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Hierarchical supramolecules and organization using boronic acids building blocks

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Current progress on hierarchical supramolecules using boronic acids has been highlighted in this feature article. Boronic acids can participate in "click reaction" with diols and their congeners with dynamic covalent functionality. By comprehensively exploring versatile sequential boronate esterification linkages between plural boronic acid-appended molecules and multiple hydroxyl counterparts, not only versatile supramolecular polymers but also structurally well-defined network nanostructures have been developed. In addition orthogonal interactions such as dative bonds of the boron center with Lewis bases has led to the formation of hierarchical nano/microstructures. Boronate systems have the potential to be used as materials involving smart gels, chemosensors, active architectures for electronics, heterogeneous catalysts, chemical-stimulus responsive systems for drug delivery, etc. Here, we fully discuss the feasibility of the structure-directing ability of boronic acids from the standpoint of the generation of new smart materials.

1. Introduction

Boron is a rare metal, while still being extremely intimate as a ubiquitous element in our life. This originates from its electron structure as well as its position in the periodic table, being adjacent to carbon. For instance, electrophilic and trigonal planar structures of boron-containing molecules are isoelectronic analogues of carbocations.[1] Their high reactivities allow additional bond formation to provide anionic tetrahedral compounds. In nature, a number of boron-containing molecules where boron covalently binds to oxygen atoms are present; boronic acids or borates participate in reactions with not only alcohols and phenols but also diols, polyols, and polysaccharides. Thus, prebiotic chemists consider that boron may have provided an essential contribution to the pre-RNA world because borate minerals[2] can associate to stabilize ribose and form boronate ester-based nucleotides.[3] The role of boron as a prebiotic element on the building process of "RNA-world" inspires supramolecular chemists to build hierarchical artificial systems.

There are a myriad of boron-containing molecules, being roughly classified as oxygen-linked boron in the form of boric acids and organoboron molecules which contain B–C covalent bonds. In the former case, boric acids and borate are close to the living systems.[4] Phenylboronic acid and its derivatives are of remarkable interest, being known as Lewis acids with a pK_a of 8.7.[5] The compounds have pH-dependent binding capability with 1,2-*cis* or 1,3-diols to form the corresponding cyclic esters. These simple yet versatile reaction modes have served as detection tools for biology-related species such as saccharides under physiological conditions.[6] Whereas organoboron molecules has been widely prepared and used in organic chemistry because of their electronic and structural properties. One of most exciting utilities is that they participate in transmetalation reactions with organopalladium compounds, a feature exemplified in the Suzuki reaction (2010 Nobel Prize in Chemistry).[7] Another fascinating feature is based on the connection

with π-conjugated systems;[8] the vacant *p*-orbital of boron enables effective p-π* conjugation to provide unique electronic and optical properties. Thus, three coordinate boryl substitutions can behave as π-electron acceptors. Subsequent "boryl functionalized chromophores" have been promising functional materials in the field of nonlinear optics, two-photon absorption, emissive systems, electronic devices, and chemosensors.[9]

Taken together, boron chemistry has been spanned very wide research areas including not only organic chemistry but also materials, medical science and their applications. Our attention in this feature article is focused on versatile reactivity of boronic acids which can serve as the connection as well as stabilisation tools for molecular organization, as inferred from the role of boron in the evaluation of the living world. Sophisticated combinations of boronate-triggered molecular organisation and boron's electronic and structural properties would lead to a more meaningful approach in the quest for new materials.

2. Scope of article

The key strategy of boron-containing hierarchical systems involves the utilisation the interaction of boronic acids with diols, which can be regarded as a reversible and controllable "click reaction".[10] The reversible and spontaneous reaction modes have been widely used in sensing and separation of biology-related species under physiological conditions (*vide supra*). Although the topic is not handled in this article, their biocompatible features are applicable for diagnostic and proteomics applications.[11] Outside of the analytical and biological fields, boronic acids have been recognized as a powerful module in self-assembly.[12] Due to recent demand for preparation of nano- and micro-architectures that can be hierarchically built up of organic molecules, namely "bottom-up approach",[13] a significant progress has been made in the synthesis and characterization of the related boronate systems where the

synergistic outcomes (functionality) are largely superior to those provided by single molecules. With this trend in mind, our feature article is focused on the pivotal engineering of boronic acid-inspired hierarchical systems, as depicted in Fig. 1, that can contribute to various field such as electronics, sensing, catalysis, and drug delivery. These reversible reaction systems with "error-checking" characteristics allow easy thermodynamic formation of ordered nanostructures, bringing about stable covalently bound molecular networks.
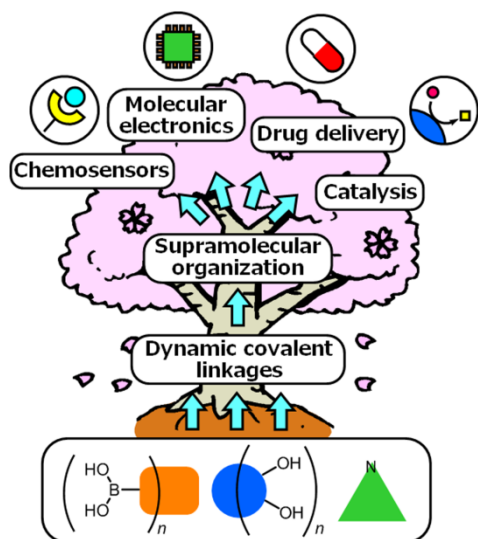

Fig. 1 Schematic overview of hierarchical systems using boronic acid building blocks.

3. Boronic acids with versatile connection modes

Since the structure of boronate anion was elucidated by Edwards and Lorand in 1959,[14] the pH-dependent binding mode of boronic acids with diol compounds involving saccharides have been well-established in aqueous solution. In this context, an excellent review has been published wherein the general principle of interactions between boronic acids and sugars in aqueous media are fully discussed.[15] Arylboronic acid derivatives are typically synthesized by following methods; (1) Grignard or lithium reagents and then organoborates; (2) palladium-catalyzed cross-coupling between aryl halides or aryl triflates and tetraalkoxydiboron or dialkoxyhydroborane.[16] In the latter case, the resultant organoboronate esters can convert to the corresponding boronic acids by reaction with potassium hydrogen fluoride and then treatment with either inorganic base or trimethylsilyl chloride and water.[17] As for molecular organization, our attention has been focused on dynamic covalent functionality of boronic acids which do not only participate in dehydration reactions with diols but also have Lewis acidity. In this context, stability of botonate ester linkages is a significant matter. Roy et al. investigated structural effects on the relative rates of the achiral cyclic phenylboronic ester.[18] Based on this study, six membered boronic esters are thermodynamically more stable than their corresponding five-membered analogs. Indeed, boronate esterification with pentaerythritol is not hindered by presence of water as a co-solvent.[19] Such a property has motivated

supramolecular chemists to develop boron-based hierarchical materials. In addition, Lewis base such as pyridine can tune the reactivity through B–N dative bond formation, with an accompanying switch in the geometry from trigonal planar complex to tetrahedral boronate. The optimized structure has been investigated by Anslyn et al. using boronate ester obtained from o-(pyrrolidinylmethyl)phenylboronic acid and catechol.[20] Computer modelling of the boronate ester indicates a B–N bond length of 1.8 Å and equivalent angle of 107 °. Furthermore, the B−O bond length was calculated to be 1.46 Å, being larger than that of the free acid (1.38 Å). B–N dative bond formation weakens back-donation from oxygen atom. Note that the reactivity is not limited to those with diols or Lewis bases. Self-condensation of boronic acids leads to the formation of boroxines.[21] The condensation reactions of boronic acids with silane diols or aromatic 1,2-diamines give borasiloxane link[22] or 1,3,2-benzodiazaborole,[23] respectively. In the latter case, ball-milling in the solid state is sometimes profitable to complete the reaction quantitatively. In the past decade, the chemistry of 1,3,2-diazaborole has been progressively developed.[24] Some of these three-coordinate boron compounds have strong luminescence properties.[25] It has also been confirmed that 1,3,2-diazaborole behaves as π-donor substituents.[26] Indeed, the introduction of electron accepting group in the borylated benzene unit induces an emission in the visible region.[27] In another intriguing example, Severin et al. have reported the reversible formation of borophosphonate by the condensation reaction of boronic acid with tert-butyl-phosphonate.[28] In this manner, versatile reaction modes of boronic acids have enabled excellent connection tools for constructing pre-organised hierarchical architectures (Scheme 1).
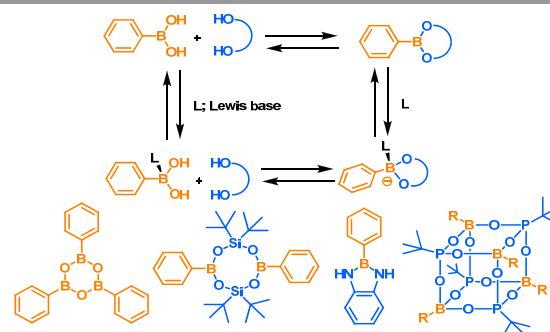
Scheme 1 Boronate esterification and the related dehydrated compounds.

4. Boronic acid-induced nano- and microarchitectures

4.1. Supramolecular polymers

Supramolecular polymers are composed of molecular units connected by reversible bonds.[29] The presence of the dynamic covalent bonds for "main chain" formation endows the polymers with smart properties such as chemical stimulus-acceptability, degradability, shape-memory, self-healing, etc.[30] Boronate-based systems have been recognized as one of most promising approaches towards this end. Since they were first report by S. Shinkai, et al.,[31] these related linear polymers have been widely developed.[32] The current trend is to build hierarchical supramolecular polymers where multiple kinds of intermolecular interactions, both in the polymeric

backbone and those oriented orthogonally, combine to form 3D aggregates.[33] Using this approach, well-tailored boronic acid-based building blocks have been designed and synthesised. Höpfl et al. have investigated supramolecular systems prepared from *N*-containing boronic acids (5-isoquinolineboronicacid (**5-iqbaH₂**) and 4-pyridineboronic acid (**4-pybaH₂**) and pentaerythritol.[34] Single-crystal X-ray diffraction of these nanostructures revealed that both compounds induced molecular networks of the compositions {[5-iqba]₂[C₅H₈]}·nEtOH and {[4-pyba]₂-[C₅H₈]} 4n EtOH·H₂O·toluene (Fig. 2). The former has a 2D layered structure while the latter system adopts a 3D network, meaning that *N*-containing boronates can serves self-complementary tectons for the generation of 2D and 3D molecular networks through coordination of dative N–B bond as secondary interactions. For the expanded research, replacing pentaerythritol with ethanol or simple diols, it was found that one tetranuclear macrocyclic and four one-dimensional polymeric boronates were formed.[35]
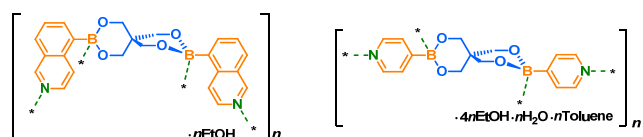

Fig. 2 Structures of {[5-iqba]₂[C₅H₈]}·nEtOH and {[4-pyba]₂-[C₅H₈]} 4n EtOH·H₂O·toluene repeating unit.

Severin, et al. have investigated supramolecular polymerization based on the combination of boronate esterification and N–B dative bond formtion.[36] Taking into account that the binding constants (K_a) between functional groups are typically required to obtain polymers with significant molecular weight are equal or more than 10^6 M^{-1}, the K_a vales of dioxaboles with pyridine were fully evaluated. As a result, the use of appropriate molecular components with both electron withdrawing substituent on the dioxabole segment and electron donor group has led to a significant improvement of the K_a values. Based on these findings, 4-(6-(methyl(pyridin-4-yl)amino)hexyl)benzene-1,2-diol (**1**) was synthesized (Fig 3). Interestingly, when polymerisation was tested with different arylboronic acids (**2**), it was found that the degree of polymerisation was affected by electronic and steric properties of the boronate esters. This study suggests that main-chain supramolecular polymers could be accessible through dative N–B bond interactions. This N–B binding motif has been applied to cross-linked supramolecular polymers.[37]
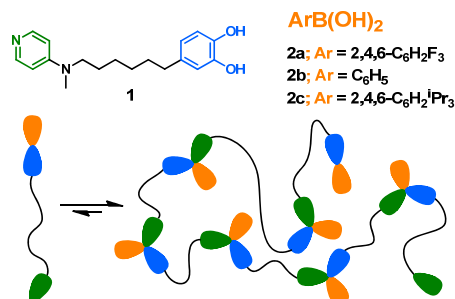

Fig. 3 Aggregation of the heteroditopic boronate ester through dative B–N bond formation.

As shown in Fig. 4, the condensation of benzene-1,4-diboronic acid with catechol gave 1,4-bis(benzodioxaborole)benzene, which aggregates with the *N*-donor tetradentate ligand, tetra(4-pyridylphenyl)ethylene through dative N–B bonds. Crystallographic analysis revealed that a 2D network polymer **3** was formed where all of the pyridyl *N* atoms of the tetradentate ligand were connected to the 1,4-bis(benzodioxaborole)benzene units through dative bonds. The individual layers of the network can be described as connections of large macrocyclic structures with ring sizes of 94 atoms. It represents a rare example of a crystalline network that is based on dative N–B bonds to boronate esters. Although tetra(4-pyridylphenyl)ethylene is known for aggregation-induced emission in the solid state (*vide infra*),[38] crystalline **3** was found to be nonfluorescent when excited at 300 nm.
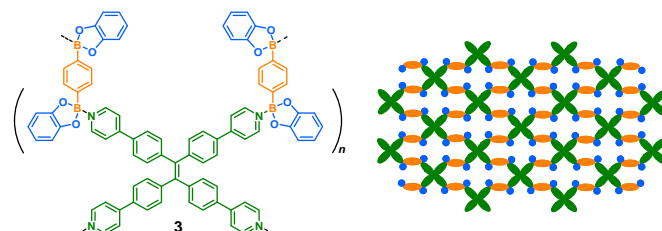

Fig. 4 Synthesis of dative B–N bond-induced 2D polymer **3**.

Well-tailored combination of reversible boronate esterification and N–B dative bond formation enables preparation of chemical stimulus-triggered interconversion system between macrocyclic boronate ester and boronate-based organo gels.[39] The azulene-containing macrocycle can be spontaneously produced from diboronic acid and indacene-type bis(1,2-diol).[40] As shown in Fig. 5, the addition of 1,3-diaminopropane into a turbid solution of guest-encapsulated boronate macrocycle (**4**) led to the formation of a boronate oligomers/polymer gel (**5**) cross-linked by the diamine where the guest (azulene) was released from the cyclic host. Interestingly, the released guest was recovered from the gel phase with a 84% recovery when treated with acidic solution. Taking advantage of dynamic covalent functionality of the boronate system, a new type of smart gel-based delivery system could be created.
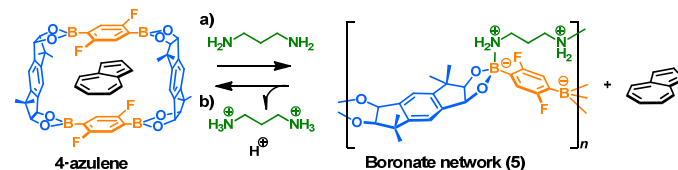

Fig. 5 a) Formation of borate gel (**5**) from the guest-included macrocyclic boronate ester (**4**) along with release of the guest molecule into the gel. b) Reconstruction of the macrocyclic boronate ester and recovery of the guest molecule from the gel.

In material science, conducting polymers with structurally well-defined metal centers have great promise for developing molecular sensors and catalysts.[41] To furnish such hybrid materials, metal-inserted cage complex as its monomer unit

were synthesised by metal-templated [3+2]–type condensation reaction of bithiophene-derived boronic acid with diphenylglyoxime.[42] Electropolymerisation produces boron-containing conducting polymeric systems for the study of charge injection and transport properties (Fig. 6a). Polymer (6) has a capability to deliver electrons to its metal centers, laying a firm foundation for exploration as a surface-bound electrocatalysis. In addition, boronic acids are effective tools for the construction of multimetallic assemblies. In molecular electronics, such assemblies composed of bimetallic complexes are desired for the realisation of a quantum cellular automaton.[43] Thus,1′,1‴-biferrocenediboronic acid (7) was synthesized as a useful organobimetallic building block,[44] which forms 1D hydrogen-bonded networks (i.e., chain) with octaatomic rings composed of the neighbouring two molecules (Fig. 6b). Insight into the association of functional bimetallic complexes without additional metal–ligand coordination chemistry has been obtained.
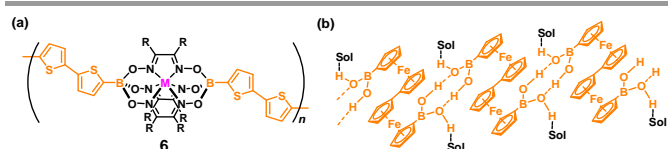

Fig.6 (a) Metal-containing boronate nonducting polymers (**6**). (b) A 1D hydrogen network with 1′,1‴-biferrocenediboronic acid (**7**).

4.2. Boronate gels as smart materials

Polymeric hydrogels, with solid-like rheology, have been widely investigated in the field of material science.[45] The biocompatibility makes them of potential use in the biomedical and pharmaceutical fields for drug delivery systems.[46] Based on the synergistic effect of both functions of boronic acids and hydrogels, biomaterials have been proposed for gluco-sensing applications and self-controlled insulin release, etc. These aspects were nicely reviewed by Y. Guan and Y. Zhang.[47] Herein, our attention is focused on poly(vinyl alcohol) (PVA) which serves as a functional gel matrix. It was reported a long time ago that mixing a PVA solution and a borax solution yielded a hydrogel, presently used in popular toys.[48] The complexation reaction is shown in Fig. 7a.[49]
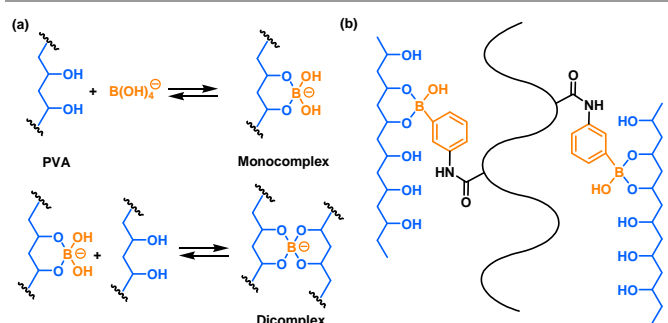

Fig. 7 (a) The PVA-borate complexation. (b) PVA cross-linking with DMAA-NAAPBA copolymer.derivatives.

In the search for new functions for PVA-borax, the related hydrogels with added organic liquids have been applied in the art conservation.[50] PVA is also known as biocompatible and widely employed as a material for a variety of medical applications because of its excellent film forming and adhesive properties.[51] Kitano et al. reported a polymer complex based on boronate-PVA interactions;[52] this complex was designed as a glucose sensitive system directed towards the regulation of insulin release. The cross-linking effect of boronate-containing copolymers has been investigated using a *N,N*-dimethylacrylamide (DMAA)–*N*-acryloyl-*m*-aminophenylboronic acid (NAAPBA) copolymer (Fig.7b).[53] The polymeric cross-linker enables gel formation at much lower concentrations of boron, due to multipoint interaction of the copolymer with PVA *via* boronate esterification. The PVA-copolymer gel exhibited much higher relaxation time than did PVA-borate gels, indicating that boronic acid-containing copolymers are more effective cross-linkers of PVA than borates. In line with these approaches, pH-responsive hydrogels were prepared from α,ω-phenylboronic acid-terminated crosslinkers and PVA.[54]

The advantage of boronate-based cross-linking was demonstrated through the fabrication of film-based chemosensors which are operated in water, because stable PVA–borate gels are not water soluble. Nishiyabu, Kubo, and co-worker prepared new type of PVA-based hydrogels in which benzene-1,4-diboronic acid was employed as a cross-linker, being stable in water.[55] The residual hydroxyl groups in the gel matrix can participate in binding sites for grafting fluorophores to produce the desired gel sensors. As a proof-of-concept study, boronate gel film (8) composed of a covalently attached dansyl indicator in a PVA–boronate matrix was fabricated (Fig. 8). As such, the film showed highly selective copper ion-induced fluorescence response in water, with minimal interference from competitive metal ions such as Hg^{2+} ions. It is noteworthy that the gel was found to be a reusable and a free-standing film capable of visually detecting Cu^{2+}, providing a simple and expedient tool for on-site Cu^{2+} monitoring in environmental applications such as water analysis.
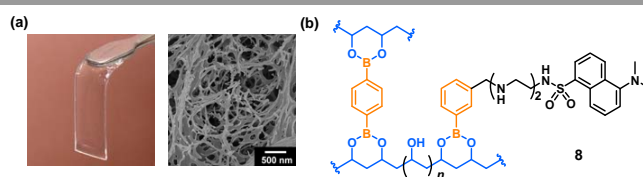

Fig. 8 (a) Photograph of the boronate hydrogel film with dansyl moieties and FE-SEM Image of the xerogel; (b) Proposed structure of the indicator hydrogel **8** wherein OH inserted sp^3-hybridized tetrahedral boronate esters would be partly produced. (Adapted from ref. 55)

For systematic extension of the research, a multicolour fluorescent hydrogel sensor (9) was successfully prepared, in which two types of fluorescent dyes with amidoquinoline and rhodamine B chromophores were incorporated (Fig. 9).[56] Amidoquinoline is known to exhibit a turn-on fluorescence response toward Zn^{2+}.[57] Although the boronate hydrogel film exhibited red fluorescence under UV-light irradiation (365 nm)

using a handheld UV lamp (Fig. 9a), adding incremental amounts of Zn^{2+} ions to the boronate gel in HEPES buffer (*N*-2-hydroxyethylpiperazine-*N'*-2-ethanesulfonic acid, pH = 7.0) induced variations in the emission color: the red emission converted to white and blue-green emission at Zn^{2+} ion concentrations of 3.0×10^{-5} M (Fig. 9b) and 9.0×10^{-5} M (Fig. 9c), respectively. The colour change was visually detectable at the upper limit of the acceptable Zn^{2+} concentration (3 ppm) in drinking water indicated by the World Health Organization (WHO).[58]

In this manner, PVA has been recognized as a suitable matrix for preparing hydrogels. From the standpoint of the field of bioengineering fields, the encapsulation of living cells into a hydrophilic polymer hydrogel will play an important role in tissue engineering. Such demand led chemists to prepare spherical PVA-based hydrogels with a highly monodisperse diameter.
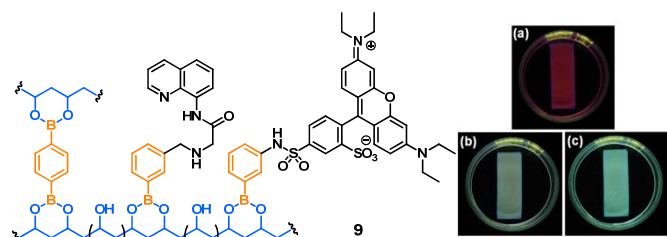

Fig. 9 Proposed structure of the film **9**. Photographs of the boronate hydrogel films after immersion in aqueous solutions (5 mM HEPES buffer, pH = 7.0, 3.0 mL) of Zn^{2+} ions ([Zn^{2+}] = (a) 0 M, (b) 3.0×10^{-5} M, and (c) 9.0×10^{-5} M) for 30 min. The photographs were taken under UV light: λ_{ex} = 365 nm. (Adapted from ref. 56.)

Making use of a flow-focusing microfluidic channel devices prepared by polydimethylsiloxane (PDMS), spherical phospholipid polymer hydrogels were formed spontaneously from 2-methacryloyloxyethyl phosphorylcholine polymer bearing phenyl boronic acid groups (PMBV) and PVA (Figs. 10a and 10b).[59] It was found that the spherical hydrogel can encapsulate human promyelocytic leukemia (HL-60) by dispersing the cells in the polymer solution prior to injection into the microfluidic device. On the other hand, the hydrogel could be dissolved within 10 min by the addition of D-sorbitol solution to the suspension (Fig. 10c). This property would be useful for recovering cells from the hydrogels under mild conditions. For an alternate approach based on interactions between PVA and PBA, Anzai et al. have prepared layer-by–layer films composed through alternate deposition of phenylboronic acid-bearing poly(allylamine hydrochloride) (PBA–PAH) and poly(vinyl alcohol) (PVA) on the surface of a quartz slide to develop thin films that can be decomposed in response to hydrogen peroxide (H_2O_2). Such films can be used as H_2O_2-sensitive delivery systems.[60]
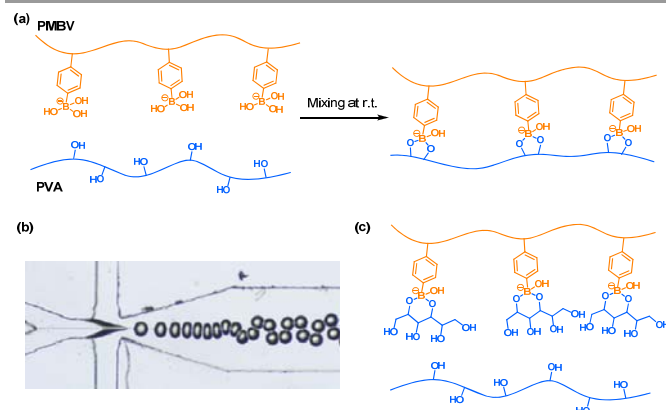

Fig. 10 (a) The gelation mechanism between PMBV and PVA. (b) Optical microscopic image of polymer solution flow in the PDMS microfluidic channel device with fluorine modification. (c) Dissociation of the hydrogel upon adding D-sorbitol. (Reproduced with permission of The American Chemical Society from ref. 59.)

Recently, interest in hierarchical molecular recognition based on macroscopic assemblies has been growing since it would open up new methodologies for developing functional materials, and contribute to the understanding of the selective organisation of functional molecules in cells.[61] Harada et al., have investigated various stimuli-responsive macroscopic assemblies based on polymeric hydrogels, using the idea that complementary complex formation should be more effective for the construction of multifunctional macroscopic self-assemblies.[62] For example, a macroscopic regulation of gel assemblies based on boronate esterification has been achieved where a phenylboronic acid-appended gel (**10**) can form an assembly with a gel possessing catechol moieties (**11**) using boronic acid−catechol interactions (Fig 11).[63] Interestingly, the assembly and disassembly of the gels are reversibly switched by varying the pH of the medium. The adhesion strength is also tunable by competitive monosaccharide molecules in accordance with their association strength with the phenylboronic acid moieties. The adhesion strength is estimated by stress–strain measurements.
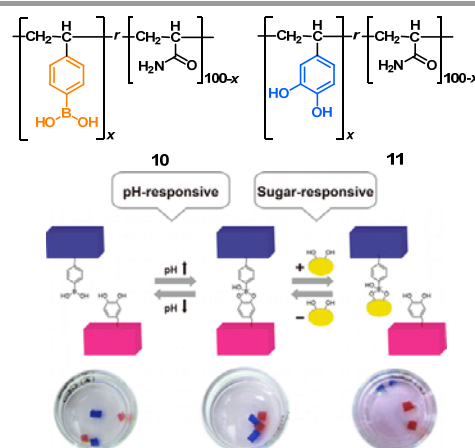

Fig. 11 (a) Structures of phenylboronic acid-appended gel **10** and gel possessing catechol moieties **11**. (b) Chemical stimulus-controlled hierarchical molecular

Low-molecular-weight-gelators (LMGs)[64] are an alternative approach in the quest for functional boronate gels. As one of the earlier examples, S. Shinkai, et al., synthesized phenylboronic acid-appended cholesterols and the gel-forming properties arising from complexation with monosacchrides.[65] As inferred from thermo-reversibility of LMGs,[66] such gels are sensitive to change in their surrounding environment. Recent progress involves pH responsive self-healing hydrogels using dynamic boronate-catechol complexation. One of the typical examples is prepared from 4-arm polyethylene glycol (PEG) catechol (**12**) and benzene-1,3-diboronic acid.[67] Its self-healing capability is shown in Fig. 12. When a cube of the hydrogel (Fig. 12a) was cut into two pieces, it healed autonomously and rapidly after the two pieces were brought into contact (Figs. 13b and 13c). Interestingly, the healed gel was strong enough to be stretched after fusion (Fig. 12d).
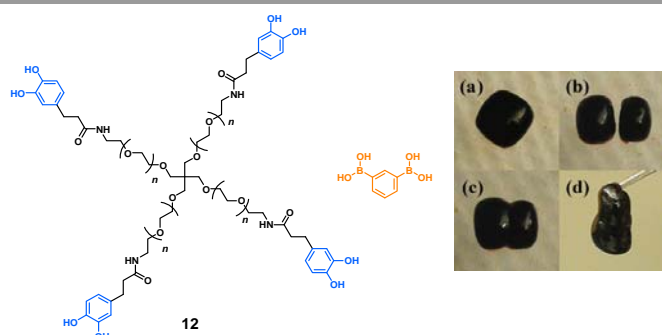

Fig. 12 Structure of catechol PEG. Self-healing properties of the covalent polymer gel formed from **12** (15 wt%) and benzene-1,3-diboronic acid at pH 9.0. The gel (a) as a cube, (b) cut into two pieces, (c) fused together, and (d) stretched without fracture 30 s after fusion.The molar ratio of **12** to benzene-1,3-diboronic acid was 1:8. (Adapted from ref. 67.)

4.3. Boronate-based covalent-organic framework as nanoporous materials

Boronic acids can participate in the construction of covalent-organic frameworks (COFs),[68] which are organic analogues of metal organic frameworks (MOFs).[69] In particular, much attention has recently been devoted to the related nanoporous materials with high surface areas because of their potential in sustainable chemistry such as gas storage and energy and luminescence devices.[70] The boronate ester bonds are stable as covalent bonds and reversible, which can induce homo- and heteropolymerisation accompanied by tunable porosity and nanostructures, giving ordered structure. In a pioneering study, Yaghi et al., produced crystalline organic polymers based on self-condensation of aromatic diboronic acids or controlled condensation of aromatic diols with aromatic diboronic acids to synthesise a number of 2D and 3D COFs via B–O bond formation.[71] In addition to versatile boronic acid-appended molecular units that can induce a variety of network structures, the subtle balance between kinetic and thermodynamic control can be influenced by the conditions used for the polycondensation reaction.[72] Most notably, the hetero

polymerization based on combination of boronic acids and diol components can provide versatile boronate COFs with different functionalities. This article overviews an intriguing approach towards boronate-based functional COFs.

Versatile synthetic strategy is important to develop desired porous crystalline materials with a well-defined pore size, Bein et al., reported systematic way to prepare a COF with large pores (**13**) having an open diameter of 4.0 nm.[73] Formed by condensation of 1,3,5-benzenetris(4-phenylboronic acid) and 2,3,6,7-tetrahudroxy-9,10-dimethyl-antharacence (Fig. 13a), the reaction parameters were systematically varied using a high throughput screening approach employing a robotic dosing system. As a result, the solvent mixture was the most important parameter for this system and using a mixture of just anisole and methanol as solvents gave the network structures. Also, by judicious choice of both boronic acid- and diol-derivatives as component precursors, a 2D COF with large 4.7 nm hexagonal pores has been synthesised.[74]

Looking at their functionalisation for materials, Dichetel et al. proposed a strategy for assembling organic semiconductors into COF networks, featuring boronate square lattices composed of phthalocyanine macrocycles.[75] Broad absorption properties of the COF over the solar spectrum enable its use as an efficient charge transport materials for application in photovoltaic devices. The film properties of boronate COFs containing π-conjugated components have been also investigated on single-layer graphene.[76] It has been recognized that 2D COFs represent a feasible platform for the molecular design of semiconducting and photoconductive materials. In particular, exploration of synthetic strategies for the construction of COFs with electron donor and acceptor components is significant for photoinduced electron transfer and photoenergy conversion.
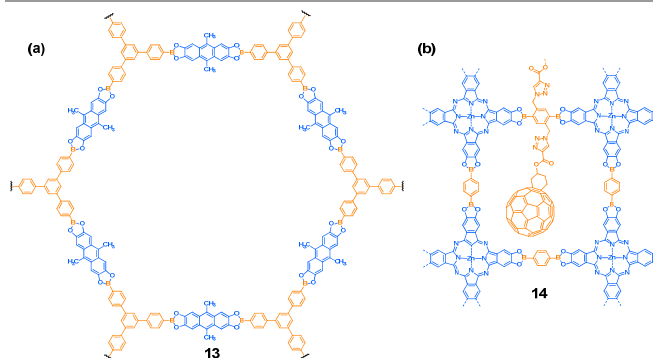

Fig. 13 (a) Synthesis of COF **13** with 4.0 nm (b) Donor-acceptor COF with C$_{60}$ (**14**).

With this in mind, photonic COFs (**14**) were prepared from electron-donating Zn(II)-phthalocyanine (ZnPc) COFs with fullerene units joined through triazole linkers (Fig. 13b).[77] The topological feature is the spatial confinement of the fullerene within the nanochannels via covalent anchoring on the channel walls. Investigation of the photoinduced electron transfer using time-resolved electron spin resonance (TR-ESR) spectroscopy revealed the charge dynamics of the donor-acceptor COFs in the solid state. Although the ZnPc-COF at 20 K without

fullerene on the walls exhibited only a broad TR-ESR signals upon a laser flash at 680 nm, integrating of electron-accepting fullerene molecules onto the channel walls drastically changed the TR-ESR patterns. Detailed investigation indicate the formation of ZnPc•[+] and C_{60}•[−] species in **14**. These results clearly indicate that the light irradiation triggers photoinduced electron transfer from ZnPc to fullerene in the COF system, and then suggest the enormous available for developing COFs for charge separation for application in photovoltaics.[78] Porphyrins with 18 π electron systems are another class of interesting planar macrocyclic compounds from the standpoint of conjugated nanoporous systems. Regulation of the macroscopic structures and control of the pore parameters of porphyrin-based COFs have been fully investigated.[79]

Bein et al., have proposed a unique strategy using host-guest interactions for fabrication of donor-acceptor heterojunction COF systems.[80] An electron acceptor, [6,6]-phenyl-C61-butyricacid methyl ester (PCBM), was encapsulated within an electro-donating thienothiophene-based COF (**15**) synthesised by condensation of 2,3,6,7,10,11-hexahydroxytriphenylene with thieno[3,2-*b*]thiophene-2,5-diyl diboronic acid. Immersion of the COF into a solution of PCBM led to incorporation of PCBM into the pore of the COF (Fig. 14). The authors examined the photovoltaic properties using **15**/PCBM layers in a cell device where ITO and Al electrodes were used. Under simulated AM1.5G full sun illumination we measured an open-circuit voltage of 622 mV was obtained, along with a short-circuit current density of 0.213 mA cm^{−2}, and a 40% fill factor, giving rise to a power conversion efficiency of 0.053%. It is noteworthy that these are the first studies of a COF-based photovoltaic device with an electron donor in the walls and the complementary electron acceptor in ordered periodic channels. This shows that light-induced charge-separation and collection is clearly feasible for these systems. However, taking into account practical applications of boronate-COFs, durability against water should be considered because the linkage is susceptible to hydrolysis.[32c]
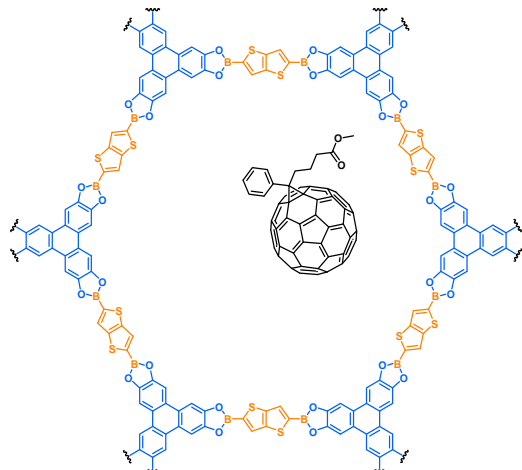

Fig. 14 Host–guest complex of **15** and a PCBM molecule.

Lavigne et al. investigated the stability and bulkproperties of 2D boronate ester-linked COFs upon exposure to an aqueous environments (Fig. 15a). Enhanced stability could be observed for

frameworks with alkylation in the pores of the COF (**16**) compared to nonalkylated frameworks, indicating that the hydrolysis is retarded to maintain porosity when alkyl substituents are present in the COF pores.[81]

In general, planar components preferably adapt 2D frameworks, whereas tetrahedral ones give 3D COFs. Thus, use of bowl-shaped components is an approach to provide distinctive COFs. Hexahydroxyl cyclotricatechylene (CTC) is an intriguing macrocyclic molecule with intrinsic cavity in host-guest chemistry which exhibits unique selective binding characteristic.[82] The catechol segments located with C_3 symmetry in the molecule can participate in boronate esterification.[83] Zheng, et al., prepared an undulated two-dimensional CTC-based COF (**17**) which stacks in an eclipsed mode in the microcrystalline state (Fig. 15b). It was reported that **17** has a surface area of 1710 m[2] g^{−1}, with a pore width of 2.26 nm calculated by a density functional theory (DFT) modelling.[84] The bowl-shaped core unit led to a larger surface area than its analogue, COF-5[71a] constructed by planar subunits. It was found that this material has higher low pressure hydrogen uptake than other 2D COFs with similar structures.
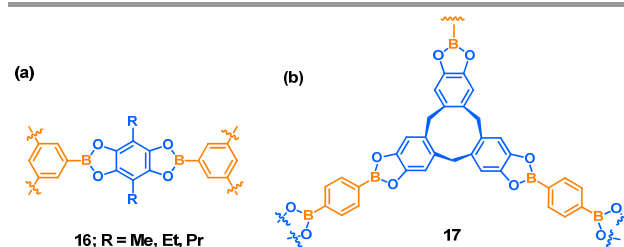

Fig. 15 (a) Partial structures of alkylated COFs (**16**). (b) CTC based two-dimensional covalent organic framework (**17**).

The use of triptycene as a catechol component afforded 2D COF with a unique morphology.[85] Zhao, et al., investigated the condensation reaction of benzene-1,4-diboronic acid with triptycene in mesitylene/dioxne (1:1) at 85 ℃ under an Ar atmosphere. After stirring for 3 days, honeycomb-shaped polymers (**18**) were produced (Fig. 16). Interestingly, the 2D polymeric monolayers were found to further evolve into monolayered or multilayered hollow spheres through wrapping of the spherical monolayers by newly produced layer. The phenomenon is attributed to very weak interlayer interactions between monolayers due to the lack of π−π interactions. This research has not only provided meaningful insight into the design of new hollow nano-materials for application in separation science, but also become a plausible model system for the transformation of graphene to fullerene.
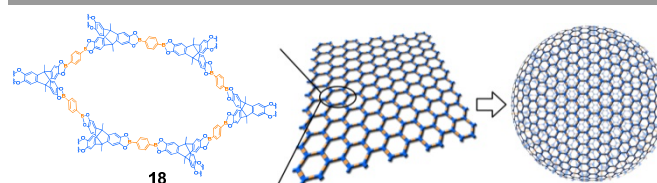

Fig. 16 The formation of 2D polymers and hollow spheres.

Taken together, COFs have become an emerging class of periodic porous materials composed of network polymers. Despite intense interest for these materials, the formation mechanism is not fully understood. In 2014, Smith and Dichtel found that the boronate ester-linked 2D framework COF-5 was readily synthesised using fully homogeneous conditions on time scales of minutes.[86] The nucleation and growth process for polymerization of 2,3,6,7,10,11-hexahydroxytriphenylene and benzene-1,4-diboronic acid monomers enabled the first rate measurements of its formation. During these mechanistic studies of 2D boronate COFs, plausible growth models were proposed (Fig. 17); the researchers favoured the scenario in which smaller oligomers stack upon larger 2D polymers (template polymerisation) may be involved. Although an understanding of the nucleation, polymerisation and crystal growth prior to aggregation has still remained incomplete, these findings will prompt further rigorous studies of COF nucleation and growth processes to create new frameworks.
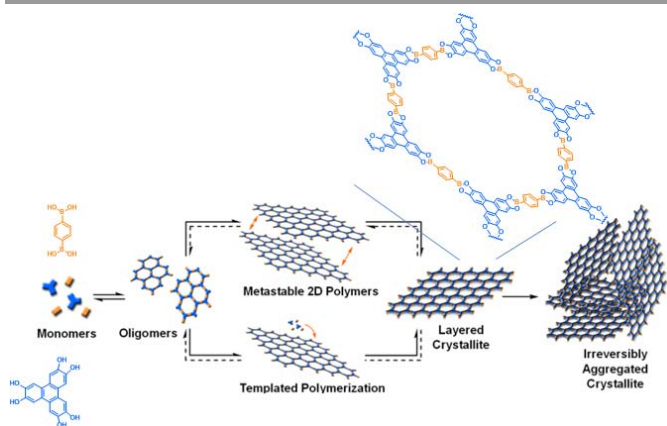

Fig. 17. Proposed models of boronate ester COF-5 growth.

Inspired by the pioneering work with graphene,[87] there is an increasing interest in the development of 2D materials that exhibit unique mechanical[88] and optical[89] properties. We believe that polymeric 2D structures prepared directly from small molecular units through clickable boronate esterification will show the most promise for the fabrication of single molecule thick 2D materials.[90] An excellent review article has been published on this topic.[91]

4.4. Three dimensional nano- and microarchitectures using boronic acid building blocks

Organic caged systems built through dynamic covalent functionality are among the most intriguing three dimensional porous materials obtainable under reversible conditions where easy access to complex structures can be thermodynamically possible.[92] Hexahydroxy tribenzotriquinacene (**19**), a known precursor for microporous polymers,[93] features a nearly rectangular orientation of the three indane moieties with respect of each other. The addition of 4Å molecular sieves into a THF solution of catechol-functionalized **19** with benzene-1,4-diboronic acids led to precipitation of a microcrystalline materials (**20**). One-pot reaction resulting in the formation of 24

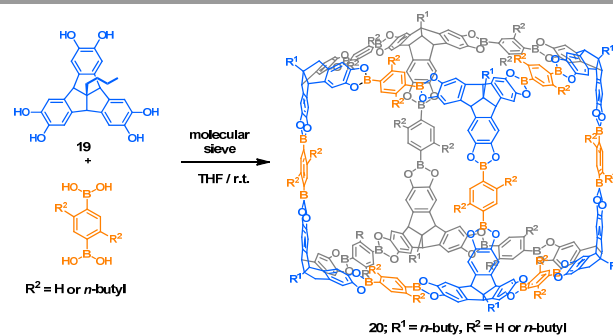boronate esters in an [8+12] co-condensation of 20 components occurred (Fig. 18).[94]

Fig. 18. Synthesis of cages **20** under water removing conditions..

M. Masalerz, et al. reported a boronate porous cage (**21**) with a very high specific surface area of 3758 m² g⁻¹ (Fig. 19).[95] The one step 48-fold condensation reaction of twelve molecules of triptycene tetraol (**22**) and eight molecules of triboronic acid produced the cuboctahedral [12 + 8] cages (**21**) with an outer diameter of 3.99 nm. The precise structure was determined by single-crystal X-ray diffraction. The cavity is very large in comparison with other porous cage compounds, with an inner diameter of 2.4–2.6 nm between the two opposite aryl rings of the triboronate ester linkage. It was found that the molecules pack through π–π interactions along the crystallographic *c* axis, which is reflected in a staggered coplanar assembly of boronate ester units of adjacent molecules at a distance of 3.2–3.4 Å. Along other axes, the packing interactions are rather weak, being mainly attributable to CH–π interactions.
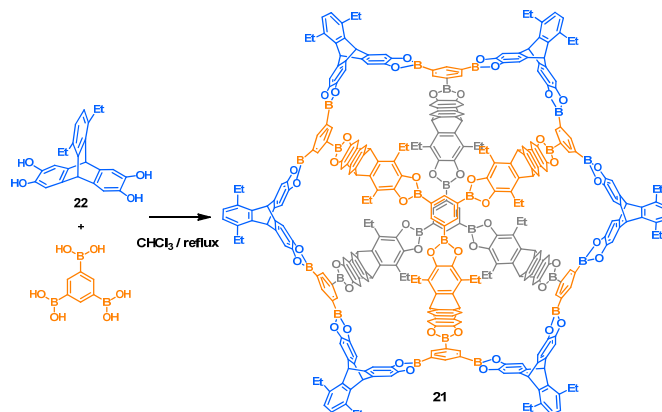
Fig. 19. Synthesis of cubotahedral [12+8] cages (**21**).

Quite interestingly, when 9,10-dihexyltriptycene was used instead of **22**, two cages were interlocked with each other in the crystalline state to provide giant catenane **23** (Fig. 20). The structure itself is of an ellipsoid, the dimension being approximately 4.6–4.7 nm in length and 4.0 nm in width. Furthermore, **23** forms a porous material with a Brunauer-Emmett-Teller (BET) surface area of 1540 m² g⁻¹. This is the first example of a porous molecular catenane.[96]

Fig. 20. Crystal structure of cage catenane **23** generated from X-ray diffraction data published in ref 91. Alkyl chains are omitted for clarity.
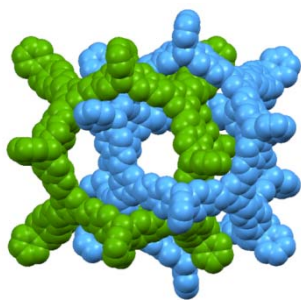
In contrast to two-component self-assemblies built through a single type of connection reaction, it is difficult to control two connection reactions in order to drive the desired self-assembled systems. Post-modification strategies have been used as a feasible way to construct discrete self-assembles for any target. Iwasawa et al. succeeded in the selective preparation of two isomeric, higher-order architectures by engineering connecting reactions of boronate esterification and [3+2] cycloaddition of nitrile oxides.[97] In one approach (Fig. 21), dehydration reactions of **24** and enantiopure (–)-**25** and gave a cylinder-type boronate self-assembly (**26**). Transesterification of (**27**) with (–)-**25** also produced the related assemblies (**28**) with a bowl shape. With the two components in hand, post-connecting reaction by [3+2] cycloaddition in the presence of proton sponge at room temperature for 7 days afforded capsule-like trimer assemblies (**29**). On the other hand, pre-connecting [3+2] cycloaddition of (**30**) with (**27**), followed by boronate esterification with (+)-**25** gave the corresponding tricyclic trimer assemblies (**31**). The measurement of BET surface areas indicates that the obtained trimeric architectures obtained have intrinsic cavities. The design of an assembly protocol with orthogonal reaction can lead to the formation of isomeric discrete nanoarchitectures having different shapes.
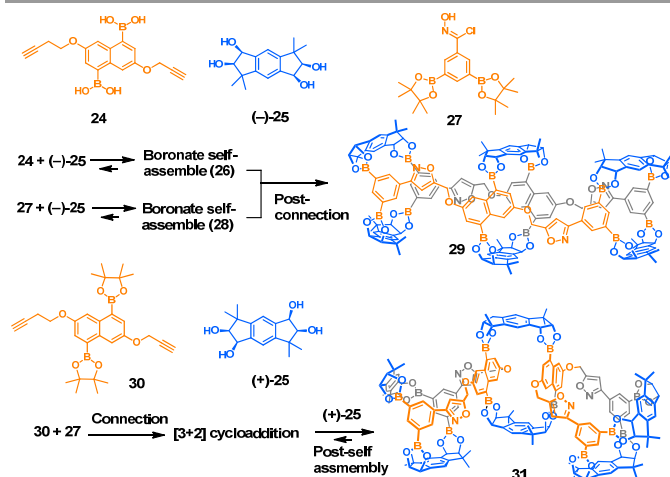

Fig. 21. Procedure-dependent trimeric boronate assembles.

To construct 3D nanosystems, the use of dendrimers, defined as highly branched, multivalent and monodisperse polymers, provides a facile scenario.[98] As part of an on-going program to develop stimulus-responsive cross-lined micelles as

nanocarrier systems for tumor-targeting drug delivery, a boronate cross-linked telodendorimer has been prepared and evaluated.[99] Telodendorimers, composed of linear polyethylene glycol (PEG) and dendritic cholic acids (CA) block copolymers, have served efficiently in anticancer drug delivery agents.[100] The stability of the micelles was improved by crosslinking using boronate ester at the core-shell interface. As shown in Fig. 22, two types of telodendrimers with boronic acid (**32**) and catechol (**33**) have been synthesised. Reaction of the boronic acid with the catechol on distinct telodendrimers in aqueous solution induced self-assembly of the entities into micelles. Despite exhibiting stability in human plasma, the resultant micelles responded to change in not only pH but also mannitol. Interestingly, when paclitaxel (PTX) was employed as a model drug, the release of PTX from the boronate crosslinked micelles was significantly slower than that from non-crosslinked micelles but can be accelerated by the acidic pH values and/or mannitol. This result demonstrates that reversible boronate esterification is useful as chemical stimulus-triggered switching of supramolecular systems in water.[101]
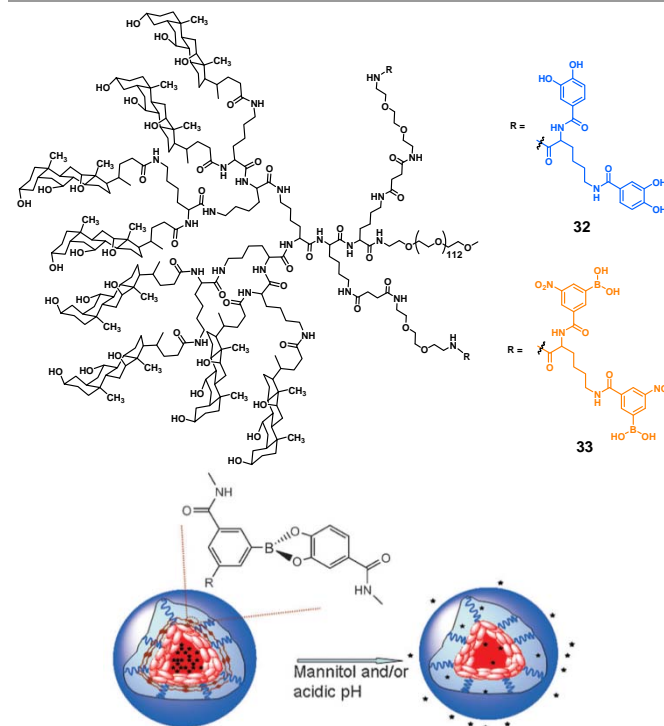
Fig. 22 Telodendorimer pair. (Reproduced with permission of Wiely from ref. 99.)

Well-ordered and boronate ester-based submicrospheres were first reported In 2012,[102] where pyridine-assisted sequential boronate esterification of benzene-1,4-diboronic acid and 1,2,4,5-tetrahydroxybenzene induced hierarchical self-assembly (Fig. 23). This result was unprecedented result since ordinary dehydration between the components provided no nucleation in toluene/10% MeOH under reflux with a Dean-Stark apparatus. The average diameter of the submicrospheres was estimated to be (870 ± 100) nm based on the field emission scanning electron microscopy (FE-SEM) images of 1000

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Fig. 23. Plausible mechanism for the formation of the submicroparticle.

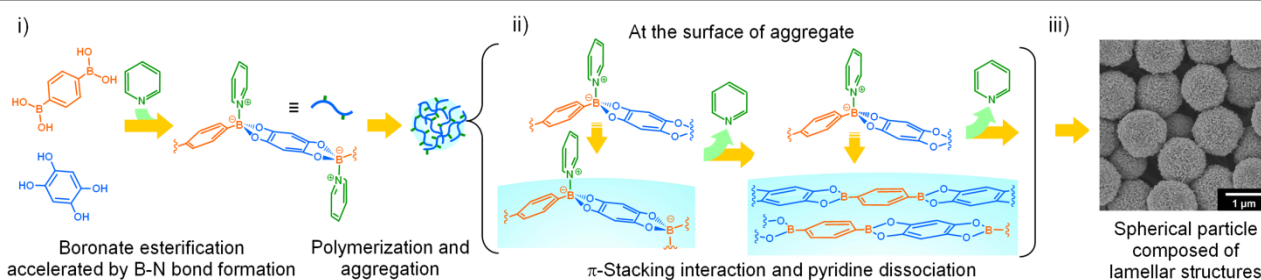particles. Spectroscopic analysis using attenuated total reflectance FTIR (ATR-FTIR) spectroscopy, NMR, and powder X-ray diffraction (XRD) indicated that the particles were composed of lamellar structures of sp^2 trigonal planar poly(dioxaborole). Pyridine is indispensable in boronate polymerisation; the B–N interaction between boronic acid and pyridine nitrogen allows boronate esterification to occur more easily than when under amine-free conditions through B–N interaction. A plausible mechanism for the particle formation is also shown in Fig. 23. Subsequent pyridine-assisted polymerisation induced a solvophobic orthogonal interaction, based on phenyl-boron-phenyl π-stacking, leading to dispersible nucleation. Upon aggregation, pyridine-coordinated boronate ester polymers are converted into planar structures via the elimination of pyridine, which is interpreted as the planar state that is composed of trigonal planer boronate ester being more thermodynamically favourable than the pyridine-coordinated tetrahedral structure. As a result, spherical particles composed of lamellar nanostructures were produced, and their size depends on minimisation of the interfacial free energy between the particles and solvent used.[103] According to Meijer's classification, the observed hierarchical growth of boronate-based aggregates may be classified as nucleation-elongation mechanism.[29] Further study is in progress to clarify two distinct nucleation and subsequent cooperative elongation processes.[104] It was also found that the dynamic covalent functionality of boronate ester linkages in the particles induced a stimulus-responsive change in their morphology. During this study, sequential boronate esterification of benzene-1,4-diboronic acid with pentaerythritol induced hierarchical molecular self-assembly to produce mono-dispersed flower-like microparticles (**BP**) with an averaged diameter of 2.3 ± 0.3 μm (Fig. 24).[105] Spectroscopic analysis indicates the formation of the particle consist of zigzag-shaped packing structure of polymeric 3-benzo-2,4,8,10-tetraoxa-3,9-diboraspiro[5.5]undecane (**34**). For the functionalisation, Kubo envisaged how such microparticles might have application in the fabrication of organic–inorganic hybrid catalysts. This is because the development of new types of catalysts in fine chemical synthesis is urgently required from the viewpoint of sustainable chemistry and green organic synthesis.[106] After several trials, the deposition of nano-gold onto the **BP** was achieved when a MeOH solution of HAuCl$_4$ was added
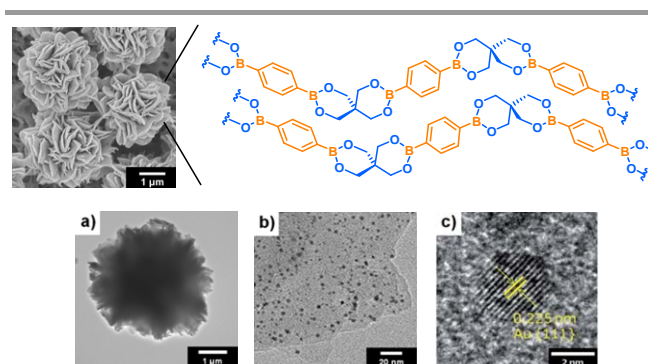

Fig. 24. Formation of flower-like microparticles (**BP**) composed of staking structures of boronate polymers **34**. (a) TEM image of **Au/BP**.(b) TEM image of the corresponding microparticle. (c) The HR-TEM image of a lattice structure observed for the {111} facet of the Au NP. (Adapted from ref. 105.)

to a turbid solution of **BP** in the presence of polyethyleneimine (PEI). **Au/BP** maintains the distinct shape (Fig. 24a) where dispersive nano-golds with a mean diameter of 2.7 nm were deposited on the **BP** (Fig. 24b). The space fringes of the Au NPs could be detected in the HR-TEM image to be $d = 0.225$ nm (Fig. 24c), which is well consistent with the {111} facet of Au. It was confirmed that highly dispersed Au NPs (2.3 wt%) could be deposited onto the boronate surface. The catalytic activity was tested through the reduction of 4-nitrophenol (**4-NP**) with NaBH$_4$, the reaction being often used as a test reaction to investigate the catalytic performance of candidate catalysts because the reaction kinetics is simultaneously recorded by absorption spectra, enabling us to easily determine the quantitative activity.[107] The reaction was conducted using Au(0), 4-NP, and NaBH$_4$ in a 1:90:1250 molar ratio, and progress was monitored by observing, the decrease in absorbance due to **4-NP** with an increase due to 4-aminophenol (**4-AP**). The reaction was nealy completed within 320 s. A linear relationship was observed between this logarithm value $\ln(A_t/A_0)$ and reaction time, the pseudo-first order rate constant (k) being estimated to be 1.6×10^{-2} s^{-1}. The turnover frequency (TOF) of **Au/BP** was estimated to be 1013 h^{-1}. Compared to conventional polymer-

supported Au nanoparticles,[108] the **Au/BP** exhibited an efficient catalytic activity for the reduction.

This successful result for the use of **BP** as a support material for inorganic/organic catalytic systems motivated the researchers to develop green catalysts based on boronate microparticles. Selective hydrogenation of α,β-unsaturated aldehydes, which has been widely investigated in catalyst chemistry.[109] It is known that Pd nanoparticle-based catalysts are one of the most promising systems for selective hydrogenation of the C=C bond; however, there are few reports on Pd catalysts that are applicable to green solvent processes in which comparatively larger amounts of catalysts[110] or higher pressures of H_2[111] are required. Considering the stable dispersion capability of boronate particles in aqueous media (*vide infra*), Pd-deposited boronate particles (**Pd/BP**) were prepared by the $NaBH_4$ reduction of $PdCl_4^{2-}$ in MeOH, in the presence of polyethyleneimine (PEI)-coated boronate particles (**BP**s), 0.66 wt% of nano-palladium being deposited on the surface, which were then applied for hydrogenation of cinnamaldehyde (**CA**) as green catalysts.[112] The hydrogenation of **CA** over **Pd/BP**s was then investigated in water under ambient conditions (0.1 MPa of H_2, 25 °C) (Scheme 2). The reaction over the catalysts proceeded significantly under the conditions; for 6 h, the hydrogenation over the hybrid catalyst afforded **HCA** in 94% yield with a reaction conversion of 100%. 3-Phenyl-1-propanol (**PPL**) was formed in only 6% yield with no detectable amount of cinnamyl alcohol (**CAL**). Taking into account the low solubility of H_2 in water,[113] **Pd/BP** showed a significant catalytic activity for hydrogenation to **HCA** with a TOF value of 33 h^{-1}. When performed in MeOH, an environmentally preferable solvent that is water-soluble, biodegradable, and occurs naturally in the environment, was employed as the reaction solvent, a more efficient catalytic activity could be obtained; the reaction was complete within 4 h to afford **HCA** in 92% yield with a TOF value of 50 h^{-1}. It is noteworthy that further reduction to **PPL** from **HCA** was not observed under these conditions, indicating that **Pd/BP** is highly selective catalyst for **HCA** via hydrogenation of **CA** using a green process. In addition, when used in MeOH, **Pd/BP** could be reused at least four times without appreciable loss of its catalytic activity or selectivity.
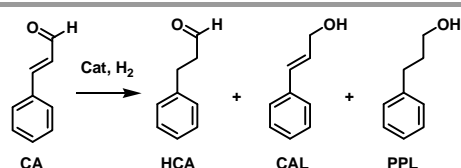
Scheme 2. Hydrogenation of cinnamaldehyde (**CA**) over **Pd/BP**.

BPs can be dispersed in aqueous media as a microparticle, and have a negative value of zeta (ξ) potential of the **BP** surface. This may indicate that terminal hydroxyl groups of the component polymers may be present at the periphery of the microparticles,[114] meaning that surface functionalization by grafting is possible. As such, due to interest in developing luminescent hierarchical materials, a white-light emissive chemosensor (**Sen-BP**) was fabricated by covalently grafting boronic acid-appended pyrene, dancyldiethylenetriamine, and rhodamine B to the surface through boronate esterification (Fig. 25).[115] The diethylenetriamine segment

serves as a metal ion-binding site[55] Upon adding Cu^{2+} in HEPES buffer at pH 7.0, the emission intensity in the wide range of the visible spectrum between 450 nm and 625 nm was efficiently decreased by adding Cu^{2+}, which suggests that the complex formation between the dansyldiethylenetriamine moiety and Cu^{2+} could not only induce fluorescence quenching of the dansyl fluorophore, but also the fluorescence intensity of the rhodamine B unit due to a reduced decrease fluorescence resonance energy transfer (FRET) from dansyl to rhodamine B units. This result indicated that boronate particles serve as a promising platform for the development of hierarchical materials with sensing/recognition capability.
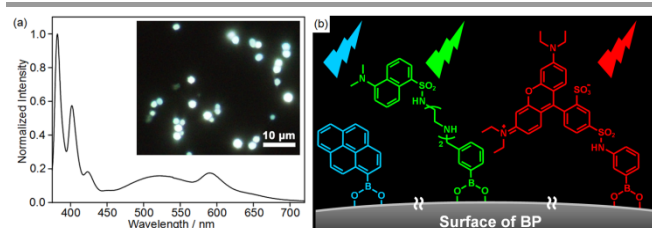
Fig. 25 Preparation of water-dispersible white-light emitting boronate microparticles. (Adapted from ref. 115.)

Interest in aggregation-induced emission (AIE) phenomena, the exact opposite of aggregation-caused quenching (ACQ), has been growing rapidly.[116] In 2001, Tang et al., firstly reported a propeller-shaped molecule with an AIE effect.[117] This interesting property can offer a versatile approach to the development of solid-state luminescence materials.[118] Tetraphenylethylene (TPE) and its derivatives are among the most promising AIE-luminogens for applications in organic light-emitting diodes,[119] stable and versatile bioprobes in medical diagonotics,[120] chemosensors in molecular recognition[121] and so on. Synergistic effects of AIE and boronic acid-based functions have been the subjects of significant interest.[122] Toward this end, considering the availability of TPE as a building block for constructing fluorescent network polymers,[123] inner functionalization of **BP** by incorporating AIE luminogen has been investigated to develop luminescent hierarchical materials where, 1,1'-di(p-dihydroxyborylpheny)-2,2'-biphenyl ethylene (**1,1-DB-TPB**) has been synthesized for the use as the component luminogen (Fig. 26a).[124]
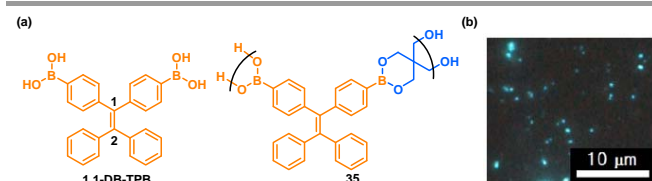
Fig. 26. (a) Chemical Structures of **1,1-DB-TPE** and Component polymer **35**. (b) a fluorescence microscopic image of **BP2**. (Adapted from ref. 124.)

Dehydration of **1,1-DB-TPE** and pentaerythritol produced an nanoparticles **BP2** in which **35** self-assembled (Fig. 26b), and displays a fluorescence with a peak at 479 nm when excited by 365 nm light in water. Taking advantageous of the facile dye-grafting of the surface of boronate aggregate,[115] multicolor emissive boronate nanoparticles (**R-BP2**) could be fabricated by tuning

amounts of rhodamine B grafted on the surface as a result of the synergistic effect of the TPE and rhodamine B units through FRET (Figs. 27a and 27b). When the amount of the dye grafted was 2.7 × 10^{-6} mol g^{-1}, white light emissive particles **R-BP2(W)** were formed. It was found that **R-BP2(W)** represent bright nanothermometer with a temperature sensitivity of 1.1%K^{-1} in water (Fig. 27c). The sensitivity is almost consistent with that of CdTe luminescence thermometry.[125] Temperature-dependent ring flipping of the unsubstituted phenyl rings in the TPE segments[126] plays a significant role in the thermo-responsive function, being followed by changes in the emission of the rhodamine B through FRET from TPE to the rhodamine B units. Such a synergistic effect of the emissive units led to a notable change in the emission color, which was easily detected by the naked eye.
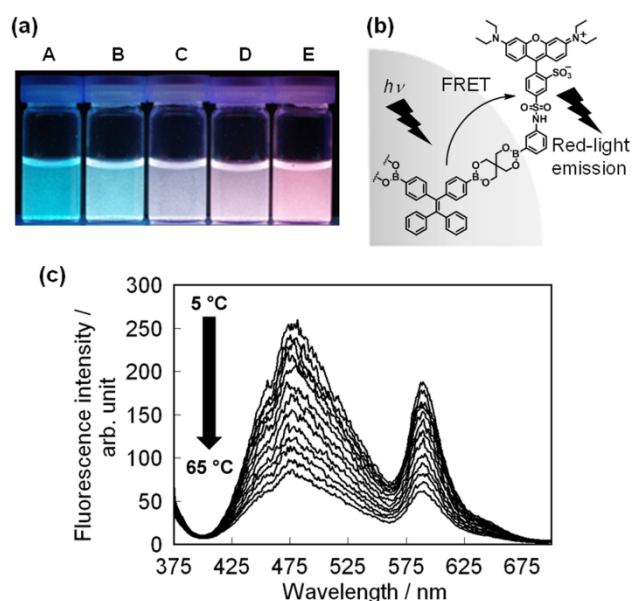

Fig. 27. (a) Photographs of the corresponding boronate nanoparticles (**R-BP2**) dispersion in aqueous media. λ$_{ex}$ = 365 nm. The amounts of grafted rhodamine B are A, 0.0 mol g^{-1}; B, 8.0 × 10^{-7} mol g^{-1}; C, 2.7 × 10^{-6} mol g^{-1}; D, 3.9 × 10^{-6} mol g^{-1} and E, 16 × 10^{-6} mol g^{-1}. (b) A plausible partial structure where FRET occurs in **R-BP2**. (c) Overall fluorescence spectra of **R-BP(W)** (0.1 mg mL^{-1}) in water at various temperatures. (Adapted from ref. 124.)

5. Conclusions and future remarks

This feature article covers recent progress of self-assembled/organised systems involving boronic acid building blocks, in which boronic acids act as connection tools with dynamic covalent functionality for the development of hierarchical supramolecular systems. Here, the emphasis is that their structure-directing properties enables easy accessible to the formation of supramolecular architectures at the nano and micro levels. This approaches are beneficial not only for constructing new network frames for applications in molecular electronics but also for support materials for heterogeneous catalysis and solid-state chemosensors. Furthermore, their biocompatibility enables application to drug delivery. The availability of boronic acids is not limited to connection tools for the fabrication of hierarchical nano- and micro structures. Other intriguing boron-based supramolecules have been

reported. For instance, in chirality manipulation, boronic acids are useful in the analysis of the enantiomeric excess of chiral amines through the assembly process.[127] Three–component chiral derivation based on boronate esterification occurs when mixing an α-chiral primary amine, *o*-formyl phenylboronic acid, and enantiopure 1,1'-bi-2-naphthol (BINOL), leading to characteristic ^{1}H-NMR spectroscopic shifts for each enantiomer of the amine. In addition, boron-based assembly protocol has been used for not only electrochemical determination of the enantiomeric excess of BINOL,[128] but also the development of a sensing array by means of circular dichroism (CD) spectroscopy[129] and CD-based sensors arising from guest-induced helical stacks.[130] Also noteworthy is that boronic acid-appended fluorophores have been used as reaction-based chemosensors.[131] A H$_2$O$_2$-triggered response, based on the oxidative conversion of boronates to phenols, is particularly significant, and is widely applied to noninvasive detection tools in biological systems.[132] In this context, recently, from the standpoint of security purposes, trace detection of peroxide-based explosives is recently growing in importance.[133] Toward this end, the synthesis of boronate systems with outstanding optical properties is worthwhile because of their highly sensitive visual detection of H$_2$O$_2$ vapor.[19,134]

Taken together, it is very exciting that boronic acid-based systems are widespread in many versatile fields of material science. However, sophisticated design and pre-organization methodology of the desired hierarchical systems arranged in fibrous, tubular, toroidal, and spherical nano- and micro structures is still in its infancy where synergistic function should be controlled in parallel accompanying with morphological control. This may be because encoding molecular modules for the construction of desired nano- and microsystems is rather difficult. We believe that the use of boronic acids as building blocks will enable chemists to engineer self-organised functional materials with inherent "softness" based on the boron-based dynamic covalent functionality. Accordingly, we are confident that in the future an ever increasing number and types of boron-based hierarchical systems will be developed.

Acknowledgements

Journal Name

Notes and references

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† Dedicated to Professor Seiji Shinkai to celebrate his 70th birthday.

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