Self-Assembly of Diboronic Esters with U-Shaped Bipyridines: “Plug-in-Socket” Assemblies

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ABSTRACT: Self-assembled complexes utilizing the ditopic dative bond acceptor 1,3-diboronic acid with catechol and complementary U-shaped donors in the form of 1,8-dipyridylnaphthalenes (1,8-bis(4-pyridyl)naphthalene (DPN), 1,8-bis(4-ethylenylpyridyl)naphthalene (DEPN), and 1,8-bis(4-ethynylpyridyl)naphthalene (DAPN)) yielded discrete two-component structures. The assemblies exhibit “plug-in-socket” geometries. DFT calculations are consistent with the donor pyridyl and acceptor catecholate being electron poor and rich, respectively. The assemblies pack via π−π interactions and support the inclusion of a solvent (i.e., DPN, DAPN). The materials may form a basis for the design of complex B-based structures (e.g., supramolecular dyads).

INTRODUCTION

Self-assembly processes involving diboronic esters are increasingly prevalent in the design of complex supramolecular assemblies and architectures. Linear diboronic acids on crystallization with di- and tritopic pyridines as linkers, for example, have generated macrocycles and cages, respectively. The materials, which also exhibit propensities to include solvent guests (e.g., aromatics) within and exterior to the self-assembled structures, are promising for applications in areas such as separations, sensing, and electronics. While noncovalent bonds such as π−π interactions, hydrogen bonding, and electrostatics have been more traditionally useful to create self-assembled structures, B−N coordination involving pyridine linkers has more recently received widespread attention. The pyridine linkers to date have been based on divergent geometries (e.g., 4,4′-bipyridine), many of which draw inspiration from studies that aim to generate hydrogen-bond and metal-mediated frameworks and solids.

U-shaped heterocyclic aza-aromatics based on the 1,8-disubstitution of naphthalenes (1,8-nap) are useful constructs in the field of molecular recognition. The hydrogen-bonding and metal-coordination capabilities of the 1,8-diacidrines have been exploited for enantioselective and fluorescence sensing of chiral carboxylic acids and metal ions, respectively. More recently, hydrogen bonding and coordination involving the 1,8-nap framework has facilitated inter- and intramolecular photocyclizations in the solid state. While the assembly properties of boronic acids can be expected to enhance the structural chemistry of members of the 1,8-nap framework, derivatives of 1,8-nap have not been applied to self-assembly using B−N bonding. Indeed, members of the 1,8-nap family of molecules are becoming more synthetically accessible, given the amenability of the bipyridines to be synthesized by mainstream cross-coupling reactions.

Herein we describe the self-assembly of a series of 1,8-dipyridylnaphthalenes with diboronic esters of 1,3-catecholates. Specifically, a combination of 1,8-bis(4-pyridyl)naphthalene (DPN), 1,8-bis(4-ethylenylpyridyl)naphthalene (DEPN), and 1,8-bis(4-ethynylpyridyl)naphthalene (DAPN) with 1,3-benzenedicarboxylic acid catechol diester (1,3-BBEC) affords the discrete 1:1 assemblies DPN-1,3-BBEC, DEPN-1,3-BBEC, and DAPN-1,3-BBEC, respectively. In all cases, the bipyridines interact with the diboron building unit akin to a macroscopic "plug-in-socket" array (Scheme 1). For DPN and DAPN, the plug-in-socket arrays generate the host–guest solids DPN-1,3-BBEC-CHCl₃ and DAPN-1,3-BBEC-2(m-xylene). We expect the U-shaped donors described here to be viable building blocks for the construction of complex B-based assemblies sustained by B−N bonding.

EXPERIMENTAL SECTION

Toluene, chloroform, and catechol were purchased from Millipore-Sigma and used as received. Benzene-1,3-diboronic acid was purchased...
from Oakwood Laboratories and used without further purification. DPN, DEPN, and DAPN were synthesized according to the literature. The formation of each assembly was accomplished by forming chloroform solutions of the corresponding bipyridine, 1,3-benzenediboronic acid, and catechol (ratio 1:1:2) and subsequently placing either toluene (DPN and DEPN) or m-xylene (DAPN) in a loosely secured screw-capped vial. Slow solvent evaporation resulted in diffraction-quality crystals of the adducts within 2 days. Crystal structures were solved using Olex2. Density functional theory (DFT) calculations (B3LYP/6-31G* level) were conducted using Spartan 18.

X-ray diffraction. Single crystals suitable for X-ray diffraction analyses were secured to X-ray transparent magnetic mounts using Paratone oil and mounted on a Bruker D8 Venture diffractometer with a Photon III detector. All single-crystal measurements were performed at 150 or 190 K or at room temperature using either Cu Kα (λ = 1.54184 Å) or Mo Kα (λ = 0.71073 Å) radiation.

■ RESULTS AND DISCUSSION

DPN, DEPN, and DAPN are attractive owing to the cofacial geometries of the 4-pyridyl groups (Scheme 2). The pyridyls are generally twisted nearly perpendicular to the naphthalene ring system. The cofacial geometry has been exploited by Wolf for molecular recognition and enantiosensing (e.g., amino acids). Interactions involving the N atoms can facilitate complexation with organohalides, hydrogen bonding, and metal complexation. We are unaware of examples wherein the bipyridines have been studied in the context of B←N coordination.

X-ray Structures of Individual Components. The crystal structures of two polymorphs of DPN have been reported, and we have described the structure of DEPN. The X-ray structure of DAPN is described here for the first time. DAPN crystallizes in the chiral orthorhombic space group P2_12_12 with one full molecule in the asymmetric unit (Figure 1 and Table 1). Both 4-

![Figure 1. X-ray structure of DAPN: (a) ORTEP diagram; (b) space-filling representation; (c) 2D packing.](image)

| Table 1. Crystallographic Data for DAPN and 1,3-BBEC |
|-----------------|-----------------|-----------------|
| compound       | DAPN            | 1,3-BBEC        |
| CCDC code      | 2074336         | 2074338         |
| formula        | C_{14}H_{14}N_{2} | C_{10}H_{8}B_{2}O_{4} |
| formula wt     | 330.37          | 313.90          |
| temp (K)       | 190(2)          | 297(2)          |
| space group    | P_{2}2_{1}2_{1} | P_{2}2_{1}2_{1} |
| a (Å)          | 9.0979(9)       | 22.542(2)       |
| b (Å)          | 11.7870(12)     | 4.7936(5)       |
| c (Å)          | 16.0856(16)     | 6.9265(7)       |
| α (deg)        | 90              | 90              |
| β (deg)        | 90              | 90              |
| γ (deg)        | 90              | 90              |
| V (Å^3)        | 1725.0(3)       | 748.46(13)      |
| Z               | 4               | 2               |
| calc density (g/cm^3) | 1.272          | 1.393          |
| μ (mm^-1)      | 0.075           | 0.096           |
| scan           | ω and φ scans   | ω and φ scans   |
| θ range for data collection (deg) | 2.532–27.918 | 2.941–26.340 |
| no. of refns mead | 35632          | 12894           |
| no. of indep obsd refns | 4109          | 1522            |
| no. of indep refns (I > 2σ) | 3070          | 1313            |
| no. of data/restraints/params | 4109/0/235   | 1522/0/110     |
| R_{int}        | 0.0466          | 0.0538          |
| final R indices (I > 2σ) | 0.0444        | 0.0319          |
| R indices (all data) | 0.0713        | 0.0403          |
| goodness of fit on F^2 | 1.057         | 1.045           |

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pyridyl groups are twisted from coplanarity (36.7, 49.1°) with respect to the naphthyl rings (Figure 1a and Table 2). The pyridyl rings are oriented approximately cofacially (19.7°) (Figure 1b). The N atoms of the stacked pyridyl rings are separated at a distance (4.49 Å) greater and less than those of DPN and DEPN, respectively. The molecule forms a 2D layered structure with adjacent bipyridines interacting via edge-to-face C–H···π forces (C–H·centroid 3.73 Å) (Figure 1c).

The diboronic ester 1,3-BBEC crystallizes in the monoclinic space group P21212 with half of a molecule in the asymmetric unit (Figure 2). The terminal catecholate groups are twisted slightly (7.35°) from the central aromatic ring system (Figure 2a). The molecule self-assembles head-to-tail along the c axis, being sustained by C–H···O hydrogen bonds (Figure 2b). 1,3-BBEC packs in a herringbone arrangement within the crystallographic ab plane (Figure 2c).

**Plug-in-Socket Assemblies.** For DPN, DEPN, and DAPN, the self-assembly process involving 1,3-BBEC affords two-component complexes with structures that conform to ”plug-in-socket” types of assemblies (Figure 3). The N atoms of the pyridyl groups of each array adopt an approximate parallel orientation and engage in B–N coordination (Table 3). The B–N bond distances are generally comparable and are only

|                  | DPN       | DEPN      | DAPN      |
|------------------|-----------|-----------|-----------|
| N···N (Å)        | 4.03 (form I), 3.99 (form II) | 5.55, 5.15 | 4.49      |
| pyridyl twist (deg) | 59.0, 51.4 (form I); 49.4, 52.3; 50.2, 36.7 | 69.2, 68.5 (form II) | 40.8, 49.1 |

**Figure 2.** X-ray structure 1,3-BBEC: (a) ORTEP diagram; (b) head-to-tail assembly; (c) herringbone packing.

**Figure 3.** X-ray structures of (a) DPN·1,3-BBEC; (b) DEPN·1,3-BBEC; and (c) DAPN·1,3-BBEC.
Table 3. Structural Metrics for 1,3-BBEC Assemblies of DPN, DEPN, and DAPN

|                  | DPN-1,3-BBEC | DEPN-1,3-BBEC | DAPN-1,3-BBEC |
|------------------|--------------|---------------|---------------|
| B–N (Å)          | 1.6688(2), 1.6680(2) | 1.6530(2), 1.6523(2) | 1.643(8), 1.645(8) |
| N1–N2 (Å)        | 4.62(1)      | 5.116(5)      | 4.857(7), 4.888(7) |
| B–B (Å)          | 5.29(1)      | 5.25(1)       | 5.31(1), 5.29(1)  |
| twist from orthogonality (α1, α2) (deg) | 63.82(3) | 59.07(8) | 109.4(2), 103.8(2) |

Dealing with the packing arrangement sustained by edge-to-face interactions (occupancies: 50:50). The complex self-assembles to form a asymmetric unit. A single catecholate ring lies disordered (occupancies: 50:50), as does the chloro- solvent inclusion compounds.17,18 In general, the shapes of the molecule (edge are also e twist angles <90°, while DAPN-1,3-BBEC exhibits a twist angle >90°. Two of the three complexes based on 1,3-BBEC are solvent inclusion compounds.15,18 In general, the shapes of the complexes are based on aromatic ring systems that alternate approximately perpendicularly to each other.

DPN-1,3-BBEC crystallizes with one full complex and one CHCl3 molecule in the asymmetric unit. A single catecholate ring lies disordered (occupancies: 50:50), as does the chloroform molecule (occupancies: 70:30). The included solvent is nestled adjacent to the B···N linkage. The Cl atoms participate in Cl···O interactions with the catecholate and C atoms of the pyridyl group. The complexes and solvent molecules form 2D layers within the ab plane (Figure 4a). The packing is manifested such that the naphthyl units point in the same direction along the c axis. Several π–π interactions define the packing of the pyridyl edges with the central phenyl ring faces of 1,3-BBEC (edge···centroid = 3.60 Å) and pyridyl edges with naphthyl faces (edge···centroid = 3.51 Å) (Table 4). The catechol rings display face-to-face π–π stacking of adjacent complexes (centroid···centroid = 3.82 Å), while the central phenyl edges and naphthyl ring faces also exhibit edge-to-face interactions (edge···centroid = 3.63 Å).

DAPN-1,3-BBEC crystallizes with two full complexes and four m-xylene molecules in the asymmetric unit. The complexes form edge-to-face dimers (Figure 4b). Edge-to-face packing between a pyridyl group and central phenyl ring forms T-shaped motifs (C–H···centroid = 3.50 Å) that alternate to form chains. Due to π–π interactions and the packing of the complexes, the included m-xylene molecules exhibit edge-to-face interactions with the assemblies. Being effectively pinched between the naphthyl adduct (edge···centroid = 3.85 Å) and central phenyl rings (edge···centroid = 3.73 Å), one molecule of m-xylene interacts by edge-to-face forces. The central phenyl ring edges of the assemblies similarly fit with one m-xylene between the complex edges (edge···centroid = 3.69 Å). The catecholate rings are also effectively sandwiched orthogonally with m-xylene molecule (edge···centroid = 3.53 Å).

DEPN-1,3-BBEC crystallizes with one full complex in the asymmetric unit. A single catecholate ring lies disordered (occupancies: 50:50). The complex self-assembles to form a packing arrangement sustained by edge-to-face interactions involving the pyridyl and naphthyl ring systems similarly to DAPN-1,3-BBEC (edge···centroid = 3.70 Å). Undulating layers of the packed complexes are present in the crystallographic bc plane resulting from twisting of adducts (59.2°) (Figure 4c).

Figure 4. X-ray structures: (a) DPN-1,3-BBEC; (b) m-xylene inclusion (purple) of DAPN-1,3-BBEC; (c) undulating layers of DEPN-1,3-BBEC.

B-Based Assemblies. While there have been several reports of discrete assemblies sustained by B···N linkages, we are unaware of a discrete B-based assembly involving the 1,8-naphthyl geometry.19 The U-shaped scaffold has been used in the assembly of Ag(I) ions, which are separated at distances shorter (Ag···Ag distance = 3.45–3.80 Å) than for the B atoms of DPN-1,3-BBEC (5.29 Å), DEPN-1,3-BBEC (5.25 Å), and DAPN-1,3-BBEC (5.31, 5.29 Å). The N···N distances of the Ag(I) complexes” (3.79–4.21 Å) are shorter than those of the B
complex (Table 2). Hydrogen (3.77–3.96 Å)- and halogen-bonded (4.20 Å) cocrystals of DPN have also reported with N···N distances that exhibit similar separations. The U-shaped bipyridines of the cocrystals exhibit shorter distances in comparison to the B complexes. Extended assemblies based on B ← N linkages have also been reported. Work by Severin involving 1,3-BBEC shows the efficacy of B ← N linkages to form networks with regenerative abilities. Utilizing an array of pyridyl- and imidazolyl-functionalized molecules, a wide range of architectures for self-assembly involving the B ← N bond were realized. DFT calculations indicate an increase in electropositivity of the coordinated pyridyl groups (Figure 5). The ranges of the electrostatic potential values (kJ/mol) for the pyridyl groups are DAPN (80–82) > DPN (71–73) > DEPN (56–58) (i.e., more electropositive). The relative electropositivity of DAPN · 1,3-BBEC is consistent with inclusion and π−π interactions involving the electron-rich m-xylene guests. We note that the C atoms of the central phenyl ring of the boronic ester display higher electron density within the bridging group. The increase in electron density is in contrast with 1,3-BBEC as a pure form. Su has reported DFT calculations that address the extent of overlap of B atoms of trigonal-planar geometry with pendant phenyl rings. We have also reported on similar electronic effects and guest inclusion involving assemblies of single boronic esters. The approximate perpendicular orientation assumed by 1,8-nap with the diboron ester moiety is also reminiscent of frameworks used to form molecular and supramolecular dyads.

**CONCLUSION**

The self-assembly of a series of U-shaped bipyridines based on 1,8-nap with the diboron ester 1,3-BBEC has resulted in the formation of novel “plug-in-socket” type architectures. We are now studying the scope of the self-assembly process to other diboron esters, as well as expanding the host–guest properties. We expect our efforts to contribute to the generation of B-based functional materials.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.1c00382.

General experimental details, synthetic procedures for DPN-1,3-BBEC, DEPN-1,3-BBEC, and DAPN-1,3-BBEC. 1H NMR and X-ray diffraction data, and
electrostatic potentials for DPN-1,3-BBEC, DEPN-1,3-BBEC, and DAPN-1,3-BBEC (PDF)

Accession Codes
CCDC 2074336–2074340 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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