.* **138**, 134315 (2013).
105. Xu, C., Cheng, L. J. & Yang, J. L. Double aromaticity in transition metal centered double-ring boron clusters  $M@B_{2n}$  ( $M = Ti, Cr, Fe, Ni, Zn; n = 6, 7, 8$ ). *J. Chem. Phys.* **141**, 124301 (2014).
106. Tam, N. M., Pham, H. T., Duong, L. V., Pham-Ho, M. P. & Nguyen, M. T. Fullerene-like boron clusters stabilized by an endohedrally doped iron atom:  $B_nFe$  with  $n = 14, 16, 18$  and  $20$ . *Phys. Chem. Chem. Phys.* **17**, 3000–3003 (2015).
107. Zhao, Y., Xin, C. & Li, J. TGMIn: a global-minimum structure search program based on a constrained basin-hopping algorithm. *Nano Res.* **10**, 3407–3420 (2017).
108. Chen, X., Zhao, Y. F., Wang, L. S. & Li, J. Recent progresses of global minimum searches of nanoclusters with a constraint basin-hopping algorithm in the TGMIn program. *Comput. Theor. Chem.* **1107**, 57–65 (2017).
109. Carencu, S., Portehault, D., Boissiere, C., Mezaillies, N. & Sanchez, C. Nanoscaled metal borides and phosphides: recent developments and perspectives. *Chem. Rev.* **113**, 7981–8065 (2013).
110. Rastgou, A., Soleymanabadi, H. & Bodaghi, A. DNA sequencing by borophene nanosheet via an electronic response: a theoretical study. *Microelectron. Eng.* **169**, 9–15 (2017).
111. Garcia-Fuente, A., Carrete, J., Vega, A. & Gallego, L. J. What will freestanding borophene nanoribbons look like? An analysis of their possible structures, magnetism and transport properties. *Phys. Chem. Chem. Phys.* **19**, 1054–1061 (2017).
112. Feng, B. *et al.* Dirac fermions in borophene. *Phys. Rev. Lett.* **118**, 096401 (2017).
113. Liu, X. *et al.* Self-assembly of electronically abrupt borophene/organic lateral heterostructures. *Sci. Adv.* **3**, e1602356 (2017).

#### Acknowledgements

The experimental work on size-selected boron clusters at Brown University was supported by the US National Science Foundation (Grant No. CHE-1263745). The theoretical work done at Tsinghua University was supported by the National Key Basic Research Special Funds (Grant No. 2013CB834603) and the National Natural Science Foundation of China (Grant Nos 21433005, 91426302 and 21590792) of China. The calculations were performed using supercomputers at the Computer Network Information Center, Chinese Academy of Sciences, Tsinghua National Laboratory for Information Science and Technology, and Guangzhou Tianhe-2 Supercomputing Center.

#### Competing interests statement

The authors declare no competing interests.

#### Publisher's note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

#### How to cite this article

Li, W.-L. *et al.* From planar boron clusters to borophenes and metalloborophenes. *Nat. Rev. Chem.* **1**, 0071 (2017).