Absorption of Hydrogen Bond Donors by Pyridyl Bis-Urea Crystals

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Supporting Information

ABSTRACT: A one-dimensional crystalline solid built from pillars of self-assembled bis-urea pyridyl macrocycles affords a close packed structure with no pores. These organic pillars contain unsatisfied urea oxygen lone pairs that can be used to drive the absorption of alcohols including trifluoroethanol, phenol, pentafluorophenol, and ethylene glycol to give well-ordered host:guest complexes with repetitive stoichiometry. The driving force for reversible solid transitions appears to be the formation of hydrogen bonds between the guest and an unsatisfied hydrogen bond acceptor, which is a lone pair of the urea oxygen. Halogen bonding with the electrophilic iodide in pentafluoriodobenzene can also drive absorption by the host to give a well-ordered host:guest complex. These results suggest that the organic solid-state is surprisingly dynamic and may have potential applications for sorbents.

KEYWORDS: ureas, porous crystals, guest absorption, solid-to-solid transformation

INTRODUCTION

Materials that can absorb gases and guests have important applications in storage,¹ separations,² and catalysis.³ Micro-porous materials such as zeolites,⁴ MOFs,⁵ or COFs,⁶ typically contain open channels and may display permanent porosity by gas absorption. Seemingly nonporous solid materials can also have the ability to uptake guests by changing their three-dimensional structure.⁷ Clays, for example, may swell or expand in presence of suitable guests.⁸ In self-assembled materials, weak supramolecular connections between building blocks may be altered and changed to accommodate the guests during the absorption process.⁹ This manuscript investigates the direct use of close packed organic crystals as sorbents for alcohols, phenols, and organohalides. Macrocyle 1 (Figure 1) assembles into pillars through hydrogen bonds between the urea NHs and two acceptors: the urea oxygen and the pyridine nitrogen leaving the urea oxygen’s second lone pair unsatisfied.¹⁰ The close packed pillars of crystalline 1 can be used directly to bind guests that can interact with this unsatisfied hydrogen bond acceptor. Specifically, we investigated guests that contain hydrogen bond donors or halogen bond donors. Alcohols with pKₐ’s that range from 5–14 were efficiently absorbed into this host. Solid-state characterization methods suggest that these guests are incorporated in between the columns, and may be similar in structure to the TFE complex obtained previously by crystallization from DMSO/TFE. Preliminary studies also suggest that activated aryl iodides, such as pentafluoriodobenzene, are absorbed but less activated halides such as iodobenzene or p-diodobenzene are not absorbed. These studies demonstrate that relatively weak interactions can be used to drive absorption in remarkably dynamic solid-state organic crystals of 1.

Frameworks that can absorb guests, bind and store gases, aid in separations, or facilitate reactions typically are porous and display permanent porosity. Barbour describes two different types of porosity: conventional porosity and porosity “without pores”.¹¹ Conventional porosity applies to materials like highly crystalline, rigid materials such as zeolites and MOFs.¹² They retain their structure after guest removal. Their porosity is generated from the atomic coordinates of the host’s framework.¹² Porosity without pores relates to nonporous materials that possess flexible frameworks.¹³ Kitagawa characterizes these dynamic processes as either guest-induced crystal to amorphous transformations, in which the framework collapses on guest

Received: August 20, 2012
Revised: November 29, 2012
Published: December 5, 2012

Figure 1. Host 1 contains hydrogen bond donors and acceptors and assemblies from DMSO into columns (shown schematically) through hydrogen bonds. Our hypothesis is that crystals and crystalline powders of host 1 can directly absorb guests that contain one or more hydrogen bond donors without significant alteration to the column’s structure.
removal, or guest-induced crystal-to-crystal transformations, in which removal of the guests induces a structural change but the structure retains its crystallinity. For example, flexible coordination frameworks may rotate around single bonds, stretch around connectors and linkers because of bond formation and or cleavage, or undergo slip and glide motions between strong individual or independent networks called “breathing” as the guest is absorbed. Binary host systems can also display guest induced structural changes.

Recently, there has been renewed interest in purely organic systems that afford porous systems. Organic systems such as clathrates may retain permanent channels and display conventional porosity or they may collapse and expand upon guest desorption or absorption. For example, calixarene derivatives show gas-induced transformations that convert the guest free form of calixarenes to host–guest inclusion complexes. The guest free crystal forms of clarithromycin and lansoprazole formations. Prior studies showed that thermodynamically stable polymorphs by gas induced transformations. Our group utilizes bis-urea macrocycles prepared from two rigid spacers and two urea units. They typically assemble through the three centered urea−urea self-association to give columnar structures. In contrast, the small pyridyl derivative that is held together by the typical three-centered hydrogen bond motif, yet it displays type 1 gas urea macrocycle microporous material. Prior studies showed that guest free crystal forms of clarithromycin and lansoprazole also display guest induced structural changes. Chemical systems that a breathing process and or cleavage, or undergo slip and glide motions which removal of the guests induces a structural change but the crystals obtained from DMSO/MeOH. However, an acceptor, a lone pair on each of the carbonyl oxygens, remains unsatisfied. In contrast, in crystals obtained by vapor diffusion of TFE into a DMSO the TFE is interpenetrated between the columnar layers. In this structure, the alcohol of TFE formed a hydrogen bond with the unsatisfied lone pair of the urea carbonyl oxygen (Figure 2d).

This manuscript examines if the higher density close packed crystals of host 1 display “breathing” processes and absorb guests in solid-to-solid transitions to form host-guest inclusion complexes. We investigate if guest interactions with the unsatisfied oxygen lone pair can be used as a general strategy to trap sizable guests and drive sorption into the crystals of 1. We found that TFE, phenol, and pentafluorophenol, which each contain a hydrogen bond donor, were absorbed into the solid to form complexes with 1:2 host-guest stoichiometry. In contrast, ethylene glycol, which contains two hydrogen bond donors, forms complexes with 1:1 host-guest stoichiometry.

![Image of a columnar structure](https://example.com/image.png)

**Figure 2.** Pyridyl bis-urea macrocycle 1 affords two forms depending on crystallization conditions. (a) Macrocycle 1 crystallized from DMSO/MeOH gives close packed pillars, (b) 1 crystallized from DMSO/TFE gives similar pillars separated by TFE layers. (c) View of the pillars and (d) view highlighting the hydrogen bond between 1 and TFE.

Crystal forms show the same columns that are held together by hydrogen bonds between the urea NHs and two different acceptors: the urea carbonyl oxygen and the pyridine nitrogen (Figure 2c). Thus, an individual macrocycle participates in four hydrogen bonds with each of its nearest neighbors to afford robust pillars with higher melting point versus the m-xylene derivative that is held together by the typical three-centered urea interactions. These columns are close packed in the crystals obtained from DMSO/MeOH. However, an acceptor, a lone pair on each of the carbonyl oxygens, remains unsatisfied. In contrast, in crystals obtained by vapor diffusion of TFE into a DMSO the TFE is interpenetrated between the columnar layers. In this structure, the alcohol of TFE formed a hydrogen bond with the unsatisfied lone pair of the urea carbonyl oxygen (Figure 2d).

**EXPERIMENTAL SECTION**

**Materials.** Triazinanone and the m-xylene bis-urea macrocycle were prepared as previously described. Macrocycle 1 was synthesized in two steps from 2,6-dibromomethylpyridine and triazinanone as previously described. All chemicals were purchased from Aldrich and used without further purification. The IR data were collected on Shimadzu 8400 FT-IR spectrometer in KBr cells of 0.2 mm to 1 mm path length.

**Loading Experiments.** We tested a range of guests to see if the simple one-dimensional pillars can move apart to take up guests. Loading experiments were carried out on samples of host 1 (5–50 mg) by several methods: (a) vapor loading, (b) soaking directly in liquid guests, or (c) soaking in guest solutions (0.1 mM in heptane). TFE could be readily loaded by exposing macrocycle 1 to TFE vapor in a sealed chamber (method a). For method b, crystals of macrocycle 1 (5–50 mg) were added to the pure liquid (1 mL) in a scintillation vial. The mixture was agitated for 5 min and kept undisturbed for equilibration (0–36 h). For method c, crystals of macrocycle 1 (5–50 mg) were added to a solution of guest (0.1 mM phenol in heptane) and equilibrated (0–72 h). Guest absorption was monitored by absorbance spectroscopy, thermogravimetric analysis (TGA), 1H-(13)C-(19)F)-CP-MAS NMR, powder X-ray diffraction (PXRD), IR and X-ray Photoelectron spectroscopy (XPS).

**UV–vis Absorption Studies.** UV absorption studies were carried out using a Shimadzu UV–vis Spectrophotometer with 50 mm and 10 mm precision cells made of Quartz Suprasil 300.

**TGA Studies.** Guest desorption studies were carried out on 5–10 mg of guest absorbed sample using a TA Instruments SDT-Q600. The TGA analysis was done at a heating rate of 4 °C/min from 20 to 200 °C under helium and then kept at 200 °C (isotherm) for 10 min. Upon completion, each sample was recollected for further characterization.

**PXRD Studies.** Both freshly recrystallized empty crystals of 1 as well as guest loaded crystals were ground to a powder and examined by PXRD. X-ray powder diffraction data was collected on a Rigaku DMAX-2100 powder X-ray diffractometers using CuKα radiation. The step scans data were collected at +0.05° steps in the angular range 20–40° 20 at ambient temperature.

**NMR Studies.** 1H NMR and 13C NMR spectra were recorded on Varian Mercury 400. 13C (125.79 MHz) solid-state NMR results were acquired on a Varian Inova 500 spectrometer using a double resonant Depty Scientific XC 4 mm magic angle spinning (MAS) probe. Linear ramped cross-polarization was performed with the vendor’s supplied pulse sequence. A 1 ms contact time was used and TTPM modulated dipolar decoupling with a 61 kHz field strength was applied during data acquisition (40 ms). One second equilibration delay was used...
between each transient. Spinning speed of 8 kHz and TOSS sideband suppression was used for all measurements.

X-ray Photoelectron Spectroscopy (XPS). XPS measurements were carried out on the Kratos AXIS Ultra DLD XPS system equipped with a hemispherical energy analyzer and a monochromated Al K$_\alpha$ source. The monochromatic Al K$_\alpha$ source was operated at 15 keV and 150 W. The pass energy was fixed at 40 eV for the detailed scans. The binding energy is calibrated using an Ag foil with Ag3d$_{5/2}$ set at 368.21 ± 0.025 eV for the monochromatic Al X-ray source.

**Synthesis of 1.** The previously described synthesis of macrocycle 1 was repeated.$^{10,13}$ Colorless crystals of 1 (35 mg) were obtained by vapor diffusion of methanol into a DMSO solution of 1 (5 mg/mL). The crystals were filtered, dried at 120 °C for 2 h, then stored in a desiccator. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ = 7.63 (t, J = 7.6 Hz, 2 H), 7.13 (d, J = 8.1 Hz, 4 H), 6.91 (br s, 4 H), 4.31 (d, J = 5.4 Hz, 8 H); $^{13}$C{1H}CP-MAS NMR (125.79 MHz) $\delta$ = 164.1, 151.5, 135.4, 123.7, 51.9. $^{13}$C{1H}CP-MAS NMR (125.79 MHz) showed a weight loss of 32.47% between 75 and 120 °C. The binding stoichiometry was determined by TGA to be 1:2, $^{13}$C(H)-CP-MAS NMR (125.79 MHz) $\delta$ = 172.8, 151.5, 129.7, 138.1, 121.6, 44.5. IR (cm$^{-1}$): 3426, 3238, 3269, 3054, 3030, 2908, 2730, 1900, 1660, 1568, 1456, 1386, 1106. PXRD: 2$\theta$ = 35, 10.8, 14.2, 18.5, 21.4, 21.7, 23.5, 23.7, 26.6, 27.1, 28.6, 30.9. HRMS (EI) calculated for formula C$_{4775}$H$_{2476}$N$_{12}$O$_{27}$ [M+]: m/z 326.3532.

1-TFE Complex. Crystals of host 1 (35 mg) were exposed to TFE vapor in a sealed chamber for 0–72 h. Samples (3 mg) were taken every 12 h and subjected to TGA analysis. The 48 h sample displayed a one-step desorption curve by TGA and showed a weight loss of 32.47% between 75 and 120 °C. The binding stoichiometry was determined by TGA to be 1:2, $^{13}$C(H)-CP-MAS NMR (125.79 MHz) $\delta$ = 178.5, 153.1, 151.5, 137.9, 121.5, 44.6. IR (cm$^{-1}$): 3344, 3274, 2925, 1639, 1577, 1521, 1456, 1426, 1369, 1308. PXRD: 2$\theta$ = 9.3, 10.1, 11.3, 14.2, 16.8, 17.8, 18.5, 19.1, 20.4, 21.3, 22.8, 23.6, 24.1, 24.4, 28.5, 29.9.

1-Phenol Complex. Phenol was absorbed into host 1 by soaking the solid host in a 0.1 mM solution of phenol in heptane. First, free host (10 mg) was soaked in 20 mL of a 0.1 mM phenol solution for 24 h. After filtration, the complex was air-dried on a filter paper for 12 h, and TGA desorption was performed. After TGA analysis, the crystals were taken and the guest was reloaded by soaking. $^{13}$C{1H}CP-MAS NMR (125.79 MHz) $\delta$ = 178.2, 159.2, 158.2, 138.9, 118.7, 137.9, 135.5, 122.8, 121.9, 119.7 43.9. IR (cm$^{-1}$): 3340, 3272, 2919, 1621, 1579, 1521, 1456, 1426, 1369, 1307. PXRD: 2$\theta$ = 8.9, 9.2, 10.7, 13.1, 13.4, 16.1, 17.4, 18.1, 18.5, 20.9, 21.3, 21.6, 23.5, 26.5, 27.0, 28.5, 29.9.

1-Pentafluorophenol Complex. Host 1 (35 mg) was exposed to TFE vapor in a sealed chamber for 0–72 h. Samples (5 mg) were taken every 12 h and subjected to TGA analysis. The 48 h sample displayed a one-step desorption curve by TGA and showed a weight loss of 32.47% between 75 and 120 °C. The binding stoichiometry was determined by TGA to be 1:2, $^{13}$C(H)-CP-MAS NMR (125.79 MHz) $\delta$ = 175.4, 162.3, 152.6, 139.8, 123.7, 51.9. IR (cm$^{-1}$): 3334, 3274, 2925, 1639, 1577, 1521, 1456, 1426, 1369, 1308. PXRD: 2$\theta$ = 9.2, 10.1, 11.3, 14.2, 16.8, 17.8, 18.5, 19.1, 20.4, 21.3, 22.8, 23.6, 24.1, 24.4, 28.5, 29.9. We investigated if the close packed structure from DMSO/MeOH could be used directly to absorb guests through a solid-to-solid transition versus through a crystallization process that was reported previously.$^{10}$ We found that host 1 crystals did reversibly absorb TFE to form the crystalline 1-TFE complex, which is shown schematically in Figure 3a. Crystals of host 1 (35 mg) were exposed to TFE vapor in a sealed chamber for 0–72 h. Samples (5 mg) were taken every 12 h and subjected to TGA analysis. The 48 h sample displayed a one-step desorption curve by TGA (Figure 3b) and showed a weight loss of 32.47% between 75 and 120 °C (Figure 3b). The binding stoichiometry was determined by TGA to be 1:2. (Figure 3b), similar to the 1:2 stoichiometry observed in the single crystal structure.$^{10}$ No difference in binding was observed at the longer exposure times, suggesting that the system had reached an equilibrium by 48 h. To check if the absorption of TFE was a surface phenomenon, host 1 crystals were ground to a microcrystalline powder and equilibrated with TFE vapor as previously described to form a 1-TFE complex. The average weight loss for 7 absorption–desorption cycles from different batches/sizes of crystals was 32.84±0.34%, which corresponds to a 1:2.06 host: TFE binding stoichiometry, suggesting that this process was not a simple surface sorption. To further investigate this binding phenomenon, host 1 (65 mg) was loaded in a capillary and equilibrated with TFE vapor for 2 days. We monitored the daily increase in volume by measuring the change in length. After 2 days, a 45% increase in volume was observed (Supporting Information, Figure S1). Analysis of a sample of this material by TGA and NMR indicated that TFE was similarly incorporated. Further evidence that supports the incorporation of TFE into the host 1 crystals was provided by solid-state NMR experiments. Solid-state cross-polarized magic angle spinning $^{13}$C(H)-CP-MAS (125.79 MHz) NMR spectra were taken on the host 1 before and after exposure to TFE. The shift of the urea carbonyl carbon of 1 is dramatically affected by self-
assembly and moves from 164.1 ppm in δ6-DMSO, where it is not assembled, to 183.6 ppm in the 13C(1H)CP-MAS NMR spectra of the crystalline host 1, where the urea carbonyl oxygen is acting as an acceptor in one hydrogen bond. Upon TFE treatment, the carbonyl peak in the 1-TFE complex moved upfield to 172.8 ppm compared to the free host. Both host 1 and 1-TFE complex are organized by hydrogen bonding; however, the urea oxygen in the host 1-TFE complex should act as an acceptor for an additional hydrogen bonding interaction with the guest TFE. In typical bis-urea macrocycles that assemble through the three-centered urea-urea interaction, such as the m-xylene macrocycle, the carbonyl carbon is observed at 167.8 ppm in the 13C(1H)CP-MAS NMR spectra. Thus, this shift of carbonyl in 1-TFE complex suggests that both the lone pairs of the urea oxygen act as hydrogen bond acceptors. This weakening of the carbonyl carbon is also reflected in the IR stretch of the carbonyl group which shifts from 1658 cm−1 in host 1 to 1639 cm−1 in the 1-TFE complex.

We next investigated if this new 1-TFE complex was similar in structure to crystal structure of host 1-TFE. The newly generated 1-TFE complex was ground to a powder and examined by PXRD (Figure 4, pattern I). Using the reported single-crystal X-ray of host 1-TFE (a = 4.6955(12) Å, b = 9.632(3) Å, c = 12.775(3) Å), we simulated the PXRD pattern for host 1-TFE using POUdRIX (Figure 4, pattern II).27 Patterns I and II are nearly identical, suggesting that TFE can be loaded into host 1 to give a host 1-TFE complex whose structure is similar to the complex crystallized by vapor diffusion of TFE into DMSO solution of 1.

Next, the guest was removed from the bulk powder by heating to 140 °C for 3 h. 1H NMR was used to independently confirm the removal of the guest. The powder was reexamined by PXRD (Figure 4, pattern III). Similarly, the coordinates from the host 1 single crystal structure (a = 9.5207(5) Å, b = 4.6948(3) Å, c = 16.3045(9) Å), were used to simulate the PXRD pattern for host 1 using POUdRIX (Figure 4, pattern IV). Patterns III and IV are nearly identical, suggesting that the two structures are similar. Taken together, these experiments suggest that host 1 absorbs TFE and undergoes a solid-to-solid transformation to afford the host 1-TFE complex. Furthermore, upon removal of TFE the host returns to its initial structure.

Our hypothesis is that guest sorption is driven by the ability of the guest to interact with the unsatisfied lone pair of the urea oxygen. Alkane should not form strong intermolecular interactions with a hydrogen bond acceptor. Thus, we expected that host 1 would not absorb alkanes. The host 1 crystals (5 mg) were soaked in 1 mL of pure pentane, cyclohexane, and heptane for 7 days. Afterward, the crystals were filtered and immediately analyzed by TGA or dissolved in DMSO-d6 and analyzed by 1H NMR. Crystalline host 1 did not absorb any of these alkanes. Because these compounds are not absorbed by 1, they were excellent solvents for loading solid guests.

Next, we examined guest binding based on their ability to form hydrogen bonds (Table 1). TFE is acidic for an aliphatic alcohol with a pK_a ∼ 12.5.28 We investigated the uptake of phenol (pK_a ∼10), pentafluorophenol (pK_a ∼ 5.5), and ethylene glycol (pK_a ∼ 14.2) in crystalline host 1. These alcohols are each more acidic than methanol (pK_a ∼15.5), which does not appear to be absorbed by host 1. Similar to TFE, phenol, and pentafluorophenol each contain one hydrogen bond donor, while ethylene glycol contains two hydrogen bond donors. We expected that the number of hydrogen bond donors would be important in determining the binding stoichiometry in the complex.

Phenol was absorbed into host 1 by soaking the solid crystalline host 1 (10 mg) in 20 mL of a 0.1 mM solution of phenol in heptane for 0–72 h. The depletion of phenol from the solution was monitored at 275 nm and reached a plateau by 48 h, suggesting that an equilibrium had been established (Figure 5a). Comparison of the absorbance at 275 nm against the Lambert–Beer’s plot of phenol gave the stoichiometry of guest absorbed by host 1, which was calculated to be 1:1.9 host:guest. Pentafluorophenol was introduced into 1 by soaking the crystals directly in the liquid guest for 0–24 h. A one step desorption curve was observed by TGA between 90 to 115 °C from the host 1-pentafluorophenol complex (Figure 5b, curve I). The average weight average loss of three separate experiments was 50.04 ± 0.31%, which gave a calculated H:G ratio of 1:2.1. It appears that guests containing one hydrogen bond donor form complexes with ~1:2 host:guest ratio regardless of the loading method or the analytical technique used to measure the binding stoichiometry. This ratio does not appear to be influenced by the acidity of the alcohol, which ranged from 5.5 to 12.5. We assume that two hydrogen bond donors are needed to interact with the two unsatisfied lone pair of the carbonyl oxygens in macrocycle 1, much like was observed in the single crystal structure of host 1-TFE.10

Next we examined the uptake of ethylene glycol (pK_a = 14.2) into host 1 by the soaking method. Crystals of 1 (5–25 mg) were added to 1 mL of pure ethylene glycol and kept undisturbed (0–72 h). After filtration, the complex was air-dried (12 h) and analyzed by TGA. The TGA showed a one-step desorption curve between 100 and 175 °C (Figure 5b, curve III). The average weight loss of three separate experiments was 20.55 ± 0.24%, which gave a calculated H:G

<table>
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<th>BP (°C)</th>
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<tr>
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</tr>
<tr>
<td>pentafluorophenol</td>
<td>1:2</td>
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*pK_a for first dissociation.
hydrogen bond with two separate columns of host can form hydrogen bonds (shown schematically in Figure 1). Hydrogen bond donors can intrude in between the columns and the guests, each complex displayed a distinct PXRD pattern with sharp and intense peaks consistent with a well-ordered crystalline structure. Comparison of the PXRD patterns of host 1 (I), host 1-phenol (II), host 1-pentafluorophenol (III), and host 1-ethylene glycol (IV) shows that there are some changes in the structure and long-range order of the host because of the addition of the guest. Each of the complexes was heated to remove the guest (120–180 °C, 30 min), and their PXRD patterns were reexamined. After guest removal, each of the samples displayed a PXRD pattern that was nearly identical to the original host pattern (see Supporting Information), suggesting that the absorption and desorption process occurs as a solid-to-solid transition and does not disrupt the columns of I.

Our hypothesis is that each of these guests is forming hydrogen bonds with host 1. Therefore, we examined these complexes by IR, which can be used to monitor both the NH and OH donors as well as the carbonyl group. Solid-state IR was used to compare host 1, host 1-TFE, host 1-phenol, host 1-pentafluorophenol, and host 1-ethylene glycol. Host 1 has the two urea NHs paired with two different acceptors and shows two stretches (3328, 3269 cm⁻¹) for the NHs that are shifted to shorter wavenumbers in comparison to the three centered urea hydrogen bonding motif, indicating that these hydrogen bonds are slightly stronger and the N–H bond is slightly weaker. Upon uptake of the guest, we observe a shifting of one of the NH groups to longer wavenumbers (Table 2), which reflects a strengthening of the N–H bond and a weakening of the hydrogen bond, consistent with the guest forming a hydrogen bond with the urea oxygen. The magnitude of this shift is largest for pentafluorophenol (3345 cm⁻¹) in host 1 versus 3328 cm⁻¹ in the host 1-pentafluorophenol complex. This effect is also large for ethylene glycol (3347 cm⁻¹), which contains two hydrogen bond donors.

The carbonyl stretch in the IR is also affected by complex formation and shifts to lower wavenumbers reflecting a weakening of the C=O as we form a hydrogen bond to the guest. The greatest shift was again observed for the most acidic donor with the carbonyl band in host 1-pentafluorophenol appearing at 1616 cm⁻¹ versus 1658 cm⁻¹ in host 1. We also investigated the structure of the host and its alcohol inclusion complexes by solid-state cross-polarized magic angle spinning ¹³C(¹H)CP-MAS (125.79 MHz) NMR spectra (see Supporting Information). We observed an upfield shift of the urea carbonyl from 183.6 ppm in host 1 to 175.4 ppm in host 1-phenol, 178.5 ppm in host 1-pentafluorophenol, and 179.4 ppm in host 1-ethylene glycol. This shift reflects a change in the urea carbonyl upon guest absorption, which is consistent with the guest forming a hydrogen bond with the urea oxygen of host 1.

The electronic structure of host 1 and its host-guest complexes (guests = phenol, pentafluorophenol, ethylene

Table 2. Indicative Peaks for Host 1 and Its Complexes from IR Spectroscopy and XPS Survey Scans

<table>
<thead>
<tr>
<th>IR bands</th>
<th>XPS survey scans</th>
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<td>C=O</td>
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<tr>
<td>host 1</td>
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<tr>
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<tr>
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<td>1639</td>
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</table>

ratio of 1:1:1. Microcrystals were also soaked in ethylene glycol and observed under a microscope over 48 h. The microcrystals did not dissolve nor change their overall morphology (Supporting Information, Figure S22); however, ethylene glycol was incorporated in ~1:1 ratio as measure by ¹H NMR. Our loading experiments support the hypothesis that hydrogen bond donors can intrude in between the columns and can form hydrogen bonds (shown schematically in Figure 1). Ethylene glycol contains two hydrogen bond donors and may hydrogen bond with two separate columns of host 1 or may adopt a conformation that allows hydrogen bond formation with neighboring macrocycles.

We next investigated the solid-state structure of these new complexes by PXRD. Figure 6 shows that upon absorption of the guests, each complex displayed a distinct PXRD pattern with sharp and intense peaks consistent with a well-ordered crystalline structure. Comparison of the PXRD patterns of host 1 (I), host 1-phenol (II), host 1-pentafluorophenol (III), and host 1-ethylene glycol (IV) shows that there are some changes in the structure and long-range order of the host because of the addition of the guest. Each of the complexes was heated to remove the guest (120–180 °C, 30 min), and their PXRD patterns were reexamined. After guest removal, each of the samples displayed a PXRD pattern that was nearly identical to the original host pattern (see Supporting Information), suggesting that the absorption and desorption process occurs as a solid-to-solid transition and does not disrupt the columns of I.

Figure 5. Loading of guests into host 1. (a) Uptake of phenol by host 1 from solution (0.1 mM in heptane) versus time monitored by UV-visible absorption spectroscopy (λ = 275 nm). (b) Comparison of TGA desorption curves for (I) host 1-phenol, (II) host 1-pentafluorophenol, (III) Host 1-TFE, and (III) host 1-ethylene glycol.

Figure 6. Comparison of the observed PXRD of host 1 and its host-guest complexes. (I) Host 1, (II) Host 1-phenol, (III) Host 1-pentafluorophenol, and (IV) Host 1-ethylene glycol.
glycol) were further probed by XPS. We used C 1s for adventitious carbon as the reference with the binding energy value at 284.6 eV.\textsuperscript{30} Survey scans of host \textit{I} and the host-guest complexes show three intense peaks for the C 1s, the O 1s, and the N 1s XPS lines (Table 2). In host \textit{I}, the N 1s peak is at 398.2 eV and O 1s peak at around 530.5 eV and C=O peak comes at 289.1 eV.\textsuperscript{10} Upon absorption of alcohols, we observed shifts in the core level spectra of O 1s, but the C 1s and N 1s XPS lines were not changed. The binding energy of O 1s shifted from 530.5 eV to larger binding energy in the host-guest complexes. The largest shift is observed for host 1-phenol (531.2 eV). In general, the larger the binding energy, the higher the oxidation state.\textsuperscript{31} This is the effect of lower electron density on the atom or ion. Our observed increase in binding energy of the O 1s suggests that the oxygen has less electron density in the host-guest complex compared to the free host. This would be expected if the oxygen acts as a hydrogen bond acceptor for the acidic hydrogen of the guest. A hydrogen bonding interaction between the lone pair of the urea oxygen and the guest’s acidic proton would decrease the electron density on oxygen and thus increase in the binding energy. Alternatively, this shift could be due to the guests themselves, which contain both carbon and oxygen. Unfortunately, we were unable to take XPS survey scans on the guests alone as the guests are either low boiling or readily sublime.

Given that the formation of hydrogen bonding interactions appear to provide a driving force for the absorption of guests into the host \textit{I} framework, we next investigated if other noncovalent interactions might also aid absorption. The halogen bonding interaction may be observed between an electrophilic halogen atom and a hydrogen bond acceptor (A\textsubscript{c}).\textsuperscript{32} Typically, the halide is an aryl iodide that also has strong electron-withdrawing groups attached to the ring.\textsuperscript{33} Halogen bonding interactions are widely used in crystal engineering and supramolecular chemistry,\textsuperscript{34} and have been recently quantified in solution.\textsuperscript{35} They have been observed in biological systems.\textsuperscript{36} For example, the 4-chlorophenyl moiety of a ligand was observed to form a halogen bond with the lone pair of a backbone amide carbonyl oxygen of Gly61 in human Cathepsin L.\textsuperscript{37} Could such interactions be used to enhance the sorption of guests into host \textit{I} where the acceptor is a urea carbonyl oxygen? Pyridines are also good acceptors for halogen bonding interactions are widely used in crystal engineering and supramolecular chemistry,\textsuperscript{33} and have been recently quantified in solution.\textsuperscript{35} They have been observed in biological systems.\textsuperscript{36} For example, the 4-chlorophenyl moiety of a ligand was observed to form a halogen bond with the lone pair of a backbone amide carbonyl oxygen of Gly61 in human Cathepsin L.\textsuperscript{37} Could such interactions be used to enhance the sorption of guests into host \textit{I} where the acceptor is a urea carbonyl oxygen? Pyridines are also good acceptors for halogen bonds; however, the pyridine group of macrocycle 1 is less accessible as it is pointing to the interior of the macrocycle making an interaction with an aryl halide less likely.

To address this question, we investigated the loading of three aryl iodides into host 1. Iodobenzene, 1,4-diiodobenzene, and pentafluoriodobenzene were investigated. Of these guests, pentafluoriodobenzene contains the most electrophilic halide.\textsuperscript{38} Host 1 was soaked in heptane solutions (0.1 mM) of iodobenzene and diiodobenzene for 0–7 days. Guest solutions were monitored intermittently by UV–visible spectroscopy at 254 nm to assess the depletion of the guest from solution. No binding was observed after 7 days suggesting that the iodines in iodobenzene and diiodobenzene are not electrophilic enough to form halogen bonds with the urea oxygen acceptor of 1.

Next, we tested pentafluoriodobenzene with its electrophilic iodine. The solid host 1 was exposed to a 0.1 mM solution of pentafluoriodobenzene in heptane for 0–80 h. The solution was monitored by UV–vis at 222 nm at 6 h intervals to assess the depletion of the guest from solution (Figure 7a). The absorbance appeared to reach a plateau by 48 h, suggesting that an equilibrium had been established. Comparison of the absorbance at 222 nm with the Lambert–Beer’s plot of pentafluoriodobenzene gave a 1:1.5 host:guest loading. Similar loading ratios were observed upon soaking host 1 directly in liquid pentafluoriodobenzene (see Supporting Information). The TGA showed a one-step desorption curve between 60 and 105 °C (Figure 7b). The average weight average loss of three separate experiments was 39.84 ± 0.29%. Assuming this weight loss is from pentafluoriodobenzene we calculated a 1:1.4 host:guest ratio similar to the ratio determined from the Lambert–Beer method.

We examined the structure of the 1-pentafluoriodobenzene complex by PXRD (Figure 7c). The host 1-pentafluoriodobenzene displays sharp and intense peaks consistent with a well-ordered crystalline structure. The electronic structure of this host 1-pentafluoriodobenzene complex was further probed by XPS. Survey scan of host 1 and host 1-pentafluoriodobenzene complex showed that there was no change for the C=O peak at 289.1 eV. The O 1s XPS lines shifted to larger binding energy from 530.47 eV in host 1 to 531.16 eV in the host 1-pentafluoriodobenzene complex. A smaller but similar shift to larger binding energy was observed for the N 1s, which shifted from 398.23 in the host to 398.36 in the complex. In this complex, the guest contains no oxygen or nitrogen. Thus, the increase in binding energy for the oxygen 1s
reflects changes in the urea oxygen of the host. This increase in binding energy for the oxygen 1s is expected if the lone pair of the urea oxygen acts as an acceptor in a halogen bond for the electrophilic iodine atom of pentafluoriodobenzene. The smaller shift for the N 1s suggests that these lone pairs may also be involved in this complex, perhaps via resonance.

Upon uptake of the halogen guest, we also observe a modest shift of the carbonyl stretch to lower wavenumbers from 1658 cm\(^{-1}\) in host 1 to 1650 cm\(^{-1}\) in the IR of host 1-pentafluoriodobenzene. The stretch of the urea NH groups shift slightly in different directions and now appear at 3321 cm\(^{-1}\) and 3278 cm\(^{-1}\) closer to the original host 1, which has NH groups at 3328 cm\(^{-1}\) and 3269 cm\(^{-1}\). We observed an upfield shift in the \(^{13}\text{C}(^1\text{H})\text{CP-MAS}\) (125.79 MHz) NMR spectra for the urea carbon from 183.6 ppm in host 1 to 178.2 ppm in the complex, similar to what was observed for the alcohol complexes of host 1. Taken together, the changes in the IR, PXRD, XPS, and NMR upon guest uptake suggest that halogen bond interactions do indeed contribute to the complex formation.

While we do not know the mechanism of this absorption process, it appears to be a solid-to-solid transition. It is possible that the specific mechanism of absorption varies for the four alcohols. Three of the alcohols are liquids at STP, and host 1 is soluble in two of these pure liquids (TFE and pentafluorophenol). Despite this solubility, the bulk powder of 1 shows no sign of dissolving and appears to expand over time in a solid-to-solid transition when treated with TFE vapor (Supporting Information, Figure S1) or when soaked in a solution of pentafluorophenol (0.5 mM in heptane). In comparison, host 1 is not soluble in ethylene glycol, and the crystals show no obvious change over the absorption time (48 h) although ethylene glycol is incorporated into the solid as confirmed by NMR. We are currently investigating if guest absorption occurs as a single-crystal-to-single crystal transformation.

**CONCLUSIONS**

In summary, we found that crystals from close packed pillars of assembled pyridyl bis-urea macrocycles are remarkably dynamic. The pyridyl bis-ureas form robust pillars where the individual macrocycles are held together by four full hydrogen bonds. This 1-dimensional solid has an unsatisfied acceptor (a lone pair on the urea oxygen). Noncovalent interactions between this acceptor and guests, such as hydrogen bonding, help to drive solid-to-solid transitions. These materials can absorb a range of alcohols from the vapor or by soaking to give solid, well-ordered host:guest inclusion complexes by PXRD. The stoichiometry of the host:guest complex formed is dependent on the number of hydrogen bond donors in the guest but was not dependent on the acidity of the alcohols, dependent on the number of hydrogen bond donors in the solid, well-ordered host:guest inclusion complexes by PXRD. Absorption of guests. Pentafluoriodobenzene was important for absorption as less activated iodobenzene and \(p\)-diiodobenzene were not absorbed. We are currently trying to grow larger single crystals to fully characterize the structure of these host:guest complexes, and hope to report on this in due time. These results suggest that both hydrogen and halogen bonding are effective for driving solid-to-solid transitions. We are now examining if this process takes place in a single crystal-to-single crystal transition and are also evaluating the selectivity of this process for mixtures of alcohols.

**ASSOCIATED CONTENT**

Supporting information

CCDC reference numbers for previously reported host 1 (781839), host 1-TFE (781840), and the meta-xylene bis-urea macrocycle (166911). Synthesis and characterization of host 1, absorption studies, and characterization of inclusion complexes. 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.

**ACKNOWLEDGMENTS**

The authors gratefully acknowledge support for this work from the NSF Award number CHE-1012298.

**ABBREVIATIONS**

MOF, metal organic framework; COF, covalent organic framework; PXRD, powder X-ray diffraction; IR, Infrared spectroscopy; TGA, thermogravimetric analysis; TFE, trifluoroethanol; NMR, Nuclear Magnetic Resonance; XPS, X-ray Photoelectron spectroscopy; MeOH, methanol; DMSO, dimethyl sulfoxide.

**REFERENCES**


