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.

Boron's interactions 2.

Boron-Diol interaction 2.1

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 1954.⁹ 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.¹⁰

Publications examining the properties and synthesis of boronic acids followed those initial early reports,¹¹ with the first quantitative investigation into the interactions between boronic acids and polyols appearing in 1959.¹² 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 and water react.^{13–15} The p K_{a} s of phenylboronic acid are reported between ~8.7 and 8.9,¹⁶ potentiometric methods refined this to 8.70 in water at 25 °C.¹⁷

Boronic esters are formed from diols when they react with esters in aqueous media,^{12,18} it was supposed that the kinetics of this reaction were faster in aqueous basic media where the boron is found in a tetrahedral anionic form.¹⁹ However, Ishihara reported that the rate constants for reactions of boronate ion with aliphatic diols are less than those with boronic acid.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.^{19,21}

2.2 Boron-Nitrogen interaction

Saccharide recognition *via* boronic acid complex formation often relies on an interaction between *o*-methylphenylboronic acids (Lewis acidic) and proximal tertiary amines (Lewis basic).²² Whilst elucidating the precise nature of the amino base–boronic acid ($N \cdots B$) interaction has been debated, it is clear that an interaction exists which provides two distinct

advantages.^{17,23} Wulff proposed that an interaction between a boronic acid and proximal amine reduces the pK_a of the boronic acid²⁴ 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_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.²⁵ *N*-Methyl-*o*-(phenylboronic acid)-*N*-benzylamine has been investigated separately by Wulff, Anslyn and others.^{17,23d,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⁻¹ in N-methyl-o-(phenylboronic acid)-Nbenzylamine.¹⁷ This agrees well with computational data which estimated the N–B interaction to be 13 kJ mol⁻¹ or less in the absence of solvent.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^{-1,28} Additionally computational and potentiometric titration data highlight that the formation of intramolecular seven-membered rings should not be ignored.^{16b,17,29} An infrared spectroscopic study of the interaction between nitrogen and boron in a related system came to a similar "tentative conclusion,"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.^{23*a*} From in depth ¹¹B-NMR spectroscopic measurements (and X-ray crystallographic data) it was



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associate professor at Tokyo Metropolitan University hosted by Professor Yuji Kubo (co-author to this article). His research interests focus on catalysis and sensing. 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.²⁷ Thanks to the investigations of Anslyn^{23a} and others.^{17,23a,23d,27,31} 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^2 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).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 Brønsted acidity of boron species becomes more important when considering covalent interactions, for example with vicinal diols. The pK_a of phenylboronic acid is 8.70 in water at 25 °C.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.³³ It has also been widely reported that boronic acids show good binding affinity with other nucleophiles such as dicarboxylic acids^{33a,34} and α -hydroxy-carboxylic acids.^{32,35} The use of boron as a Lewis acid extends to formation of coordinate bonds with a wide variety of hetero-atoms including oxygen, sulfur,³⁶ phosphorus³⁷ and nitrogen.³⁸ Such compounds have widespread use in organic synthesis.39

The earliest example of a dative nitrogen boron interaction is the complex formed between ammonia and trimethylborane, first documented in 1862.⁴⁰ One of the earliest examples of a compound containing an intramolecular $N \rightarrow B$ bond was reported in 1968 by Dunn *et al.*^{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 Boronate esterification

Lewis base coordination





Hydrogen Bonding



Spiroborate formation



Fig. 1 Key interactions of boron, with respect to the self-assembly discussed in this article.

certain external chemical stimuli. The reversible nature of boronate formation enables reversible molecular assembly. Self-condensation of boronic acids forming boroxines of six-membered B_3O_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.⁴⁴ For example, the condensation of 1 with 2 afforded a dimeric macrocyclic compound 3 in 71% yield (Scheme 1).^{44h} They demonstrated formation of a variety of dimeric macrocycles from combinations of 2-salicylideneaminoetanol derivatives (Fig. 2).^{44d/g,h,45}

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



Scheme 1 Condensation reaction of 1 with 2 to form macrocycle 3.

resulted in dynamic covalent self-assembly to quantitatively afford macrocyclic Schiff base boracycles containing bridging boron–oxygen–boron functionality (Scheme 2).⁴⁶ 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.^{5r,s,47}

Farfan and Hopfl reported [4+4] type tetrameric^{44b,h} and [3+3] trimeric macrocyclic compounds by condensation reactions between boronic acids and diols assisted with boron–nitrogen interactions.^{44c,e,48} Tetrameric macrocycle **4** 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



Fig. 2 Boronic acid macrocycles obtained by condensation reaction of imino alcohols with phenylboronic acid derivatives.^{44b}



Scheme 2 Synthesis of macrocyclic Schiff base boracycles containing bridging boron–oxygen–boron bond from [2+2] type condensation of 2-formyl-aryl-boronic acids and 1,2-amino alcohols.

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).⁴⁹ The [4+4] type self-assembly of phenylboronic acids with 2,3-dihydroxypyridine afforded tetrameric macrocycles as evidenced by X-ray crystallography (Fig. 5).^{49a} On the other hand, the [5+5] self-assembly of phenylboronic acids with 3,4-dihydroxypyridine resulted in a pentameric macrocycle (Fig. 5).^{49b} By using the [4+4] type



Fig. 3 Crystal structure of compound 4.



Scheme 3 Synthesis of tetrameric macrocycle 4 obtained a by condensation reaction.



Scheme 4 Synthesis of trimeric macrocycles 5.



Fig. 4 Crystal structure of inclusion complex of 5 (X = 4-OH, Y = Me) with dichloromethane.

condensation, Severin developed an analogous strategy for the preparation of dendritic nanostructures (Scheme 6). 49b

Severin also prepared multicomponent [4+2+2] type macrocycles by using boronic ester and imine condensation reactions. 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).⁵⁰

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).⁵¹

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).⁵² When



Scheme 5 Formation of tetrameric and pentameric macrocycles from [4+4] and [5+5] type condensation reactions.



Fig. 5 Crystal structures of tetrameric and pentameric macrocycles.

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



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.

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



Fig. 6 Crystal structure of macrocycle 6.



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



Fig. 7 Crystal structure of macrocycle 7.

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



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.

Dreos prepared macrocycles by condensation reactions between boronic acids and diols assisted by metal–ligand coordination interactions.⁵⁴ An organobis(dimethylglyoximato) cobalt(III) complex [Co(CH₃)(dmgH)₂L] [dmg = bis(dimethylglyoxime)] 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 **9**. On the other hand, a condensation reaction between the organocobaloxime and 4-pyridinylboronic acid resulted in formation of a [3+3] type macrocycle **10** (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 [ReBr(CO)₅] were heated in a flask equipped with a Dean–Stark trap, a macrocycle **11** was isolated in 58% yield (Scheme 12 and Fig. 11).⁵⁰

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.⁵⁵ The system consists of cyclotricatechylene and a boronic acid-appended hexahomotrioxacalix[3]arene. The two components do not interact with each other until Et₄NOAc is added to the solution. On addition of Et₄NOAc 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 Et₄N⁺ template. Reversible boronate esterification also allowed for



Fig. 9 Crystal structure of metal containing macrocycle 8.



Scheme 11 Formation of coordination assisted macrocycles 9 and 10.



Fig. 10 Molecular structures of metal-ligand coordination assist dimeric and trimeric boronate ester macrocycles 9 and 10.

selective control of capsule formation as a function of pH (Scheme 13).

Kobayashi *et al.* have investigated the reaction of a bowlshaped tetraboronic acid with a biscatechol linker. Upon heating a suspension of bowl-shaped tetraboronic acid and biscatechol linker in chloroform, a molecular cage was obtained in quantitative yield.⁵⁶ 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



Scheme 12 Metal–ligand coordination assisted boronic acid based macrocycle 11, from twelve molecular building blocks.



Fig. 11 Molecular structure of 11.

and cyclotricatechylene in a [6+3+2] reaction in deuterated DMF evidenced by *in situ* NMR experiments (Scheme 15).⁵¹

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).⁵⁰

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 tetraol and the triamine for 1 h at 20 Hz, cage **14** was formed almost quantitatively and was isolated in 94% yield after an



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

additional heating step to remove the generated water. Similarly, larger cage 15 was isolated in 71% yield after ballmilling 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 crystalised 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 B_3O_3 ring structures formed by selfcondensation reaction of three boronic acids (Scheme 19) and have been attracting attention as a platform for molecular assemblies. In the recent progress of boroxine



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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.

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 C_3 -symmetric molecular assemblies^{23a,61} including dendritic⁶² and rotaxane⁶³ structures have been reported that include and rely on boroxine formation.



Scheme 15 Formation of the molecular cage 12 in a [6+3+2] reaction.



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



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.



Scheme 20 Formation of a 1:1 complex of triphenyl boroxine and pyridine.

Anslyn and co-workers synthesised a boroxine from o-(pyrrolidinylmethyl)phenylboronic acid,^{23a} a similar boroxine was also prepared by Bosch *et al.*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).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).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.⁶² More recently, construction of rotaxane⁶³ and cage^{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.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.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 selfassembly. Since formation of boronate ester occurs rapidly and is a robust, supramolecular self-assembly tool boronate



Scheme 21 A boroxine structure from *o*-(pyrrolidinylmethyl)phenylboronic acid.



Scheme 22 A boroxine structure from 2-(*N*-ferrocenylmethyl-*N*-methylaminomethyl)phenylboronic acid.



Scheme 23 Synthesis of hetero-arylboroxines.

esters can be easily prepared *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).^{21*a*,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.⁶⁹ A series of dye molecules bearing boronic acid groups were synthesised for this aim (Fig. 14). When certain sacharides 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 amphiphilic boronic acids with saccharides was also reported.⁷⁰ Boronic acid appended amphiphilic 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.⁷¹



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.

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.⁷² This molecule form 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).⁷³ 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.



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



Fig. 15 Molecular structure of an amphiphilic boronic acid organogelator.



Fig. 16 Molecular structure of a cholesterylboronic boronic acid organogelator.



19: R = Me: Prepared by reaction of **18** with (1*R*, 2*R*)-2,3-butanedione **20**: R = Ph: Prepared by reaction of **18** with (1*R*, 2*R*)-hydrobenzoin

Fig. 17 Molecular structure of bolaboronic acid 18 and chiral bolaboronate esters 19 and 20.

Barboiu prepared G-quartet-type supramolecular superstructures from a macromonomeric guanosine dimer.74 A bisiminoboronic macromolecule 21 was synthesised by reacting 2-formylphenylboronic acid with bis(3-aminopropyl) polytetrahydrofuran (Scheme 25). Boronic esterification between the bisiminoboronic 21 and guanosine afforded macromonomeric guanosine dimer 22 and resulted in polymeric membrane films in the presence or absence of potassium chloride, respectively (Scheme 25).74 The macromonomeric guanosine dimer formed H-bond ribbontype 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^+ 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⁺ and K⁺.

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



Scheme 25 Synthesis of a bisiminoboronate-guanosine macromonomer 22.

3.1.5 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).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 **24** and **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.⁷⁶ Phenylboronic acids with polyoxaalkyl substituents at the *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).



Fig. 18 Hierarchical supramolecular self-assemblies of bisiminoboronateguanosine macromonomer 22 through hydrogen bonding in the absence and presence of templating K^+ ions.

Tetraboronic acids **27a** and **27b** have four $-B(OH)_2$ groups oriented tetrahedrally with cores derived from tetraphenylmethane and tetraphenylsilane respectively.⁷⁷ 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 hydrogenbonded dimers in the solid state (Scheme 30). Five-fold interpenetration of the networks is observed.

Strongin reported hydrogen-bonded supramolecular solidstate networks comprised of a tetraarylboronic acid resorcinarene.⁷⁸ 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.



Scheme 26 Synthesis of a supramolecular gelator 23 based on boronate esterification.



Fig. 19 (a) FE-SEM image of xerogel of 23. Photographs of the toluene gel of 23, which responded to Et_2NH . (b) Toluene gel (1.5 wt% 23). (c) Toluene gel containing Et_2NH (3 equiv. based on 23); the gel was then sonicated for 3 min. (d) Solution (c) was evaporated, and its residue was dried at 90 °C *in vacuo*, cooled, and dissolved in toluene.



Scheme 27 Formation of boronic acid dimers through hydrogen bonds.

Seetha-Lekshmi reported supramolecular assemblies of phenylboronic acids and bipyridine compounds in the solid state (Fig. 21).⁷⁹ 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



Scheme 28 Formation of a stimuli-responsive supramolecular organogelator.



Scheme 29 Formation of boronic acid hydrogen bonding dimers 26.

networks were observed in the crystals obtained from an aqueous methanol solution of a monosodium salt of 4-carboxyphenylboronic acid and $Co(NO_3)_2$ ·6H₂O (Scheme 31).⁸⁰ 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}



Scheme 30 Supramolecular hydrogen networks formed from selfassembly of tetraboronic acids.



Fig. 20 Solid-state supramolecular structures of resorcin-arylboronic acid compound based on a hydrogen bonding network.⁷⁸



Fig. 21 Formation of supramolecular hydrogen networks from boronic acid and 4,4'-bipyridine.⁷⁹



Scheme 31 Formation of hydrogen bonding tapes of 4-carboxyphenylboronic acid between boronic acids and carboxylates.

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



$$HO = HO = HO = R$$

$$HO = R$$

Scheme 32 Formation of a spiroborate by reaction of a borax with diols.

 $H_2PO_4^-$ 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).^{85a} A helicate consisting of two tetraphenol strands bridged by two spiroborate groups sandwiches a sodium ion. On



Scheme 33 Colour and luminescent responsive anion receptors based on spiroborate linkage having plural hydrogen bonding sites.



Scheme 34 Formation of an spiroborate 30 from 2,2'-dihydroxybiphenyl and boric acid.



Scheme 35 Formation of a square macrocycle from 31 and B(OMe)₃.



Scheme 36 Synthesis of double-helical supramolecular architectures **33** from *ortho*-linked oligophenols **32** *via* spiroborate formation.^{40c}

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.⁸⁶ The 3:3 self-assembly of



Scheme 37 The removal of the central Na^+ ion from X– Na^+ by cryptand [2.2.1].

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 macrocylic assemblies *via* boron–dipyrin complexation (Scheme 39).⁸⁷ Dipyrrin **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 BCl₃ 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 K⁺, Rb⁺, and Cs⁺ in organic solvent with the association constants for 1 : 1 complexation of 1.5×10^4 M⁻¹, 5.7×10^4 M⁻¹ and 5.5×10^6 M⁻¹, respectively.

3.2 Boronic acid based polymeric structures

Boronate esterification and boroxine formation have been utilised to construct polymeric structures that exhibit a variety of structural and functional properties.⁸⁸ 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.⁸⁹ Shinkai investigated polymeric



Scheme 38 Synthesis of spiroborate D_3 -symmetric macrocyclic hosts and formation of supramolecular chains through interaction with $[Ir(tpy)_2](PF_6)_3$.

interactions of boronic acid-appended poly(L-lysine) with saccarides 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.⁹⁰ 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.⁹⁰*c* 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.



OR

Scheme 39 Synthetic scheme of cyclic boron-dipyrrin oligomers.

Shinkai and co-workers constructed a boronic acid linear polymer by polycondensation of a diboronic acid and chiral tetraol.⁹¹ 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



Fig. 22 Structures of boronic acid-appended poly(L-lysine) and amphiphilic sugars.



Scheme 40 Formation of a three-arm polymer structure and polymeric networks by boroxine formation.

sugar backbone polymers (Fig. 23).⁹² 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* tetrahydroxycyclo-octane (Scheme 43).⁵³

Severin has developed a novel three component selfassembled polymeric system using monoarylboronic acids, 1,2,4,5-tetrahydroxybenzene and 1,2-bis(4-pyridyl)ethylene or



Scheme 41 Formation of a three-arm polymer structure by Lewis base-promoted boroxine formation.



Scheme 42 Linear boronic acid polymer by polycondensation of diboronic acid and chiral tetraol.⁹¹



Fig. 23 Building blocks of ditopic boronic acid and sugar-based bipolaramphiphiles for pH-dependent reversible polymer formation.⁹²

4,4-bipyridine,⁹³ 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



Scheme 43 Formation of a linear organometallic polymer base on boronate esterification.

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-dihidroxyfluorene-2, 7-dibironic 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 postpolymerisation processing. The molecular weight of the polymer increased under reduced pressure while exposed to hydrolytic conditions in a wet solvent. Acidic conditions led to



Scheme 44 Formations and molecular structure of boronate ester polymers by three-component reaction.⁹³



Scheme 45 Reversible polymer formation and dissociation.93

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 H_2O_2 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 $p-\pi^*$ orbital overlap (Scheme 48).



Scheme 46 Formation of a linear boronic acid polymer showing self-healing properties.



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

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.⁹⁷ The potential applications of porous covalent organic materials include gas storage,⁹⁸ catalysis⁹⁹ and separation.¹⁰⁰

Ding prepared fluorescent oligofluorenes which have two boronic acid groups.¹⁰¹ In the solid state these oligomers



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

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 anydrides and diol esterification to generate a number of open organic frameworks.¹⁰² 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).^{102a} The obtained materials possesses a surface area of S_{BET} = 711 m^2 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).^{102a} This porous material (42) showed a larger surface area of S_{BET} = 1590 m^2g^{-1} . Yaghi also prepared a series of COFs using a variety of boronic acids such as 1,3,5-benzenetriboronic acid, 1,3,5-benzenetris(4-phenylboronic acid), and 4,4'-biphenyl boronic acid with surface areas of 980, 1400, and 2080 m² g⁻¹, respectively.102b

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, ^{54a,103}



Scheme 49 Preparation of luminescent fluorene networks through boroxine formation in the solid state.



Scheme 50 Porous covalent organic frameworks based on boroxine (**41**) from condensation of 1,4 benzenedi(boronic acid).^{102a}



Scheme 51 Porous covalent organic frameworks based on boronic esterification between 1,4 benzenedi(boronic acid) and 2,3,6,7,10,11-hexahydroxytriphenylene (42).^{102a}

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.^{102c}

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 Smit and Wang reported lithium-doped 3D COFs for high-capacity hydrogen storage materials.^{105a} The group of Cooper demonstrated



Scheme 52 Synthesis and structures of alkyl functionalised covalent organic frameworks through condensation of benzene-1,3,5-triboronic acid and 2,6-disubstituted-1,2,4,5-tetrahydroxybenzene.

synthesis of covalent organic frameworks under mild conditions by adapting microwave synthesis showing rapid production of COFs 200 times faster than solvothermal methods.^{105b}

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 acidcatalysed protocol.¹⁰⁸ This method affords COFs directly from protected catechols and aryboronic acids by in situ deprotection of protected catechols. They prepared a twodimensional 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.^{102c}



Scheme 55 Pyrene containing boronate ester based covalent organic framework.



Scheme 54 Synthesis of covalent organic frameworks from borosilicate linkages.¹⁰⁴



Scheme 56 Pyrene containing boroxine based covalent organic framework.



Scheme 57 Synthesis of COF by Lewis acid-catalysed deprotection– condensation from phthalocyanine tetra(acetonide) and 1,4phenylenediboronic acid.

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, 5q-x catalysts (nanoreactors), nano architectures, 109 separation and delivery. 110 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. 111 There has been growing interest in such systems from material chemistry point of view.

On another front, for the furtherance of boronic acidfacilitated 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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