Boronic acid building blocks: tools for self assembly

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Dynamic covalent functionality has been acknowledged as a powerful tool for the construction of organised architectures, the reversible nature thermodynamically facilitates self-control and self-correction. The use of boronic acids complexation with diols and their congeners has already shown great promise in realising and developing reversible boron-containing multicomponent systems with dynamic covalent functionality. The structure-directing potential has lead to the development of a variety of self-organisation involving not only macrocycles, cages and capsules, but also porous covalent organic frameworks and polymers. Structure controls as well as remarkable synthesis are highlighted in this feature article.

1. Introduction

The first synthesis of an organoboron compound, ethylboronic acid was reported by Frankland in 1860.1 Some twenty years after dichlorophenyl borane was reported by Michaelis and Becker, which on hydrolysis allowed phenylboronic acid to be prepared.2 Subsequently Grignard reagents were used with trialkyl borates to prepare boronic acids establishing the classical synthesis we use today.3 The reversible interactions that boronic acids can take part in has seen a significant increase in the applications of boronic acid based systems in self-assembly4 sensing,5 and separation science,6 recent developments pertaining to self assembly are discussed herein.

1.1 Scope of article

In this feature article recent developments in the boronic acid arena pertaining to self assembly are surveyed. This article represents one of a two part contribution, sensors and separations facilitated by boronic acids are discussed in the partner manuscript.7 This report highlights, but is not limited to, work of the co-authors, and whilst not a comprehensive review attention is given to seminal and historically key publications as well as recent work in the area of others to set the stage for the following discussion.

2. Boron’s interactions

2.1 Boron–Diol interaction

Since boric acid has significance in determining saccharide configurations,8 it is somewhat surprising that analogous

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features were not reported with boronic acids until 1954.\textsuperscript{9} Kuivila and co-workers revealed a new compound formed on addition of phenylboronic acid to a saturated solution of mannitol, and postulated correctly that a cyclic boronic ester analogous to that observed with boric acid and polyhydroxyls was formed. Illustrating the wider implications of boronate ester formation, an interesting hypothesis has recently emerged pertaining to theories on the origins of life on Earth and the role of boron and its interactions with saccharides.\textsuperscript{10}

Publications examining the properties and synthesis of boronic acids followed those initial early reports.\textsuperscript{11} with the first quantitative investigation into the interactions between boronic acids and polyols appearing in 1959.\textsuperscript{12} Lorand and Edwards then concluded that the conjugate base of phenylboronic acid has a tetrahedral, rather than trigonal structure. Water is integral in the mechanism for the dissociation of a proton from phenylboronic acid, a hydrated proton is liberated when phenylboronic acid and water react.\textsuperscript{13–15} The pK\textsubscript{a} of phenylboronic acid are reported between \( \sim 8.7 \) and 8.9.\textsuperscript{16} potentiometric methods refined this to 8.70 in water at 25 °C.\textsuperscript{17}

Boron esters are formed from diols when they react with esters in aqueous media.\textsuperscript{12,18} It was supposed that the kinetics of this reaction were faster in the basic aqueous media where the boron is found in a tetrahedral anionic form.\textsuperscript{19} However, Ishihara reported that the rate constants for reactions of boronate ion with aliphatic diols are less than those with boronic acid.\textsuperscript{20} Six-membered rings can be formed with 1,3-diol groups, although the stability of these cyclic diesters is lower than their five-membered congeners.\textsuperscript{19,21}

### 2.2 Boron–Nitrogen interaction

Saccharide recognition \textit{via} boronic acid complex formation often relies on an interaction between o-methylphenylboronic acids (Lewis acidic) and proximal tertiary amines (Lewis basic).\textsuperscript{22} Whilst elucidating the precise nature of the amino base–boronic acid (N–B) interaction has been debated, it is clear that an interaction exists which provides two distinct advantages.\textsuperscript{17,23} Wulff proposed that an interaction between a boronic acid and proximal amine reduces the pK\textsubscript{a} of the boronic acid\textsuperscript{24} allowing binding to occur at neutral pH, thus useful for some biological scenarios. Secondly the contraction of the O–B–O bond angle upon complex formation with a saccharide and the concomitant increase in acidity at the boron atom. The increase in acidity of the already Lewis acidic boron increases the N···B interaction which in turn influences the fluorescence of nearby fluorophores. A reduction in pK\textsubscript{a} at boron on saccharide binding has the overall effect of modulating fluorescence intensity.

A study of 144 compounds with coordinative N–B bonds concluded that steric interactions along with ring strain (in the case of cyclic diesters) weakens and elongates the N–B bond, which are accompanied by a reduction in the tetrahedral geometry of the boron atom.\textsuperscript{25} N-Methyl-o-(phenylboronic acid)-N-benzylamine has been investigated separately by Wulff, Anslyn and others.\textsuperscript{17,23a,24,26}

From these analyses it was shown that the upper and lower limits of the N–B interaction must be between approximately 15 and 25 kJ mol\textsuperscript{-1} in N-methyl-o-(phenylboronic acid)-N-benzylamine.\textsuperscript{17} This agrees well with computational data which estimated the N–B interaction to be 13 kJ mol\textsuperscript{-1} or less in the absence of solvent.\textsuperscript{27} To qualify this in terms of more a recognisable bonding regime the energy of the N–B interaction, in these systems, is approximately the same as a hydrogen bond. This is much lower than the calculated and experimentally derived dative N–B bond energy of 58–152 kJ mol\textsuperscript{-1}.\textsuperscript{28} Additionally computational and potentiometric titration data highlight that the formation of intramolecular seven-membered rings should not be ignored.\textsuperscript{16,17,29} An infrared spectroscopic study of the interaction between nitrogen and boron in a related system came to a similar “tentative conclusion,”\textsuperscript{30} with an experimental rationale based on comparing two emergent peaks in IR spectra to similar peaks of known model systems. Anslyn has performed detailed structural investigations of the N–B interaction in o-(N,N-dialkyl aminomethyl) arylboronate systems.\textsuperscript{23a} From in depth \( ^{11} \)B-NMR spectroscopic measurements (and X-ray crystallographic data) it was

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shown that in aprotic media, the dative N–B bond is usually present. However, in protic solvent, insertion of the solvent into the N–B bond occurs to afford a hydrogen-bonded zwitterionic species. Wang and co-workers had also suggested that solvolysis instead of N–B bond formation could occur upon sugar binding.\textsuperscript{27} Thanks to the investigations of Anslyn\textsuperscript{23} and others\textsuperscript{17,22a,23,27} the N–B interaction can in many cases be ascribed to a hydrogen bonding interaction mediated through a bound solvent molecule.

### 2.3 Boron–Anion interaction

A small but significant contribution to anion recognition chemistry—particularly pertinent to the chemistry disclosed in this article—came in 1967 when Shriver and Ballas, identified the complex formed between a bidentate Lewis acid and a methoxide anion, similar if opposite to the situation of a central metal ion accepting electron density from a difunctional base.

The boron atom of trisubstituted boron species possesses an sp\textsuperscript{3} trigonal planar geometry with an empty p orbital perpendicular to the plane of the molecule. This feature dominates both the synthetic and receptor chemistry of boron compounds. Nucleophiles are able to interact with or donate into this vacant site, causing a subsequent change in geometry and hybridisation. The tetrahedral nature of the phenylboronate anion was confirmed by Lorand and Edwards in 1959 (see section 2.1).\textsuperscript{12}

The relatively weak Lewis acidity of the boron centre creates a wealth of synthetic chemistry but also allows boron to act as a receptor for hard anions, particularly cyanide, hydroxide and fluoride. The Bronsted acidity of boron species becomes more important when considering covalent interactions, for example with vicinal diols. The pK\textsubscript{a} of phenylboronic acid is 8.70 in water at 25°C.\textsuperscript{32} It is known that boronic acids react rapidly and reversibly with diols to afford cyclic boronate esters in non-aqueous or basic aqueous conditions.\textsuperscript{33} It has also been widely reported that boronic acids show good binding affinity with other nucleophiles such as dicarboxylic acids\textsuperscript{33a,34} and \(\alpha\)-hydroxy-carboxylic acids.\textsuperscript{32,33} The use of boron as a Lewis acid extends to formation of coordinate bonds with a wide variety of hetero-atoms including oxygen, sulfur,\textsuperscript{36} phosphorus\textsuperscript{37} and nitrogen.\textsuperscript{38} Such compounds have widespread use in organic synthesis.

The earliest example of a dative nitrogen boron interaction is the complex formed between ammonia and trimethylborane, first documented in 1862.\textsuperscript{40} One of the earliest examples of a compound containing an intramolecular N \(\rightarrow\) B bond was reported in 1968 by Dunn et al.\textsuperscript{41–43}

### 3. Boronic acids as self assembly building blocks

Boron has the potential to interact with a variety of molecular motifs, within the context of this article the key interactions are summarised below (Fig. 1).

As already discussed the fast and stable bond formation between boronic acids and diols to form boronate esters can be utilised to build molecular assemblies. In spite of the stability of boronate esters covalent B–O bonds their formation is reversible under certain conditions or under the action of certain external chemical stimuli. The reversible nature of boronate formation enables reversible molecular assembly. Self-condensation of boronic acids forming boroxines of six-membered \(\text{B}_3\text{O}_3\) ring structures is also a powerful tool for construction of molecular assemblies. Beside covalent bond forming properties of boronic acids, they also possess the potential to non-covalently interact through hydrogen bonds. Hydroxyl groups of hydrogen bond donors in boronic acids enable the formation of a variety of supramolecular self-assembly in the solid state. In addition to boronic acids, in this article, recent development in the construction of supramolecular architectures utilising spiroborate and boron-dipyrrin linkages are also discussed.

#### 3.1 Macrocycles and capsules

##### 3.1.1 Macrocycles.

Farfan, Hopfl, and Barba have designed and synthesised a series of boronic acid macrocycles through condensation reactions between boronic acids and diols assisted by boron–nitrogen interactions. They reported a variety of boronic acid macrocycles by \([2+2]\) condensation reaction of 2-salicylideneaminoethanol derivatives with phenylboronic acid derivatives.\textsuperscript{44} For example, the condensation of 1 with 2 afforded a dimeric macrocyclic compound 3 in 71% yield (Scheme 1).\textsuperscript{44b}

They demonstrated formation of a variety of dimeric macrocycles from combinations of 2-salicylideneaminoetanol derivatives and phenylboronic acid derivatives (Fig. 2).\textsuperscript{44a–d,h,i}

James, Bull and co-workers have demonstrated that reaction of 2-formyl-aryl-boronic acids with 1,2-amino alcohols

![Fig. 1 Key interactions of boron, with respect to the self-assembly discussed in this article.](image-url)
resulted in dynamic covalent self-assembly to quantitatively afford macrocyclic Schiff base boracycles containing bridging boron–oxygen–boron functionality (Scheme 2). It was also revealed that a similar self assembly protocol with chiral constituents was a versatile and robust probe for enantiomeric excess of either chiral amines or chiral diols by NMR spectroscopy and electrochemical methods.

Farfan and Hopfl reported [4+4] type tetrameric and [3+3] trimeric macrocyclic compounds by condensation reactions between boronic acids and diols assisted with boron–nitrogen interactions. Tetrameric macrocycle was obtained by condensation of 2,6-pyridinedimethanol with 3-nitrophenylboronic acid in chloroform (Fig. 3 and Scheme 3). Combination of 3-aminophenylboronic acid and salicylaldehyde derivatives afforded trimeric macrocycle compounds (Scheme 4). The structures of trimeric macrocycles from X-ray crystallographic analyses revealed that these compounds possessed a calix-like shape and inclusion of small organic molecules in the cavities were identified (Fig. 4).

Severin prepared tetrameric and pentameric boronic acid macrocycles through combining both the formation of cyclic boronate esters and intramolecular N–B interactions (Scheme 5). The [4+4] type self-assembly of phenylboronic acids with 2,3-dihydroxypyridine afforded tetrameric macrocycles as evidenced by X-ray crystallography (Fig. 5). On the other hand, the [5+5] self-assembly of phenylboronic acids with 3,4-dihydroxypyridine resulted in a pentameric macrocycle (Fig. 5). By using the [4+4] type
condensation, Severin developed an analogous strategy for the preparation of dendritic nanostructures (Scheme 6). When a THF–toluene solution of 3-formylphenylboronic acid, pentaerythritol and 1,4-diaminobenzene was heated in a flask equipped with a Dean–Stark trap, macrocycle 6 was isolated in 44% yield (Scheme 7 and Fig. 6). Nitschke reported multicomponent [4+2+2] type macrocycle formation from 2-formylphenylboronic acid, pentaerythritol and 1,4-diaminobenzene to give macrocycle 7 (Scheme 8 and Fig. 7). Iwasawa demonstrated guest induced boronic acid macrocycle formation from a racemic polyol compound containing two sets of fixed 1,2-diol units and 1,4 benzenedi(boronic acid). When equimolar amounts of these two compounds were mixed in a 2 : 1 ratio of methanol and toluene, [2 + 2] macrocycle was obtained (Fig. 8). The macrocycle included one molecule of toluene in its core. On the other hand, when a 2 : 1 mixture of methanol and benzene was employed, [3 + 3] macrocycle was obtained with two molecules of benzene inside (Fig. 8). These results suggested that formation of macrocycle depend on, or is influenced by the presence of the guest molecule. This system showed dynamic conversion of macrocyclic structure of the [2 + 2] macrocycle to the [3 + 3] macrocycle when the [2 + 2] macrocycle was suspended in...
methanol–benzene (2 : 1), and vice versa confirming dynamic behaviour.

Severin prepared rotaxanes utilising boronic esters as stoppers. The multicomponent reaction of 1,2-di(4-pyridyl)ethylene, catechol, 3,5-bis(trifluoromethyl)phenylboronic acid and 1,5-dinaphtho-38-crown-10 resulted in the formation of rotaxanes that are formed in a multicomponent assembly process from a dipyridyl linker, an arylboronic acid, catechol and crown ethers (Scheme 9).

Organometallic compounds in conjunction with metal–ligand interactions have also been exploited in the generation of boronic acid based macrocycles. The \([2+2]\) type condensation of organometallic boronic acid of 1,1'-ferrocenediboronic acid with pentaerythritol was used by Aldridge to generate a dimeric macrocycle (Scheme 10 and Fig. 9).53

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**Scheme 6** Formation of dendritic nanostructures based on \([4+4]\) type self-assembly of formylphenylboronic acids with 2,3-dihydroxypyridine.

**Scheme 7** Formation of macrocycle 6 in a \([4+2+2]\) condensation reaction.

**Scheme 8** Formation of macrocycle 7 by a \([4+2+2]\) condensation reaction.

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Fig. 6 Crystal structure of macrocycle 6.

Fig. 7 Crystal structure of macrocycle 7.
Dreos prepared macrocycles by condensation reactions between boronic acids and diols assisted by metal–ligand coordination interactions. An organobis(dimethylglyoximato) cobalt(III) complex \([\text{Co(CH}_3\text{)(dmgH)_2L}]\) known as organocobaloxime was used as a building block of boronate ester macrocycles. A condensation reaction between the organocobaloxime and 4-pyridinylboronic acid afforded \([2+2]\) type macrocycles. On the other hand, a condensation reaction between the organocobaloxime and 4-pyridinylboronic acid resulted in formation of a \([3+3]\) type macrocycle (Scheme 11 and Fig. 10).

Severin also showed how metal–ligand coordination could assist boronic acid based macrocycle formation, an impressive twelve building blocks were cyclised in this manner. When a THF–benzene solution of 3-aminophenylboronic acid, pentaerythritol, 3-chloro-4-formylpyridine and \([\text{ReBr(CO)}_5]\) were heated in a flask equipped with a Dean–Stark trap, a macrocycle was isolated in 58% yield (Scheme 12 and Fig. 11).

### 3.1.2 Molecular capsule

Boronate esterification can be utilised in the construction of capsule structures which display three dimensional cavities. Kubo and co-workers have described ion pair-driven heterodimeric capsule formation. The system consists of cyclotricatechylene and a boronic acid-appended hexahomotrioxacalix[3]arene. The two components do not interact with each other until \(\text{Et}_4\text{NOAc}\) is added to the solution. On addition of \(\text{Et}_4\text{NOAc}\) quantitative capsule formation by boronate esterification is observed. The self-assembly process is a direct result of anion directed boronate ester formation and the presence of the \(\text{Et}_4\text{N}^+\) template. Reversible boronate esterification also allowed for

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**Fig. 8** Formation of \([2+2]\) macrocycle in methanol–toluene (2:1) and \([3+3]\) macrocycle in methanol–benzene (2:1).

**Scheme 9** Synthesis of a rotaxane from a multicomponent reaction.

**Scheme 10** Formation of a metal containing macrocycle 8.

**Fig. 9** Crystal structure of metal containing macrocycle 8.
selective control of capsule formation as a function of pH (Scheme 13).

Kobayashi et al. have investigated the reaction of a bowl-shaped tetraboronic acid with a bis catechol linker. Upon heating a suspension of bowl-shaped tetraboronic acid and bis catechol linker in chloroform, a molecular cage was obtained in quantitative yield. The capsule contains one molecule of a guest such as 4,4'-disubstituted-biphenyl or 2,6-disubstituted-anthracene derivative in a highly selective recognition event. Kinetic studies of guest encapsulation using 2D EXSY analysis as well as structural analysis of a complex suggested a partial linker dissociation mechanism for guest uptake and release into and out of the host ensemble. On/off control of capsule formation with guest encapsulation by removal and addition of methanol was also demonstrated (Scheme 14).

Nitschke reported formation of a molecular cage 12 by reaction of 2-formylphenylboronic acid $m$-xylylenediamine and cyclotricatechylene in a $[6+3+2]$ reaction in deuterated DMF evidenced by in situ NMR experiments (Scheme 15).

Severin also reported multicomponent assembly of boronic acid based molecular cage in a $[6+3+2]$ reaction. When 4-formylphenylboronic acid, pentaerythritol and tris (2-aminoethyl)amine were heated in a flask equipped with a Dean–Stark trap, molecular cage 13 was formed in 82% yield (Scheme 16).

Severin reported solvent-free syntheses of two molecular cages. They were obtained by polycondensation of eleven building blocks in a ball mill. When 4-formylphenylboronic acid, pentaerythritol, and 1,3,5-trisaminomethyl-2,4,6-triethylbenzene were heated for 2 h in ethanol using a Dean–Stark trap, the corresponding molecular cage was isolated in 54% yield. On the other hand, when formylboronic acid was ball-milled with the tetaol and the triamine for 1 h at 20 Hz, cage 14 was formed almost quantitatively and was isolated in 94% yield after an
additional heating step to remove the generated water. Similarly, larger cage 15 was isolated in 71% yield after ball-milling for 1 h and subsequent heating (Scheme 17).50

Guest induced boronic acid molecular cage formation was also demonstrated by Iwasawa et al.57 When a racemic tetraol and 1,3,5-benzenetri(boronic acid) were mixed in methanol at room temperature, a cage structured 3:2 complex of tetraol and triboronic acid (homo-[3+2]) was obtained. When the homo-[3+2] was crystallised by the slow vapor diffusion of n-pentane into a toluene solution of homo-[3+2], the complex included one molecule of toluene at its core (Scheme 16). Whereas, when 13 equivalents of m-xylene or o-xylene were employed as a guest molecule, hetero-[3+2], the diastereomer, was obtained (Scheme 18).

3.1.3 Boroxine based molecular self-assembly. Boroxines58 are six-membered B₃O₃ ring structures formed by self-condensation reaction of three boronic acids (Scheme 19) and have been attracting attention as a platform for molecular assemblies. In the recent progress of boroxine chemistry, structural and functional properties have been reviewed by Korich and Iovine.59 as such only structural variations of boroxine based molecular assemblies and their functional properties are discussed here. After Snyder et al. reported the synthesis of a 1:1 complex of triphenyl boroxine and pyridine (Scheme 20),60 a variety of C₃-symmetric molecular assemblies²³,6¹ including dendritic6² and rotaxane6³ structures have been reported that include and rely on boroxine formation.

Scheme 13  Amine-triggered molecular capsules via dynamic boronate esterification.

Scheme 14  Formation of capsule from bowl-shaped tetraboronic acid and biscatechol linker and on/off control of capsule formation with guest encapsulation by removal/addition of methanol.
Scheme 15  Formation of the molecular cage 12 in a [6 + 3 + 2] reaction.

Scheme 16  Formation of the molecular cage 13 in a [6 + 3 + 2] reaction, and its crystal structure.

Scheme 17  Formation of the molecular cage 14 and 15 in a [6 + 3 + 2] reaction in a ball mill, and their crystal structures.

Scheme 18  Guest-induced selective formations of homo-[3 + 2] and hetero-[3 + 2].

Scheme 19  Formation of boroxine by condensation of three boronic acids.
Anslyn and co-workers synthesised a boroxine from $\alpha$-(pyrrolidinylmethyl)phenylboronic acid, a similar boroxine was also prepared by Bosch et al.\textsuperscript{64} The crystal structure of the boroxine revealed that two of the three boron atoms adopt a tetrahedral configuration with the pyrrolidinyl nitrogen atoms coordinated. The other boron center adopts a trigonal planar configuration, with nitrogen atom left unbound (Scheme 21).

On the other hand, a boroxine formed by self-condensation reaction of 2-($N$-ferrocenylmethyl-$N$-methylaminomethyl)phenylboronic acid revealed that all boron atoms adopt a tetrahedral configuration with the nitrogen atoms coordinated (Scheme 22).\textsuperscript{65}

Iovine reported hetero-arylboroxines, which were synthesised by condensation reaction of ortho-($N$, $N$-dimethylaminomethyl)-phenylboronic acid with two molar equivalents of arylboronic acids (Scheme 23).\textsuperscript{61f}

Based on boroxine formation, a variety of unique molecular assemblies have been developed. Iovine synthesised a series of dendritic structured phenylacetylene boroxine core compounds. More recently, construction of rotaxane\textsuperscript{63} and cage\textsuperscript{61g} structures based on boroxines have been reported (Fig. 12).

The functional properties of several boroxine based $C_3$-symmetric molecular assemblies have been studied. The Lewis acidic property of the boroxine ring has led to this class of molecular assembly being studied as anion conductive materials, in batteries for example.\textsuperscript{66} Triboroxines have also been investigated as non-linear optical materials, since there is conjugation between peripheral aryl groups via the planar boroxine core and the electron deficient property of boroxine.\textsuperscript{67}

### 3.1.4 Supramolecular aggregations triggered by formation of boronate esters

Supramolecular structures can be also constructed from molecular self-assembly of boronate esters, whereby boronate esterification triggers molecular self-assembly. Since formation of boronate ester occurs rapidly and is a robust, supramolecular self-assembly tool boronate esters can be easily prepared \textit{in situ} by mixing boronic acids and diol compounds (Scheme 24).

Shinkai and co-workers prepared a series of boronic acids having long alkyl chains (Fig. 13).\textsuperscript{21a,68} They investigated the self-assembled monolayers of the boronic acids at the air-water interface. The monolayers selectively respond to saccharides in the subphase. These results indicated that formation of boronate esters led to molecular self-assembly.

After that, Shinkai demonstrated that a variety of supramolecular aggregations of boronic acids were induced by boronate esterification.\textsuperscript{69} A series of dye molecules bearing boronic acid groups were synthesised for this aim (Fig. 14). When certain saccharides were added to aggregations of nonchiral dyes such as 16 and 17, chiral supramolecular aggregation was induced by boronate esterification of boronic acids with saccharides which were monitored by CD spectroscopy.

The formation of supramolecular chiral fibres by complexation of amphipilic boronic acids with saccharides was also reported.\textsuperscript{70} Boronic acid appended amphipilic azobenzenes and porphyrins formed fibrous structures upon complexation of saccharides. Furthermore gelation was observed when certain saccharides were added to a boronic-acid-appended chiral amphiphile (Fig. 15) in solution, while this molecule precipitated in the absence of saccharides.\textsuperscript{71}
Electron microscopic observations of the gels revealed formation of nanoscale helical strings.

Boronate esterification triggered gelation was also observed when a cholesterylboronic acid (Fig. 16) was employed. This molecule forms gels in a variety of solvents by complexation with certain saccharides.

Supramolecular structures based on boronic acids were triggered not only by saccharides but also other diol compounds. Shinkai synthesised a bolaamphiphilic compound bearing two boronic acid groups at the two ends (18, Fig. 17). The bolaamphiphile is insoluble in many solvents, however boronate esterification of this molecule with chiral diols afforded new amphiphiles end-capped with the chiral substituents. The resultant end-capped 19 and 20 formed fibrous super-structures that acted as gelators of organic solvents. These results indicate that a variety of diol compounds can lead boronic acids to form supramolecular structures by boronate esterification.

Fig. 12 Structures of dendritic, rotaxane and cage structures based on boroxine formation.

Fig. 13 Molecular structures of boronic acids having long alkyl chains for forming monolayers at the air–water interface.

Fig. 14 Molecular structures of chromophoric boronic acids 16 and 17.

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Electron microscopic observations of the gels revealed formation of nanoscale helical strings.

Boronate esterification triggered gelation was also observed when a cholesterylboronic acid (Fig. 16) was employed. This molecule forms gels in a variety of solvents by complexation with certain saccharides.

Supramolecular structures based on boronic acids were triggered not only by saccharides but also other diol compounds. Shinkai synthesised a bolaamphiphilic compound bearing two boronic acid groups at the two ends (18, Fig. 17). The bolaamphiphile is insoluble in many solvents, however boronate esterification of this molecule with chiral diols afforded new amphiphiles end-capped with the chiral substituents. The resultant end-capped 19 and 20 formed fibrous super-structures that acted as gelators of organic solvents. These results indicate that a variety of diol compounds can lead boronic acids to form supramolecular structures by boronate esterification.

Fig. 12 Structures of dendritic, rotaxane and cage structures based on boroxine formation.

Scheme 24 Induction of supramolecular aggregations upon formation of boronic esters.

Fig. 13 Molecular structures of boronic acids having long alkyl chains for forming monolayers at the air–water interface.

Fig. 14 Molecular structures of chromophoric boronic acids 16 and 17.
Barboiu prepared G-quartet-type supramolecular superstructures from a macromonomeric guanosine dimer.\textsuperscript{74} A bisiminoboronic macromolecule \textsuperscript{21} was synthesised by reacting 2-formylphenylboronic acid with bis(3-aminopropyl) polytetrahydrofuran (Scheme 25). Boronic esterification between the bisiminoboronic and guanosine afforded macromonomeric guanosine dimer \textsuperscript{22} and resulted in polymeric membrane films in the presence or absence of potassium chloride, respectively (Scheme 25).\textsuperscript{74} The macromonomeric guanosine dimer formed H-bond ribbon-type superstructure of the quinine moieties in the film in the absence of potassium chloride. In the presence of potassium chloride self-assembly of the macromonomeric guanosine dimer afforded G-quartet-type supramolecular superstructure by K\textsuperscript+ ion templating (Fig. 18). The G-quadruplex ordered membrane materials contribute to the fast electron/proton transfer by the formation of directional conduction pathway. The G-quartet membrane exhibited different cation transport behavior for Na\textsuperscript+ and K\textsuperscript+.

Kubo developed a chemical stimuli-responsive supramolecular organogel using boronate ester-substituted cyclotricatehylene. The gelator was synthesised by reacting boronic acid with cyclotricatehylene (Scheme 26).\textsuperscript{75} The structure-directing property of the boronic acid-diol interactions is responsible for the shuttlecock-shaped structure of \textsuperscript{23}, which led to the gelation of several solvents (Fig. 19). The distribution control of trigonal and tetrahedral boronate esters allows phase transition \textit{via} chemical stimulus such as anion and amine (Fig. 19).

3.1.5 \textbf{Other types of supramolecular self-assembly based on boronic acid.} The hydrogen bonding properties of boronic acid have also been utilised in the formation of molecular assemblies in solution and the solid state (Scheme 27).\textsuperscript{32} Anslyn reported formation of boronic acid dimers through hydrogen bonding. Crystals of boronic acid dimers were prepared by diffusing pentane or hexane into concentrated chloroform solutions. In the crystals of boronic acids \textsuperscript{24} and \textsuperscript{25}, these molecules dimerised through hydrogen bonds between the trigonal planar boronic acid moieties. In these crystal structures, the N–B dative bond is not observed, the nitrogen atoms interact with boronic hydroxyl groups through hydrogen bonding (Scheme 28).

Sporzyński reported formation of boronic acid dimers in the solution and solid state.\textsuperscript{76} Phenylboronic acids with polyoxaalkyl substituents at the \textit{ortho} positions were synthesised and crystallised. The crystal structures of these boronic acids dimers (26) displayed oxygen atoms which interact with boronic hydroxyl groups through hydrogen bonds in addition to hydrogen bonds between boronic acid moieties (Scheme 29).
Tetraboronic acids 27a and 27b have four –B(OH)2 groups oriented tetrahedrally with cores derived from tetraphenylmethane and tetraphenylsilane respectively. Crystallization produces isostructural diamondoid networks held together by hydrogen bonding of the –B(OH)2 groups, in accord with the tendency of simple arylboronic acids to form cyclic hydrogen-bonded dimers in the solid state (Scheme 30). Five-fold interpenetration of the networks is observed.

Strongin reported hydrogen-bonded supramolecular solid-state networks comprised of a tetraarylboronic acid resorcinarene. When 28a is recrystallised from 9:1 MeOH:EtOH, partial esterification takes place to give compound 28b, the corresponding half methyl ester, which forms an infinite two-dimensional array (Fig. 20). Each molecule participates in twelve hydrogen bonds with other macrocycles.

Seetha-Lekshmi reported supramolecular assemblies of phenylboronic acids and bipyridine compounds in the solid state (Fig. 21). Self-assembly of 4-methoxyphenylboronic acids with 4,4′-bipyridine was observed due to the formation of hydrogen bonds between nitrogen atoms and the boronic hydroxyl groups.

Supramolecular hydrogen bonds of boronic acids were also generated from hydrogen bonds between boronic acid groups and carboxylate groups. Supramolecular hydrogen
networks were observed in the crystals obtained from an aqueous methanol solution of a monosodium salt of 4-carboxyphenylboronic acid and Co(NO$_3$)$_2$·6H$_2$O (Scheme 31). In the crystals, molecular tapes of hydrogen bonding between the boronic acids and the carboxylates are observed. Interestingly, there is no coordination bond between the boronic acid and Co(II) ions. Instead, the Co(II) ions form a hexahydrate by coordinating to six water molecules. The coordinating water molecules were further associated with the boronic acid tapes through hydrogen bonds.

### 3.1.6 Supramolecular structures via spiroborate linkage and other boron containing linkages

In recent years boronic esterification has been attracting much attention as a mode of linkage for the synthesis of molecular assemblies. Spiroborate linkage and other boron containing linkage have also been utilised for the construction of supramolecular assemblies. Spiroborate linkage is a class of boron containing bond between borax and diols.$^{12,81}$ In the spiroborate system, one borate binds two diol molecules to form a spiroborate linkage (Scheme 32).$^{12,81}$
Kameta and Hiratani synthesised spiroborate based supramolecular architectures that exhibit anion recognition and sensing properties.82 The molecules were synthesised by forming spiroborate bonds between B(OH)$_3$ and catechol ligands having plural hydrogen bonding sites (Scheme 33). The resultant receptor 29a showed selective binding to H$_3$PO$_4^-$ accompanied with colour change of solution from colourless to yellow in acetonitrile. Anthracene appended receptor 29b shows an excimer emission selectively accompanied with capture of anions.

Wuest synthesised simple molecular assemblies by reacting boric acid with 2,2'-dihydroxybiphenyl in the presence of various cations.83 In the spiroborate formation, spiroborate 30 favors chiral rather than meso structures, a flattened $D_2$ geometry was observed (Scheme 34).

Robson synthesised a macrocyclic square by utilising spiroborate linkages.84 Reaction of 31 with B(OMe)$_3$ and triethylamine in methanol at 160 °C afforded a square macrocycle (Scheme 35). The crystal structure revealed the highly symmetric nature of the macrocyclic structure.

Yashima and Furusho synthesised spiroborate-based double-helical supramolecular architectures 33 by using ortho-linked oligophenols 32 as ligands (Scheme 36).85 It was shown that sodium ions can trigger the reversible anisotropic twisting of an enantiomeric double-stranded helicate (Scheme 37).85 A helicate consisting of two tetraphenol strands bridged by two spiroborate groups sandwiches a sodium ion. On
removal of the central sodium by adding a [2.2.1] cryptand to the solution, the double helicate expands. Crystallographic and nuclear magnetic resonance studies reveal that the expanded helicate is over twice as long as the initial contracted molecule. This anisotropic extension–contraction process is reversibly triggered by the successive addition and removal of sodium ions in solution.

Danjo and Yamaguchi have designed and prepared $D_3$-symmetric macrocycles via spiroborate linkages, that exhibit molecular recognition behavior. The 3:3 self-assembly of 2,2',3,3'-tetrahydroxy-1,1'-binaphthyls and boric acids resulted in macrocycles evidenced by X-ray crystallography, where a dual host–guest interaction is observed (Scheme 38).

Nabeshima prepared novel boron containing macrocyclic assemblies via boron–dipyrin complexation (Scheme 39). Dipyrin 37 was prepared from a protected catechol-OMe precursor which was synthesised via acid catalysed condensation of 2-phenylpyrrole and 2,3-dimethoxybenzaldehyde followed by oxidation. The reaction of 37 with $\text{BCl}_3$ in refluxing toluene gave a mixture of oligomers which upon permeation chromatography gave 38, 39 and 40. Compound 38 is able to complex alkali-metal ions of $\text{K}^+$, $\text{Rb}^+$, and $\text{Cs}^+$ in organic solvent with the association constants for 1:1 complexation of $1.5 \times 10^4 \text{ M}^{-1}$, $5.7 \times 10^4 \text{ M}^{-1}$ and $5.5 \times 10^6 \text{ M}^{-1}$, respectively.

### 3.2 Boronic acid based polymeric structures

Boronic esterification and boroxine formation have been utilised to construct polymeric structures that exhibit a variety of structural and functional properties. Such polymeric structures have been constructed through multiple boronate esterification and boroxine formations between boronic acid and diol molecules bearing multiple boronic acid moieties and/or diol moieties in each building block, respectively.

#### 3.2.1 Polymeric structures based on polymer scaffolds

Polymeric structures from boronic acids were studied by Shinkai and co-workers using boronic acid-appended polymers as building blocks. Shinkai investigated polymeric structures from boronic acids were studied by Shinkai and co-workers using boronic acid-appended polymers as building blocks.89
interactions of boronic acid-appended poly(L-lysine) with saccharides and sugar-based amphiphiles (Fig. 22). D-Fructose has a high affinity for boronic acids, when it was added to an aqueous solution of boronic acid-appended poly(L-lysine), the helix content of boronic acid-appended poly(L-lysine) increased. This indicated that the helicity was stabilised or enhanced by binding to D-fructose. Furthermore, a series of studies utilising sugar-based amphiphiles revealed that structural changes of the amphiphiles were induced by binding to boronic acid-appended poly(L-lysine).

Boronic acid polymeric structures were also prepared through boroxine formation from boronic acid functionalised polymers. Jäkle synthesised boronic acid-end-functionalised polystyrenes, the mono-functionalised polymer was converted to the three-arm structure by boroxine formation (Scheme 40). When an α,ω-boronic acid functionalised polymer was employed, polymeric networks were obtained. The polymeric structures were reversibly formed. Sumerlin synthesised homopolymers and block copolymers with boronic acid-functional end groups. Lewis base-promoted boroxine formation of the boronic acid end groups led to three-arm star polymers with boroxine junction points (Scheme 41).

3.2.2 Polymeric 1D structures

Polymeric structures can be constructed from multi-functional small molecule building blocks containing boronic acids and diols. A variety of supramolecular polymer structures have been constructed from small molecules the structural features and functional properties are discussed herein.

Shinkai and co-workers constructed a boronic acid linear polymer by polycondensation of a diboronic acid and chiral tetraol. Spectroscopic studies and theoretical calculations established that the polymeric structures possess a DNA-like helical structure (Scheme 42).

Shimizu has also used boronic acids in conjunction with glucuronamide bipoloramphiphiles to prepare self-assembled
sugar backbone polymers (Fig. 23). This system realised reversible polymer formation through tuning the pH of the aqueous solution.

Aldridge reported boronic acid based linear polymeric structure containing organometallic units by condensation of 1,1'-ferrocenediboronic acid with a meso tetrahydroxycyclooctane (Scheme 43).

Severin has developed a novel three component self-assembled polymeric system using monoarylboronic acids, 1,2,4,5-tetrahydroxybenzene and 1,2-bis(4-pyridyl)ethylene or 4,4-bipyridine, where the polymeric backbone is held together by N–B bonds. The resulting crystalline polymers are deeply coloured due to intrastrand charge-transfer transitions. However, the weak N–B interaction means the polymers are not stable in solution. It was noted that the
reversible formation of the polymer backbone could in itself be useful from a processing point of view (Schemes 44 and 45).

The reversible nature of boronate esterification was taken advantage of by Lavigne who has exploited this property to create self-healing polymers.94 A self-healing polymer was synthesised through the condensation of 9,9-dihydroxyfluorene-2,7-dibronic acid and pentaerythritol in toluene with azeotropic removal of water (Scheme 46). The length of the polymer was controlled by the ratio of each monomer and post-polymerisation processing. The molecular weight of the polymer increased under reduced pressure while exposed to hydrolytic conditions in a wet solvent. Acidic conditions led to a decrease of the polymer’s molecular weight. Furthermore, self-repair of these hydrolytically damaged materials was accomplished under reduced pressure without any other treatment.94c

Trogler prepared linear boronic ester polymers from 3',6', bis(pinacolatoboron)fluoran and pentaerythritol.95 This polymer was designed and synthesised as a self-interrogating sensor for the selective detection of H2O2 by a fluorescence-on mechanism. In this system, the fluorescent response resulted from oxidative deprotection of the boronate functionalities forming green luminescent fluorescene (Scheme 47).

Lee reported conjugated polymer sensors where oligothiophene units were linked by borasiloxane cages.96 This boron-containing conjugated polymer undergoes reversible colour change from green to orange upon exposure to volatile amines. The observed colour change was explained by involving reversible N–B dative bond formation that profoundly influences the p–π* orbital overlap (Scheme 48).
3.2.3 Polymeric 2D and 3D structures

The development of porous covalent organic frameworks (COFs) is an important area in which the boronic acid–diol interaction are beginning to play an important role. The potential applications of porous covalent organic materials include gas storage, catalysis and separation.

Ding prepared fluorescent oligofluorenes which have two boronic acid groups. In the solid state these oligomers undergo cross-linking reactions through dehydration of the boronic acid groups. The cross-linked amorphous networks showed bright photoluminescence in the solid state under UV irradiation (Scheme 49), which exhibit high thermal and morphological stability.

Yaghi has used both the formation of boronic acid trimeric anhydrides and diol esterification to generate a number of open organic frameworks. The frameworks developed by Yaghi can be broken down into two main classes either planar layered or three dimensional honeycombed. The planar layered structures are derived from the trimeric anhydride formed when phenylboronic acid is dehydrated or a cyclic ester is formed between phenyl boronic acid and hexahydroxy triphenylene. The planar layered structures are derived from the trimeric anhydride which is formed when phenylboronic acid is dehydrated or when cyclic esters between phenyl boronic acid and hexahydroxy triphenylene are formed. Porous covalent organic frameworks based on boroxine (41) were synthesised by heating of 1,4 benzenedi(boronic acid) at 120 °C for 72 h in a sealed Pyrex tube (Scheme 50). The obtained materials possesses a surface area of $S_{BET} = 711 \text{ m}^2 \text{ g}^{-1}$. Yaghi expanded this methodology by using boronic esterification between boronic acids and diol compounds. The condensation of 1,4 benzenedi(boronic acid) and 2,3,6,7,10,11-hexahydroxytriphenylene also afforded porous covalent organic frameworks (Scheme 51). This porous material (42) showed a larger surface area of $S_{BET} = 1590 \text{ m}^2 \text{ g}^{-1}$. Yaghi also prepared a series of COFs using a variety of boronic acids such as 1,3,5-benzentriboronic acid, 1,3,5-benzenetris(4-phenylboronic acid), and 4,4'-biphenyl boronic acid with surface areas of 980, 1400, and 2080 m$^2$ g$^{-1}$, respectively.

Lavigne reported the incorporation of alkyl groups in covalent organic frameworks (Scheme 52). This modification provides a simple way of tailoring the microporosity of the resultant frameworks. Modification of the pore interior with increasingly larger alkyl groups caused a decline in nitrogen uptake but an increase in the molar amount of hydrogen adsorbed into the network. This work provides a model for the systematic study of the functionalisation of microporous COFs.

Scheme 47  Synthesis of boronic acid fluoran polymer, and its turn-on detection of hydrogen peroxide vapour.

Scheme 48  Formation of borasiloxane conjugated polymer, a colourimetric sensing of volatile amine.

Scheme 49  Preparation of luminescent fluorene networks through boroxine formation in the solid state.
Three-dimensional covalent organic frameworks (3D COFs) were synthesised by targeting two nets based on triangular and tetrahedral nodes (Scheme 53). The respective 3D COFs were synthesised by condensation reactions of tetrahedral tetra(4-dihydroxyborylphenyl)methane or tetra(4-dihydroxyborylphenyl)silane and by co-condensation of triangular 2,3,6,7,10,11-hexahydroxytriphenylene.102

Yaghi also reported a robust covalent organic framework constructed from borosilicate linkages (B–O–Si) that possessed comparably high porosity and thermal stability (Scheme 54).104 After Yaghi’s reports of boronic acid based COFs, this type of construct has been developed elsewhere.105 Yaghi and Wang reported lithium-doped 3D COFs for high-capacity hydrogen storage materials.105a The group of Cooper demonstrated synthesis of covalent organic frameworks under mild conditions by adapting microwave synthesis showing rapid production of COFs 200 times faster than solvothermal methods.106

Jiang prepared boronic acid based COFs by employing pyrene-2,7-diboronic acid and boronic ester formation with 2,3,6,7,10,11-hexahydroxytriphenylene106 that exhibited blue fluorescence (Scheme 55). Jiang also prepared luminescent boroxine based COFs by self-condensation of pyrene-2,7-diboronic acid (Scheme 56).107 Furthermore, these luminescent COFs harvest visible photons and trigger photocurrent generation, and are capable of repetitive on-off photocurrent switching cycles with a large on-off ratio.

Spitler and Dichtel reported a new preparative methodology for the synthesis of boronate ester based COFs by a Lewis acid-catalysed protocol.108 This method affords COFs directly from protected catechols and aryboronic acids by in situ deprotection of protected catechols. They prepared a two-dimensional phthalocyanine COF by heating a mixture of phthalocyanine tetra(acetonide) and 1,4-phenylenediboronic acid in solution in the presence of BF₃·OEt₂ as a deprotecting agent (Scheme 57). The resultant eclipsed 2D COF displayed thermal stability to 500 °C and broad absorption bands up to the near infrared region. The presented method enables direct use of unstable...
Scheme 53 Synthesis of three-dimensional covalent organic frameworks (3D COFs), synthesised by targeting two nets based on triangular and tetrahedral nodes.\textsuperscript{102}

Scheme 54 Synthesis of covalent organic frameworks from borosilicate linkages.\textsuperscript{104}

Scheme 55 Pyrene containing boronate ester based covalent organic framework.

Scheme 56 Pyrene containing boroxine based covalent organic framework.
This feature article overviews a variety of self-assembled systems based on boron’s dynamic covalent functionality. It emerges that sophisticated design of building blocks and reaction conditions are a prerequisite for highly complex and functional architectures. In other words, judicious choice of building blocks and or templates is required. Furthermore, combination of the assembled structures with the possible change or modulation of the coordination mode of boron results in systems which are responsive to chemical-stimuli such as Lewis bases, function-controllable molecular systems have been developed, which can be employed in applications including sensors,

polyfunctional catechol reactants as building blocks for boronate ester based COFs.

4. Conclusions

This feature article overviews a variety of self-assembled systems based on boron’s dynamic covalent functionality. It emerges that sophisticated design of building blocks and reaction conditions are a prerequisite for highly complex and functional architectures. In other words, judicious choice of building blocks and or templates is required. Furthermore, combination of the assembled structures with the possible change or modulation of the coordination mode of boron results in systems which are responsive to chemical-stimuli such as Lewis bases, function-controllable molecular systems have been developed, which can be employed in applications including sensors, catalysts (nanoreactors), nano architectures, separation and delivery. For example, stimulus-controllable encapsulation is of particular interest, since it can provide insight towards the further development of molecular delivery vectors in material science. Also, the development of boronic acid-based combinatorial libraries is another appealing aspect, which led to the fabrication of a sensor array for the use in bioanalysis. There has been growing interest in such systems from material chemistry point of view.

On another front, for the furtherance of boronic acid-facilitated self-assembly and self-organisation, facile synthesis of trigonal dioxaboroles still remains to be explored. The discovery of catalysis to promote the linkage and fast exchange of the covalent bond would provide unique and varied systems in this field.

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Notes and references