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Utilizing the π-Acidity of Boron Subphthalocyanine To Achieve Novel Solid-State Arrangements

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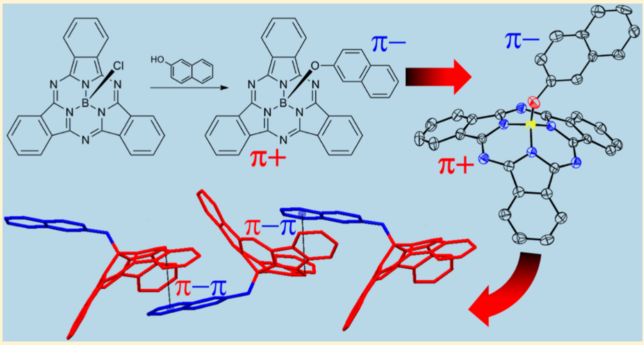
Ⓢ *Supporting Information*

ABSTRACT: The ability to control the solid-state structure of organic electronic materials can have a large effect on the quality of the devices to which they are applied. In this paper, we describe the use of $\pi-\pi$ interactions to direct the crystal structure/solid-state arrangement of boron subphthalocyanine (BsubPc) derivatives by taking advantage of the π-electron-deficiency (π-acidity) of the BsubPc molecular fragment. First, we outline why BsubPc is a π-acid by looking at its chemical characteristics and the structure of crystals formed with other π-acidic moieties. Then we show how the solid-state arrangement of BsubPc can be purposefully altered by adding π-basic substituents. We found that adding a naphthoxy substituent provides an interaction that is strong enough to direct BsubPc into a novel solid-state arrangement made up of ribbons (or catemers) of molecules linked through π-stacking interactions between the naphthoxy and neighboring BsubPc molecular fragments. A similar effect was also seen when the naphthoxy fragment was added to the stronger π-acid perfluoro-BsubPc (F_{12}BsubPc).



■ INTRODUCTION

Crystal engineering can use non-covalent interactions of varying strength (such as hydrogen bonding, dipole−dipole interactions, van der Waals interactions, and $\pi-\pi$ interactions) to rationally plan and acquire specific solid-state arrangements of targeted materials. Such interactions can be designed and incorporated into a targeted molecular material if a certain amount of information is known in advance about the molecule and/or its fragments. Although these interactions may be relatively weak in energetic terms, having many weak, non-covalent intermolecular interactions can provide sufficient impetus for stabilization of specific and desired solid-state arrangements.

The use of $\pi-\pi$ interactions in crystal engineering is not as common as the use of other non-covalent interactions such as hydrogen bonding, which might be due to the debate surrounding the nature of these interactions.[1] Nonetheless, the ubiquity of $\pi-\pi$ interactions in the crystal structures of aromatic molecules, as well as the recognition of the contribution of other intermolecular interactions involving π-electron systems in crystal structures (for example N$\cdots\pi$, C−H$\cdots\pi$, and X$\cdots\pi$), has undoubtedly demonstrated the importance of π electrons in directing the solid-state arrangement of molecules. Thus, more recently, the use of $\pi-\pi$ interactions in crystal engineering has been gaining broader acceptance.[2]

The potential benefit from control of $\pi-\pi$ interactions has been established in the field of organic electronics. There have been a number of studies correlating intermolecular $\pi-\pi$ distances with charge carrier mobility.[3] The pioneering work by Anthony and co-workers on silyl-derivatized pentacenes has shown that smaller intermolecular distances in the solid state lead to an increase in electron mobility and better performance of the material in organic electronic devices such as organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs).[4] Others have shown that the crystal polymorph,[5] the crystal orientation,[6] the quality of the crystal,[6] and the solid-state packing density of the material[7] used in an organic electronic device all affect the device performance. For example, OPV devices have been fabricated with active layers consisting of mixtures of C_{60} and boron subphthalocyanine (BsubPc). It was shown that BsubPc forms crystallites in the devices that are linked with an increase in the device performance versus the same BsubPc in an amorphous form.[8]

Most crystal engineering techniques to control the solid-state arrangement of small molecules rely on the addition of functional groups, which adds additional molecular mass that dilutes the concentration of π electrons in the resulting

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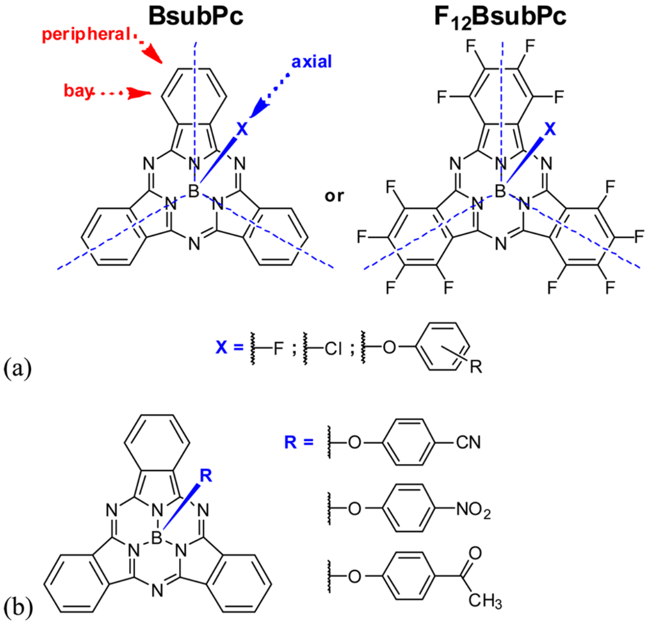


Figure 1. (a) Scheme of generic BsubPcs showing C_{3v} symmetry lines, the peripheral and bay positions, and the difference between the perhydrogenated (BsubPc) and perfluorinated (F_{12}BsubPc) variants. (b) Previously reported phenoxy-BsubPcs containing π-acidic phenoxy molecular fragments.[26−28]

materials. The use of $\pi-\pi$ interactions alone to control the solid-state arrangement of aromatic materials such as BsubPcs would be ideal, as one could then minimize the number of nonaromatic groups in the molecular structure. There is evidence to suggest that a combination of electron-rich (π-basic) and electron-deficient (π-acidic) aromatic groups present within a single molecule can be used to engineer the solid-state arrangement of the material; one example resulted in a material with a hole mobility greater than 2 $cm^2\ s^{-1}\ V^{-1}$.[9] In that reported crystal structure, the π-rich thiophene and the π-deficient pyridinyl fragments stack on top of each other, displaying a π-electron acid−base/acceptor−donor interaction. Another study showed that a mixture of tetracene with phenyl substituents (π-bases) and tetracene with fluorinated pendant groups (π-acids) co-crystallizes in a 1:1 ratio with alternating units of halogenated and non-halogenated pendant groups in a π-stacked motif within the solid state.[10] This type of arene−perfluoroarene interaction is well-known, and many studies in crystal engineering have used it to obtain desired solid-state arrangements through co-crystallization.[2,9,11,12] That the perfluoroarene molecules alternate with the corresponding non-halogenated arenes demonstrates a preference for an energetically attractive π-stacking interaction between different molecules of differing π-acidity/π-basicity rather than between two of the same molecule. Thus, one can conclude on the basis of these two representative examples that the π-acid/π-base association preferentially occurs when π-acids and π-bases are present together either within the same molecule or as co-crystallites.

Recently, our group outlined how the charge-carrier mobilities of a series of BsubPc derivatives with various numbers of fluorine atoms in their chemical structures could be correlated to their solid-state arrangement and the associated crystallographic parameters. The series of BsubPcs had a consistent packing motif in the solid state, but variation in the distances between neighboring molecules and the overall crystal density could be correlated to variations in their measured charge-carrier mobilities in thin films.[3b]

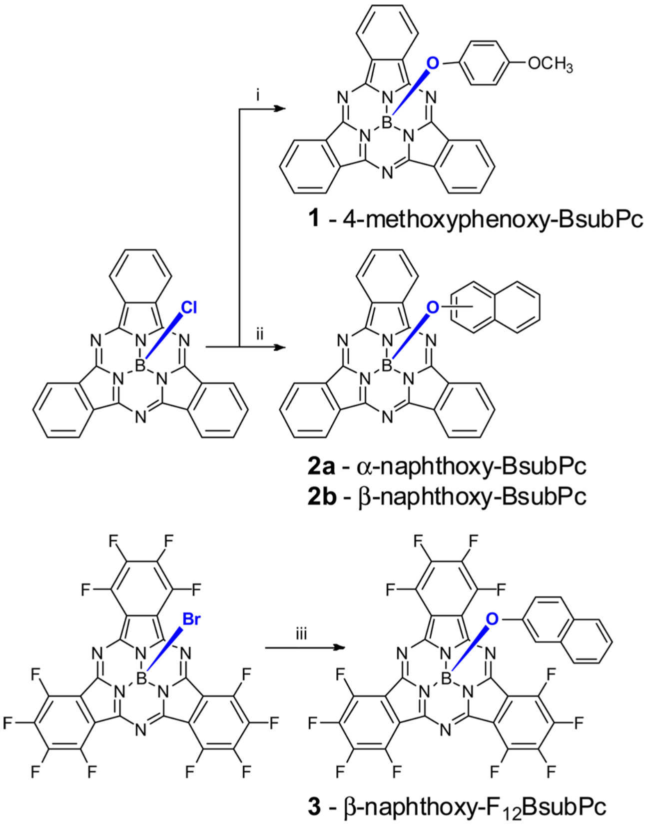
Typically, BsubPcs exist in two common varieties, a perhydrogenated version that we will denote simply as BsubPc and a perfluorinated version that we will denote as F_{12}BsubPc (see Figure 1a). If one considers how the more common BsubPcs arrange in the solid state, then BsubPcs can be grouped into one of four categories depending on the nature of their axial and peripheral substituents: halo-BsubPcs, phenoxy-BsubPcs, halo-F_{12}BsubPcs, and phenoxy-F_{12}BsubPcs. Halo-BsubPcs (X = F,[13a] Cl,[13b] Br;[13a] see Figure 1a) are all practically isostructural in the solid state, crystallizing into a head-to-tail concave-face to concave-face arrangement in well-defined rows. When the halide group is replaced with a phenoxy group (X = $-OC_6H_5$ in Figure 1a), the arrangement is entirely different, with phenoxy-BsubPcs generally arranged in such a manner that they form head-to-head concave−concave dimers that repeat throughout the extended solid state.[14] We have recently published two studies illustrating that halides present on the phenoxy molecular fragment can produce novel solid-state arrangements of phenoxy-BsubPc. This first was observed in the solid-state arrangement of *p*-bromophenoxy-BsubPc, which has one novel polymorph stabilized by a π-Br interaction.[15] The second was observed for a wide variety of *m*-halophenoxy-BsubPcs (halo = iodo, bromo, chloro) that exhibited novel solid-state arrangements through the formation of halogen bonds.[16] Halo-F_{12}BsubPcs, whether X = F,[17] Cl,[18] or Br[19] (Figure 1a), arrange in columns running in a direction perpendicular to the plane of the F_{12}BsubPc fragment. The halide is located immediately underneath the boron atom in the concave face of the BsubPc at a distance of less than the sum of the van der Waals radii. Finally, phenoxy-F_{12}BsubPcs (X = RPhO; Figure 1a) arrange in a similar fashion to their halide counterparts, except that is the phenoxy fragment that occupies the concave face and displays $\pi-\pi$ interactions with the F_{12}BsubPc moiety.[20] A similar structure was found for 4-methylphenoxy-F_{12}BsubPc,[21] pentafluorophenoxy-F_{12}BsuBPc,[22] and 4-ferrocenylphenoxy-F_{12}BsubPc.[23]

In this paper, we demonstrate a method for crystal engineering of BsubPc derivatives using π-acid/π-base interactions to generate an entirely unique and novel solid-state arrangement of the BsubPc molecular fragment. We begin by outlining why we believe BsubPc is a π-acid. This is supported by several observations, including the electrochemical behavior of BsubPcs and the positions of the hydrogen resonances in the ^{1}H NMR spectrum of a BsubPc. Following that discussion, we outline the synthesis and crystallization four novel BsubPc compounds with π-basic substituents (Scheme 1): 4-methoxyphenoxy-BsubPc (**1**), α-naphthoxy-BsubPc (**2a**), β-naphthoxy-BsubPc (**2b**), and β-naphthoxy-F_{12}BsubPc (**3**). We show that attachment of π-basic substituent groups axially to the boron atom of a BsubPc molecular fragment creates a π-acid/π-base interaction within the crystal. This interaction results in a novel solid-state arrangement for a BsubPc, as the concave-face to concave-face π-stacking motif seen in many phenoxy-BsubPc crystal structures[14,15,20,24] is replaced with a ribbonlike (or catemeric) arrangement.

■ RESULTS AND DISCUSSION

To make the case that BsubPcs are π-acids, we begin by considering the electrochemical behavior of BsubPcs. We have previously shown that BsubPc is preferentially an n-type

Scheme 1. Synthesis of BsubPcs 1−3[a]



[a]Conditions: (i) toluene, 4-methoxyphenol, reflux, 48 h; (ii) toluene, naphthol, reflux, 24−72 h; (iii) chlorobenzene, 2-naphthol, reflux, 20 h.

organic electronic semiconductor in an OLED, an observation supported by the fact that BsubPc generally accepts an electron rather than giving up an electron under cyclic voltammetry conditions.[22] A reversible reduction is seen for a typical phenoxy-BsubPc over many cycles, whereas an oxidation is observed to be nonreversible. The inclination to accept an electron without degradation yet degrade upon giving up an electron is a property of a π-acidic molecule (i.e., a molecule that is deficient in π-electron density).

Second, when we consider the ^{1}H NMR spectrum of a typical phenoxy-BsubPc, we observe that the peripheral and bay protons (defined in Figure 1a) resonate at ∼7.85 and ∼8.85 ppm, respectively (confirmed also in DMSO-d_6).[14,20,24] Each of these resonances lies either at or well beyond the downfield boundary of what would be expected for a standard aromatic compound. As ^{1}H NMR analysis can be considered a measure of the acidity of a particular proton, the positions of the ^{1}H resonances of the peripheral protons of a typical BsubPc suggest that they are acidic relative to other aromatic compounds, including other phthalocyanines. We would note that the significant ring currents of BsubPc and more generally phthalocyanines also play a role in the downfield positions of the proton resonances relative to other aromatic compounds. However, if one considers the position of the proton resonances of zinc phthalocyanine, for example,[25] the peripheral proton resonances appear at ∼5.8 and ∼6.8 ppm (DMSO-d_6), still significantly upfield from those of BsubPc. Therefore, we would suggest that it is not simply ring current considerations that place the proton resonances of BsubPc this far downfield.

Third, evidence for the π-acidity of BsubPc can be obtained by looking at the crystal structures of its derivatives with other π-acidic moieties. We previously reported the synthesis and crystal structure of 4-cyanophenoxy-BsubPc (R = *p*-CNPhO; Figure 1b).[26] The 4-cyanophenoxy unit is π-acidic because of the strong electron-withdrawing character of the cyano group. By coupling it with the BsubPc unit, we observed the formation of large void spaces in the single crystal (which were filled with disordered solvent). Benzene/heptane and acetone/heptane gave identical crystals, thus indicating that the disordered solvent is likely heptane. A distorted B−O−C bond angle of 128.89(11)° was also observed, which is significantly different than the typical 115°. One can explain these unique observations by considering that within this molecule there

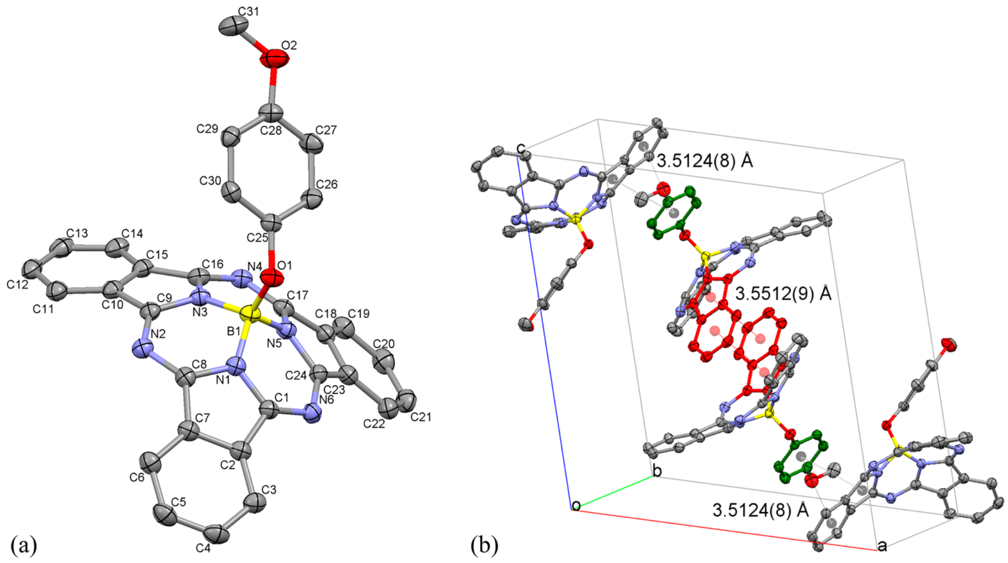


Figure 2. (a) Displacement ellipsoid plot of compound **1** at the 50% probability level and (b) its populated unit cell showing π-stacking interactions between BsubPcs (red) and between methoxy (green) and a BsubPc. H atoms have been omitted for clarity. Colors: carbon, gray; nitrogen, blue; oxygen, red; boron, yellow. The isoindoline units are colored in red in (b) for clarity of presentation.

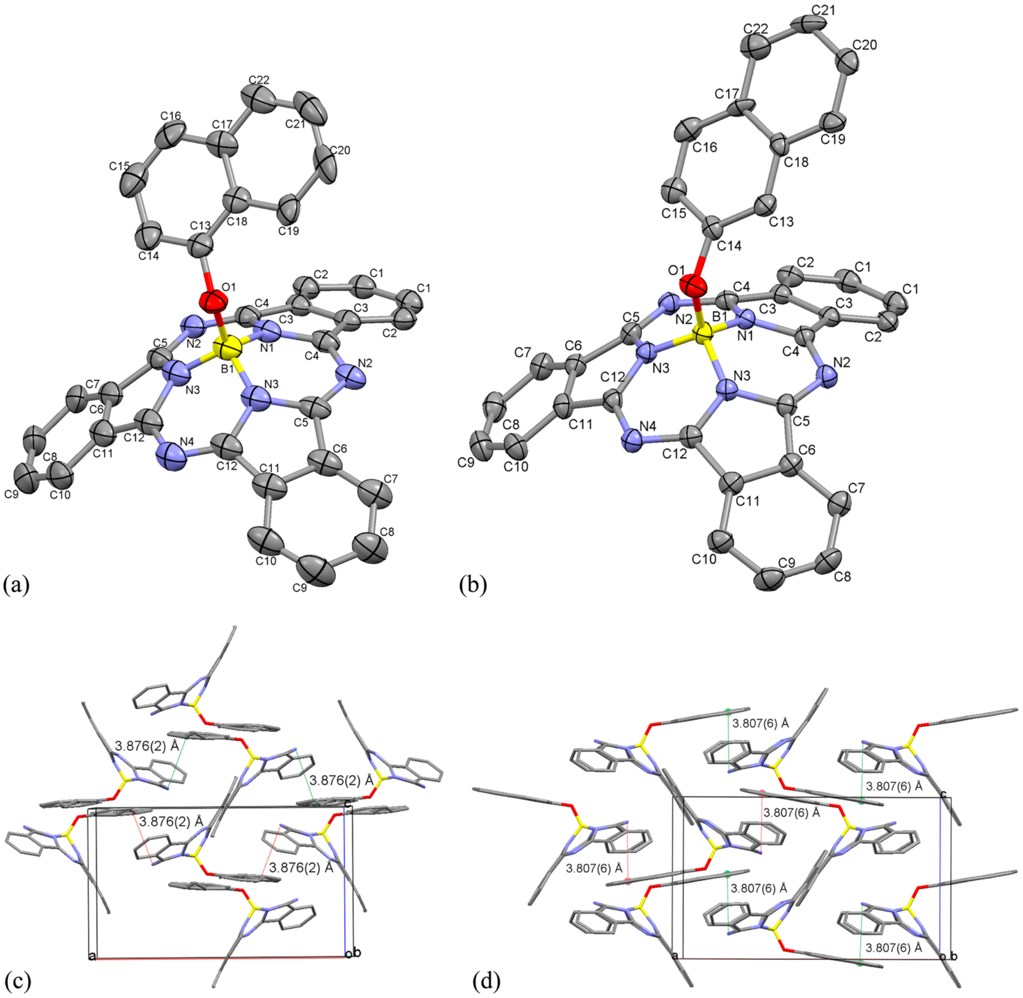


Figure 3. (a, b) Displacement ellipsoid plots of (a) compound **2a** and (b) compound **2b** at the 50% probability level. (b, c) Extended packing structures showing π-stacking interactions between naphthoxy units and BsubPcs (red and green lines) for (c) **2a** and (d) **2b**. H atoms have been omitted for clarity. Colors: carbon, gray; nitrogen, blue; oxygen, red; boron, yellow.

are two π-acidic fragments that do not benefit from associating with one another. Rather, the molecule in the solid state seeks to associate with heptane instead (likely by C−H···π interactions), but this requires a significant distortion of its molecular conformation. Similar observations regarding the distortion of the B−O−C bond angle can be seen when other π-acidic groups are present on the phenoxy fragment of a phenoxy-BsubPc. For example, B−O−C bond angles of 124.6(1)° and 130.3(2)° are seen for 4-nitrophenoxy-BsubPc (R = p-NO_2PhO)[27] and 4-acetylphenoxy-BsubPc (R = p-CH_3COPhO),[28] respectively, although in these cases there is not an accompanying solvent-filled void volume present within the crystal.

The crystallographic data for cyanophenoxy-BsubPc, the typical electrochemical behavior, and the ^1H NMR spectroscopic behavior of BsubPcs are all consistent with the idea that BsubPcs are π-acids. Given this, we can then move to the rational design of novel BsubPc derivatives that utilize the π-acidity to obtain previously unknown solid-state arrangements for BsubPc derivatives.

As stated above, it is best to use the most mass-efficient means to alter the solid-state arrangement of BsubPcs in order to avoid diluting the specific concentration of the BsubPc chromophore. For this reason, we considered π-basic aryloxy units that could be placed in the axial position of BsubPc (see Figure 1) to complement the π-acidity of the BsubPc and form robust π-acid/π-base interactions in the solid state.

We began by considering 4-methoxyphenoxy-BsubPc (**1**) which was synthesized using previously published procedures[14,20,24] (Scheme 1). Briefly, Cl-BsubPc was reacted with 4-methoxyphenol in toluene at reflux. The reaction was monitored by HPLC until complete. Purification via Kauffman column chromatography on standard basic alumina with dichloromethane as the eluent gave the final product. Full experimental details for all of the compounds are provided in the Supporting Information. Crystals suitable for X-ray diffraction were obtained via vapor diffusion using benzene/heptane (solvent/antisolvent, a system we have used before). Within 2 weeks, high-quality single crystals suitable for X-ray diffraction were grown, diffracted, and solved (Figure 2a).

In examining the solid-state arrangement of **1** (Figure 2b), we see that in addition to the typical molecular pairing between adjacent isoindoline fragments (colored in red in Figure 2b) observed in other phenoxy-BsubPcs, there is an extra π−π interaction between the methoxyphenoxy (shown in green) and BsubPc fragments in the neighboring molecule at a distance of 3.5124(8) Å (Figure 2b). In this structure, the distance of the π−π interaction between the isoindoline fragments of adjacent

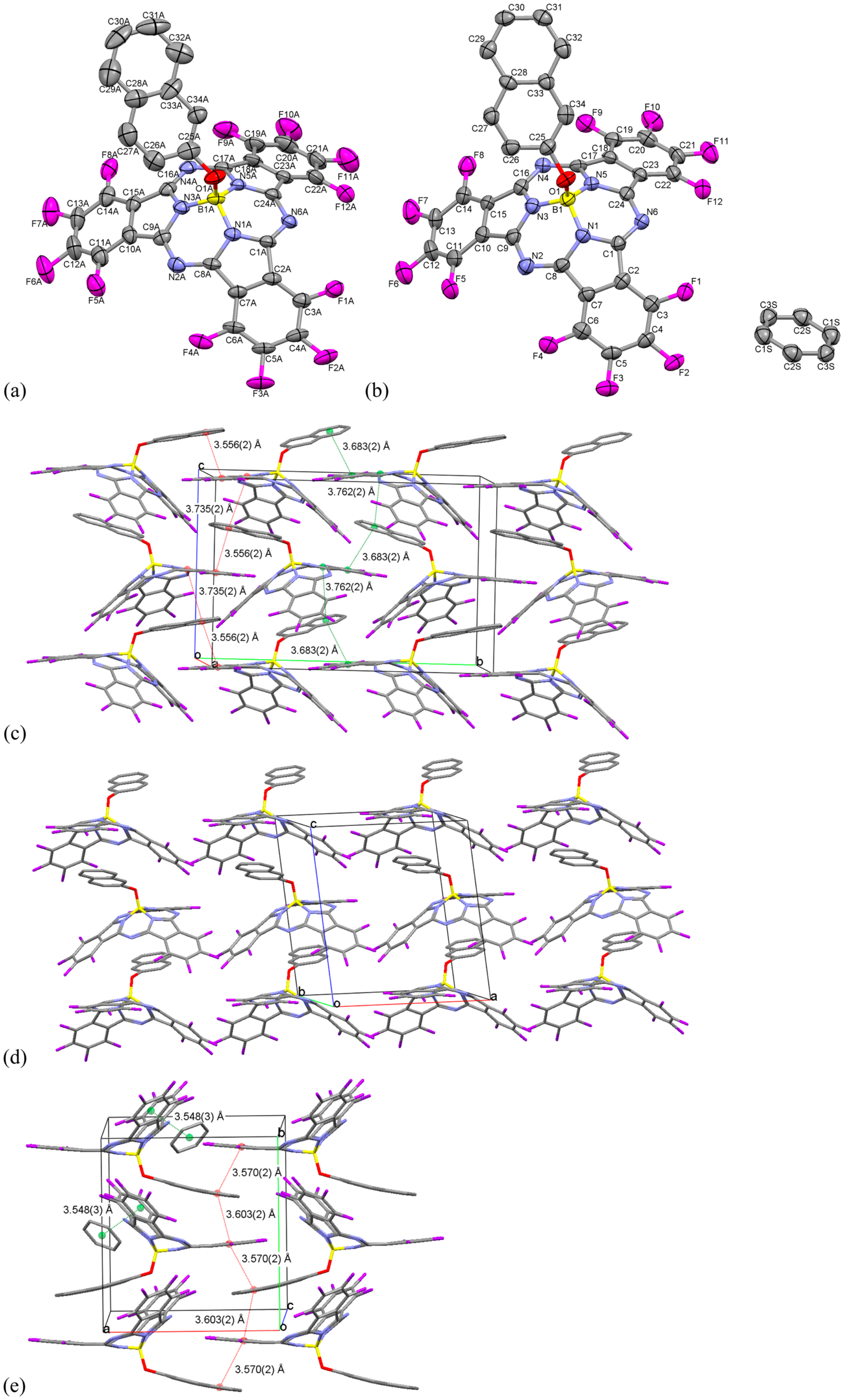


Figure 4. continued

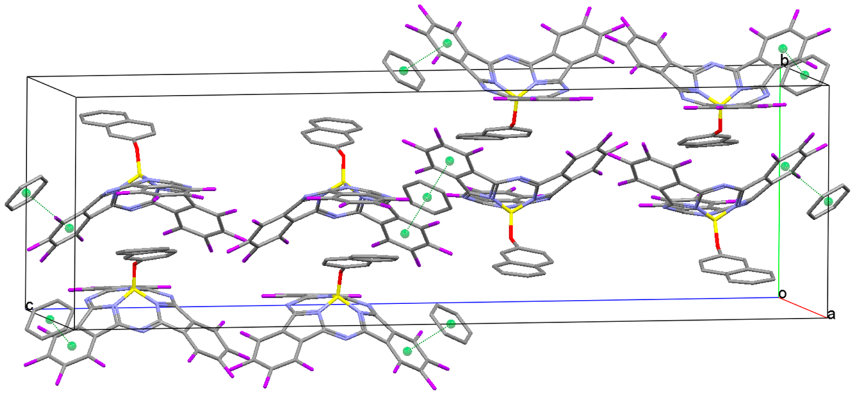


Figure 4. (a, b) Displacement ellipsoid plots for (a) compound **3** and (b) compound **3** benzene solvate at the 50% probability level. (c, d) Extended solid-state arrangement of **3** showing π−π interactions between naphthoxy units and F_{12}BsubPcs. (e, f) Extended solid-state arrangement of **3** benzene solvate showing π−π interactions between naphthoxy units and F_{12}BsubPcs and between the benzene solvent and F_{12}BsubPcs. H atoms have been omitted for clarity. Colors: carbon, gray; nitrogen, blue; oxygen, red; boron, yellow; fluorine, purple.

BsubPcs is 3.5512(9) Å, which is slightly shorter than that observed in other phenoxy-BsubPcs. In view of the relative π-basicity of the methoxyphenoxy fragment over a standard phenoxy fragment, the presence of a new π−π interaction not otherwise seen in crystals grown under identical conditions initially demonstrated to us the potential for using π-acid/π-base interactions to alter the solid-state arrangement of aryloxy-BsubPcs, although this example still contains the often seen dimerization of adjacent BsubPc fragments.[14]

We then turned our attention to other π-basic substituents that may be slightly less mass-efficient yet provide for a wider π-basic footprint. Specifically, we incorporated α-naphthoxy and β-naphthoxy fragments into the BsubPc molecular structure. The naphthoxy group is only slightly larger than the 4-methoxyphenoxy group (144 vs 124 amu, respectively) yet provides for a larger π-system by area. The synthesis was as described above. Reaction of Cl-BsubPc with commercially available α-naphthol and β-naphthol gave the two naphthoxy-BsubPcs **2a** and **2b**, respectively (Scheme 1; same conditions as for **1**). Again, single crystals of **2a** and **2b** were obtained by slow vapor diffusion using a benzene/heptane solvent system, and their X-ray crystal structures are shown in Figures 3a,b, respectively.

The solid-state arrangements of **2a** and **2b** do not at all resemble the typical phenoxy-BsubPc arrangement. The BsubPc molecules are arranged in one-dimensional ribbons (or catemers) parallel to the crystallographic axis, directed by the presence of a π−π interaction between the naphthoxy fragment and the concave face of the BsubPc (Figure 3c,d). These ribbons show close-packing N···π distances of 3.876(2) and 3.807(6) Å between the centroid of the outermost ring of the naphthoxy unit and the closest imine nitrogen in the next BsubPc ligand in the crystal structures of **2a** and **2b**, respectively. Interestingly, in the structures of both the α- and β-naphthoxy derivatives there exists disorder in the naphthoxy unit across the mirror plane of each row. This disorder does not affect the region in which there is intermolecular close contact between the naphthoxy group and the neighboring BsubPc ligand. Furthermore, there is no disorder in the BsubPc ligands themselves. Taken together, these results suggest a strong intermolecular interaction between the naphthoxy and BsubPc.

Further evidence of the strength of the naphthoxy−BsubPc aromatic interactions is provided by the prevalence of the crystal structure. While some BsubPc structures show varying crystal structure or solvates[15,29] with variation of the crystallization conditions, a polymorph search on the naphthoxy-derivatized BsubPcs yielded only the crystal structure described above. We attempted crystallization by liquid-layering, classic crystallization, evaporation, and slow vapor diffusion using a variety of different solvents. We also formed crystals of the naphthoxy derivatives using sublimation. In all cases, we were able to form high-quality crystals, and in all cases the crystals exhibited the same structure.

We next looked at perfluorinated BsubPcs (F_{12}BsubPcs), which should be even more π-acidic than the perhydrogenated BsubPcs discussed above. By attachment the naphthoxy substituent to F_{12}BsubPc, we again expected to see crystals that possess π-acid/π-base interactions. β-Naphthoxy-F_{12}BsubPc (**3**) (Scheme 1) was synthesized using procedures similar to those described above. We successfully grew crystals via both sublimation and vapor diffusion of heptane into a benzene solution. These methods gave two different structures, the former a solvent-free structure and the latter a benzene solvate. Displacement ellipsoid plots of these structures are shown in Figure 4a,b, respectively. Interestingly, aside from the benzene molecules in the solvate, the interactions seen in the two structures are same, as described below.

In the solvent-free structure (Figure 4a,c,d), the naphthoxy unit is located beneath the concave side of an indole unit and interacts through π−π interactions at a distance of 3.735(2) Å; however, the same indole unit also interacts through its convex side with another naphthoxy group at a π−π stacking distance of 3.556(2) Å. This second interaction joins two neighboring columns within the structure. There are two sets of these interactions in the structure because two molecules of the compound in slightly different conformations appear in the asymmetric unit. The Cg−Cg distances of the π−π interaction in the second set are 3.762(2) and 3.683(2) Å, respectively. These stacked molecules form two-dimensional sheets of molecules that do not appear to have specific interactions between them.

The benzene solvate of **3** (Figure 4b,e,f) shows identical π−π interactions, but at separation distances of 3.603(2) and 3.570(2) Å. The main difference between the two crystals of **3** is that in the solvated structure there is also an equidistant convex face to solvent (benzene) π−π stacking at 3.548(3) Å that joins adjacent sheets of stacked molecules.

The consistency between the two structures shows that the preferred interaction in this molecule is between the π-acidic F_{12}BsubPc and the π-basic naphthoxy substituent. Both of these arrangements are similar to what is typically observed in the solid-state arrangements of phenoxy-F_{12}BsubPcs (as described above), but the structures of **3** show more π-stacking overlap. In the structures of phenoxy-F_{12}BsubPc[20] and 4-methylphenoxy-F_{12}BsubPc,[21] the phenol π-stacks with the concave face of the neighboring F_{12}BsubPc unit at Cg−Cg distances of 3.6048(19) and 3.5320(18) Å, respectively. Because of the smaller area of the π-basic phenoxy unit compared to the naphthoxy group, however, there are no additional interactions with the convex face of the F_{12}BsubPc moiety. In other words, the increased π-basicity of the naphthoxy substituent over the phenoxy substituent allows greater π-acid/π-base interactions for β-naphthoxy-F_{12}BsubPc in the solid state.

■ CONCLUSIONS

The addition of a π-basic substituent onto both BsubPc and F_{12}BsubPc produces increased π-stacking interactions at shorter distances over those with less π-basic substituents. These additional interactions produce variations in the crystal packing motifs of typical phenoxy-BsubPcs[14] and phenoxy-F_{12}BsubPcs,[20,21] suggesting that an increase in the available π-electron density interacts favorably with any BsubPc. It has been shown that BsubPc is π-electron-deficient and thus is a π-acid. For this reason, we believe that the increased π-electron stacking is due to a π-acid/π-base interaction between the π-basic axial derivatives of naphthoxy and methoxyphenoxy and the π-acidic BsubPc and F_{12}BsubPc. This conclusion is further supported by the increased number of $\pi-\pi$ interactions seen in the crystal structure of compound **3** and the decreased number of interactions seen in the structures of other phenoxy-BsubPc derivatives having π-acidic phenols as the axial substituent.[26−28]This study provides evidence that π-acid/π-base interactions can successfully be used in the crystal engineering of BsubPc. In fact, the three naphthoxy derivatives display a one- or two-dimensional infinite ribbon structure in the solid state that may provide improved electronic properties. For this reason, these materials possess great potential for use as electronic materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials, synthetic procedures, crystallographic data, and CIFs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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