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Communication

Single-Crystal-to-Single-Crystal [2 + 2] Photodimerization Involving B←N Coordination with Generation of a Thiophene Host

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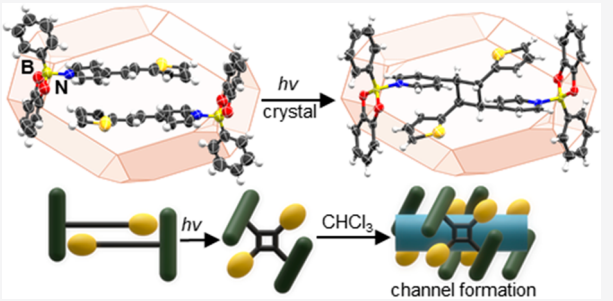
ABSTRACT: We report on B←N coordination to support a single-crystal-to-single-crystal reaction in the solid state. A [2 + 2] photodimerization is achieved with face-to-face π-stacks of monotopic B←N adducts composed of a phenylboronic acid catechol ester and an alkene with a terminal thiophene group. The photoreaction generates a ditopic B-adduct involving a head-to-tail cyclobutane regio- and stereoselectively. The photodimerization is accompanied by an increase in the tetrahedral character of the B atom. The resulting boron enables channel confinement of chloroform upon recrystallization.

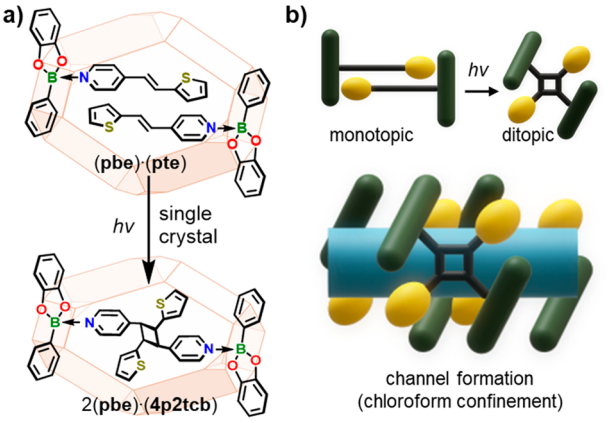


Boronic esters have gained increased attention as building blocks of functional supramolecular architectures (e.g., cages,[1] polymers,[2] tweezers[3]) via dative coordination with N-donor ligands. The orthogonal B←N coordination is generally accompanied by a change in geometry of the B atom from trigonal planar to approximately tetrahedral.[4]

Recently, B←N coordination has been reported to support a [2 + 2] photocycloaddition in the solid state to form a molecular bis-tweezer.[5] The resulting B-based tweezer was used to separate thiophene from benzene, a vital separation in petrochemistry.[6] Whereas the photochemical transformation proceeded in a polycrystalline solid (i.e., powder), the ability of B←N coordination of boronic esters to support a photochemical reaction in a single-crystal process has yet to be demonstrated.

As part of our efforts to engineer photoactive solids,[7] we report here the capacity of B coordination involving a phenylboronic acid catechol ester (**pbe**) to support a solid-state [2 + 2] photodimerization of *trans*-1-(4-pyridyl)-2-(2-thienyl)ethylene (**pte**) that occurs regio- and stereoselectively in a single-crystal-to-single-crystal (SCSC) reaction (Scheme 1). Photodimerizations of thiophenes are extremely rare in both solution and the solid state, with thiophenes also being integral components of organic semiconductors.[8] More specifically, we reveal the ability of monotopic (**pbe**)·(**pte**) formed by B←N coordination to generate ditopic *ht-rctt*-1,2-bis(4-pyridyl)-3,4-bis(2-thienyl)cyclobutane 2(**pbe**)·(**4p2tcb**) (*ht* = head-to-tail) via a SCSC transformation (Scheme 1a). The SCSC reaction involves a 7% increase in tetrahedral character (THC)[4b] of the B center. The resulting ditopic B complex is shown to act as a channel former with confinement of chloroform in the solid state (Scheme 1b).

Scheme 1. (a) SCSC [2 + 2] Photodimerization of (pbe)·(pte) to 2(pbe)·(4p2tcb) and (b) Change in Boron Coordination Modes from Monotopic to Ditopic and Channel Formation



SCSC transformations are rare and intriguing phenomena that involve structural changes in a crystal lattice without appreciable loss of crystal mosaicity.[9] Crystal-to-crystal (i.e., topotactic) reactivity has provided valuable mechanistic insight of chemical reactions in solids (e.g., [2 + 2] and [4 + 4]

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photodimerizations,[7c,10] ring-closing and opening isomerization,[11] *trans*−*cis* photoisomerization[12]), and enabled the development of resilient solids with unique properties (e.g., photochromism,[13] porosity,[14] conductivity,[15] and chemical patterning[16]). In contrast to a relatively large number of recent reports of SCSC reactivity[17] involving metal−ligand coordination, single-crystal reactivity involving a B atom has only been observed in a tricoordinate B←N aminoborane.[18] To our knowledge, SCSC reactivity in tetracoordinate B←N boronic ester based adducts is unknown.

Initially, we focused to evaluate the reactivity of pure **pte** in the solid state (Figure S3 in the Supporting Information).[19] Single-crystal X-ray diffraction (SCXRD) analysis revealed **pte** to crystallize in the monoclinic space group *Pc* as yellow plates (Figure 1). The **pte** molecules self-assemble in a herringbone

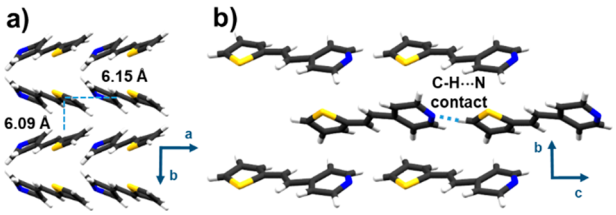

Figure 1. X-ray structure thiophene **pte**: (a) herringbone arrangement; (b) hydrogen-bonded layers.

arrangement with nearest-neighbor carbon−carbon double (C═C) bonds separated by 6.09 Å (Figure 1a). The **pte** molecules define layers sustained by C−H···N interactions in the *bc* plane (Figure 1b). Upon exposure to UV radiation (72 h, 450 W, medium-pressure Hg lamp), **pte** was photostable, as confirmed by ^{1}H NMR spectroscopy (Figure S1 in the Supporting Information).

To promote solid-state reactivity, B←N coordination was achieved by combining **pbe** (20 mg, 0.010 mmol) with **pte** (19.1 mg, 0.010 mmol) in hot acetonitrile (2 mL). Single crystals in the form of pale yellow prisms suitable for X-ray diffraction (SCXRD) formed upon slow solvent evaporation after a period of 2 days.

SCXRD analysis of (**pbe**)·(**pte**) reveals the components to crystallize in the monoclinic space group $P2_1/n$ (Figure 2). The asymmetric unit consists of a T-shaped adduct composed of **pbe** coordinated to **pte** via a B←N bond (1.646(8) Å). The thiophene molecule **pte** in the adduct is disordered over two sites (site occupancies 0.603 and 0.397). The THC of the B atom (68%) is slightly weaker in comparison to similar boronic ester based adducts.[3,20] The pyridyl and thiophenyl rings adopt a nearly coplanar conformation (twist angle 6.3°). Two (**pbe**)·(**pte**) molecules self-assemble into discrete head-to-tail dimers through $\pi\cdots\pi$ and C−H···π forces (Figure 2a). The (**pbe**)·(**pte**) molecules form a herringbone-arrangement in the *ab* plane through C−H···S and C−H···O interactions (Figure 2b). The dimers further organize into sheets parallel to the *b* axis in the *bc* plane. The alkenes stack with C···C distances of 3.70 Å, which satisfies the criteria for a [2 + 2] photocycloaddition reaction.[21] C═C bonds of neighboring dimers are separated by 10.4 Å (Figure 2c).[5a]

When single crystals of (**pbe**)·(**pte**) were exposed to UV radiation (UV light gel nail dryer) for 2 h,[22] a ^{1}H NMR spectroscopic analysis confirmed the complete conversion of **pte** to a cyclobutane, as evidenced by the appearance of cyclobutyl resonance signals at δ 4.86 and 4.45 ppm and

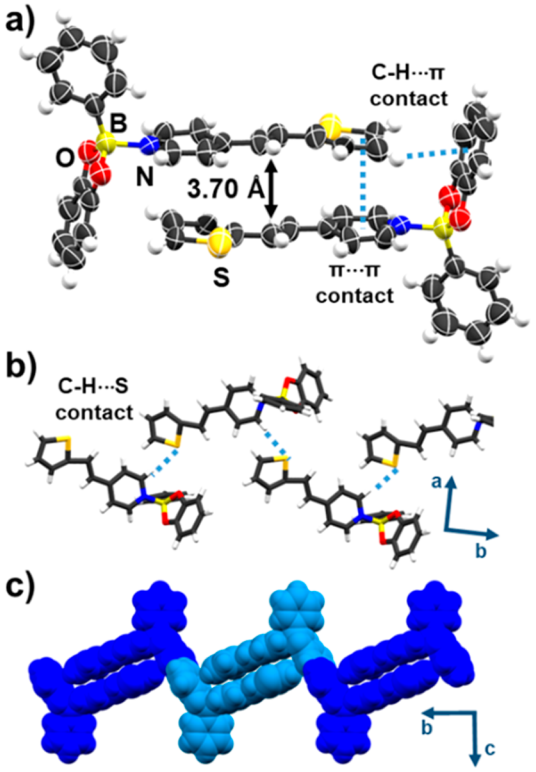

Figure 2. X-ray structure of adduct (**pbe**)·(**pte**): (a) ORTEP view; (b) herringbone arrangement; (c) dimeric assemblies.

disappearance of the olefinic signals (Figure S2 in the Supporting Information). A powder X-ray diffraction analysis was supportive of a change in the phase of the solid (Figures S4 and S5 in the Supporting Information).

SCXRD analysis revealed the components (**pbe**)·(**pte**) to undergo a SCSC [2 + 2] photodimerization to form 2(**pbe**)·(**4p2tcb**) regio- and stereoselectively, in quantitative yield (Figure 3). Importantly, the crystal-to-crystal photoreaction generated a ditopic B adduct with two **pbe** units that effectively act as "hinges" and with two pendant α-thiophenyl rings (Figure 3a). The bipyridine **4p2tcb** is disordered over two sites (site occupancies: 0.637(4) and 0.363(4)). Whereas the B←N bond length does not differ considerably (1.659(4) Å) from that of (**pbe**)·(**pte**), the THC of boron (75%) increased after the photoreaction, which is indicative of a stronger coordination bond.[4b] The increase in the THC is consistent with an increase in electron density. The formation of the electron-donating cyclobutyl ring, which acts as an efficient through-bond donor,[23] can be ascribed to the increase in THC. The B···B distance in 2(**pbe**)·(**4p2tcb**) (13.27 Å) is slightly shorter than that of the (**pbe**)·(**pte**) dimers (13.64 Å), consistent with a decrease in carbon−carbon atom distances conferred by the cyclobutyl ring (Figure 3b). The conformational change enables the formation of intermolecular C−H···O contacts between the cyclobutyl ring and **pbe**. The formation of the adduct is also accompanied by tilting of the thiophenyl ring (18.4°) and a slight rotation of the aryl ring (1.3°) (Figure 3c). To our knowledge, (**pbe**)·(**pte**) is the first example of a solid with a boronic ester that participates in a SCSC reaction.

2(**pbe**)·(**4p2tcb**) acts as a channel former for the solid-state confinement of chloroform.[24] Recrystallization of 2(**pbe**)·(**4p2tcb**) (30 mg, 0.039 mmol) in chloroform (2.5 mL)

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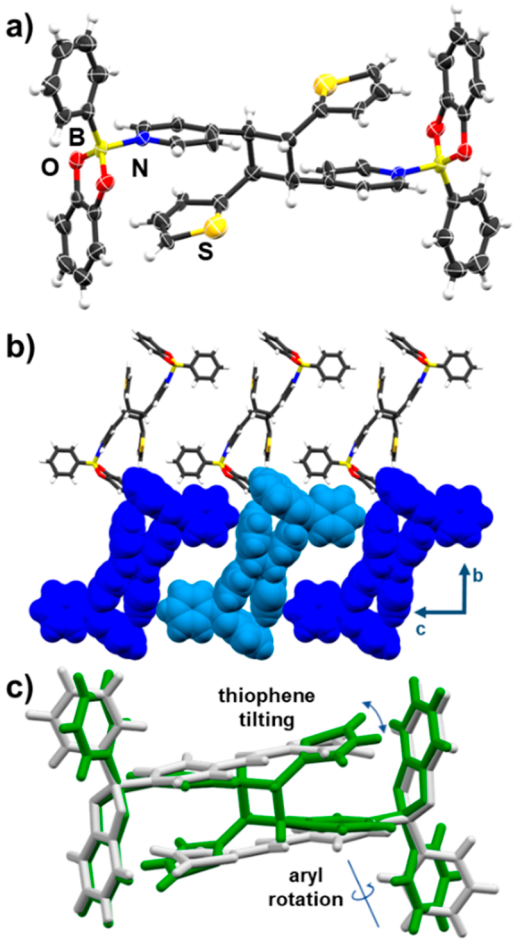

Figure 3. X-ray structure of bis-tweezer adduct 2(**pbe**)·(**4p2tcb**): (a) ORTEP view; (b) supramolecular chains; (c) overlay with (**pbe**)·(**pte**) depicting conformational changes along with the SCSC transformation.

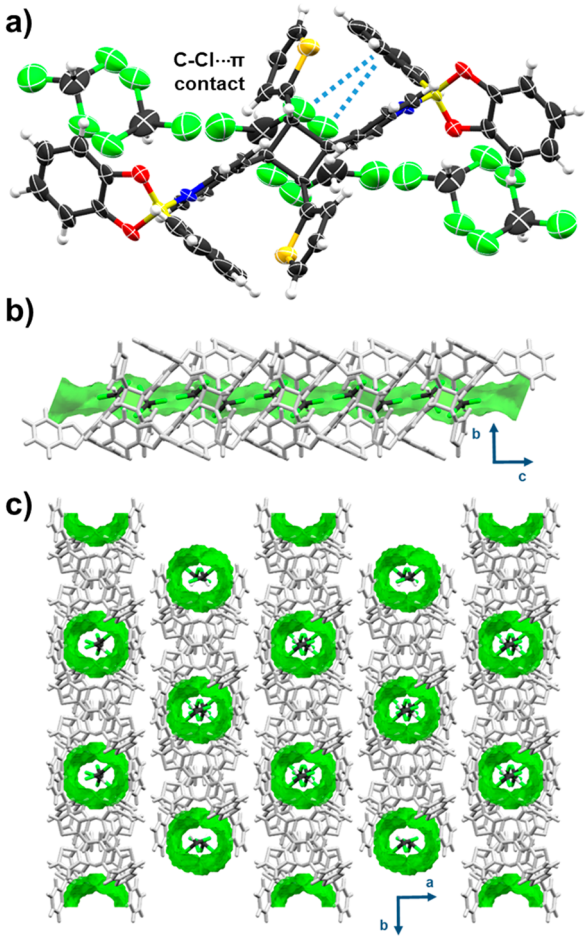

Figure 4. X-ray structure of the diboron adduct 2(**pbe**)·(**4p2tcb**)⊃**CHCl$_3$**: (a) ORTEP view and C−Cl···π contacts with $CHCl_3$ solvate molecules; (b) channel occupied by chloroform; (c) adjacent channels in the *ab* plane.

afforded 2(**pbe**)·(**4p2tcb**)⊃**CHCl$_3$**, as confirmed by ^{1}H NMR spectroscopy and SCXRD. The components of 2(**pbe**)·(**4p2tcb**)⊃**CHCl$_3$** crystallize in the monoclinic space group *C*2/*c*. The asymmetric unit consists of two chloroform molecules per host molecule (Figure 4). The B←N bond distance (1.646(8) Å) and THC of boron (68%) are identical with those of the unreacted adduct (**pbe**)·(**pte**), which is consistent with loss of strain.[25] In the solid, the chloroform molecules are stabilized by C−Cl···π and C−H···Cl contacts with aryl and pyridyl groups, respectively (Figure 4a). The guest molecules[5a] are entrapped in channels formed between adjacent cyclobutyl rings (Figure 4b). Collectively, the channels facilitate confinement of chloroform that accounts for 14.0% of the total unit cell volume (i.e., contact surface) (Figure 4c).

In conclusion, B←N coordination in (**pbe**)·(**pte**) supports a SCSC [2 + 2] photodimerization of (**pte**). The photoreaction occurs regio- and stereoselectively in quantitative yield to generate 2(**pbe**)·(**4p2tcb**). The photoproduct enables channel confinement of chloroform upon crystallization through C−Cl···π contacts. We envisage the development of additional photoresponsive boron materials with the ability to modulate conductivity, porosity, and luminescence through single-crystal reactivity via B←N coordination.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00258.

Experimental information, PXRD patterns, and additional SCXRD data (PDF)

Accession Codes

CCDC 1993366−1993369 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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