Opportunities Using Boron to Direct Reactivity in the Organic Solid State

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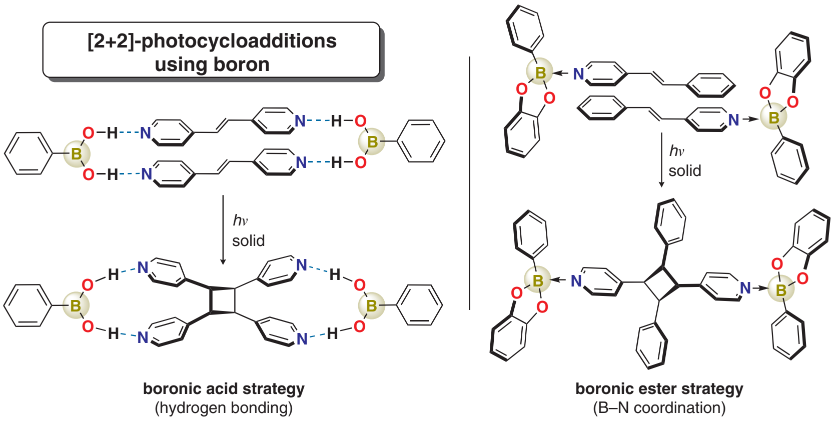

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Abstract This Account describes work by our research group that highlights opportunities to utilize organoboron molecules to direct chemical reactivity in the organic solid state. Specifically, we convey a previously unexplored use of hydrogen bonding of boronic acids and boron coordination in boronic esters to achieve [2+2]-photocycloadditions in crystalline solids. Organoboron molecules act as templates or 'shepherds' to organize alkenes in a suitable geometry to undergo regio- and stereoselective [2+2]-photocycloadditions in quantitative yields. We also provide a selection of publications that served as an inspiration for our strategies and offer challenges and opportunities for future developments of boron in the field of materials and solid-state chemistry.

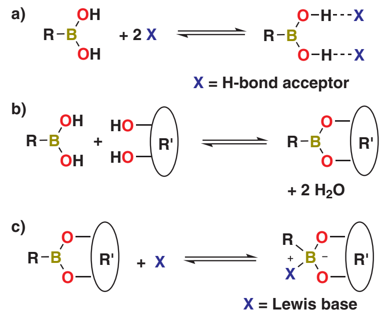
Key words boron, [2+2]-photocycloadditions, solid-state chemistry, supramolecular chemistry, hydrogen bond, boron coordination

1 Introduction

Organoboron compounds represent a long-standing class of auxiliary molecules for organic synthetic transformations. A testament of the synthetic value of this class of molecules is the development of C–C bonds through the Suzuki–Miyaura coupling (or Suzuki coupling) through metal-catalyzed cross-coupling reactions with boronic acid derivatives (i.e., 2010 Nobel Prize in Chemistry).[1] Although boron reagents continue to inspire new methodologies in synthetic chemistry,[2] the potential of supramolecular chemistry of boron compounds, particularly from boronic acids and derivatives, has remained largely underexplored in the context of synthetic transformations.

Versatility of supramolecular chemistry of boronic acid and derivatives relies on the unique electronic properties resulting from the trivalent boron that possess one carbon-based substituent (i.e., C–B bond). The boron atom possesses a vacant p-orbital due to sp^2 hybridization, which is orthogonal to the substituents.[3] Depending on reaction conditions, boronic acids and derivatives can act as either Brønsted–Lowry or Lewis acids.[4]

For instance, boronic acids can act as hydrogen-bond donors with suitable bases (e.g., pyridines) (Scheme 1a) or can form *reversible* covalent chelates (i.e., boronic esters)



Scheme 1 Supramolecular interactions of boronic acids and boronic esters: (a) hydrogen bonding, (b) esterification, (c) Lewis base coordination.

upon condensation with diols (Scheme 1b). In turn, boronic esters can coordinate Lewis bases *via* the empty p-orbital to generate adducts (Scheme 1c).[3,5]

All of the observations above inspired us to introduce the use of boronic acids (Figure 1a) and boronic esters (Figure 1b) as templates or 'shepherds' to position alkenes in suitable geometries for [2+2]-photocycloadditions in the organic solid state through hydrogen bonding and boron coordination (i.e., B←N interaction), respectively. By doing so, the capacity of boronic acid derivatives to function as tools to make use of organic solids as media to construct unique and novel molecules can be realized.

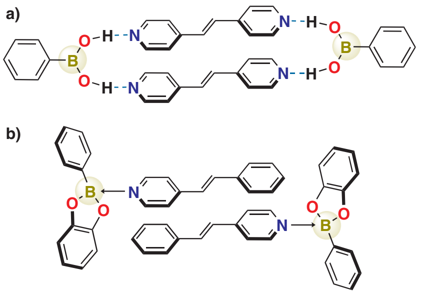


Figure 1 Template strategy using (a) hydrogen bonds in boronic acids and (b) B←N interactions in boronic esters.

1.1 Template Strategy for [2+2]-Photocycloadditions in the Solid State

The template strategy has mostly involved the use of ditopic molecules to direct chemical reactivity in the organic solid state. The approach exploits weak, noncovalent interactions to align otherwise photostable alkenes parallel and within a distance of 4.2 Å according to the geometry criteria of Schmidt (Scheme 2a).[6] Specifically, we introduced the use of molecules in form of linear templates to reliably stack C=C bonds into positions to react and, at the same time, enable the modular construction and access a variety of products.[7] The first example of a linear molecular template involved the cocrystallization of resorcinol (res) with *trans*-1,2-bis(4-pyridyl)ethene (bpe). The resulting cocrystals consisted of four-component assemblies, or macrocycles, wherein two res molecules (templates) organizes bpe molecules (reactants) through (C)O–H···N hydrogen bonds. UV-light irradiation resulted in the quantitative formation of *rctt*-tetrakis(2-pyridyl)cyclobutane (tpcb) stereoselectively and gram scale (Scheme 2b). The molecular template can be conveniently removed from tpcb following photoreaction by basic extraction.[7a]

The inherent modularity of the template strategy was subsequently exploited to assemble and preorganize polyenes to generate [2.2]cyclophanes[8] and [*n*]ladderanes[9]

Biographical Sketches

Gonzalo Campillo-Alvarado is a DRIVE postdoctoral research associate in the Illinois Distinguished Postdoctoral and Visiting Scholar Program at the University of Illinois at Urbana-Champaign mentored by Prof. Ying Diao (Department of Chemical & Biomolecular Engineering). He obtained his BSc in biopharmaceutical chemistry at Universidad Veracruzana in Xalapa, Veracruz, Mexico. He later completed a MSc in chemistry at Universidad Autónoma del Estado de Morelos, Mexico. In 2020, he received his PhD in chemistry from the University of Iowa under the supervision of Prof. Leonard R. MacGillivray as a CONACyT fellow. His research interests gravitate toward the design of functional materials (e.g., electronics, pharmaceutics, photoactive solids, and materials for separation) with emphasis on boron using elements of crystal engineering.

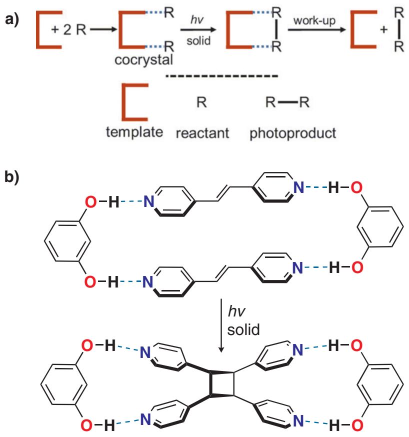
Len MacGillivray is a Professor and Chair of the Department of Chemistry and Professor in the College of Pharmacy at the University of Iowa. He obtained his BSc (Hons) at Saint Mary's University in Halifax, Nova Scotia, Canada (1994) and then went on to obtain a PhD in chemistry as a NSERC 1967 Science and Engineering Scholarship recipient at the University of Missouri-Columbia (1998). Following his PhD he was a research associate at the Steacie Institute of Molecular Sciences at the National Research Council of Canada, Ottawa, Canada (1998–2000). The current research of Professor MacGillivray focuses on applications of supramolecular chemistry to the crystal engineering of co-crystals for applications in organic chemistry, materials science, and pharmaceutics. Professor MacGillivray received an Arthur C. Cope Scholar Award of the American Chemical Society in 2007 and is currently a fellow of the Royal Society of Chemistry (RSC, 2007), American Association for the Advancement of Science (2012), and the American Chemical Society (2015). He has published over 230 manuscripts and is currently a co-editor of the International Union of Crystallography Journal (IUCrJ).

(Figure 2a,d), where n = 3 (Figure 2b) and 5 (Figure 2c) whose solution-phase organic syntheses had been a challenge and largely limited to exceptionally low yields.[10]

Our group has since expanded the library of organic and inorganic molecular templates to promote [2+2]-photocycloadditions in solids (e.g., halophenols,[11] catechol,[12] halogenated molecules,[13] diacids,[14] silver,[15] and gold[16] salts). The use of boron molecules to aid photochemical transformations in solids had not been explored.

2 Boronic Acids as Templates for [2+2]-Photocycloadditions in the Solid State

Boronic acids are a quintessential class of reagents, being based on the –B(OH)$_2$ moiety.[3] The ability of boronic acids to engage in supramolecular recognition has rapidly surfaced after reports of boron-based pharmaceuticals[17] and saccharide receptors.[18] Seminal work by Pedireddi and collaborators,[19] for instance, provided the first evidence for the potential of boronic acids to act as receptors for aza-donor molecules in the solid state. In the study, phenylboronic acid (**ba**) was cocrystallized with 4,4′-bipyridine (**bpy**), *trans*-1,2-bis(4-pyridyl)ethene (**bpe**) affording a series of cocrystals facilitated by (B)O–H···N hydrogen bonds and π···π interactions (Figure 3a). An extension to the recognition capacity of boronic acids was realized by the generation of polymeric supramolecules (Figure 3b).



Scheme 2 (a) Template strategy for [2+2]-photocycloadditions in the solid state through cocrystallization; (b) formation of **tpcb** from **bpe** using **res** as template.

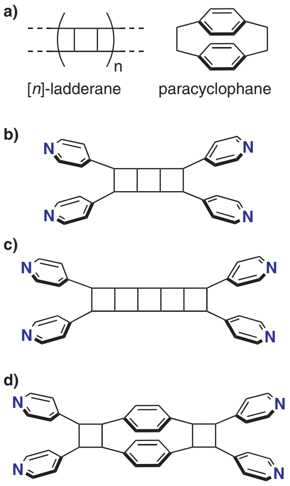


Figure 2 (a) Targets of [2+2]-photocyloadditions using template strategy, (b) [3]-ladderane, (c) [5]-ladderane, and (d) [2.2]paracyclophane.

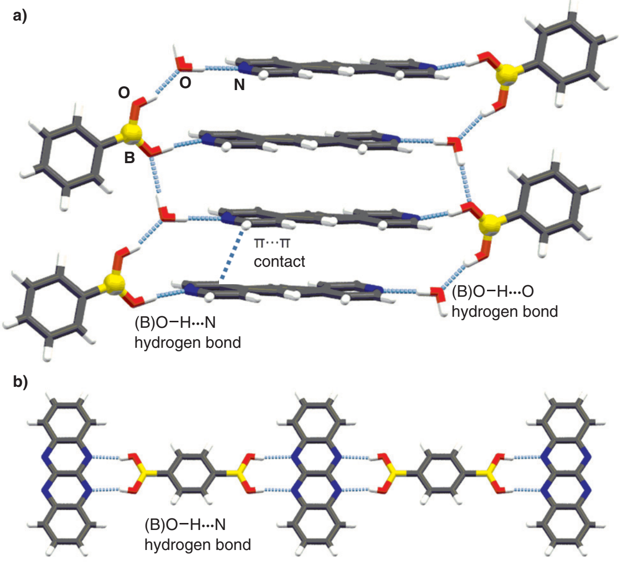


Figure 3 Supramolecular assemblies of boronic acids (H-bond donors) with acceptors: (a) infinite stacks and (b) polymers.

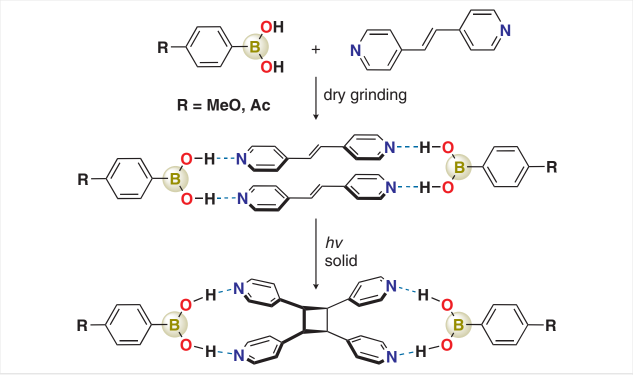
The close structural similarity of linear templates (e.g., **res**) used to achieve [2+2]-photocycloadditions in the solid state inspired our group to employ phenylboronic acids as templates.[20]

Our initial studies to achieve [2+2]-photocycloadditions in solids involved the formation of cocrystals through dry mortar-and-pestle grinding of 4-methoxy- and 4-acetylphenylboronic acids (**4-MeO** and **4-AcO**, respectively) with **bpe** (Scheme 3). In the solids, the boronic acids organize **bpe** into four-component discrete assemblies sustained by (B)O–H···N hydrogen bonds and π···π interactions (Figure 4, a and b). The assemblies in the solid were photoactive. Specifically, UV irradiation generated **tpcb** stereoselectively and in up to 96% yield. Dry grinding – a process in the field of mechanochemistry[21] – of the components after photoreaction and subsequent UV-light irradiation generated **tpcb** quantitatively.

Remarkably, the templated reaction using the boronic acid proceeded as a rare single-crystal-to-single-crystal (SCSC) transformation that provided insight into the photochemical process in the solid state (Figure 4c). The SCSC demonstrated that hydrogen bonding in boronic acids display flexibility in single crystals that promote crystal reactivity.[20]

2.1 Supramolecular Catalysis of [2+2]-Photocycloadditions in the Solid State Using Boronic Acids

[2+2]-Photodimerization of **bpe** was also achieved by supramolecular organocatalysis in the solid state[22] using boronic acids. A combination of dry grinding and continuous UV irradiation using substoichiometric **4-MeO** and **4-AcO** with **bpe** resulted in the quantitative formation of **tpcb** in a catalytic cycle (Scheme 4). Our observations demonstrated that mechanochemistry facilitates turnover (i.e., displacement of **tpcb** from cocrystal and stacking of additional **bpe**) and supports full conversion of reactants to products.[20]



Scheme 3 Template strategy using hydrogen bonds in boronic acids.

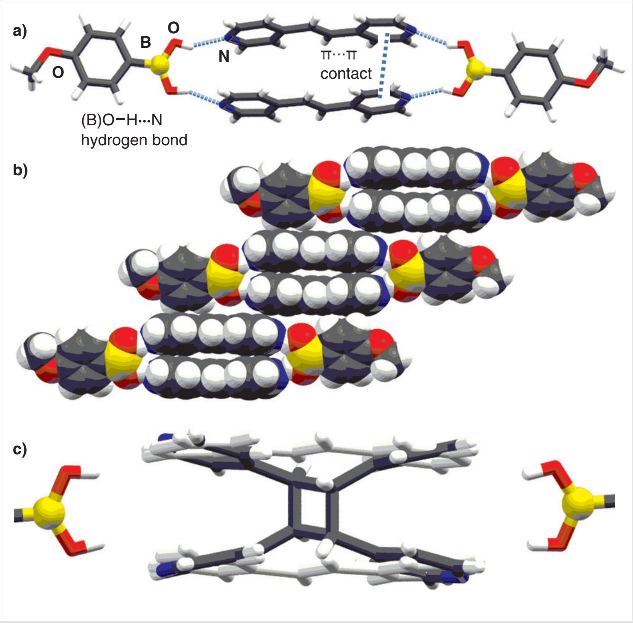
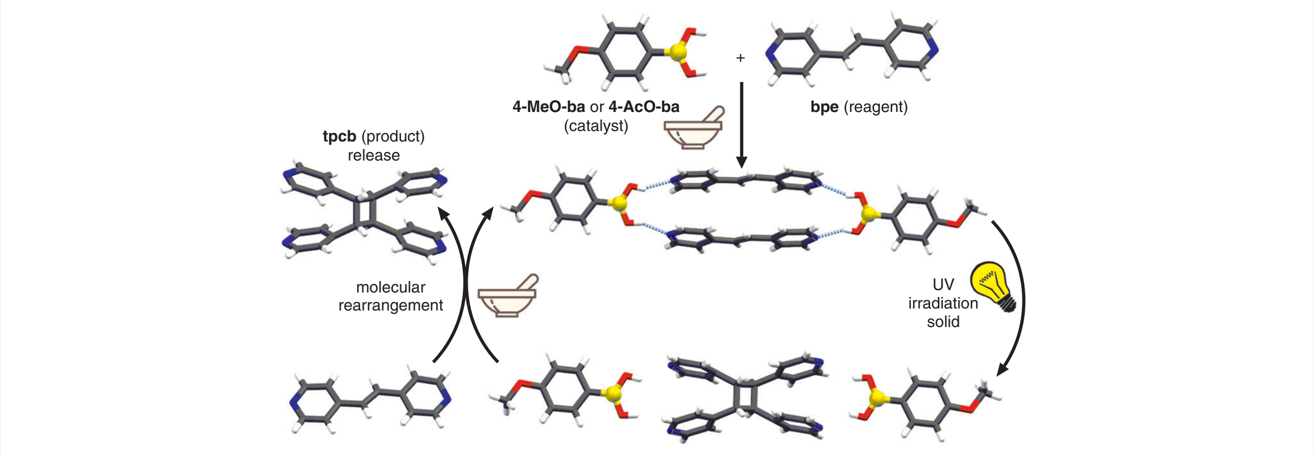


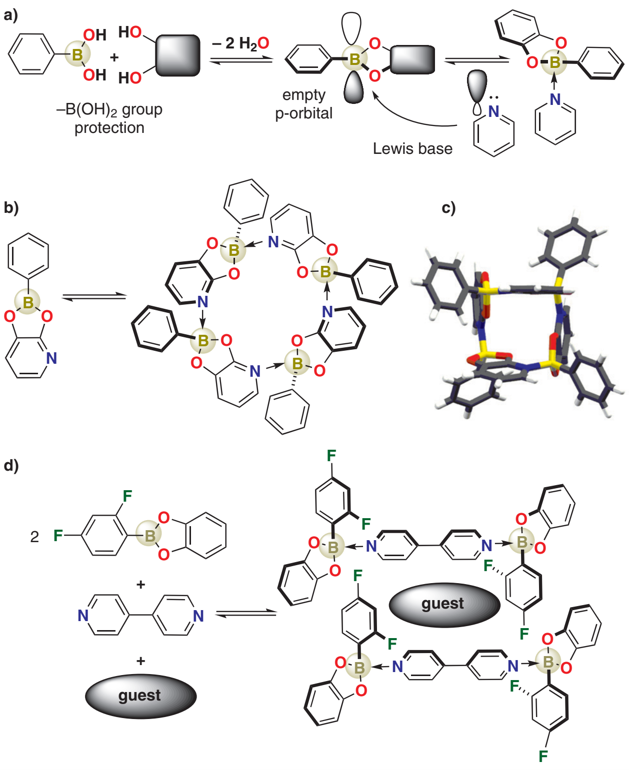
Figure 4 Crystal structure of (**4-MeO**)·(**bpe**): (a) discrete assembly, (b) space-filling view of adjacent assemblies, and (c) SCSC [2+2]-photocycloaddition.

3 Boronic Esters as Templates for [2+2]-Photocycloadditions in the Solid State

Boronic esters are an exceptional class of molecules that exhibit dynamic covalent chemistry (i.e., ability of covalent bond to form or break upon external stimuli).[23] Owing to the protection of the $-B(OH)_2$ moiety, the empty p-orbital of boron, located orthogonally to the substituents, becomes readily available for dative bonding with suitable Lewis bases (e.g., pyridines).[24] Boron coordination is accompanied with a change in geometry of the boron center from trigonal planar to tetrahedral (Scheme 5a).[25]



Scheme 4 Supramolecular catalysis of [2+2]-photocycloadditions in the solid state using boronic acids.

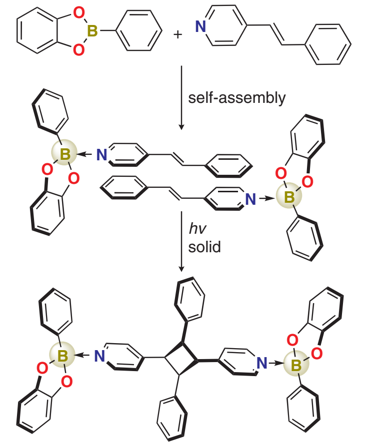


Scheme 5 (a) B←N interaction between the empty p-orbital of boron with a Lewis base (e.g., pyridine), (b) macrocycle formation through B←N interaction, (c) crystal structure of macrocycle, and (d) host–guest complexes based on B←N interaction.

In this context, B←N interaction has been an emerging supramolecular force in the last decade for the construction of supramolecular materials (e.g., optical,[26] conductive,[27] porous[28]). Although the B←N interaction is relatively weak in solution,[25] it has been demonstrated to be a reliable and directional force in the solid state.[24a] Pioneering studies by Severin and Höpfl demonstrated that the B←N interaction can lead to the construction of diverse extended architectures such as discrete macrocycles (Scheme 5b),[29] as well as 2D[30] and 3D[28] extended networks.

The potential of the B←N interaction to form host-guest systems had also been evaluated by us in collaboration with the groups of Höpfl and Morales-Rojas.[31] In our study, two units of 2,4-difluorophenylboronic acid catechol ester were coordinated to 4,4′-bipyridine (**bpy**) through B←N interaction. The electron-deficient surface of **bpy** in combination with C–H···F contacts facilitated the π-stacking of electron-rich aromatics (Scheme 5c). The adaptability of the host towards guests of different size and electronic properties has enabled the formation separation of materials for separation of petrochemicals[31] and organic semiconductors (Figure 5).[27]

Motivated by the above observations, we turned to make use of the B←N interaction to facilitate reactivity in the solid state. Our strategy involved the combination of 4-stilbazole (**4-sbz**) with phenylboronic acid catechol ester (**be**). Specifically, we showed the adduct (**be**)·(**4-sbz**) to assemble into a dimer based on electronic complementarity. Stacking of the C=C bonds in the dimer fulfilled the geometric criteria of Schmidt for a [2+2]-photocycloaddition affording *rctt*-1,3-bis(4′-pyridyl)-2,4-bis(phenyl)cyclobutane (**ppcb**) upon UV irradiation (Scheme 6).[32]



Scheme 6 Template strategy using the B←N interaction in boronic esters to afford **ppcb**.

Crystallization of the components afforded a T-shaped boronic ester adduct of composition (**be**)·(**4-sbz**) wherein **4-sbz** was positioned orthogonally to **be**. Self-assembly of two monoboron adducts generated a discrete dimer with a head-to-tail geometry (ht) sustained by π···π and C–H···π contacts (Figure 6a,b). The dimers interact through C–H···π contacts. The crystalline powder (**be**)·(**4-sbz**) was highly photoactive upon UV irradiation as revealed by complete conversion into the diboron adduct 2(**be**)·(**ht-ppcb**) in a period of 20 min.

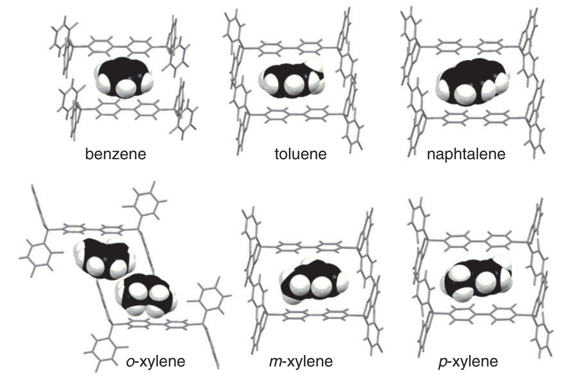


Figure 5 Crystal structures of host–guest complexes based on B←N boronic ester adducts with aromatics.

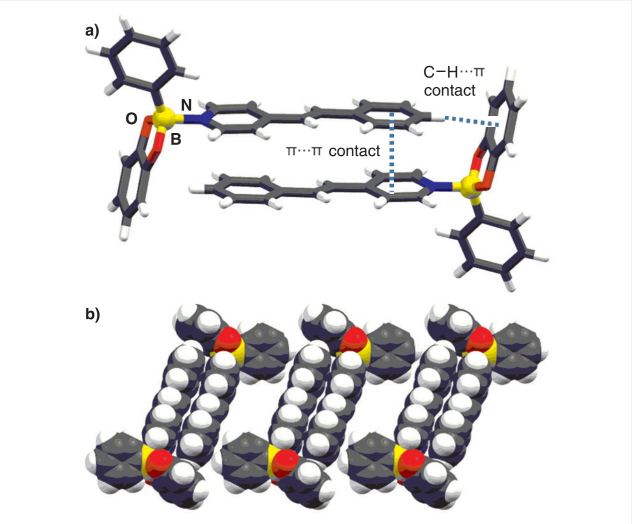


Figure 6 Crystal structure of (**be**)·(**4-sbz**): (a) supramolecular dimer, (b) space-filling view of discrete dimeric assemblies.

3.1 Application of Photoproducts: Separation of Thiophene from Benzene through Crystallization

Photoproduct 2(**be**)·(**ht-ppcb**) was determined to act as a supramolecular sponge when recrystallized with benzene (2(**be**)·(**ht-ppcb**)$\supset$2($\mathbf{C_6H_6}$), Figure 7a) and thiophene (2(**be**)·(**ht-ppcb**)$\supset$6($\mathbf{C_4H_4S}$), Figure 7b). Specifically, solvent molecules were confined within cavities generated from the be units and the terminal phenyl rings of ppcb. The solvent molecules were sustained by a combination of face-to-face and edge-to-face π···π contacts. In the case of 2(**be**)·(**ht-ppcb**)$\supset$6($\mathbf{C_4H_4S}$), a higher affinity of the boron host was ascribed to additional C–H···S forces.

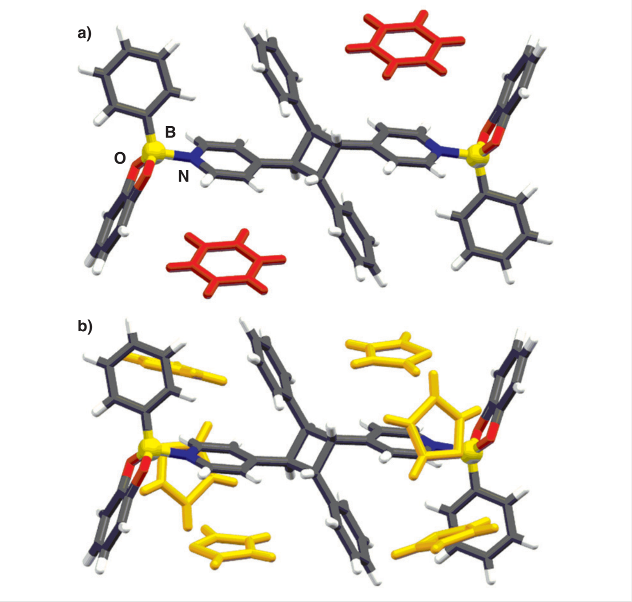
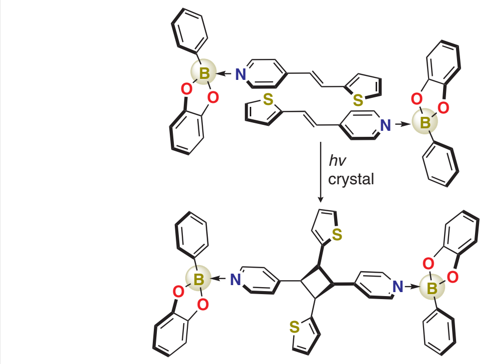


Figure 7 Crystal structures of (a) 2(**be**)·(**ht-ppcb**)$\supset$2($\mathbf{C_6H_6}$) and (b) 2(**be**)·(**ht-ppcb**)$\supset$6($\mathbf{C_4H_4S}$).

The higher affinity of the diboron sponge towards thiophene was exploited for the separation of a mixture of benzene/thiophene, an important and challenging process in petrochemistry due to close similarities in the physicochemical properties of both solvents.[33] Specifically, fractional crystallization resulted in a 94% thiophene enrichment after five cycles as indicated by ^{1}H NMR spectroscopy.

3.2 Crystal Reactivity of B←N-Bonded Adducts: The Case of Styrylthiophenes

Generality of the approach using the B←N interaction of boronic esters to achieve [2+2]-photocycloadditions was evaluated with thiophene *trans*-1-(4-pyridyl)-2-(2-thienyl)ethylene (**pte**).[34] [2+2]-Photodimerizations of thiophenes are extremely rare both in solution and in the solid state despite being desirable for the fields of electronics and organic semiconductors.[35] The template approach to perform [2+2]-photodimerizations involved B←N coordination of **pte** with **be** to afford a T-shaped monoboron adduct (**be**)·(**pte**). Photoreaction generates a diboron host with a ht geometry *rctt*-1,2-bis(4-pyridyl)-3,4-bis(2-thienyl)cyclobutane 2(**be**)·(**4p2tcb**) (Scheme 7).



Scheme 7 Template strategy using the B←N interaction in boronic esters to afford **4p2tcb**.

Single-crystal X-ray diffraction analysis revealed that [2+2]-photodimerization of (**be**)·(**pte**) to proceed as a SCSC transformation to generate 2(**be**)·(**4p2tcb**) (Figure 8a). The SCSC behavior of (**be**)·(**pte**) enabled us to gain unique mechanistic insight into structural changes that occur during the [2+2]-photodimerization involving B←N coordination. The formation of the cyclobutyl ring in 2(**be**)·(**4p2tcb**) was accompanied with titling of the thiophenyl ring and rotation of the aryl ring. The photoproduct 2(**be**)·(**4p2tcb**) was also employed as a host for chloroform solvent molecules, which were accommodated in channels formed by adjacent hosts and sustained by C–Cl···π contacts (Figure 8b).

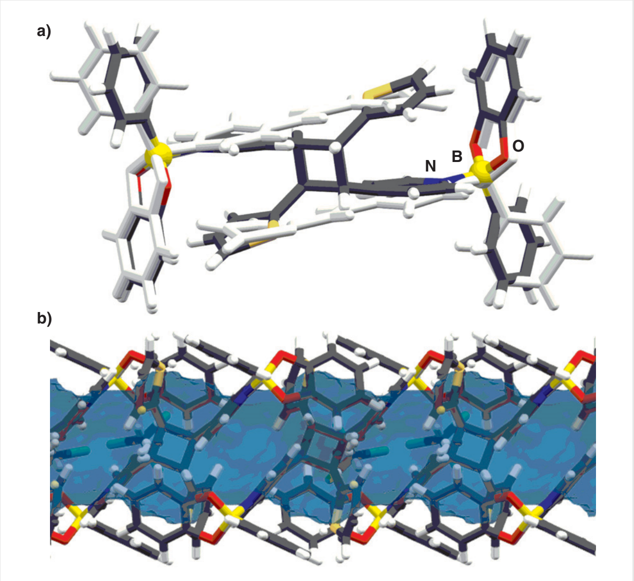


Figure 8 (a) Overlay of crystal structures of (**be**)·(**pte**) and 2(**be**)·(**4p2tcb**), and (b) channel formation involving 2(**be**)·(**4p2tcb**) with chloroform molecules.

4 Conclusions and Perspectives

In this Account we have described the ability of organoboron molecules to direct and support reactivity in the organic solid state. Hydrogen bonding using boronic acids and boron coordination using boronic esters organize olefins in a suitable geometry for [2+2]-photocycloadditions. The work has expanded on original synthetic uses of organoboron molecules as synthetic intermediates and provides a platform to generate synthetic targets of increasing complexity in solids (e.g., ladderanes, [2.2]cyclophanes). Cyclobutanes are also core architectures of pharmaceutics and natural products.[36] Solid-state reactivity using the template strategy has further enabled structural diversification of cyclobutane architectures that has resulted in functional molecular materials with intriguing properties (i.e., multi-responsive solids,[37] chemical patterning,[38] photoactuators[39]).

Looking forward, we envision pathways to new uses and applications of supramolecular chemistry to organoboron molecules in the context of solid-state reactivity. The fields of organic synthetic chemistry and crystal engineering stand to benefit from synthetic efforts that aim to diversify uses of boronic acids and derivatives.[2] The recognized ability to chemically decorate and functionalize organoboron molecules can be expected to result in the discovery of additional molecular boron-based templates that could be incorporated into an everyday toolbox of the synthetic organic chemists for the design and syntheses of creative and previously unattainable cyclobutane architectures.

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References

(1) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Lennox, A. J. J.; Lloyd-Jones, G. C. *Chem. Soc. Rev.* **2014**, *43*, 412. (c) Miyaura, N. *Synlett* **2009**, 2039.

(2) (a) Li, C.; Wang, J.; Barton, L. M.; Yu, S.; Tian, M.; Peters, D. S.; Kumar, M.; Yu, A. W.; Johnson, K. A.; Chatterjee, A. K.; Yan, M.; Baran, P. S. *Science* **2017**, 356. (b) Wang, J.; Shang, M.; Lundberg, H.; Feu, K. S.; Hecker, S. J.; Qin, T.; Blackmond, D. G.; Baran, P. S. *ACS Catal.* **2018**, *8*, 9537.

(3) Hall, D. G. *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials, 2nd ed*; John Wiley & Sons: Hoboken, **2006**, 571.

(4) Bentley, K. W.; Proano, D.; Wolf, C. *Nat. Commun.* **2016**, *7*, 12539.

(5) (a) Fujita, N.; Shinkai, S.; James, T. D. *Chem. Asian J.* **2008**, *3*, 1076. (b) Nishiyabu, R.; Kubo, Y.; James, T. D.; Fossey, J. S. *Chem. Commun.* **2011**, *47*, 1124. (c) Bull, S. D.; Davidson, M. G.; van den Elsen, J. M. H.; Fossey, J. S.; Jenkins, A. T. A.; Jiang, Y.-B.; Kubo, Y.; Marken, F.; Sakurai, K.; Zhao, J.; James, T. D. *Acc. Chem. Res.* **2013**, *46*, 312.

(6) MacGillivray, L. R.; Papaefstathiou, G. S.; Friščić, T.; Hamilton, T. D.; Bučar, D.-K.; Chu, Q.; Varshney, D. B.; Georgiev, I. G. *Acc. Chem. Res.* **2008**, *41*, 280.

(7) (a) MacGillivray, L. R.; Reid, J. L.; Ripmeester, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 7817. (b) MacGillivray, L. R. *J. Org. Chem.* **2008**, *73*, 3311.

(8) (a) Friščić, T.; MacGillivray, L. R. *Aust. J. Chem.* **2006**, *59*, 613. (b) Elacqua, E.; Friščić, T.; MacGillivray, L. R. *Isr. J. Chem.* **2012**, *52*, 53.

(9) Gao, X.; Friščić, T.; MacGillivray, L. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 232.

(10) Hopf, H. *Angew. Chem. Int. Ed.* **2003**, *42*, 2822.

(11) Campillo-Alvarado, G.; Li, C.; Swenson, D. C.; MacGillivray, L. R. *Cryst. Growth Des.* **2019**, *19*, 2511.

(12) (a) Quentin, J.; MacGillivray, L. R. *ChemPhysChem* **2020**, *21*, 154. (b) Papaefstathiou, G. S.; Duncan, A. J. E.; MacGillivray, L. R. *Chem. Commun.* **2014**, *50*, 15960.

(13) Sinnwell, M. A.; Blad, J. N.; Thomas, L. R.; MacGillivray, L. R. *IUCrJ* **2018**, *5*, 491.

(14) Hutchins, K. M.; Sumrak, J. C.; Swenson, D. C.; MacGillivray, L. R. *CrystEngComm* **2014**, *16*, 5762.

(15) (a) Chu, Q.; Swenson, D. C.; MacGillivray, L. R. *Angew. Chem. Int. Ed.* **2005**, *44*, 3569. (b) Kole, G. K.; Medishetty, R.; Koh, L. L.; Vittal, J. J. *Chem. Commun.* **2013**, *49*, 6298. (c) Kole, G. K.; Tan, G. K.; Vittal, J. J. *Cryst. Growth Des.* **2012**, *12*, 326.

(16) (a) Li, C.; Campillo-Alvarado, G.; Swenson, D. C.; MacGillivray, L. R. *Inorg. Chem.* **2019**, *58*, 12497. (b) Nagarathinam, M.; Peedikakkal, A. M. P.; Vittal, J. J. *Chem. Commun.* **2008**, 5277. (c) Mir, M. H.; Ong, J. X.; Kole, G. K.; Tan, G. K.; McGlinchey, M. J.; Wu, Y.; Vittal, J. J. *Chem. Commun.* **2011**, *47*, 11633.

(17) (a) Campillo-Alvarado, G.; Didden, T.; Oburn, S.; Swenson, D. C.; MacGillivray, L. R. *Cryst. Growth Des.* **2018**, *18*, 4416. (b) Campillo-Alvarado, G.; Staudt, C. A.; Bak, M. J.; MacGillivray, L. R. *CrystEngComm* **2017**, *19*, 2983. (c) Richardson, P. G.; Barlogie, B.; Berenson, J.; Singhal, S.; Jagannath, S.; Irwin, D.; Rajkumar, S. V.; Srkalovic, G.; Alsina, M.; Alexanian, R. *N. Engl. J. Med.* **2003**, *348*, 2609.

(18) (a) James, T. D.; Phillips, M. D.; Shinkai, S. *Boronic Acids in Saccharide Recognition*; RSC: Cambridge, **2006**, 174. (b) James, T. D.; Sandanayake, K.; Shinkai, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1910.

(19) Pedireddi, V.; SeethaLekshmi, N. *Tetrahedron Lett.* **2004**, *45*, 1903.

(20) Campillo-Alvarado, G.; Brannan, A. D.; Swenson, D. C.; MacGillivray, L. R. *Org. Lett.* **2018**, *20*, 5490.

(21) Friščić, T.; Mottillo, C.; Titi, H. M. *Angew. Chem. Int. Ed.* **2020**, *59*, 1018.

(22) (a) Sokolov, A. N.; Bučar, D. K.; Baltrusaitis, J.; Gu, S. X.; MacGillivray, L. R. *Angew. Chem. Int. Ed.* **2010**, *49*, 4273. (b) Oburn, S. M.; Quentin, J.; MacGillivray, L. R. *Molecules* **2019**, *24*, 3059.

(23) (a) Iwasawa, N.; Takahagi, H. *J. Am. Chem. Soc.* **2007**, *129*, 7754. (b) Nishimura, N.; Yoza, K.; Kobayashi, K. *J. Am. Chem. Soc.* **2009**, *132*, 777. (c) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. *Angew. Chem. Int. Ed.* **2002**, *41*, 898.

(24) (a) Luisier, N.; Bally, K.; Scopelliti, R.; Fadaei, F. T.; Schenk, K.; Pattison, P.; Solari, E.; Severin, K. *Cryst. Growth Des.* **2016**, *16*, 6600. (b) Campillo-Alvarado, G.; D'mello, M. M.; Sinnwell, M. A.; Höpfl, H.; Morales-Rojas, H.; MacGillivray, L. R. *Front. Chem.* **2019**, *7*, 695. (c) Cruz-Huerta, J.; Campillo-Alvarado, G.; Höpfl, H.; Rodríguez-Cuamatzi, P.; Reyes-Márquez, V.; Guerrero-Álvarez, J.; Salazar-Mendoza, D.; Farfán-García, N. *Eur. J. Inorg. Chem.* **2016**, 355.

(25) Höpfl, H. *J. Organomet. Chem.* **1999**, *581*, 129.

(26) Ono, T.; Taema, A.; Goto, A.; Hisaeda, Y. *Chem. Eur. J.* **2018**, *24*, 17487.

(27) Ray, K. K.; Campillo-Alvarado, G.; Morales-Rojas, H.; Höpfl, H.; MacGillivray, L. R.; Tivanski, A. V. *Cryst. Growth Des.* **2020**, *20*, 3.

(28) Stephens, A. J.; Scopelliti, R.; Tirani, F. F.; Solari, E.; Severin, K. *ACS Mater. Lett.* **2019**, *1*, 3.

(29) Christinat, N.; Scopelliti, R.; Severin, K. *Chem. Commun.* **2004**, 1158.

(30) Cruz-Huerta, J.; Salazar-Mendoza, D.; Hernández-Paredes, J.; Ahuactzi, I. F. H.; Höpfl, H. *Chem. Commun.* **2012**, *48*, 4241.

(31) Campillo-Alvarado, G.; Vargas-Olvera, E. C.; Höpfl, H.; Herrera-España, A. D.; Sánchez-Guadarrama, O.; Morales-Rojas, H.; MacGillivray, L. R.; Rodríguez-Molina, B.; Farfan, N. *Cryst. Growth Des.* **2018**, *18*, 2726.

(32) Campillo-Alvarado, G.; D'mello, K. P.; Swenson, D. C.; Santhana Mariappan, S. V.; Höpfl, H.; Morales-Rojas, H.; MacGillivray, L. R. *Angew. Chem. Int. Ed.* **2019**, *58*, 5413; *Angew. Chem.* **2019**, *131*, 5467.

(33) Fu, H.; Wang, Y.; Zhang, T.; Yang, C.; Shan, H. *J. Phys. Chem. C* **2017**, *121*, 25818.

(34) Campillo-Alvarado, G.; Li, C.; Feng, Z.; Hutchins, K. M.; Swenson, D. C.; Höpfl, H.; Morales-Rojas, H.; MacGillivray, L. R. *Organometallics* **2020**, *39*, 2197.

(35) (a) Hutchins, K. M.; Sumrak, J. C.; MacGillivray, L. R. *Org. Lett.* **2014**, *16*, 1052. (b) Green, B. S.; Heller, L. *J. Org. Chem.* **1974**, *39*, 196. (c) Dai, Y.; Tan, J.; Ye, N.; Yang, Z. *CrystEngComm* **2014**, *16*, 636.

(36) Li, J.; Gao, K.; Bian, M.; Ding, H. *Org. Chem. Front.* **2020**, *7*, 136.

(37) Claassens, I. E.; Barbour, L. J.; Haynes, D. A. *J. Am. Chem. Soc.* **2019**, *141*, 11425.

(38) Park, I.-H.; Lee, E.; Lee, S. S.; Vittal, J. J. *Angew. Chem. Int. Ed.* **2019**, *58*, 14860.

(39) Mandal, R.; Garai, A.; Peli, S.; Datta, P. K.; Biradha, K. *Chem. Eur. J.* **2020**, *26*, 396.