

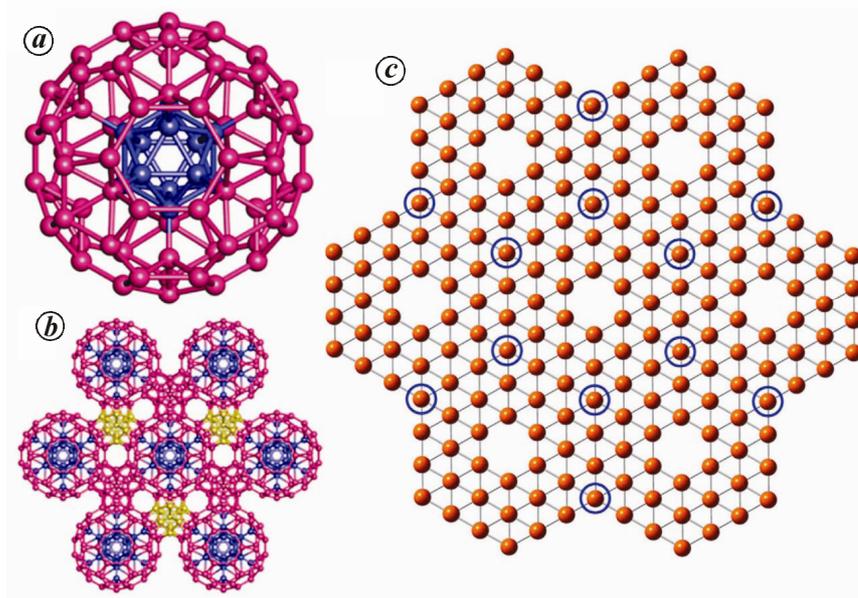
## Borophene: a new paradigm!

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The chemistry of boron-containing compounds is quite unique and incomparable to that of any other element in the periodic table. The strong tendency of boron to form 3D clusters is quite noticeable from the library of boranes and metalloboranes<sup>1</sup>. Owing to their stability, 3D-aromaticity, etc., these boron-rich compounds find important applications in medicine (e.g. BNCT or boron-neutron-capture-therapy, etc.) as well as in material research (e.g. high temperature stable materials, luminescent components, LASERs, etc.)<sup>2</sup>. On the other hand, a significant recent development in the intriguing organometallic chemistry of boron is the emergence of Frustrated Lewis acids, containing electron-deficient boron centres and their applications in catalysis<sup>3</sup>. Further, these Lewis acid-base adduct systems and simple donor-acceptor (D-A) architectures of boron-containing molecules are also of interest from as materials in optoelectronic devices<sup>4</sup>. The vast chemistry of boronic-acids as reagents and drugs is also expanding at a rapid pace<sup>5</sup>. Inorganic boron-compounds (e.g. boron-nitride (BN)) are finding importance in nano-sciences<sup>6</sup>. Last but not the least, boron-containing organic materials, e.g. triarylboranes (TABs), boron-dipyrromethenes (BODIPY) have been successfully utilized in the developments of families of bright luminescent, photostable and fine-tunable dyes, which find applications in solid-state lighting, security, forensic analysis, sensing, stimuli-responsive and light-harvesting systems<sup>7</sup>. Verily, boron-chemistry has grown by leaps and bounds and is full of surprises which continue to astound researchers. In a previous article, we had described different bonding tendencies of boron in the formation of various stable organic/organometallic compounds<sup>8</sup>. Even after two centuries of the discovery of boron, there is no consensus among chemists in describing the phase diagrams of elemental boron<sup>9</sup>. Although boron displays a large number of allotropes, only a few of them (e.g.  $\alpha$ -rhombohedral boron,  $\beta$ -rhombohedral boron,  $\gamma$ -boron and T-192) have been confirmed to be thermodynamically stable. The thermodynamically favourable  $\beta$ -boron has

tremendously complex structure, with greater than 300 atoms per hexagonal unit cell that consists of a combination of icosahedra and fused icosahedra (Figure 1). However, a phase transition from  $\beta$ -boron to other phases by cooling or annealing at ambient pressure has never been reported. However, the unresolved issues of partial occupancies (as observed by X-ray crystallography) at two different sites even of this structure has spurred a large number of theoretical investigations<sup>9</sup>. Even though our understanding of the structure of elemental boron is incomplete, the progress of boron chemistry has not ceased and continued to expand. In understanding boron, theoretical knowledge and computational approaches have contributed to a great extent<sup>1b</sup>. Electronic predictions and validations of experimental structures have often compelled experimental chemists to get back to their work benches.

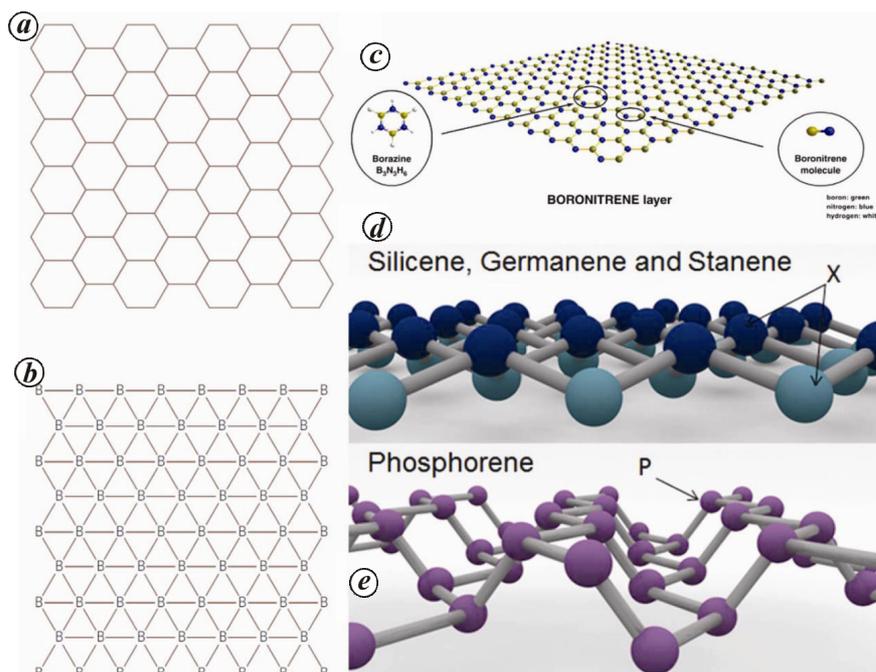
The synergistic feedback between theory and experiment has greatly enriched boron chemistry. For instance, Prasad and Jemmis<sup>10</sup> had proposed theoretical models for stabilizing fullerene-like boron clusters in 2008 and in 2014, Wang *et al.*<sup>11</sup> published the first report on the experimental observation of an all boron-fullerene. The intriguing 3D-structural features of boron and its clusters make it quite unintuitive to even stumble upon the idea of 2D boron sheets. However, in 2014, Wang *et al.*<sup>12</sup> proposed theoretical models based on experimental observations which predicted planar hexagonal B<sub>36</sub> as a potential basis for extended single-atom layer of boron sheets (Figure 1). The vacancies and the bending of the overall structure are expected to be of fundamental importance for the enhanced stability of the B<sub>36</sub> cluster<sup>12,13</sup>. Based on the results, the authors predicted that the electronic structure of the 2D boron sheets can be either metallic or semiconducting.



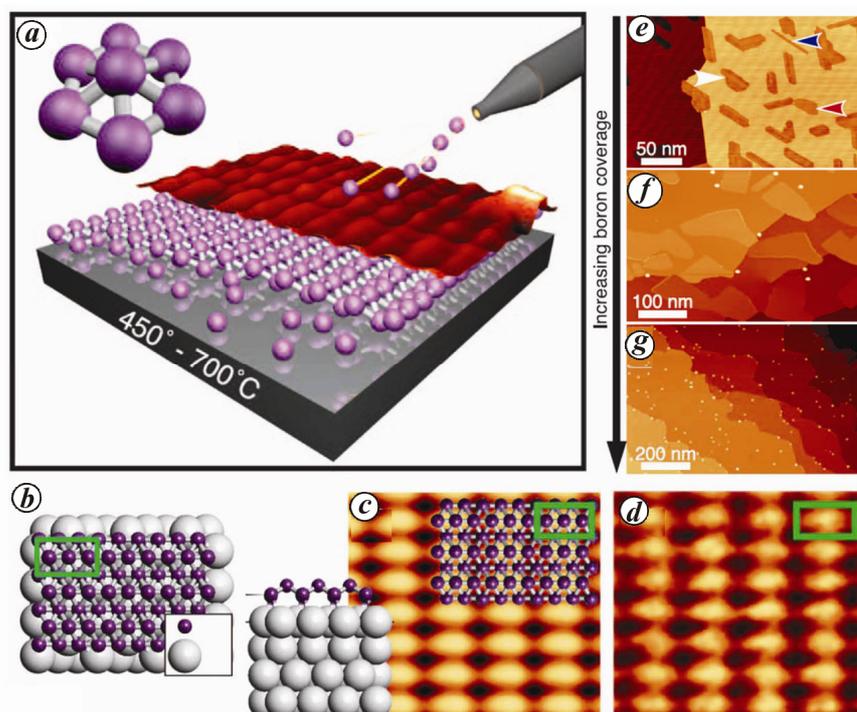
**Figure 1.** The crystal structure of  $\beta$ -rhombohedral boron in terms of B<sub>84</sub> and B<sub>10</sub> units. **a**, B<sub>84</sub> consists of a central B<sub>12</sub> icosahedron (blue) surrounded by 12 half icosahedra (pink). **b**, B<sub>84</sub> units in adjacent rhombohedral unit cells connected via B<sub>10</sub> cluster units (gold). This view is from the c-axis (perpendicular to the page). These layered structures stick to each other along this axis, and interstitial boron atoms (not drawn) lie between B<sub>10</sub> clusters connecting the layers. **c**, A schematic view of part of an extended one-atom-thick boron sheet, named borophene, as constructed from the planar hexagonal B<sub>36</sub> unit. The circles represent the apex atoms in the B<sub>36</sub> unit that are shared by three units. Removal of these atoms would lead to the a-sheet. Adapted with permission from ref. 9 (Copyright 2013, American Chemical Society) and ref. 12 (Copyright 2014, Nature Publishing Group).

This idea of achieving a 2D sheet of ordered boron atoms is quite intriguing. Current research on 2D materials such as graphene, boronitrene layers, phosphorene, silicene, or transition-metal dichalcogenides is focused on the tuning of their electronic and photonic properties combined with high-quality film syntheses (Figure 2)<sup>14</sup>. Major goals are the fabrication of semiconducting films for nanoscale electronic devices and applications to improve the performance of energy conversion and storage systems<sup>14c</sup>. The mechanical properties of graphene and MoS<sub>2</sub> are also being considered for their nano- and meso-scale tribological aspects. The prospect of exploiting the fascinating electro-dynamics of the quantum realm using two-dimensional (2D) materials has initiated a paradigm shift towards the exploration of sophisticated 2D systems<sup>14b</sup>.

The outstanding achievement in 2D materials has been the development of graphene, the hexagonal planar allotrope of carbon which has driven the hunt for high speed nano-electronics. Its isolated 2D nature gives rise to some of its striking and favourable properties that are absent in its bulk counterpart (graphite)<sup>14-16</sup>. The superior electronic properties of graphene arise because of the quantum confinement of the carriers along the plane and carriers acting as relativistic massless Dirac fermions, where they can cover remarkable distances without scattering<sup>15</sup>. Even at a free carrier concentration of zero, the presence of such Dirac fermions ensures a minimum (quantum) electrical conductivity. These remarkable aspects of graphene are projected to be the basis for the future generation of nano-electronics. However, the semi-metallic and chemically inactive nature of graphene remains an impediment in utilizing its full potential. In recent years, elemental sheets of silicon and germanium (silicene and germanene respectively) have been developed as strong contenders in the realm of 2D materials<sup>16</sup>. Although semi-metallic, silicene and germanene, unlike graphene, do not form van der Waals layered structures in their bulk phase and this has posed a major hurdle in realizing their applications. Hence, they do not exist as freestanding sheets and till now can be only synthesized as ad-layer structures on ordered substrates. Recently, phosphorene (the fundamental 2D structure that constitutes black phosphorus



**Figure 2.** Chemical structure of single layers of (a) graphene, (b) borene, (c) boronitrene. 3D views showing conformations of (d) silicene, germanene, stanene and (e) phosphorene. Adapted with permission from ref. 16a. Copyright 2010; Elsevier.



**Figure 3.** a, Schematics of distorted B<sub>7</sub> cluster and growth setup with atomic structure model and STM topography rendering. b, Top and side views of the low-energy monolayer structure (unit cell indicated by green box). c, Simulated empty states STM image ( $V_{\text{sample}} = 1.0$  V), with overlaid atomic structure and unit cell of 0.500 nm by 0.289 nm and d, Experimental STM images ( $V_{\text{sample}} = 0.1$  V,  $I_t = 1.0$  nA), with overlaid unit cell of 0.51 nm by 0.29 nm. e-g, Series of large-scale STM topography (left) images of borophene sheets. Adapted with permission from ref. 18b. Copyright 2015, The American Association for the Advancement of Science.

crystals) which exists as a freestanding 2D nano-sheet and displays exceptional semiconductor with graphene like properties, has been added to the family of elemental material<sup>17</sup>.

Very recently in 2015, Guisinger *et al.*<sup>18b</sup> first demonstrated experimental characterization of boron monolayers by scanning tunnelling microscopy and low-energy electron diffraction (Figure 3). The authors used physical vapour deposition (PVD) method to create atomically thin, borophene sheets under ultrahigh-vacuum (UHV) conditions, using a solid boron atomic source (99.9999% purity) over an atomically clean Ag(111) substrate which provided a well-defined and inert surface for borophene growth. Probing by *in situ* scanning tunnelling microscopy (STM) images showed planar structures exhibiting anisotropic corrugation consistent with first-principles structure predictions. The borophene sheets are theoretically expected to be metallic with highly anisotropic electronic properties. This anisotropy is predicted to result in mechanical stiffness comparable to that of graphene. However, thorough experimental confirmations of such properties are yet to be explored. Such unique properties are complementary to those of existing 2D materials available at current times. The lowest-energy monolayer structure is presented in Figure 3b, and is constituted from distorted B<sub>7</sub> clusters using the Aufbau principle. The freestanding sheets are expected to show instability against long wavelength transversal thermal vibrations, which would likely distort the structure of the borophene sheet upon removal from the growth substrate. This substrate-induced stability makes borophene as an in-between class of templated, covalently bound sheets with characteristics distinct from those of conventional 2D materials. The authors also demonstrated that electronic band structure calculations predict metallic conduction of the material within the 2D Brillouin zone of the relaxed, freestanding monolayer. It is notable that all known bulk boron allotropes are semi-

conductors at standard conditions, only becoming metallic at enormously high pressures. It is expected that the reactivity of the boron atoms can be beneficial in the further modifications of borophene by introducing other chemical groups or by sandwiching it between other materials to fine-tune its properties. Boron containing compounds are well known for their extreme hardness and thus they may be easier to handle than the more fragile 2D materials such as silicene and germanene.

These explorations have remarkably brought boron to the forefront of the competitive field of 2D nano-materials and have attracted the attention of physicists and material scientists. We should expect further investigations of this remarkable material leading to further surprises and enrichment of chemistry in general and boron chemistry in particular.

- (a) Wade, K., *J. Chem. Soc. D*, 1971, 792; (b) Williams, R. E., *Chem. Rev.*, 1992, **92**, 177; (c) Jemmis, E. D. and Balakrishnarajan, M. M., *J. Am. Chem. Soc.*, 2001, **123**, 4324; (d) Jemmis, E. D., Balakrishnarajan, M. M. and Pancharatna, P. D., *Chem. Rev.*, 2002, **102**, 93.
- (a) Dash, B. P., Satapathy, R., Maguire, J. A. and Hosmane, N. S., *New J. Chem.*, 2011, **35**, 1955; (b) Cerdan, L., Braborec, J., Garcia-Moreno, I., Costela, A. and Londesborough, M. G. S., *Nat. Commun.*, 2014; doi:10.1038/ncomms6958; (c) Mukherjee, S. and Thilagar, P., *Chem. Commun.*, 2016, **52**, 1070.
- (a) Welch, G. C., Juan, R. R. S., Masuda, J. D. and Stephan, D. W., *Science*, 2006, **314**, 1124; (b) Stephan, D. W. and Erker, G., *Angew. Chem. Int. Ed.*, 2010, **49**, 46.
- (a) Hudson, Z. M. and Wang, S., *Acc. Chem. Res.*, 2009, **42**, 1584; (b) Sudhakar, P., Mukherjee, S. and Thilagar, P., *Organometallics*, 2013, **32**, 3129.
- (a) Miyaura, N. and Suzuki, A., *Chem. Rev.*, 1995, **95**, 2457; (b) Trippier, P. C. and McGuigan, C., *Med. Chem. Commun.*, 2010, **1**, 183.
- (a) Corso, M., AuwKrter, W., Muntwiler, M., Tamai, A., Greber, T. and Osterwalder, J., *Science*, 2004, **303**, 217; (b)

Berner, S. *et al.*, *Angew. Chem. Int. Ed.*, 2007, **46**, 5115.

- (a) Ulrich, G., Ziessel, R. and Harriman, A., *Angew. Chem., Int. Ed.*, 2008, **47**, 1184; (b) Jakle, F., *Chem. Rev.*, 2010, **110**, 3985; (c) Loudet, A. and Burgess, K., *Chem. Rev.*, 2007, **107**, 4891; (c) Mukherjee, S. and Thilagar, P., *J. Mater. Chem. C*, 2016, **4**, 2647.
- (a) Mukherjee, S. and Thilagar, P., *Curr. Sci.*, 2013, **104**, 1601; (b) Thilagar, P., *Curr. Sci.*, 2015, **109**, 1541.
- Ogitsu, T., Schwegler, E. and Galli, G., *Chem. Rev.*, 2013, **113**, 3425.
- Prasad, D. L. V. K. and Jemmis, E. D., *Phys. Rev. Lett.*, 2008, **100**, 165504.
- Zhai, H.-J. *et al.*, *Nat. Chem.*, 2014, **6**, 727.
- Piazza, Z. A., Hu, H.-S., Li, W.-L., Zhao, Y.-F., Li, J. and Wang, L.-S., *Nat. Commun.*, 2014; doi:10.1038/ncomms4113.
- Tang, H. and Ismail-Beigi, S., *Phys. Rev. Lett.*, 2007, **99**, 115501.
- (a) Spear, J. C., Ewers, B. W. and Batteas, J. D., *Nano Today*, 2015, **10**, 301; (b) Balendhran, S., Walia, S., Nili, H., Sriram, S. and Bhaskaran, M., *Small*, 2015, **11**, 640; (c) Franklin, A. D., *Science*, 2015, **349**, 704.
- (a) Novoselov, K. S. *et al.*, *Science*, 2004, **306**, 666; (b) Novoselov, K. S. *et al.*, *Nature*, 2005, **438**, 197.
- (a) Sachdev, H., Müller, F. and Hüfner, S., *Diamond Related Mater.*, 2010, **19**, 1027; (b) Vogt, P. *et al.*, *Phys. Rev. Lett.*, 2012, **108**, 155501; (c) Wang, Q. H., Kalantar-zadeh, K., Kis, A., Coleman, J. N. and Strano, M. S., *Nat. Nanotechnol.*, 2012, **7**, 699; (d) Chhowalla, M., Shin, H. S., Eda, G., Li, L. J., Loh, K. P. and Zhang, H., *Nat. Chem.*, 2013, **5**, 263; (e) Gibney, E., *Nature*, 2015, **522**, 274; (f) Tao, L. *et al.*, *Nat. Nanotechnol.*, 2015, **10**, 227.
- Li, L. *et al.*, *Nat. Nanotechnol.*, 2014, **9**, 372.
- (a) Sachdev, H., *Science*, 2015, **350**, 1468; (b) Mannix, A. J. *et al.*, *Science*, 2015, **350**, 1513.

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