Dynamic Transformation between Covalent Organic Frameworks and Discrete Organic Cages

Zhen Shan,^{\perp} Xiaowei Wu,^{\perp} Bingqing Xu, You-lee Hong, Miaomiao Wu, Yuxiang Wang, Yusuke Nishiyama, Junwu Zhu, Satoshi Horike, Susumu Kitagawa, and Gen Zhang^{*}

Cite This: https://dx.doi.org/10.1021/jacs.0c11073		Read Online		
ACCESS	III Metrics & More	Article Recommendations		s Supporting Information

ABSTRACT: We propose a dynamic covalent chemistry (DCC)-induced linker exchange strategy for the structural transformation between covalent organic frameworks (COFs) and cages for the first time. Studies have shown that the COF-to-cage and cage-to-COF transformations were realized by using borate bonds and imine bonds, respectively, as linkages. Self-sorting experiments suggested that borate cages and imine COFs are thermodynamic minimum compounds. This research builds a bridge between discrete and polymeric organic scaffolds and broadens the knowledge of chemistry and materials for porous materials science.

D ynamic covalent chemistry (DCC) involves a series of reversible chemical reactions controlled by thermodynamic equilibrium.¹ In light of the principle of DCC, small organic building blocks are covalently assembled into complex molecular architectures such as discrete assemblies (macrocycles,² cages,³ molecular knots,⁴ rotaxanes,⁵ catenanes,⁶ etc.) and infinite polymeric scaffolds⁷⁻⁹ (amorphous and crystalline polymers). The nature of DCC enables the dynamic transformation of discrete assemblies under homogeneous phase equilibrium-controlled conditions. However, the dynamic transformation of infinite polymers in heterogeneous phases remains a significant challenge.

Covalent organic frameworks (COFs) are an emerging class of crystalline porous materials constructed by covalent linking of organic building blocks into two-dimensional (2D) sheets or three-dimensional (3D) frameworks.⁹ Thanks to their tunable and designable structures and properties, COFs have attracted extensive research attention in the fields of gas separation and storage,¹⁰ sensing,¹¹ catalysis,¹² organic electronics,¹³ energy conversion and storage,¹⁴ and environmental¹⁵ and biological applications.¹⁶ Although the formation of COFs follows the DCC principle and many dynamic covalent bonds have been used in their construction, there are few studies on their transformations compared with their analogues, metal-organic frameworks (MOFs).¹⁷ Very recently, Zhao et al.¹⁸ described the first examples of COFto-COF transformations through linker exchange. Horike and co-workers¹⁹ achieved the transformation of single COFs to hierarchical/composite COFs via postsynthetic modification. Amorphous organic polymers can also be transformed into COFs, as disclosed by Zeng and co-workers.²⁰ Nevertheless, to date these studies have mainly been focused on the transformation between framework materials with similar structures and properties or the conversion of one discrete architecture into another. However, the transformation between crystalline framework materials and discrete structures has never been investigated.²

Covalent organic cages are constructed by connecting organic building blocks via reversible covalent bonds into zero-dimensional (0D) discrete architectures with tunable, designable, and functionalizable nanospace.²² Since organic cages and COFs follow the principle of DCC and share many common precursor building blocks such as amines, aldehydes, and boronic acid molecules for their synthesis,²³ we assume that the dynamic transformation between these two crystalline materials could occur via reversible bond exchanges under thermodynamic control. In this contribution, we chose boronate ester-bonded and imine-bonded COFs and cages as framework materials and discrete architectures, respectively, and systematically studied the dynamic transformation between these two distinct crystalline porous materials via the linker exchange process.

To investigate the dynamic transformation between COFs and cages, we initially synthesized boronate ester-linked COFs built from catechol-functionalized tribenzotriquinacene (**TBTQ**),²⁴ a core-twisted nonplanar polyphenolic compound, and *p*-phenylene diboronic acid (**DP**), denoted as COF-**NUST-1** (Scheme 1). In the FT-IR spectra, strong stretching vibration bands attributed to the formation of a boronate ester ring of B–O linkages were observed at ~1324 cm⁻¹, and the almost disappearance of characteristic O–H stretching bands (~3284 cm⁻¹) indicated the complete condensation of two monomers (Figure S2), which was also confirmed by 1D ¹H,¹¹B single-pulse NMR spectra and 2D ¹H-¹³C heteronuclear correlation solid-state NMR spectrum (Figures S4, S5, and S7). Thermogravimetric analysis (TGA) revealed that COF-**NUST-1** exhibited no weight loss under N₂ upon heating to

Received: October 20, 2020



Scheme 1. Synthesis of COF-NUST-1 and Cage-NUST-1 and the Structural Transformation



Figure 1. (a) PXRD pattern and Le Bail fitting for COF-NUST-1. (b) Top and (c) side views of COF-NUST-1. (d) ¹H NMR spectra of Cage-NUST-1 (500 MHz, CDCl₃ for Cage-NUST-1, THF- d_8 for TBTQ and TP). (e, f) Structure of discrete Cage-NUST-1 showing the cage cavity.

300 °C (Figure S29). Scanning electron microscopy (SEM) images and optical pictures showed that COF-NUST-1 possessed a uniform cubic morphology (see Figures 2b and S31), and TEM images showed a layered structure (Figure 2c).

The crystalline nature and structure of COF-NUST-1 was elucidated by PXRD analysis (Cu K α) (Figure 1). The PXRD pattern for COF-NUST-1 (Figure 1a, black curve) exhibited main diffraction peaks at 3.5°, 5.9°, and 6.8°, which were assigned to the (100), (001), and (110) facets, respectively, along with other minor peaks at 8–20°. Structural modeling and Le Bail refinement fitting (Figure S9) were conducted to build the crystal structure for COF-NUST-1, and it was predicted that the most probable structure is a 2D net with the eclipsed AA stacking, which is mainly contributed by the structural self-complementarity of the twisted nodes and the

wavy lattice propensity²⁵ (Figure 1b,c). The experimental PXRD pattern showed good agreement with the simulated pattern, which was confirmed by low residual values and acceptable profile differences ($R_{wp} = 5.6\%$ and $R_p = 3.3\%$).

The porosity of COF-**NUST-1** was measured by nitrogen sorption analysis at 77 K. The adsorption curves exhibited the type-IV isotherm (Figure 2e), a characteristic of mesoporous materials. Application of the Brunauer–Emmett–Teller (BET) model resulted in a surface area of 410 m² g⁻¹ for COF-**NUST-1**. A QSDFT²⁶ calculation provided a narrow pore size of about 24 Å for COF-**NUST-1**, in good agreement with the simulated value from the eclipsed AA stacking model (Figure S8).

Cage-NUST-1 was prepared from TBTQ and *o*-phenylene diboronic acid (TP) with monitoring by ¹H NMR spectros-



Figure 2. (a) Transformation from COF-NUST-1 to Cage-NUST-1 with the obvious color change. (b) Optical image of COF-NUST-1. (c) TEM image of COF-NUST-1. (d) Optical image of Cage-NUST-1. (e) N_2 sorption curves at 77 K for COF-NUST-1 and Cage-NUST-1. (f) Time-dependent ¹H NMR spectra for the transformation from COF-NUST-1 to Cage-NUST-1 (500 MHz, CDCl₃).

copy (Figure 1d). The disappearance of characteristic signals of -OH in TBTQ and the chemical shift of protons in the benzene ring of TP were observed, which proved the formation of Cage-NUST-1. ¹H NMR spectra showed only one set of signals for the individual protons, indicating the high symmetry of the structure. SEM images revealed that Cage-NUST-1 showed a rhombic morphology (Figure S31). The porosity of Cage-NUST-1 was much lower than that of COF-NUST-1 (Figure 2e), consistent with the results from reported work and demonstrating that infinite framework materials possess the natural merit regarding porosity and capacity compared with discrete cage compounds. Currently the obtained crystals were too small (Figure 2d), so we were not able to determine the structure by X-ray diffraction. It is worth noting that Cage-NUST-1 is isostructural to a reported cage.² Atmospheric-pressure chemical ionization mass spectrometry showed a peak at m/z = 1518.32556 as the dominant signal, which correlated exactly to the molecular mass of Cage-NUST-1 (Figures 1e,f and S13).

To study the possible transformation between COFs and cages, COF-NUST-1 was put into a flask containing THF and molecular sieves (MS), a typical condition that was used in COF/Cage-NUST-1 growth, followed by the addition of TP (equivalent mole ratio; Figure S17). It should be noted that COF-NUST-1 is stable and cannot be dissolved in THF, remaining as a precipitate in the bottom while the upper THF solution is clear (Figure 2a). Interestingly, the THF solution quickly became turbid in 30 min, and as time went on, the turbidity gradually turned clear and the color switched from light blue to bluish-violet within 48 h (Figure 2a). Timedependent ¹H NMR spectra were recorded to further understand the transformation process, and they revealed that with the passing of time, the characteristic peaks of TP at 6.6-7.1 ppm (H_b, H_c, H_d, H_e) shifted gradually to 7.2-7.9 ppm and the peak for TBTQ (H_a, 7.38 ppm) also shifted to 7.24 ppm, accompanied by the emergence of a characteristic peak of DP (H $_{\rm p}$ 6.8 ppm) (Figure 2f). This phenomenon suggested that the transformation was a step-by-step process of exchange with the significant color changes (Figure 2a). Cage-NUST-1 was obtained by removing the solvent and purified by a recrystallization procedure. The FT-IR and ¹H NMR results for Cage-NUST-1 validated the successful COF-to-cage transformation (Figure S16).

The experiment aiming to realize the conversion from Cage-NUST-1 to COF-NUST-1 was also performed using a similar method (Figure \$18). Unfortunately, we were not able to obtain the COF through this effort. The addition of DP into the THF solution of Cage-NUST-1 yielded no precipitate (no COF) at room temperature, and a small amount of solid was collected as an amorphous polymer upon heating of the system (Figure S19). We supposed that the feasibility of the change from COF-NUST-1 to Cage-NUST-1 may be due to the thermodynamic self-sorting issue. To prove this point, we combined TBTQ, TP, and DP together in THF and MS for 72 h. Only Cage-NUST-1 was obtained in this self-sorting process (Figure S20), which demonstrated that DCC exchange of precursor building blocks was the main driving force for the COF-to-cage transformation, and the hindrance in going from cages to COFs is mainly determined by thermodynamic and kinetic control. To test the generality of this transformation, we synthesized another borate-linked COF, COF-NUST-2 (Figure S3). The transformation from COF-NUST-2 to Cage-NUST-1 was also successfully realized (Figure S17b).

Encouraged by above achievements, we sought to explore whether other types of linkages in the COF/cage family can undergo such dynamic transformation. The use of imine linkages has been the most prevalent strategy to construct COFs/organic cages since 2009,^{23,28} so we turned to two reported imine-linked COF/cage systems, COF-LZU-1^{12b} and **Cage-1** for further studies. **Cage-1** was synthesized from triformylbenzene (**TFB**) and ethylenediamine (**ED**) as described previously.^{28a} The ¹H NMR spectrum and PXRD peak of **Cage-1** were consistent with those of reported work (Figures 3b and S15). Optical micromorphology revealed that



Figure 3. (a) Synthesis of **Cage-1** and COF-**LZU-1** and the structural transformation. (b) Time-dependent PXRD patterns for the transformation from **Cage-1** to COF-**LZU-1**. (c) Nitrogen sorption curves for COF-**LZU-1** and **Cage-1**.

Cage-1 has a needlelike shape (Figure S30). COF-LZU-1 was prepared from TFB and *p*-phenylenediamine (PD) through solvothermal reactions according to a reported procedure. First, the transformation experiments from COF-LZU-1 to **Cage 1** were implemented following a similar strategy as used in the boronate ester-linked system. COF-LZU-1 was combined with solvent (ethyl acetate, 1,4-dioxane, etc.) and ED, and with or without acetic acid as a catalyst at room temperature, no **Cage-1** was afforded, as characterized by PXRD analysis (Figure S25). Since the imine (>C=N-) bond is stronger than that of -B-O- (615 vs 515 kJ/mol),²⁹ we surmised that it might not be possible to manipulate these transformations at room temperature, and thus, control of the temperature was involved in this respect.

We then further carried out the transformation from Cage-1 to COF-LZU-1 by solvothermal reactions. An ampule containing Cage-1 was combined with 1,4-dioxane and PD in the presence of acetic acid as a catalyst (Figure 3a). After 3 days at 120 °C, a yellow solid was harvested at the bottom, which was verified to be COF-LZU-1 as ascertained by PXRD analysis together with other techniques (Figures 3b, S21, and S22).

Time-dependent PXRD patterns were characterized to study the kinetic transformation (Figure 3b). A yellow precipitate was afforded as an amorphous polymer within the first period of 12 h. The diffraction peak of the (100) facet at 4.8° appeared in 24 h, indicating that ordered frameworks emerged. After 72 h, highly crystalline COF-LZU-1 with (100), (110), and (001) diffraction peaks at 4.8°, 8.1°, and 26.0°, respectively, was formed. SEM images revealed that **Cage-1** possessed a spherical morphology while COF-LZU-1 showed a coralloid shape (Figure S31). The N₂ adsorption curve exhibited the microporous characteristic of COF-LZU-1. The BET surface area was 823 m² g⁻¹, which is almost the same as that for the COF synthesized directly (Figure S22c), and the porosity was significantly improved in going from **Cage-1** to COF-LZU-1 (Figure 3c).

In addition, other imine-linked 2D COFs can also be obtained by this method. For a proof-of-concept study, conducting solvothermal reactions among **Cage-1**, 1,4-dioxane, and 1,3,5-tris(4-aminophenyl)benzene in the presence of acetic acid led to the successful construction of COF-**TFPA** (Figures S23 and S24).

A self-sorting experiment was also performed. **TFB**, **ED**, and **PD** were dissolved into ethyl acetate in a molar ratio of 2:3:3 at room temperature, and a yellow solid precipitated with or without the presence of acetic acid. The precipitate could be partially dissolved in chloroform and was detected as **Cage-1** by ¹H NMR spectroscopy (Figure S26), and the remaining undissolved material was confirmed to be amorphous polymer as checked by PXRD (Figure S27). When a temperature of 120 °C was imposed on this system, COF-**LZU-1** was obtained in the presence of acetic acid as a catalyst (Figure S28). The self-sorting results indicated that the DCC process plays a crucial role in determining the final products via different routes (temperature, catalyst, etc.).

In summary, we have developed a DCC-induced linker exchange strategy for the structural transformation between infinite COFs and discrete cages. The transformation mainly depends on the reversible covalent bonds linking COFs and cages. The studies showed that when boronate esters were used as linkages, the COF-to-cage transformation could be achieved, and when imine bonding was applied, the cage-toCOF conversion was accomplished. The transformation process was determined by time-dependent NMR spectroscopy and PXRD analysis. Self-sorting experiments indicated that the boronate ester COFs and imine cages are the thermodynamic minimum compounds that controlled the transformation. This work paves a new way to study the crystalline nature of organic materials. Further studies involving insightful experiments/mechanisms that show how to control the transformations in a more elaborate way to prepare more crystalline materials (MOFs, COFs, cycles, cages, etc.) are greatly needed and are proceeding in our lab.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c11073.

Experimental procedures and characterization data (PDF)

AUTHOR INFORMATION

Corresponding Author

Gen Zhang – Key Laboratory for Soft Chemistry and Functional Materials of Ministry of Education, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China; orcid.org/ 0000-0001-5948-8635; Email: zhanggen@njust.edu.cn

Authors

- **Zhen Shan** Key Laboratory for Soft Chemistry and Functional Materials of Ministry of Education, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China
- Xiaowei Wu Key Laboratory for Soft Chemistry and Functional Materials of Ministry of Education, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China; © orcid.org/ 0000-0003-2141-3448
- **Bingqing Xu** Key Laboratory for Soft Chemistry and Functional Materials of Ministry of Education, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China
- You-lee Hong RIKEN–JEOL Collaboration Center and RIKEN SPring-8 Center, Yokohama, Kanagawa 230-0045, Japan; Institute for Integrated Cell-Material Sciences, Institute for Advanced Study, Kyoto University, Kyoto 606-8501, Japan
- Miaomiao Wu Key Laboratory for Soft Chemistry and Functional Materials of Ministry of Education, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China
- Yuxiang Wang Key Laboratory for Soft Chemistry and Functional Materials of Ministry of Education, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China
- Yusuke Nishiyama RIKEN–JEOL Collaboration Center and RIKEN SPring-8 Center, Yokohama, Kanagawa 230-0045, Japan; JEOL RESONANCE Inc., Akishima, Tokyo 196-8558, Japan; © orcid.org/0000-0001-7136-1127
- Junwu Zhu Key Laboratory for Soft Chemistry and Functional Materials of Ministry of Education, School of Chemical Engineering, Nanjing University of Science and

Technology, Nanjing, Jiangsu 210094, China; orcid.org/0000-0002-7518-9683

- Satoshi Horike Institute for Integrated Cell-Material Sciences, Institute for Advanced Study, Kyoto University, Kyoto 606-8501, Japan; o orcid.org/0000-0001-8530-6364
- Susumu Kitagawa Institute for Integrated Cell-Material Sciences, Institute for Advanced Study, Kyoto University, Kyoto 606-8501, Japan; orcid.org/0000-0001-6956-9543

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.0c11073

Author Contributions

pubs.acs.org/JACS

 $^{\perp}$ Z.S. and X.W. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by startup funding from Nanjing University of Science and Technology (AE89991/194, AE89991/258, AE89991/259, AD41913, and AD41960) and the Natural Science Foundation of Jiangsu Province (BK20200472 and BK20200476). G.Z. acknowledges the support of the Thousand Young Talent Plan.

REFERENCES

(1) (a) Corbett, P. T.; Leclaire, J.; Vial, L.; West, K. R.; Wietor, J.-L.; Sanders, J. K. M.; Otto, S. Dynamic combinatorial chemistry. *Chem. Rev.* 2006, 106, 3652–3711. (b) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. Dynamic covalent chemistry. *Angew. Chem., Int. Ed.* 2002, 41, 898–952. (c) Jin, Y.; Yu, C.; Denman, R. J.; Zhang, W. Recent advances in dynamic covalent chemistry. *Chem. Soc. Rev.* 2013, 42, 6634–6654.

(2) Xue, M.; Yang, Y.; Chi, X.; Zhang, Z.; Huang, F. Pillararenes, a new class of macrocycles for supramolecular chemistry. *Acc. Chem. Res.* **2012**, *45*, 1294–1308.

(3) Acharyya, K.; Mukherjee, P. S. Organic imine cages: Molecular marriage and applications. *Angew. Chem., Int. Ed.* **2019**, *58*, 8640–8653.

(4) Forgan, R. S.; Sauvage, J.-P.; Stoddart, J. F. Chemical topology: Complex molecular knots, links, and entanglements. *Chem. Rev.* **2011**, *111*, 5434–5464.

(5) Mena-Hernando, S.; Pérez, E. M. Mechanically interlocked materials. Rotaxanes and catenanes beyond the small molecule. *Chem. Soc. Rev.* **2019**, *48*, 5016–5032.

(6) Gil-Ramírez, G.; Leigh, D. A.; Stephens, A. J. Catenanes: Fifty years of molecular links. *Angew. Chem., Int. Ed.* **2015**, *54*, 6110–6150. (7) Lee, J.-S. M.; Cooper, A. I. Advances in conjugated microporous polymers. *Chem. Rev.* **2020**, *120*, 2171–2214.

(8) (a) Cote, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. Porous, crystalline, covalent organic frameworks. *Science* 2005, *310*, 1166–1170. (b) Geng, K.; He, T.; Liu, R.; Dalapati, S.; Tan, K. T.; Li, Z.; Tao, S.; Gong, Y.; Jiang, Q.; Jiang, D. Covalent organic frameworks: Design, synthesis, and functions. *Chem. Rev.* 2020, *120*, 8814–8933. (c) Kandambeth, S.; Mallick, A.; Lukose, B.; Mane, M. V.; Heine, T.; Banerjee, R. Construction of crystalline 2D covalent organic frameworks with remarkable chemical (acid/base) stability via a combined reversible and irreversible route. *J. Am. Chem. Soc.* 2012, *134*, 19524–19527.

(9) Guan, X.; Chen, F.; Fang, Q.; Qiu, S. Design and applications of three dimensional covalent organic frameworks. *Chem. Soc. Rev.* 2020, 49, 1357–1384.

(10) (a) Furukawa, H.; Yaghi, O. M. Storage of hydrogen, methane, and carbon dioxide in highly porous covalent organic frameworks for clean energy applications. J. Am. Chem. Soc. 2009, 131, 8875–8883.

(b) Wang, Z.; Zhang, S.; Chen, Y.; Zhang, Z.; Ma, S. Covalent organic frameworks for separation applications. *Chem. Soc. Rev.* **2020**, *49*, 708–735.

(11) (a) Ascherl, L.; Evans, E. W.; Gorman, J.; Orsborne, S.; Bessinger, D.; Bein, T.; Friend, R. H.; Auras, F. Perylene-based covalent organic frameworks for acid vapor sensing. *J. Am. Chem. Soc.* **2019**, *141*, 15693–15699. (b) Jhulki, S.; Evans, A. M.; Hao, X.-L.; Cooper, M. W.; Feriante, C. H.; Leisen, J.; Li, H.; Lam, D.; Hersam, M. C.; Barlow, S.; Brédas, J.-L.; Dichtel, W. R.; Marder, S. R. Humidity sensing through reversible isomerization of a covalent organic framework. *J. Am. Chem. Soc.* **2020**, *142*, 783–791. (c) Wu, X.; Han, X.; Xu, Q.; Liu, Y.; Yuan, C.; Yang, S.; Liu, Y.; Jiang, J.; Cui, Y. Chiral binol-based covalent organic frameworks for enantioselective sensing. *J. Am. Chem. Soc.* **2019**, *141*, 7081–7089.

(12) (a) Bi, S.; Thiruvengadam, P.; Wei, S.; Zhang, W.; Zhang, F.; Gao, L.; Xu, J.; Wu, D.; Chen, J.-S.; Zhang, F. Vinylene-bridged twodimensional covalent organic frameworks via knoevenagel condensation of tricyanomesitylene. J. Am. Chem. Soc. 2020, 142, 11893-11900. (b) Ding, S.-Y.; Gao, J.; Wang, Q.; Zhang, Y.; Song, W.-G.; Su, C.-Y.; Wang, W. Construction of covalent organic framework for catalysis: Pd/cof-lzu1 in suzuki-miyaura coupling reaction. J. Am. Chem. Soc. 2011, 133, 19816-19822. (c) Han, X.; Yuan, C.; Hou, B.; Liu, L.; Li, H.; Liu, Y.; Cui, Y. Chiral covalent organic frameworks: Design, synthesis and property. Chem. Soc. Rev. 2020, 49, 6248-6272. (13) (a) Yu, F.; Liu, W.; Li, B.; Tian, D.; Zuo, J.-L.; Zhang, Q. Photostimulus-responsive large-area two-dimensional covalent organic framework films. Angew. Chem., Int. Ed. 2019, 58, 16101-16104. (b) Xiong, Y.; Liao, Q.; Huang, Z.; Huang, X.; Ke, C.; Zhu, H.; Dong, C.; Wang, H.; Xi, K.; Zhan, P.; Xu, F.; Lu, Y. Ultrahigh responsivity photodetectors of 2D covalent organic frameworks integrated on graphene. Adv. Mater. 2020, 32, 1907242. (c) Chen, L.; Furukawa, K.; Gao, J.; Nagai, A.; Nakamura, T.; Dong, Y.; Jiang, D. Photoelectric covalent organic frameworks: Converting open lattices into ordered donor-acceptor heterojunctions. J. Am. Chem. Soc. 2014, 136, 9806-9809. (d) Haug, W. K.; Moscarello, E. M.; Wolfson, E. R.; McGrier, P. L. The luminescent and photophysical properties of covalent organic frameworks. Chem. Soc. Rev. 2020, 49, 839-864.

(14) (a) Li, J.; Jing, X.; Li, Q.; Li, S.; Gao, X.; Feng, X.; Wang, B. Bulk COFs and COF nanosheets for electrochemical energy storage and conversion. *Chem. Soc. Rev.* **2020**, *49*, 3565–3604. (b) Wu, X.; Hong, Y.-l.; Xu, B.; Nishiyama, Y.; Jiang, W.; Zhu, J.; Zhang, G.; Kitagawa, S.; Horike, S. Perfluoroalkyl-functionalized covalent organic frameworks with superhydrophobicity for anhydrous proton conduction. *J. Am. Chem. Soc.* **2020**, *142*, 14357–14364. (c) Zhang, G.; Hong, Y.-l.; Nishiyama, Y.; Bai, S.; Kitagawa, S.; Horike, S. Accumulation of glassy poly(ethylene oxide) anchored in a covalent organic framework as a solid-state Li⁺ electrolyte. *J. Am. Chem. Soc.* **2019**, *141*, 1227–1234.

(15) Wang, J.; Zhuang, S. Covalent organic frameworks (COFs) for environmental applications. *Coord. Chem. Rev.* **2019**, *400*, 213046.

(16) Guan, Q.; Wang, G.-B.; Zhou, L.-L.; Li, W.-Y.; Dong, Y.-B. Nanoscale covalent organic frameworks as theranostic platforms for oncotherapy: Synthesis, functionalization, and applications. *Nanoscale Advances.* **2020**, *2*, 3656–3733.

(17) Stock, N.; Biswas, S. Synthesis of metal-organic frameworks (MOFs): Routes to various MOF topologies, morphologies, and composites. *Chem. Rev.* 2012, *112*, 933–969.

(18) Qian, C.; Qi, Q.-Y.; Jiang, G.-F.; Cui, F.-Z.; Tian, Y.; Zhao, X. Toward covalent organic frameworks bearing three different kinds of pores: The strategy for construction and COF-to-COF transformation via heterogeneous linker exchange. *J. Am. Chem. Soc.* **2017**, *139*, 6736–6743.

(19) Zhang, G.; Tsujimoto, M.; Packwood, D.; Duong, N. T.; Nishiyama, Y.; Kadota, K.; Kitagawa, S.; Horike, S. Construction of a hierarchical architecture of covalent organic frameworks via a postsynthetic approach. J. Am. Chem. Soc. **2018**, 140, 2602–2609.

(20) Miao, Z.; Liu, G.; Cui, Y.; Liu, Z.; Li, J.; Han, F.; Liu, Y.; Sun, X.; Gong, X.; Zhai, Y.; Zhao, Y.; Zeng, Y. A novel strategy for the construction of covalent organic frameworks from nonporous

covalent organic polymers. Angew. Chem., Int. Ed. 2019, 58, 4906–4910.

(21) Liang, R.-R.; A, R.-H.; Xu, S.-Q.; Qi, Q.-Y.; Zhao, X. Fabricating organic nanotubes through selective disassembly of twodimensional covalent organic frameworks. *J. Am. Chem. Soc.* **2020**, 142, 70–74.

(22) (a) Greenaway, R. L.; Santolini, V.; Pulido, A.; Little, M. A.; Alston, B. M.; Briggs, M. E.; Day, G. M.; Cooper, A. I.; Jelfs, K. E. From concept to crystals via prediction: Multi-component organic cage pots by social self-sorting. *Angew. Chem., Int. Ed.* **2019**, *58*, 16275–16281. (b) Leonhardt, V.; Fimmel, S.; Krause, A.-M.; Beuerle, F. A covalent organic cage compound acting as a supramolecular shadow mask for the regioselective functionalization of C60. *Chem. Sci.* **2020**, *11*, 8409–8415.

(23) Beuerle, F.; Gole, B. Covalent organic frameworks and cage compounds: Design and applications of polymeric and discrete organic scaffolds. *Angew. Chem., Int. Ed.* **2018**, *57*, 4850–4878.

(24) He, L.; Ng, C.-F.; Li, Y.; Liu, Z.; Kuck, D.; Chow, H.-F. Trefoilshaped porous nanographenes bearing a tribenzotriquinacene core by three-fold scholl macrocyclization. *Angew. Chem., Int. Ed.* **2018**, *57*, 13635–13639.

(25) Martínez-Abadía, M.; Stoppiello, C. T.; Strutynski, K.; Lerma-Berlanga, B.; Martí-Gastaldo, C.; Saeki, A.; Melle-Franco, M.; Khlobystov, A. N.; Mateo-Alonso, A. A wavy two-dimensional covalent organic framework from core-twisted polycyclic aromatic hydrocarbons. J. Am. Chem. Soc. **2019**, *141*, 14403–14410.

(26) Neimark, A. V.; Lin, Y.; Ravikovitch, P. I.; Thommes, M. Quenched solid density functional theory and pore size analysis of micro-mesoporous carbons. *Carbon* **2009**, *47*, 1617–1628.

(27) Klotzbach, S.; Beuerle, F. Shape-controlled synthesis and selfsorting of covalent organic cage compounds. *Angew. Chem., Int. Ed.* **2015**, 54, 10356–10360.

(28) (a) Tozawa, T.; Jones, J. T. A.; Swamy, S. I.; Jiang, S.; Adams, D. J.; Shakespeare, S.; Clowes, R.; Bradshaw, D.; Hasell, T.; Chong, S. Y.; Tang, C.; Thompson, S.; Parker, J.; Trewin, A.; Bacsa, J.; Slawin, A. M. Z.; Steiner, A.; Cooper, A. I. Porous organic cages. *Nat. Mater.* **2009**, *8*, 973–978. (b) Uribe-Romo, F. J.; Hunt, J. R.; Furukawa, H.; Klöck, C.; O'Keeffe, M.; Yaghi, O. M. A crystalline imine-linked 3D porous covalent organic framework. *J. Am. Chem. Soc.* **2009**, *131*, 4570–4571. (c) Segura, J. L.; Mancheño, M. J.; Zamora, F. Covalent organic frameworks based on schiff-base chemistry: Synthesis, properties and potential applications. *Chem. Soc. Rev.* **2016**, *45*, 5635–5671.

(29) Jiang, J.; Zhao, Y.; Yaghi, O. M. Covalent chemistry beyond molecules. J. Am. Chem. Soc. 2016, 138, 3255–3265.