

A Journal of the Gesellschaft Deutscher Chemiker A DOCH International Edition Market Chemiker CDCh Chemiker Ch

Accepted Article

- Title: A Heteromeric Carboxylic-acid-based Single Crystalline Crosslinked Organic Framework
- Authors: Rongran Liang, Jayanta Samanta, Baihao Shao, Mingshi Zhang, Richard Staples, Albert Chen, Miao Tang, Yuyang Wu, Ivan Aprahamian, and Chenfeng Ke

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202109987

Link to VoR: https://doi.org/10.1002/anie.202109987

WILEY-VCH

COMMUNICATION

WILEY-VCH

A Heteromeric Carboxylic-acid-based Single Crystalline Crosslinked Organic Framework

Rongran Liang,^[a] Jayanta Samanta,^[a] Baihao Shao,^[a] Mingshi Zhang,^[a] Richard J. Staples,^[b] Albert D. Chen,^[a] Miao Tang,^[a] Yuyang Wu,^[c] Ivan Aprahamian^{*[a]}, and Chenfeng Ke^{*[a]}



Abstract: The development of large pore single-crystalline covalently linked organic frameworks is critical in revealing the detailed structureproperty relationship with substrates. One emergent approach is to photo-crosslink hydrogen-bonded molecular crystals. Introducing complementary hydrogen-bonded carboxylic acid building blocks is promising to construct large pore networks, but these molecules often form interpenetrated networks or non-porous solids. Herein, we introduced heteromeric carboxylic acid dimers to construct a noninterpenetrated molecular crystal. Crosslinking this crystal precursor with dithiols afforded a large pore single-crystalline hydrogen-bonded crosslinked organic framework H_cOF-101. X-ray diffraction analysis revealed H_cOF-101 as an interlayer connected hexagonal network, which possesses flexible linkages and large porous channels to host a hydrazone photoswitch. Multicycle Z↔E-isomerization of the hydrazone took place reversibly within H_cOF-101, showcasing the potential use of H_cOF-101 for optical information storage.

Developing covalently connected porous organic framework materials with high crystallinity,^[1] good chemical stability,^[2] and large porosity^[3] is highly desired to not only establish precise structure-property relationships between porous materials and sorbates, but also advance their practical applications in gas separation,^[4] catalysis,^[5] and optoelectronics.^[6] While one approach of fine-tuning the reversible reactions to obtain singlecrystalline covalent organic frameworks^[7] (COFs) has been demonstrated successful,^[1b] the small crystal sizes of COFs often limit their diffraction data quality to fully unveil the detailed atomic level information.^[8] Another emerging approach to generate single-crystalline porous organic materials is covalently crosslinking hydrogen-bond pre-organized molecular crystals. This approach generates a family of hydrogen-bonded crosslinked organic framework (H_cOF) materials,^[9] which combined the advantages of hydrogen-bonded organic frameworks^[10] (HOFs) and COFs.^[11] To date, reported H_COFs are constructed using non-complementary hydrogen-bonding motifs such as diallyl- and dipropargyl-diaminotriazines (DATs). The formed hydrogen-bonded networks possess limited pore sizes due to undesired side-on hydrogen-bonding interactions^[9b] formed in the solid-state, making it challenging to construct H_cOFs with large pores.

One attempt to address the challenge was to introduce selfcomplementary hydrogen-bonding functional groups such as carboxylic acids^[12] to direct the network topology. However, the framework architectures formed by homo-carboxylic acid derivatives often encounter undesired network interpenetrations and they are susceptible to even a slight structural modification.^[13] The problem is well illustrated in the various interpenetrated networks generated by 1,3,5-tris(4-carboxyphenyl)benzene





(b) Synthesis of large pore H_cOF-101 single crystals



Figure 1. (a) Illustration of the heteromeric assembly of carboxylic acid derivatives of mis-matched sizes and pK_a values. (b) Synthesis of the non-interpenetrated H_cOF -101 through co-crystallization of size-mismatched monomers followed by a thiol-ene single-crystal to single-crystal transformation.

COMMUNICATION

(TCPB) derivatives in the solid-state (Scheme S3).^[14] Herein, we introduce, for the first time, heteromeric size-mismatched carboxylic acid derivative M1 and trimesic acid TA to construct a single-crystalline covalently linked organic framework H_cOF-101, which features large pore and non-interpenetrated hydrogenbonded network (Figure 1). H_cOF-101 was synthesized through a single-crystal to single-crystal (SCSC) transformation^[15] from a 2D hexagonal hydrogen-bonded network through the thiol-ene crosslinking. Compared to electron diffraction (ED) data that mostly reveal the framework topology for COFs,^[8,16] the highquality single-crystal X-ray diffraction data of H_cOF-101 enabled the precise determination of the pore sizes with flexible crosslinkages connecting a large pore 2D network in four different interlayer ways. The large 1D porous channels (D = 1.4 nm, Figure 1b) of H_cOF-101 was not only capable of adsorbing a hydrazone photoswitch of nearly one nanometer in size but also enabled the hydrazone photo-isomerizations in these channels. In multi-cycle writing-erasing experiments, the hydrazone-loaded H_cOF-101 demonstrated switchable solid-state fluorescent emissions, manifesting the potential use of this platform as a solid-state information storage device.

Triallylether-based monomer **M1** was synthesized from 1,3,5tribromobenzene in four steps with 53% overall yield (see the Supporting Information). Slow vapor diffusion of methanol into the 1,4-dioxane solution of **M1** afforded **M1**_{crystal} that is suitable for single-crystal X-ray diffraction (SCXRD) analysis. **M1**_{crystal} crystallized in the P3 space group, and three of the carboxyphenyl rings are rotated out of the plane to the central phenyl ring with a dihedral angle of 46° (Figure 2a). The carboxylic acids of **M1** formed intermolecular hydrogen bonds with the upper layer allylether (OH•••O = 2.46 Å, Figure 2a) and the carboxylic acid of **M1** (OH•••O = 1.99 Å). The typical carboxylic acid dimer was not formed in the solid-state, and **M1** stacked into 1D columns through interlayer hydrogen bonding interactions. These **M1** columns are packed hexagonally via van der Waals interactions with narrow 1D porous channels (Figure 2a). The allylethers of **M1** prevented the formation of carboxylic acid dimers in the solid-state, which confirmed that the substitution of the TCPB drastically altered its solid-state superstructure.

To prevent the undesired close-packing of **M1** and direct its solid-state assembly to form a large porous hydrogen-bonded network, we sought to introduce a carboxylic acid-based filler molecule that features a similar C_3 geometry but of different size. Surprisingly, no prior example has yet shown heteromeric co-crystallization of two carboxylic acid derivatives in the construction of porous hydrogen-bonded network. Limited successful examples of non-porous heteromeric dimerization of benzoic acid derivatives with electron-donating and electron-withdrawing groups^[12,17] suggested that introducing a filler molecule of different pK_a to **M1** would favor the heteromeric carboxylic acid dimerization against homo-self-sorting.

The p K_a of **M1** was measured as 8.9 ± 0.1 , 9.9 ± 0.1 , and 10.9 ± 0.2 in MeOD at 298 K using ¹H NMR spectroscopy (Figure S1).^[18] We chose trimesic acid **TA** as the template molecule to form heteromeric carboxylic acid co-assembly with **M1** because of its different p K_a (3.1, 3.9 and 4.7) to **M1** analog 2-propoxybenzoic acid (4.2) in water.^[19] The p K_a of **TA** in MeOD were measured as 8.0 ± 0.1 , 9.4 ± 0.1 , and 10.6 ± 0.1 ,



Figure 2. (a) Crystal structures of M1_{crystal} connected via intermolecular hydrogen bonds. (b) PXRD profiles of (co-)crystals generated at different M1/TA feeding ratios. (c) Crystal structures of M1-TA_{crystal}. Top: asymmetric unit, middle: an image of the crystal, bottom: packed structures viewed along the *a/b* plane and *c*-axis, hydrogens were omitted for clarity.

COMMUNICATION

respectively (Figure S2). When a less-than-stoichiometric amount of TA was added to M1, powder X-ray diffraction (PXRD, Figure 2b) experiments showed a self-sorted crystallization outcomeonly $M1_{crystal}$ was formed. When $TA/M1 \ge 1:1$, a new crystalline phase emerged and remained the same at higher TA/M1 ratios. Single crystals of this new crystalline phase were obtained, and SCXRD analysis revealed that M1 and TA co-crystallized in a 1:1 ratio in the P6₅ space group with unit cell parameters of a = b =24.0075(2) Å, c = 19.5118(2) Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$. Heteromeric carboxylic acid dimers were formed between M1 and TA, affording a 2D hexagonal hydrogen-bonded network. This result suggested that, when TA reached over stoichiometric amount to M1, the more acidic carboxylic acid group of TA ($pK_a = 8.4$) could stabilize the heteromeric carboxylic acid dimer formed between M1 and TA. Allylether moieties of M1 were crystallographically disordered with equal probabilities on either side of the carboxyphenyl groups due to the phenyl-phenyl free rotations (Figure 2c). The pore size of M1-TAcrystal is measured to be 16 Å when accounting for the allylethers, which is smaller than the d =21 Å calculated from the (100) diffraction (Figure 2b-c). The carboxyphenyl groups of M1 were found to be nearly co-planar with the central phenyl ring, with small dihedral angles of 6.8°, 9.6°, and 27.9°, respectively. This conformation of M1 enabled alternating TA/M1 π - π stacking along the c-axis (centroid to centroid, 3.66-3.73 Å). Interestingly, this alternating M1 and TA stacking is not perfectly eclipsed, and there are small offsets between the phenyl rings of different layers (Figure 2c), which provide some structural insights to previously proposed eclipsed 2D COFs.^[3a,3c,20] The M1-TA co-crystal consists of 47% void space as 1D porous channels, which is sufficiently large for ethanedithiol (EDT, HSCH₂CH₂SH) diffusion. Multiple pairs of allyl groups (Table S4) were found within the suitable distances for EDT crosslinking.

Single crystals of M1-TA_{crystal} were soaked in MeCN solutions with various concentrations of EDT in the dark for 4 d to reach equilibrium before they were irradiated under UV light. The crystals were washed extensively and then soaked in hot, degassed DMSO-d₆ (140 °C) before ¹H NMR analysis at 25 °C. The TA moiety was removed from the crystal and dissolved in DMSO- d_6 (Figure S3), and its proton signals were used as an internal ¹H NMR reference. A stoichiometric EDT/allyl = 1:2 reaction would afford fully crosslinked H_cOF-101 (Figure 3a), but reactions that drifted from the stoichiometry would afford oligomeric species. Experimentally, these species were extracted from the crosslinked crystals using hot DMSO-d₆, and they were observed at higher EDT feeding concentrations (Figure S3). Decreasing the EDT concentrations to 60-203 µmol/mL resulted in extensive crosslinking of M1, as no appreciable amount of soluble species was extracted according to ¹H NMR analysis (Figure S3). After reaction optimization (Table S2), a close-tostoichiometric crosslinking (EDT/allyl = 1:1.9) was achieved with H_cOF-101 as revealed by elemental analyses. Further evidence supports the successful crosslinking of H_cOF-101. In the FT-IR spectrum of H_cOF-101 (Figure S5), bending vibrations of the allyl groups at 995 cm⁻¹ (-CH=) and 927 cm⁻¹ (=CH₂) disappeared. In the solid-state ¹³C CPMAS NMR spectrum of H_cOF-101, carbon resonances of C11-C13 at ~30 ppm (Figure 3b), attributed to thioether moieties, were identified. Due to several overlapped carbon signals at 120-135 ppm in the solid-state ¹³C NMR, we sought to confirm the complete consumption of allylethers through a digestion experiment. H_cOF-101 crystals were digested



Figure 3. (a) Synthesis of H_COF-101. (b) Stacked ¹³C NMR spectra (298 K) of **M1/TA**_{crystal} dissolved in DMSO- d_6 and H_COF-101 recorded in the solid-state. (c) Stacked ¹H NMR spectra (298 K) of **M1** in DMSO- d_6 and fully digested H_COF-

.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 ppm

completely into soluble species in DCI-DMSO- d_6 solution at 75 °C. ¹H NMR analysis (Figure 3c) showed only trace amounts of proton signals at 4.8-6.2 ppm, which may be attributed to trace amounts of hydrolyzed allylethers (Figure S7).

Transparent crystals of H_cOF-101 retained the needle-like morphology (Figure 4a). Its symmetry was reduced to the monoclinic C2 space group due to the generated dithioethers, with the unit-cell parameters of a = 24.0134(2), b = 41.5667(2), c = 13.42270(10) Å, $\alpha = \gamma = 90^{\circ}$, $\beta = 104.2590(10)^{\circ}$. The hydrogenbonded TCPB and **TA** skeleton was well refined in the SCXRD analysis (Figure 4a), and it remained nearly identical to the parent **M1-TA**_{crystal} (Figure S13). The dithioether crosslinkages inherited the disorders from the parent **M1-TA**_{crystal}, and they were found at both sides of the carboxyphenyl groups. Fortunately, high-quality synchrotron SCXRD data allowed us to model most of the crosslinkages despite some of them overlapping (Figure 4b).

101 in DCI/DMSO-d₆.

COMMUNICATION



Figure 4. (a) Single-crystal structure of H_cOF -101 viewed along the c-axis (left) and its highlighted pore surfaces (right). Inset: an image of H_cOF -101 crystals. (b) Dissected sections of H_cOF -101, illustrating different interlayer crosslinkages. (c) PXRD profiles of H_cOF -101 soaked in various solvents. (d) Vapor sorption isotherms of H_cOF -101.

In H_cOF-101, the dithioether crosslinkage A was found to connect M1 in the non-adjacent 1,4-layers (Figure 4b), reflecting the distances between two allyls that are 7.1 Å apart in M1-TAcrystal (Table S4). Linkages C and D were found to connect two allyl groups in 1,3-layers that are 8.6 and 7.2 Å apart in M1-TA_{crystal}, respectively. Linkages B consist four possible 1,2- and 1,3-layer linkages, which are super-imposed crystallographically (Figure S15). These dithioether moieties were weakly associated to the pore surfaces along the 1D channels. The pore size and void space of H_cOF-101 were measured as ~14 Å and 27%, respectively (Figure 4a). Comparison between the clearly modeled multiple linkages in H_cOF-101 and the conformations of allylethers in M1-TA_{crystal} (Figure S13) revealed two key factors to allow extensive thiol-ene crosslinking, despite allylethers are randomly distributed at each side of the carboxyphenyl group in M1-TA_{crystal}. Firstly, the allyl ether moieties are reasonably dynamic for efficient crosslinking during the H_cOF-101 synthesis, because the formed dithioethers adopt different conformations compared to their precursors. This result provides detailed structural information of the flexible auxiliaries in changing the size and chemical environment of the 1D porous channels in H_cOF-101, and more broadly post-modified 2D COFs.^[21] Secondly, each allyl group has two or more nearby allyls for crosslinking, and the large 1D porous channel allows the crosslinking to take place extensively. This result highlights the benefit of large pore, because limited pore size could severely impact the extensiveness of crosslinking as evident in the synthesis of H_cOF-4.^[9b] These covalent crosslinkages significantly enhanced the chemical stability of H_cOF-101 in various solvents as revealed by the PXRD analysis (Figure 4c). In comparison, the solid state structure of **M1-TA**_{crystal} was disrupted upon exposing to various solvents (Figure S25-26). The supercritical CO₂-activated H_cOF-101 demonstrated good vapor uptake^[22] (Figure 4d and S26a) of water, methanol, and toluene as 91, 92, and 105 cm³/g (P/P₀ = 0.9) at 297 K, respectively.

The pore size of H_cOF-101 is sufficiently large to accommodate a fluorescent photoswitch Z-H1 (Figure 5a),^[23] which features a cross-section width of 9.5 Å. Immersing H_cOF-101 in an acetone/MeOH solution of hydrazone Z-H1 afforded orange-colored H_cOF-101•Z-H1 with an uptake capacity of 0.15

COMMUNICATION

 \pm 0.022 mmol/g. Z-H1 emits at λ_{em} = 560 nm in toluene, but its emission is red-shifted to 620 nm in crystalline form because of



Figure 5. (a) Structure of a hydrazone switch **H1**. (b) Solid-state fluorescence emission spectra of H_cOF-101•*Z*-**H1** before and after 442 nm irradiation (λ_{ex} = 470 nm). (c) Multicycle patterning and erasing experiments performed on an H_cOF-101•*Z*-**H1** crystal strip (9 × 1.5 mm). Fluorescent images were recorded under 365 nm light.

its head-to-tail packing.^[23] H_cOF-101•*Z*-H1 emits ($\lambda_{em} = 575$ nm, Figure 5b) in the solid-state upon 470 nm excitation, similar to what is observed in the solution. Moreover, the large pore size of H_cOF-101 allows an effective *Z*- to *E*-H1 photoisomerization upon 442 nm irradiation with a photostationary state (PSS₄₄₂) of 70% *E*-H1. This observation contrasts with what happens in the crystalline form of *Z*-H1, where no appreciable isomerization was observed even after prolonged photoirradiation. Clearly, the inclusion of *Z*-H1 in H_cOF-101 makes H1 behave like it does in solution rather than in its neat crystalline state.

The photoswitching of H_cOF-101•Z-H1 is accompanied with a fluorescent color change from yellow to greenish-blue, which results from the emission of H_cOF-101 with minor contributions from the remaining Z-H1 at PSS442 (E-H1 is non-emissive). Reverse $E \rightarrow Z$ photoisomerization of H1 in H_cOF-101 takes place upon photoirradiation with 375 nm light or heating at 95 °C. The reversible solid-state switching of H_cOF-101•H1 enabled us to use it in multicycle solid-state photo-patterning. When a strip of H_cOF-101•Z-H1 crystals was irradiated at 442 nm under a photomask, the mask pattern was written into the solid-state material (Figure 5c). This pattern was erased upon heating at 95 °C, followed by applying a new double-strip pattern, which was also transferred to the crystal. The third cycle generated a triangleshaped pattern. The solid-state photo-isomerizations of H1 in H_cOF-101 have been repeated for five cycles (Figure S30), demonstrating that H_cOF-101•Z-H1 can be used as a rewriteable information storage material.

In summary, a large-pore single-crystalline H_cOF material was successfully synthesized by assembling heteromeric sizemismatched carboxylic acid-monomers followed by single-crystal to single-crystal thiol-ene crosslinking. In the first step, a 2D hexagonal porous co-crystal was formed by a 1,3,5-tris(4carboxyphenyl)benzene derivative **M1** and a trimeric acid. After crosslinking the allylethers in the co-crystal, a hexagonally porous H_cOF -101 was synthesized. High-quality single-crystal diffraction data revealed the architecture of H_cOF -101 as a 3D crosslinked network and the configured conformations of rather flexible interlayer crosslinkages. H_cOF -101 demonstrated superior chemical stability compared to its molecular crystal precursor, and its permanent porosity was confirmed by vapor sorption analysis. By including a photoswitch into H_cOF -101, a solid-state inclusion material with switchable fluorescent emissions was obtained, which is not possible in the neat crystal of the hydrazone. Overall, our work not only successfully introduced heteromeric carboxylic acid for the construction of porous crystalline network for the first time, this method also demonstrated a practical way to suppress network interpenetration. The detailed atomic level structure information of H_cOF -101 allowed us to precisely identify suitable sorbents, enabling the formation of hydrazon+ H_cOF -101 as a solid-state potential optical information storage device.

Acknowledgements

This work is supported by the National Science Foundation (NSF) CAREER award (DMR-1844920) and the Beckman Young Investigator Program. I. A. thanks the NSF MSN program (CHE-1807428). C.K., R.L. acknowledges support from the NSF EPSCoR-1757371. J.S., C.K. thanks the American Chemical Society Petroleum Research Fund (58377-DNI10). Funding for the Single Crystal X-ray diffractometer at MSU was provided by the MRI program by the NSF under Grant No. 1919565. This research used resources of the Advanced Photon Source and the Advanced Light Source, which are DOE Office of Science User Facility under contract no. DE-AC02-06CH11357 and DE-AC02-05CH11231. Professor Yuebiao Zhang at Shanghai Tech University and Professor Omar Farha at Northwestern University for helpful discussions.

Keywords: heteromeric carboxylic acid dimer • hydrogenbonded crosslinked organic framework • photo-switch • singlecrystalline porous organic material • single-crystal to singlecrystal transformation

- a) D. Beaudoin, T. Maris, J. D. Wuest, *Nat. Chem.* **2013**, *5*, 830-834; b)
 T. Ma, E. A. Kapustin, S. X. Yin, L. Liang, Z. Zhou, J. Niu, L.-H. Li, Y. Wang, J. Su, J. Li, X. Wang, W. D. Wang, W. Wang, J. Sun, O. M. Yaghi, *Science* **2018**, *361*, 48-52; c) A. M. Evans, L. R. Parent, N. C. Flanders, R. P. Bisbey, E. Vitaku, M. S. Kirschner, R. D. Schaller, L. X. Chen, N. C. Gianneschi, W. R. Dichtel, *Science* **2018**, *361*, 52-57.
- [2] a) A. Halder, S. Karak, M. Addicoat, S. Bera, A. Chakraborty, S. H. Kunjattu, P. Pachfule, T. Heine, R. Banerjee, *Angew. Chem.* 2018, *130*, 5899-5904; *Angew. Chem. Int. Ed.* 2018, *57*, 5797-5802; b) P.-F. Wei, M.-Z. Qi, Z.-P. Wang, S.-Y. Ding, W. Yu, Q. Liu, L.-K. Wang, H.-Z. Wang, W.-K. An, W. Wang, *J. Am. Chem. Soc.* 2018, *140*, 4623-4631; c) S. Xu, G. Wang, B. P. Biswal, M. Addicoat, S. Paasch, W. Sheng, X. Zhuang, E. Brunner, T. Heine, R. Berger, X. Feng, *Angew. Chem.* 2019, *131*, 859-863; *Angew. Chem. Int. Ed.* 2019, *58*, 849-853.

[3] a) E. L. Spitler, B. T. Koo, J. L. Novotney, J. W. Colson, F. J. Uribe-Romo,
G. D. Gutierrez, P. Clancy, W. R. Dichtel, *J. Am. Chem. Soc.* 2011, 133, 19416-19421; b) R.-R. Liang, S.-Y. Jiang, R.-H. A, X. Zhao, *Chem. Soc. Rev.* 2020, *49*, 3920-3951; c) S. B. Alahakoon, K. Tan, H. Pandey, S. D. Diwakara, G. T. McCandless, D. I. Grinffiel, A. Durand-Silva, T. Thonhauser, R. A. Smaldone, *J. Am. Chem. Soc.* 2020, *142*, 12987-12994; d) H. Li, J. Ding, X. Guan, F. Chen, C. Li, L. Zhu, M. Xue, D. Yuan, V. Valtchev, Y. Yan, S. Qiu, Q. Fang, *J. Am. Chem. Soc.* 2020, *142*, 13334-13338.

COMMUNICATION

- [4] Z. Wang, S. Zhang, Y. Chen, Z. Zhang, S. Ma, Chem. Soc. Rev. 2020, 49, 708-735.
- [5] a) X. Wang, L. Chen, S. Y. Chong, M. A. Little, Y. Wu, W.-H. Zhu, R. Clowes, Y. Yan, M. A. Zwijnenburg, R. S. Sprick, A. I. Cooper, *Nat. Chem.* **2018**., 10, 1180-1189; b) Q. Sun, Y. Tang, B. Aguila, S. Wang, F.-S. Xiao, P. K. Thallapally, A. M. Al-Enizi, A. Nafady, S. Ma, *Angew. Chem.* **2019**, *131*, 8762-8767; *Angew. Chem. Int. Ed.* **2019**, *58*, 8670-8675; c) R. Chen, Y. Wang, Y. Ma, A. Mal, X.-Y. Gao, L. Gao, L. Qiao, X.-B. Li, L.-Z. Wu, C. Wang, *Nat. Commun.* **2021**, *12*, 1354.
- [6] N. Keller, T. Bein, Chem. Soc. Rev. 2021, 50, 1813-1845.
- [7] A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger, O. M. Yaghi, *science* **2005**, *310*, 1166-1170.
- [8] Z. Huang, T. Willhammar, X. Zou, Chem. Sci. 2021, 12, 1206-1219.
- [9] a) Y. Lin, X. Jiang, S. T. Kim, S. B. Alahakoon, X. Hou, Z. Zhang, C. M. Thompson, R. A. Smaldone, C. Ke, *J. Am. Chem. Soc.* 2017, *139*, 7172-7175; b) X. Jiang, X. Cui, A. J. E. Duncan, L. Li, R. P. Hughes, R. J. Staples, E. V. Alexandrov, D. M. Proserpio, Y. Wu, C. Ke, *J Am Chem Soc* 2019, *141*, 10915-10923.
- [10] a) P. Brunet, M. Simard, J. D. Wuest, J. Am. Chem. Soc. 1997, 119, 2737-2738; b) Y. He, S. Xiang, B. Chen, J. Am. Chem. Soc. 2011, 133, 14570-14573; c) M. Mastalerz, I. M. Oppel, Angew. Chem. 2012, 124, 5345-5348; Angew. Chem. Int. Ed. 2012, 51, 5252-5255; d) M. Mastalerz, Chem. Eur. J. 2012, 18, 10082-10091. e) I. Hisaki, C. Xin, K. Takahashi, T. Nakamura, Angew. Chem. 2019, 131, 11278-11288; Angew. Chem. Int. Ed. 2019, 58, 11160-11170; f) R.-B. Lin, Y. He, P. Li, H. Wang, W. Zhou, B. Chen, Chem. Soc. Rev. 2019, 48, 1362-1389; g) B. Wang, R.-B. Lin, Z. Zhang, S. Xiang, B. Chen, J. Am. Chem. Soc. 2020, 142, 14399-14416; h) I. Brekalo, D. E. Deliz, L. J. Barbour, M. D. Ward, T. Friščić, K. T. Holman, Angew. Chem. 2020, 132, 2013-2018; Angew. Chem. Int. Ed. 2020, 59, 1997-2002.
- [11] E. Jin, M. Asada, Q. Xu, S. Dalapati, M. A. Addicoat, M. A. Brady, H. Xu, T. Nakamura, T. Heine, Q. Chen, D. Jiang, *Science* **2017**, 357, 673-676.
- [12] O. Ivasenko, D. F. Perepichka, Chem. Soc. Rev. 2011, 40, 191-206.
- [13] P. Li, M. R. Ryder, J. F. Stoddart, Acc. Mater. Res. 2020, 1, 77-87.
- [14] a) A. Bajpai, P. Venugopalan, J. N. Moorthy, *Cryst. Growth Des.* 2013, *13*, 4721-4729; b) A. Bajpai, P. Venugopalanb, J. N. Moorthy, *CrystEngComm* 2014, *16*, 4853-4860; c) C. A. Zentner, H. W. H. Lai, J. T. Greenfield, R. A. Wiscons, M. Zeller, C. F. Campana, O. Talu, S. A. FitzGerald, J. L. C. Rowsell, *Chem. Commun.* 2015, *51*, 11642-11645; d) H. W. H. Lai, R. A. Wiscons, C. A. Zentner, M. Zeller, J. L. C. Rowsell, *Cryst. Growth Des.* 2016, *16*, 821-833; e) T.-U. Yoon, S. B. Baek, D. Kim, E.-J. Kim, W.-G. Lee, B. K. Singh, M. S. Lah, Y.-S. Bae, K. S. Kim, *Chem. Commun.* 2018, *54*, 9360-9363; f) W. Yang, W. Zhou, B. Chen, *Cryst. Growth Des.* 2019, *19*, 5184-5188.
- [15] a) V. Athiyarath, K. M. Sureshan, Angew. Chem. 2019, 131, 622-627; Angew. Chem. Int. Ed. 2019, 58, 612-617; b) V. Athiyarath, K. M. Sureshan, Angew. Chem. 2020, 132, 15710-15715; Angew. Chem. Int. Ed. 2020, 59, 15580-15585.
- [16] a) Y. B. Zhang, J. Su, H. Furukawa, Y. Yun, F. Gandara, A. Duong, X. Zou, O. M. Yaghi, J. Am. Chem. Soc. 2013, 135, 16336-16339; b) Y. Liu, Y. Ma, Y. Zhao, X. Sun, F. Gándara, H. Furukawa, Z. Liu, H. Zhu, C. Zhu, K. Suenaga, P. Oleynikov, A. S. Alshammari, X. Zhang, O. Terasaki, O. M. Yaghi, Science 2016, 351, 365-369; c) T. Ma, J. Li, J. Niu, L. Zhang, A. S. Etman, C. Lin, D. Shi, P. Chen, L.-H. Li, X. Du, J. Sun, W. Wang, J. Am. Chem. Soc. 2018, 140, 6763-6766; d) C. Gao, J. Li, S. Yin, G. Lin, T. Ma, Y. Meng, J. Sun, C. Wang, Angew. Chem. 2019, 131, 9872-9877; Angew. Chem. Int. Ed. 2019, 58, 9770-9775; e) T. Sun, L. Wei, Y. Chen, Y. Ma, Y.-B. Zhang, J. Am. Chem. Soc. 2019, 141, 10962-10966.
- [17] C. V. K. Sharma, K. Panneerselvam, T. Pilati, G. R. Desiraju, J. Chem. Soc., Perkin Trans. 2, 1993, 2209-2216.
- [18] M. Wallace, D. J. Adams, J. A. Iggo, Anal. Chem. 2018, 90, 4160-4166.
- [19] H. C. Brown, D. H. McDaniel, O. Häfliger, in *Determination of Organic Structures by Physical Methods, Chapter 14 Dissociation Constants* (Eds.: E. A. Braude, F.C. Nachod) Academic Press, New York, **1955**, pp. 567-662.
- [20] a) B. T. Koo, W. R. Dichtel, P. Clancy, J. Mater. Chem. 2012, 22, 17460-17469; b) T. Sick, J. M. Rotter, S. Reuter, S. Kandambeth, N. N. Bach, M. Döblinger, J. Merz, T. Clark, T. B. Marder, T. Bein, D. D. Medina, J. Am. Chem. Soc. 2019, 141, 12570-12581; c) A. M. Pütz, M. W. Terban,

S. Bette, F. Haase, R. E. Dinnebier, B. V. Lotsch, *Chem. Sci.* **2020**, *11*, 12647-12654; d) C. Kang, Z. Zhang, V. Wee, A. K. Usadi, D. C. Calabro, L. S. Baugh, S. Wang, Y. Wang, D. Zhao, *J. Am. Chem. Soc.* **2020**, *142*, 12995-13002.

- [21] a) J. L. Segura, S. Royuela, M. M. Ramos, *Chem. Soc. Rev.* 2019, *48*, 3903-3945; b) D.-G. Wang, N. Li, Y. Hu, S. Wan, M. Song, G. Yu, Y. Jin, W. Wei, K. Han, G.-C. Kuang, W. Zhang, *ACS Appl. Mater. Interfaces* 2018, *10*, 42233-42240.
- [22] No appreciable N_2 and low CO_2 adsorptions were observed for $H_COF-101$, Figure S16.
- [23] B. Shao, H. Qian, Q. Li, I. Aprahamian, J. Am. Chem. Soc. 2019, 141, 8364-8371.

COMMUNICATION

Table of Contents



Heteromeric dimer inhibited interpenetration. A large pore single-crystalline hydrogen-bonded crosslinked organic framework was synthesized through heteromeric monomers co-crystallization followed by thiol-ene crosslinking. The crosslinked porous crystals featured large pores to host a hydrazone switch for solid-state photo-patterning.