CRYSTAL GROWTH & DESIGN

pubs.acs.org/crystal

Article

Assembling Guests as Cyclic Tetramers in a Porous Hydrogen-Bonded Organic Framework

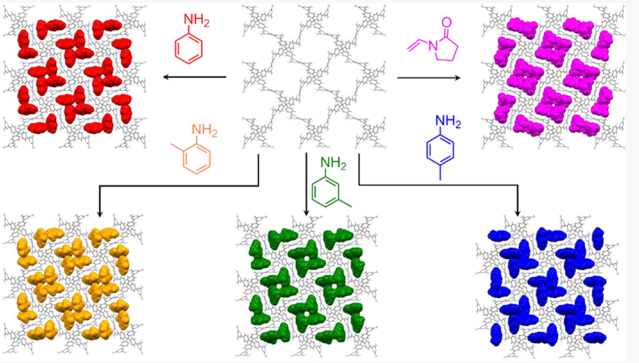
Mingshi Zhang, Jayanta Samanta, and Chenfeng Ke*

Cite This: *Cryst. Growth Des.* 2022, 22, 3421−3427

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Arranging multiple guests in large-pore organic framework materials relies on a fundamental understanding of the framework−substrate and substrate−substrate interactions. In this work, we prepared a series of hydrogen-bonded organic framework complexes (HOF-1·guests) with aniline, *o*-toluidine, *m*-toluidine, *p*-toluidine, toluene, and *N*-vinyl-2-pyrrolidone. Single-crystal structural analyses revealed that these guests formed similar cyclic tetramers in HOF-1 due to the strong HOF-1-guest hydrogen bonding and N-H···π interactions. Weak C-H···π or C-H···O interactions between guests were found to further stabilize these cyclic tetramers. The strong framework−substrate interaction enabled the uptake of aniline and *N*-vinyl-2-pyrrolidone in the same voids of HOF-1, and the residual acid in HOF-1 catalyzed an alkylation reaction within the voids.



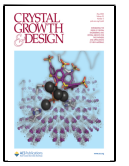
INTRODUCTION

Host−guest interactions are widely found in supramolecular systems[1,2] in solution[3] and the solid state.[4] Depending on the cavity size of the host molecule, one or multiple guests could be encapsulated via hydrogen bonding,[5−7] hydrophobic effects,[8,9] and electrostatic interactions.[10,11] Macrocycles including γ-cyclodextrin,[12,13] cucurbit[8]uril,[14,15] and cyclobisparaquats[16,17] have been reported to form ternary complexes in solution, respectively. These ternary complexes are further stabilized through guest−guest interactions. In the solid state, organic cages[18,19] and porous crystals[20−22] have also been reported to include multiple guests. Sometimes, these guests are arranged in unique geometries through multivalent host−guest and guest−guest interactions. For example, Kim et al. reported a fullerene tetramer and a porphyrin cage assembly in the solid state,[23] and Kubik et al. stabilized a dihydrogenphosphate tetramer using a cyclic pseudopeptide.[24]

In porous framework materials, such as metal−organic frameworks (MOFs),[25−28] covalent organic frameworks (COFs),[29,30] and hydrogen-bonded organic frameworks (HOFs),[31−34] the large and interconnected voids allow for the adsorption of multiple guests. In HOFs, discrete guest molecules, including organic solvents[35,36] and aromatic compounds,[37−40] have been identified to bind the functional groups decorated on the pore surfaces. This phenomenon is well illustrated in HOF-1 (Figure 1),[41,42] which binds acetylene selectively through framework−substrate hydrogen bonding for ethylene/acetylene separation.[42] Apart from gaseous substrates, the large one-dimensional (1D) porous channels of HOF-1 also allow for the uptake of multiple guest molecules either in the liquid or solid form. Therefore, the investigation of nongaseous substrates and HOF-1 complexes in the solid state will provide important structural insights into the understanding of multivalent host−guest and guest−guest interactions in porous organic materials.

In this work, we chose HOF-1 as the crystalline framework host and aniline and its analogues toluidine and toluene as guests for the investigation. Different from the reported aniline or toluidines complexes formed in MOFs[43] or HOFs,[38,44] the single-crystal X-ray structure of HOF-1·PhNH$_2$ revealed that anilines were assembled in the voids of HOF-1 as cyclic tetramers. Furthermore, cyclic guest tetramers are found in five other HOF-1·guest complexes, including toluidine isomers (*o*-, *m*-, *p*-Tld), toluene (Tol), and *N*-vinyl-2-pyrrolidone[45] (VP) (Figure 1a), respectively. We have discovered that the strong HOF-1/substrate interactions, including hydrogen bonding and N-H···π interactions, direct the assembly of guests as cyclic tetramers. They are further stabilized via C-H···π interactions. We noticed that the strong HOF-1/substrate interaction dominates the arrangement of guests in the voids of HOF-1. This feature allows for the coadsorption of different guests in

Received: February 19, 2022
Revised: March 17, 2022
Published: April 5, 2022



https://doi.org/10.1021/acs.cgd.2c00217
Cryst. Growth Des. 2022, 22, 3421−3427

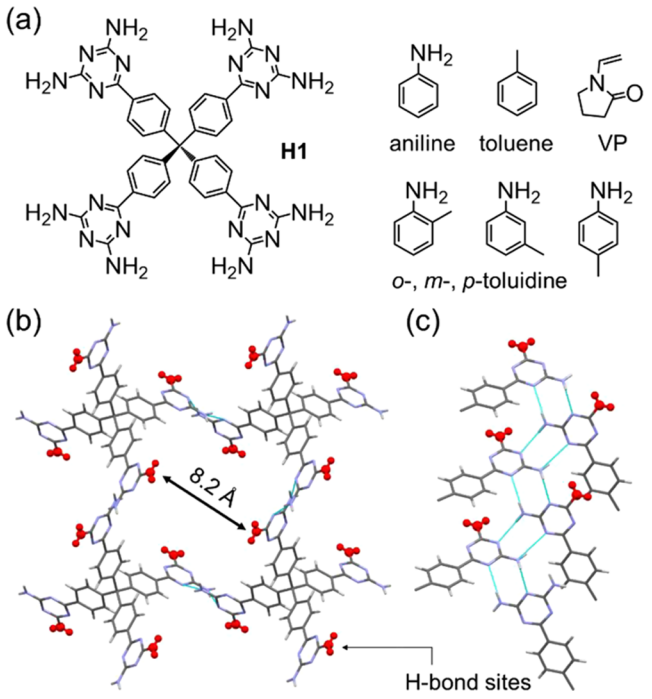


Figure 1. (a) Chemical structures of **H1** and substrates used in this investigation. (b) Solid-state structure of HOF-1 viewed along the *c*-axis. Vacant amino groups are highlighted in red color. Disordered solvent molecules are omitted for clarity. (c) Hydrogen-bonding arrays formed between 2,4-diamino-1,3,5-triazine (DAT) arms.

the same porous channel, as evident from the alkylation[46] of the coadsorbed aniline and VP in HOF-1.

EXPERIMENTAL SECTION

HOF-1 and HOF-1·Guest Complexes. A solution of **H1** (100.0 mg, 0.132 mmol, in 0.75 mL of 1,4-dioxane and 1 mL of formic acid) in a 4 mL vial was placed in a 20 mL vial with 8 mL 1,4-dioxane for solvent diffusion. After 10 days at room temperature, transparent needle-like HOF-1 crystals were obtained (~60 mg). HOF-1 single crystals (~5 mg) were picked and transferred to a vial containing 2 mL of neat guest liquid (aniline, toluene, *o*-toluidine, *m*-toluidine, *p*-toluidine, *N*-vinyl-2-pyrrolidone). The samples were kept at 25 or 50 °C for 24 h. Crystals of HOF-1·guest complexes were selected for single-crystal X-ray diffraction (SCXRD) analysis.

Coadsorption of Guest Mixtures. HOF-1 single crystals (~5 mg) were selected, transferred to a mixture of guests, and kept at room temperature for 48 h. The crystals were washed with water and dried under reduced pressure. The crystals were dissolved in DMSO-d_6 for ^{1}H NMR analysis. Fed $PhNH_2$/Tol mixture: $PhNH_2$ (1.112 g, 1.09 mL, 12 mmol) and Tol (1.104 g, 1.27 mL, 12 mmol); found **H1**/$PhNH_2$/Tol = 1:3.4:0.7. Fed $PhNH_2$/Tld isomer mixtures: $PhNH_2$ (0.556 g, 0.51 mL, 6 mmol), *o*-Tld (0.642 g, 0.64 mL, 6 mmol), *m*-Tld (0.642 g, 0.66 mL, 6 mmol), and *p*-Tld (0.556 g, 0.61 mL, 6 mmol); found **H1**/$PhNH_2$/*o*-Tld/*m*-Tld/*p*-Tld = 1:1.1 ± 0.1:1.0 ± 0.0:1.0 ± 0.0:1.2 ± 0.1.

Alkylation of Aniline and *N*-Vinyl-2-pyrrolidone in HOF-1. HOF-1 single crystals (~5 mg) were selected, washed with water, and transferred to a mixture of $PhNH_2$ (1.112 g, 1.09 mL, 12 mmol) and VP (1.332 g, 1.28 mL, 12 mmol). After 48 h at room temperature, the mixture of $PhNH_2$ and VP was carefully removed for ^{1}H NMR analysis. The crystals were washed with water and dried under reduced pressure. These crystals were dissolved in DMSO-d_6 for ^{1}H NMR analysis. 1-(1-Anilinoethyl)-2-pyrrolidinone (AEP) was not detected in the mother liquid. Found **H1**/$PhNH_2$/VP/AEP = 1:3.1 ± 0.1:0.8 ± 0.1:0.3 ± 0.0.

RESULTS AND DISCUSSION

The compound **H1**, which is the molecular building block of HOF-1, was synthesized according to previous reports.[42] **H1** consists of a tetraphenyl methane (TPM) core and four DAT arms (Figure 1a). Diffusing 1,4-dioxane into the mixed solution of formic acid/dioxane of **H1** afforded HOF-1 crystals that are suitable for SCXRD analysis. In HOF-1, each DAT arm is hydrogen-bonded with two adjacent **H1** molecules. One vacant amino group of DAT (red, Figure 1b) points toward the pore surface. There are square-shaped 1D porous channels[42] with an aperture of 8.2 Å in HOF-1, which allows for the uptake of multiple guest molecules.

The HOF-1·$PhNH_2$ complex was prepared by immersing solvent-filled HOF-1 crystals in neat aniline at 25 °C. After 24 h diffusion, the obtained crystal sample was subjected to SCXRD analysis. In HOF-1·$PhNH_2$, four aniline molecules are packed in an edge-to-face manner (Figure 2a) as a cyclic tetramer at the cross section of the 1D channel. SCXRD and ^{1}H NMR analyses showed that the molar ratio between **H1** and aniline is 1:4 (Table 1). Compared to HOF-1, the unit cell volume of HOF-1·$PhNH_2$ contracted by 2.1%, indicating that the uptake of aniline does not significantly impact the hydrogen-bonded network of HOF-1. The vacant amino groups of **H1** form hydrogen bonds (Figure 2b) with anilines via an N(5)-H···N(6)-Ph interaction (2.48 Å, Table 1). Additional N-H···π interactions (Figure 2c) are also noticeable between the amino groups and aniline (3.68 Å, Table 1). Within the pore voids, four anilines are bonded to each other as a cyclic tetramer (Figure 2d) via C-H···π interactions (3.68 Å, Table 1). The cyclic tetramers are repeated along the *c*-axis of HOF-1 (Figure 2e). Compared to the solid-state structure of aniline (Figure 2f),[47] the spatial arrangement of anilines in HOF-1 is very different, suggesting that the strong HOF-1-to-aniline interaction competes against the aniline−aniline hydrogen bonding (2.51 and 2.36 Å) in the solid state. To understand the framework−substrate interactions, we replaced aniline with toluene and prepared a toluene-filled HOF-1 crystal (HOF-1·Tol) for SCXRD analysis. Surprisingly, cyclic toluene tetramers were also formed within the voids of HOF-1 (Figure 2g), similar to HOF-1·$PhNH_2$. Only N-H···π interactions (4.29 Å, Table 1) are established between the vacant amino groups of HOF-1 and toluene (Figure 2h). The Ph-H···π distance (3.95 Å, Table 1) between toluene molecules (Figure 2i) is larger than those of the aniline molecules (3.68 Å). These analyses suggest much weaker framework−substrate and substrate−substrate interactions in HOF-1·Tol compared to that of HOF-1·$PhNH_2$. When HOF-1 single crystals were immersed in a 1:1 mixture of aniline/toluene at 25 °C for 24 h, the adsorbed aniline/toluene ratio was measured as 4.9:1 by ^{1}H NMR spectroscopy (Figure S26).[48] In vapor sorption experiments (Figure S31), the adsorption of toluene in HOF-1 is relatively low at the lower−pressure range, but the adsorption amount rapidly increased at higher pressure. This phenomenon is also observed in MOFs,[49,50] suggesting that the guest−guest interaction prompts the guest uptake in HOF-1 voids.

Expanding the substrate scope from aniline to *o*-Tld, *m*-Tld, and *p*-Tld, we sought to investigate the co-conformations of toluidine regioisomer assemblies in HOF-1. Three HOF-1·toluidine complexes were prepared by immersing solvent-filled HOF-1 crystals in neat *o*-Tld, *m*-Tld at 25 °C, and *p*-Tld melt at 50 °C, respectively. Despite different shapes of toluidine

https://doi.org/10.1021/acs.cgd.2c00217
Cryst. Growth Des. 2022, 22, 3421−3427

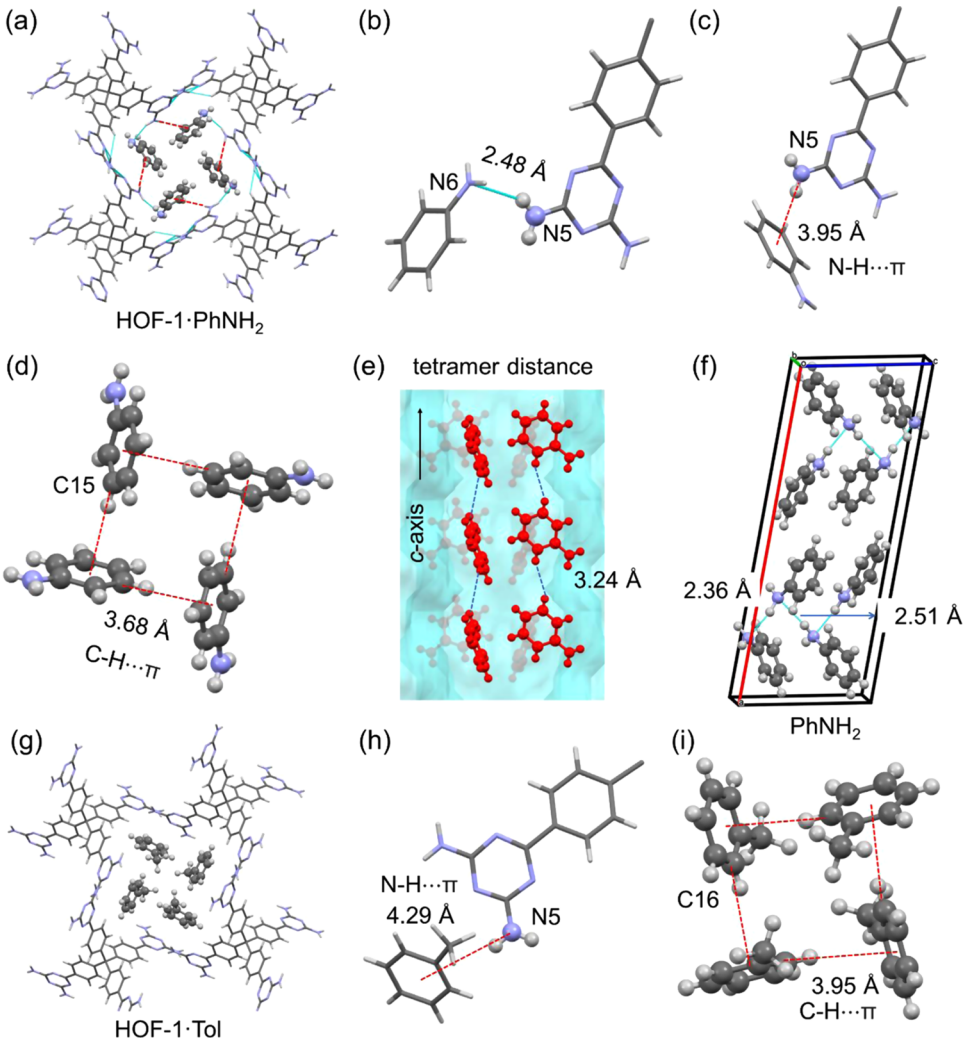


Figure 2. (a) Solid-state structure of HOF-1·$PhNH_2$ viewed along the *c*-axis. (b) Hydrogen bonding and (c) N-H···π interaction between HOF-1 and aniline. The N-H···π distance is measured as the distance between the N atom and the center of the phenyl ring. (d) Cyclic aniline tetramer in HOF-1·$PhNH_2$ with C-H···π interactions highlighted. (e) Layered packing of cyclic aniline tetramers in HOF-1·$PhNH_2$. Anilines are highlighted in red color. (f) Solid-state structure of aniline.[47] (g) Solid-state structure of HOF-1·Tol viewed along the *c*-axis. (h) N-H···π interaction between HOF-1 and toluene. (i) Cyclic toluene tetramer in HOF-1·Tol, with C-H···π interactions highlighted.

isomers, cyclic toluidine tetramers were found in HOF-1·*o*-Tld, HOF-1·*m*-Tld, and HOF-1·*p*-Tld (Figure 3a). The amino groups of *o*-Tld, *m*-Tld, and *p*-Tld are hydrogen-bonded to the vacant amino group of DAT in HOF-1 (Figure 3b), and the N(5)-H···N(6) distances are measured as 2.45, 2.44, and 2.43 Å, respectively (Table 1). The N(5)-H···π interactions were also found in HOF-1·*o*-Tld (4.01 Å), HOF-1·*m*-Tld (3.92 Å), and HOF-1·*p*-Tld (3.96 Å) (Figure 3c). Both Ph-H···π and CH_3···π interactions were found between the neighboring toluidine molecules in HOF-1·*o*-Tld and HOF-1·*p*-Tld (Figure 3d), while only a Ph-H···π interaction was found in HOF-1·*m*-Tld. The short hydrogen bonds and N-H···π interactions between the *p*-toluidine tetramer and HOF-1 and the 2-fold C-H···π interactions within the cyclic tetramer suggest that HOF-1·*p*-Tld possesses slightly stronger host−guest and guest−guest interactions among the HOF-1·Tld complexes. Experimentally, when HOF-1 crystals were immersed in an equal amount of $PhNH_2$, *o*-Tld, *m*-Tld, and *p*-Tld mixture, the uptake ratio of $PhNH_2$, *o*-Tld, *m*-Tld, and *p*-Tld was measured as 1:1.1 ± 0.1:1.0 ± 0.0:1.0 ± 0.0:1.2 ± 0.1 using ^{1}H NMR spectroscopy (Figure S27).[48] The greater uptake amount of *p*-Tld in the adsorption experiment is consistent with SCXRD analyses.

When the substrates were changed from toluidine isomers (both hydrogen bonding donors and acceptors) to *N*-vinyl-2-pyrrolidone (a hydrogen bonding acceptor), tetrameric cyclic assemblies of VP were also found in the solid state (Figure 4a). In the HOF-1·VP crystal, the carbonyl groups of VP tetramers form hydrogen bonds via a N(5)-H···O(1) interaction (2.13 Å, Figure 4b), directing the vinyl groups to point toward the pore surface of HOF-1. The closest vinyl-to-vinyl distance is measured as 6.37 Å. In the VP tetramer, only weak C(14)-H···O(1) dipole interactions (2.68 Å, Figure 4c) were discovered, suggesting the assembly of VP molecules in HOF-1 is primarily driven by the framework−substrate interaction.

The strong framework-guest and weak guest−guest interactions within HOF-1·$PhNH_2$, HOF-1·Tol, HOF-1·*o*-Tld, HOF-1·*m*-Tld, HOF-1·*p*-Tld, and HOF-1·VP complexes directed the formation of guest cyclic tetramers. These cyclic tetramers were weakly packed along the 1D voids of HOF-1. Therefore, we speculated that the voids of HOF-1 could

https://doi.org/10.1021/acs.cgd.2c00217
Cryst. Growth Des. 2022, 22, 3421−3427

Table 1. Summary of Crystallographic Data of HOF-1 and HOF-1·Guest Complexes[a]

	HOF-1	HOF-1·$PhNH_2$	HOF-1·Tol	HOF-1·*o*-Tld	HOF-1·*m*-Tld	HOF-1·*p*-Tld	HOF-1·VP
formula	**H1**·4dioxane· HCO_2H	**H1**·4$PhNH_2$	**H1**·4Tol	**H1**·4*o*-Tld	**H1**·4*m*-Tld	**H1**·4*p*-Tld	**H1**·4VP
unit cell (Å)							
a	20.466(8)	20.3468(10)	20.1754(6)	20.2713(4)	20.1198(3)	20.2017(4)	20.3140(7)
b	20.466(8)	20.3468(10)	20.1754(6)	20.2713(4)	20.1198(3)	20.2017(4)	20.3140(7)
c	7.185(2)	7.1118(6)	7.2479(4)	7.1255(2)	7.20870(10)	7.1518(2)	7.3565(4)
cell volume change (%)		−2.1	−2.0	−2.7	−3.0	−3.0	0.9
H1:guest							
SCXRD[b]		1:4.0	1:4.0	1:4.0	1:4.0	1: 4.0	1:4.0
^{1}H NMR[c]		1:3.9	1:3.2[d]	1:4.0	1:4.2	1:4.1	1:3.9
N-H···N distance (Å)		2.48		2.45	2.44	2.43	2.13 (N-H···O)[e]
N-H···π distance[f] (Å)		3.95	4.29	4.01	3.92	3.96	
C-H···π distance[g] (Å)		3.68	3.95	3.79[h]	3.65	3.79[h]	
				4.01[h]		4.15[h]	
distance of tetramers[i] (Å)		3.24	2.60	2.23	2.30	2.22	2.92

[a]All Crystals are Tetragonal in the *I*-4 Space Group with $\alpha = \beta = \gamma = 90°$. [b]**H1**:guest ratios determined by X-ray crystallography. [c]**H1**:guest ratios determined by ^{1}H NMR experiment. [d]Fewer toluene molecules per **H1** measured in ^{1}H NMR analysis, attributed to the high volatility of toluene. [e]The N-H···N hydrogen bond distance between the vacant amino group of **H1** and nitrogen atoms of the substrate. [f]The N-H···π distance is measured as the distance between the N(5) atom and the center of the phenyl ring. [g]The C-H···π distance is measured as the distance between the carbon atom and the center of the phenyl ring. [h]Measured Ph-H···π and CH_3···π distances, respectively. [i]The measured distance between the nearest atoms of two cyclic tetramers.

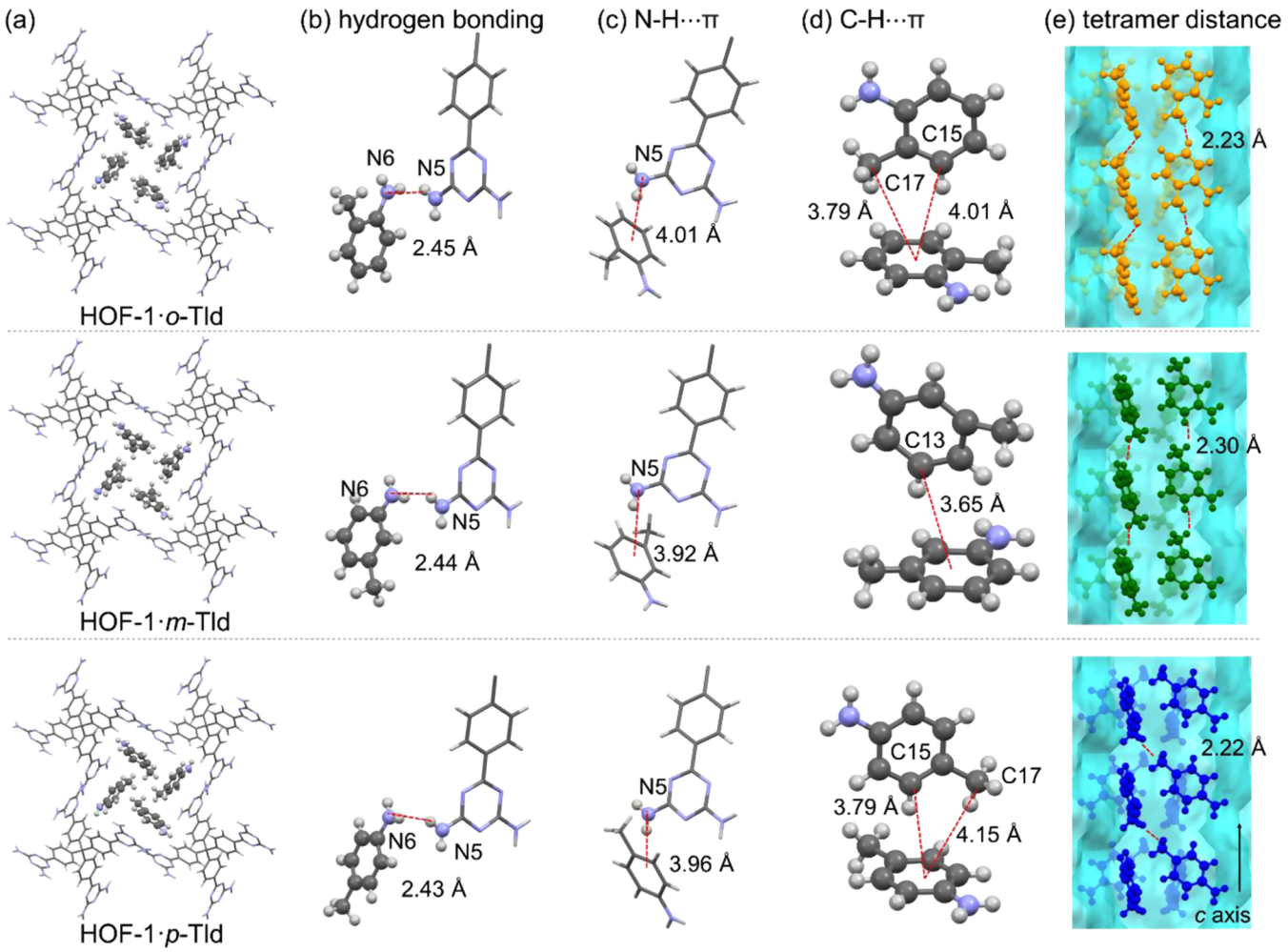


Figure 3. Crystal structures of HOF-1·*o*-Tld, HOF-1·*m*-Tld, and HOF-1·*p*-Tld in descending order. (a) Solid-state structure of HOF-1·*o*-Tld, HOF-1·*m*-Tld, and HOF-1·*p*-Tld viewed along the *c*-axis. (b) Hydrogen-bonding interactions and (c) N-H···π interaction between HOF-1 and *o*-Tld, *m*-Tld, and *p*-Tld, respectively. (d) C-H···π interactions in the cyclic tetramers of *o*-Tld, *m*-Tld, and *p*-Tld, respectively. (e) Layered packing structures of cyclic tetramers of *o*-Tld, *m*-Tld, and *p*-Tld from top to bottom. The *o*-Tld, *m*-Tld, and *p*-Tld are highlighted in yellow, green, and blue colors, respectively.

https://doi.org/10.1021/acs.cgd.2c00217
Cryst. Growth Des. 2022, 22, 3421−3427

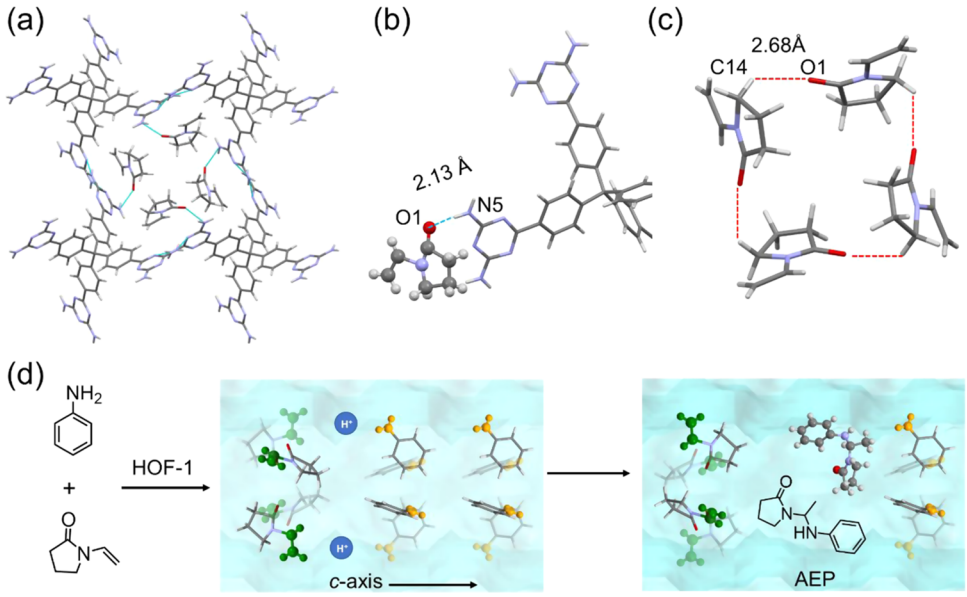


Figure 4. (a) Solid-state structure of HOF-1·VP complex viewed along the *c*-axis. (b) Hydrogen-bonding interactions between HOF-1 and VP (c) C-H···O interactions between VP molecules in the channels of HOF-1. (d) Process by which aniline and VP meet and react with each other in the channels of HOF-1. Aniline and VP are first coadsorbed into HOF-1, and they are catalyzed by the residual formic acid within HOF-1 to afford 1-(1-anilinoethyl)-2-pyrrolidinone (AEP). The amino and olefin groups are highlighted in yellow and green colors, respectively.

accommodate two different guests simultaneously as a mixture of cyclic tetramers.[51] To confirm this, we immersed HOF-1 crystals in the mixture of two reactive substrates ($PhNH_2$ and VP). $PhNH_2$ and VP could undergo an alkylation[46] to form 1-(1-anilinoethyl)-2-pyrrolidinone (AEP, Figure 4d) in the presence of an acid. In the solvent-filled HOF-1 crystals, formic acid residuals are present in the 1D voids, which could catalyze the formation of AEP when $PhNH_2$ and VP are adsorbed in the same channel. Experimentally, we immersed HOF-1 crystals in a 1:1 mixture of $PhNH_2$ and VP at room temperature. After 48 h, the crystals and mother liquid were subjected to ^{1}H NMR analysis (Figures S22–S23). No AEP was detected in the mother liquid mixture, and ^{1}H NMR analysis shows the **H1**/$PhNH_2$/VP/AEP ratio in the dissolved crystal sample as 1:3.1 ± 0.1:0.8 ± 0.1:0.3 ± 0.0 (Figure S30). The formation of AEP in HOF-1 confirmed that $PhNH_2$ and VP molecules were coadsorbed within the same 1D channel of HOF-1. The found **H1**/$PhNH_2$/VP ratio revealed that HOF-1 binds $PhNH_2$ stronger than VP, and VP was not consumed completely. This incomplete alkylation in HOF-1 indicates that $PhNH_2$ and VP are coadsorbed as cyclic tetramer aggregates, and the alkylation only occurred at the interface of $PhNH_2$ and VP aggregates (Figure 4d).

CONCLUSIONS

In summary, a series of HOF-1·guest complexes with aniline, *o*-, *m*-, *p*-toluidine, toluene, and *N*-vinyl-2-pyrrolidone were prepared, and their corresponding single-crystal X-ray structures are reported here. Despite the different sizes of guests, the strong HOF-1–substrate interactions, including hydrogen bonding and N-H···π interactions, direct the assembly of guests as cyclic tetramers within the 1D voids of HOF-1. These cyclic tetramers are further stabilized through the guest–guest interactions, which include C-H···π and van der Waals interactions. By comparing the packing structures of *o*-, *m*-, *p*-toluidines in HOF-1, we discovered that the methyl groups of toluidine regioisomers only resulted in very small changes in the HOF-1·toluidine interactions. These cyclic tetramers are packed along with the 1D voids of HOF-1. No specific interactions are noticed between neighboring cyclic tetramers, which allowed for the coadsorption of different guests inside the same 1D voids of HOF-1. This coadsorption of different guest molecules in HOF-1 was confirmed by the alkylation between aniline and VP inside HOF-1. Our work suggests that strong framework–substrate interactions could effectively arrange multiple guests in desired co-conformations, while guest–guest interactions differ depending on the size and functional groups of the guests. These results provide important structural insights into multiple guests inclusion and methods for conducting chemical reactions in confined environments.[52,53]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.2c00217.

Experimental and general methods, ^{1}H NMR spectra, X-ray diffraction details, and crystal structures (PDF)

Accession Codes

CCDC 2153022–2153028 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.

AUTHOR INFORMATION

Corresponding Author

Chenfeng Ke – *Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755, United States;* orcid.org/0000-0002-4689-8923; Email: chenfeng.ke@dartmouth.edu

https://doi.org/10.1021/acs.cgd.2c00217
Cryst. Growth Des. 2022, 22, 3421–3427

Authors

Mingshi Zhang − *Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755, United States*

Jayanta Samanta − *Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.cgd.2c00217

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the National Science Foundation CAREER award (DMR 1844920) and Arnold & Mabel Beckman Foundation Beckman Young Investigator program. In addition, the authors thank Dr. Qianming Lin and Mr. Albert D. Chen for their help in preparing the manuscript.

■ DEDICATION

This work is dedicated to Sir Fraser Stoddart on the occasion of his 80th birthday.

■ REFERENCES

(1) Kyba, E. P.; Helgeson, R. C.; Madan, K.; Gokel, G. W.; Tarnowski, T. L.; Moore, S. S.; Cram, D. J. Host-guest complexation. 1. Concept and illustration. *J. Am. Chem. Soc.* **1977**, *99*, 2564−2571.

(2) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*, 3rd ed.; John Wiley & Sons, 2022.

(3) Oshovsky, G. V.; Reinhoudt, D. N.; Verboom, W. Supramolecular chemistry in water. *Angew. Chem., Int. Ed.* **2007**, *46*, 2366−2393.

(4) Ramamurthy, V.; Eaton, D. F. Perspectives on solid-state host-guest assemblies. *Chem. Mater.* **1994**, *6*, 1128−1136.

(5) Weber, E.; Franken, S.; Puff, H.; Ahrendt, J. Enclave inclusion of nitromethane by a new crown host - X-ray crystal-structure of the inclusion complex and host selectivity properties. *J. Chem. Soc., Chem. Comm.* **1986**, 467−469.

(6) Ashton, P. R.; Ballardini, R.; Balzani, V.; GomezLopez, M.; Lawrence, S. E.; MartinezDiaz, M. V.; Montalti, M.; Piersanti, A.; Prodi, L.; Stoddart, J. F.; Williams, D. J. Hydrogen-bonded complexes of aromatic crown ethers with (9-anthracenyl)methylammonium derivatives. Supramolecular photochemistry and photophysics. pH-controllable supramolecular switching. *J. Am. Chem. Soc.* **1997**, *119*, 10641−10651.

(7) Nangia, A.; Desiraju, G. R. Pseudopolymorphism: occurrences of hydrogen bonding organic solvents in molecular crystals. *Chem. Commun.* **1999**, 605−606.

(8) Southall, N. T.; Dill, K. A.; Haymet, A. D. J. A view of the hydrophobic effect. *J. Phys. Chem. B* **2002**, *106*, 521−533.

(9) Gibb, C. L. D.; Gibb, B. C. Well-defined, organic nanoenvironments in water: The hydrophobic effect drives a capsular assembly. *J. Am. Chem. Soc.* **2004**, *126*, 11408−11409.

(10) Plieger, P. G.; Tasker, P. A.; Galbraith, S. G. Zwitterionic macrocyclic metal sulfate extractants containing 3-dialkylaminomethylsalicylaldimine units. *Dalton Trans.* **2004**, 313−318.

(11) Mahoney, J. M.; Beatty, A. M.; Smith, B. D. Selective recognition of an alkali halide contact ion-pair. *J. Am. Chem. Soc.* **2001**, *123*, 5847−5848.

(12) Hashimoto, S.; Thomas, J. K. Fluorescence study of pyrene and naphthalene in cyclodextrin amphiphile complex-systems. *J. Am. Chem. Soc.* **1985**, *107*, 4655−4662.

(13) Nakamura, A.; Inoue, Y. Electrostatic manipulation of enantiodifferentiating photocyclodimerization of 2-anthracenecarboxylate within gamma-cyclodextrin cavity through chemical modification. Inverted product distribution and enhanced enantioselectivity. *J. Am. Chem. Soc.* **2005**, *127*, 5338−5339.

(14) Kim, H. J.; Heo, J.; Jeon, W. S.; Lee, E.; Kim, J.; Sakamoto, S.; Yamaguchi, K.; Kim, K. Selective inclusion of a hetero-guest pair in a molecular host: Formation of stable charge-transfer complexes in cucurbit[8]uril. *Angew. Chem., Int. Ed.* **2001**, *40*, 1526−1529.

(15) Biedermann, F.; Scherman, O. A. Cucurbit[8]uril mediated donor-acceptor ternary complexes: A model system for studying charge-transfer interactions. *J. Phys. Chem. B* **2012**, *116*, 2842−2849.

(16) Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. Cyclobis(paraquat-para-phenylene) - a tetracationic multipurpose receptor. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1547−1550.

(17) Cao, J.; Guo, J. B.; Li, P. F.; Chen, C. F. Complexation between pentiptycene derived bis(crown ether)s and $CBPQT^{4+}$ Salt: Ion-controlled switchable processes and changeable role of the $CBPQT^{4+}$ in host-guest systems. *J. Org. Chem.* **2011**, *76*, 1644−1652.

(18) Ning, G. H.; Cui, P.; Sazanovich, I. V.; Pegg, J. T.; Zhu, Q.; Pang, Z. F.; Wei, R. J.; Towrie, M.; Jelfs, K. E.; Little, M. A.; Cooper, A. I. Organic cage inclusion crystals exhibiting guest-enhanced multiphoton harvesting. *Chem* **2021**, *7*, 3157−3170.

(19) Little, M. A.; Chong, S. Y.; Schmidtmann, M.; Hasell, T.; Cooper, A. I. Guest control of structure in porous organic cages. *Chem. Commun.* **2014**, *50*, 9465−9468.

(20) Rizzuto, F. J.; von Krbek, L. K. S.; Nitschke, J. R. Strategies for binding multiple guests in metal-organic cages. *Nat. Rev. Chem.* **2019**, *3*, 204−222.

(21) Taylor, C. G. P.; Train, J. S.; Ward, M. D. Interactions of small-molecule guests with interior and exterior surfaces of a coordination cage host. *Chemistry* **2020**, *2*, 510−524.

(22) Yan, K. K.; Dubey, R.; Arai, T.; Inokuma, Y.; Fujita, M. Chiral crystalline sponges for the absolute structure determination of chiral guests. *J. Am. Chem. Soc.* **2017**, *139*, 11341−11344.

(23) Yu, X.; Wang, B. Z.; Kim, Y.; Park, J.; Ghosh, S.; Dhara, B.; Mukhopadhyay, R. D.; Koo, J.; Kim, I.; Kim, S.; Hwang, I. C.; Seki, S.; Guldi, D. M.; Baik, M. H.; Kim, K. Supramolecular fullerene tetramers concocted with porphyrin boxes enable efficient charge separation and delocalization. *J. Am. Chem. Soc.* **2020**, *142*, 12596−12601.

(24) Mungalpara, D.; Valkonen, A.; Rissanen, K.; Kubik, S. Efficient stabilisation of a dihydrogenphosphate tetramer and a dihydrogenpyrophosphate dimer by a cyclic pseudopeptide containing 1,4-disubstituted 1,2,3-triazole moieties. *Chem. Sci.* **2017**, *8*, 6005−6013.

(25) Deria, P.; Bury, W.; Hupp, J. T.; Farha, O. K. Versatile functionalization of the NU-1000 platform by solvent-assisted ligand incorporation. *Chem. Commun.* **2014**, *50*, 1965−1968.

(26) Qin, J. S.; Yuan, S.; Alsalme, A.; Zhou, H. C. Flexible zirconium MOF as the crystalline sponge for coordinative alignment of dicarboxylates. *ACS Appl. Mater. Interfaces* **2017**, *9*, 33408−33412.

(27) Pei, X. K.; Burgi, H. B.; Kapustin, E. A.; Liu, Y. Z.; Yaghi, O. M. Coordinative alignment in the pores of MOFs for the structural determination of N-, S-, and P-containing organic compounds including complex chiral molecules. *J. Am. Chem. Soc.* **2019**, *141*, 18862−18869.

(28) Kato, S.; Otake, K.; Chen, H. Y.; Akpinar, I.; Buru, C. T.; Islamoglu, T.; Snurr, R. Q.; Farha, O. K. Zirconium-based metal-organic frameworks for the removal of protein-bound uremic toxin from human serum albumin. *J. Am. Chem. Soc.* **2019**, *141*, 2568−2576.

(29) Sun, Q.; Fu, C. W.; Aguila, B.; Perman, J.; Wang, S.; Huang, H. Y.; Xiao, F. S.; Ma, S. Q. Pore environment control and enhanced performance of enzymes infiltrated in covalent organic frameworks. *J. Am. Chem. Soc.* **2018**, *140*, 984−992.

(30) Chen, Y. C.; Shi, Z. L.; Wei, L.; Zhou, B. B.; Tan, J.; Zhou, H. L.; Zhang, Y. B. Guest-dependent dynamics in a 3D covalent organic framework. *J. Am. Chem. Soc.* **2019**, *141*, 3298−3303.

(31) Wang, B.; Lin, R. B.; Zhang, Z. J.; Xiang, S. C.; Chen, B. L. Hydrogen-bonded organic frameworks as a tunable platform for functional materials. *J. Am. Chem. Soc.* **2020**, *142*, 14399−14416.

(32) Li, P. H.; Ryder, M. R.; Stoddart, J. F. Hydrogen-bonded organic frameworks: A rising class of porous molecular materials. *Acc. Mater. Res.* **2020**, *1*, 77−87.

(33) Yang, Y. S.; Li, L. B.; Lin, R. B.; Ye, Y. X.; Yao, Z. Z.; Yang, L.; Xiang, F. H.; Chen, S. M.; Zhang, Z. J.; Xiang, S. C.; et al. Ethylene/ethane separation in a stable hydrogen-bonded organic framework through a gating mechanism. *Nat. Chem.* **2021**, *13*, 933−939.
(34) Li, P.; He, Y. B.; Guang, J.; Weng, L. H.; Zhao, J. C. G.; Xiang, S. C.; Chen, B. L. A homochiral microporous hydrogen-bonded organic framework for highly enantioselective separation of secondary alcohols. *J. Am. Chem. Soc.* **2014**, *136*, 547−549.
(35) Xiao, W. C.; Hu, C. H.; Ward, M. D. Guest exchange through single crystal-single crystal transformations in a flexible hydrogen-bonded framework. *J. Am. Chem. Soc.* **2014**, *136*, 14200−14206.
(36) Wahl, H.; Haynes, D. A.; le Roex, T. Guest exchange in a robust hydrogen-bonded organic framework: Single-crystal to single-crystal exchange and kinetic studies. *Cryst. Growth. Des.* **2017**, *17*, 4377−4383.
(37) Huang, Q. Y.; Li, W. L.; Mao, Z.; Qu, L. J.; Li, Y.; Zhang, H.; Yu, T.; Yang, Z. Y.; Zhao, J.; Zhang, Y.; Aldred, M. P.; Chi, Z. G. An exceptionally flexible hydrogen-bonded organic framework with large-scale void regulation and adaptive guest accommodation abilities. *Nat. Commun.* **2019**, *10*, No. 3074.
(38) Wang, B.; He, R.; Xie, L. H.; Lin, Z. J.; Zhang, X.; Wang, J.; Huang, H. L.; Zhang, Z. J.; Schanze, K. S.; Zhang, J.; Xiang, S. C.; Chen, B. L. Microporous hydrogen-bonded organic framework for highly efficient turn-up fluorescent sensing of aniline. *J. Am. Chem. Soc.* **2020**, *142*, 12478−12485.
(39) Liu, T.; Wang, B.; He, R.; Arman, H.; Schanze, K. S.; Xiang, S. C.; Li, D.; Chen, B. L. A novel hydrogen-bonded organic framework for the sensing of two representative organic arsenics. *Can. J. Chem.* **2020**, *98*, 352−357.
(40) Ma, L.; Xie, Y.; Khoo, R. S. H.; Arman, H.; Wang, B.; Zhou, W.; Zhang, J.; Lin, R. B.; Chen, B. L. An adaptive hydrogen-bonded organic framework for the exclusive recognition of p-xylene. *Chem.-Eur. J.* **2022**, *28*, No. e202104269.
(41) Brunet, P.; Simard, M.; Wuest, J. D. Molecular tectonics. Porous hydrogen-bonded networks with unprecedented structural integrity. *J. Am. Chem. Soc.* **1997**, *119*, 2737−2738.
(42) He, Y. B.; Xiang, S. C.; Chen, B. L. A Microporous hydrogen-bonded organic framework for highly selective C_2H_2/C_2H_4 separation at ambient temperature. *J. Am. Chem. Soc.* **2011**, *133*, 14570−14573.
(43) Liu, Q. K.; Ma, J. P.; Dong, Y. B. Adsorption and separation of reactive aromatic isomers and generation and stabilization of their radicals within cadmium(II)-triazole metal-organic confined space in a single-crystal-to-single-crystal fashion. *J. Am. Chem. Soc.* **2010**, *132*, 7005−7017.
(44) Ke, Z. J.; Chen, K. X.; Li, Z. Z.; Huang, J.; Yao, Z. Z.; Dai, W.; Wang, X. F.; Liu, C. L.; Xiang, S. C.; Zhang, Z. J. Dual-functional hydrogen-bonded organic frameworks for aniline and ultraviolet sensitive detection. *Chinese Chem. Lett.* **2021**, *32*, 3109−3112.
(45) Perrin, A.; Goodwin, M. J.; Musa, O. M.; Berry, D. J.; Corner, P.; Edkins, K.; Yufit, D. S.; Steed, J. W. Hydration behavior of polylactam clathrate hydrate inhibitors and their small-molecule model compounds. *Cryst. Growth.Des.* **2017**, *17*, 3236−3249.
(46) Ziyaei Halimehjani, A.; Goudarzi, M.; Nosood, Y. L. Alkylation of aromatic amines by tert-enamides: Direct access to protected aminals. *Syn. Commun.* **2017**, *47*, 2022−2029.
(47) Funnell, N. P.; Dawson, A.; Marshall, W. G.; Parsons, S. Destabilisation of hydrogen bonding and the phase stability of aniline at high pressure. *CrystEngComm* **2013**, *15*, 1047−1060.
(48) Van de Voorde, B.; Munn, A. S.; Guillou, N.; Millange, F.; De Vos, D. E.; Walton, R. I. Adsorption of N/S heterocycles in the flexible metal-organic framework MIL-53(Fe-III) studied by in situ energy dispersive X-ray diffraction. *Phys. Chem. Chem. Phys.* **2013**, *15*, 8606−8615.
(49) Coudert, F. X.; Jeffroy, M.; Fuchs, A. H.; Boutin, A.; Mellot-Draznieks, C. Thermodynamics of guest-induced structural transitions in hybrid organic-inorganic frameworks. *J. Am. Chem. Soc.* **2008**, *130*, 14294−14302.
(50) Aguado, S.; Bergeret, G.; Titus, M. P.; Moizan, V.; Nieto-Draghi, C.; Bats, N.; Farrusseng, D. Guest-induced gate-opening of a zeolite imidazolate framework. *New J. Chem.* **2011**, *35*, 546−550.
(51) Natarajan, R.; Magro, G.; Bridgland, L. N.; Sirikulkajorn, A.; Narayanan, S.; Ryan, L. E.; Haddow, M. F.; Orpen, A. G.; Charmant, J. P. H.; Hudson, A. J.; Davis, A. P. Nanoporous organic alloys. *Angew. Chem., Int. Ed.* **2011**, *50*, 11386−11390.
(52) Kobayashi, Y.; Horie, Y.; Honjo, K.; Uemura, T.; Kitagawa, S. The controlled synthesis of polyglucose in one-dimensional coordination nanochannels. *Chem. Commun.* **2016**, *52*, 5156−5159.
(53) Begum, S.; Hassan, Z.; Bräse, S.; Tsotsalas, M. Polymerization in MOF-confined nanospaces: Tailored architectures, functions, and applications. *Langmuir* **2020**, *36*, 10657−10673.

https://doi.org/10.1021/acs.cgd.2c00217
Cryst. Growth Des. 2022, 22, 3421−3427