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Authors

Zhao, Chenfei
Diercks, Christian S
Zhu, Chenhui
[et al.](#)

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Urea-Linked Covalent Organic Frameworks

Chenfei Zhao,[†] Christian S. Diercks,[†] Chenhui Zhu,[‡] Nikita Hanikel,[†] Xiaokun Pei,[†] and Omar M. Yaghi^{*,†,||}

[†]Department of Chemistry, University of California–Berkeley; Materials Sciences Division, Lawrence Berkeley National Laboratory; Kavli Energy NanoSciences Institute at Berkeley; Berkeley Global Science Institute, Berkeley, California 94720, United States

[‡]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

^{||}UC Berkeley-KACST Joint Center of Excellence for Nanomaterials for Clean Energy Applications, King Abdulaziz City for Science and Technology, Riyadh 11442, Saudi Arabia

ABSTRACT: 2D covalent organic frameworks (COFs) with flexible urea linkages have been synthesized by condensation of 1,3,5-triformylphloroglucinol (TFP) with 1,4-phenylenediurea (BDU) or 1,1'-(3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diyl)diurea (DMBDU). The resulting COF-117 and COF-118 undergo reversible structural dynamics within their layers, in response to inclusion and removal of guest molecules, emanating from urea C–N bond rotation and interlayer hydrogen-bonding interactions. These compounds are the first urea-linked COFs, serving to expand the scope of reticular chemistry.

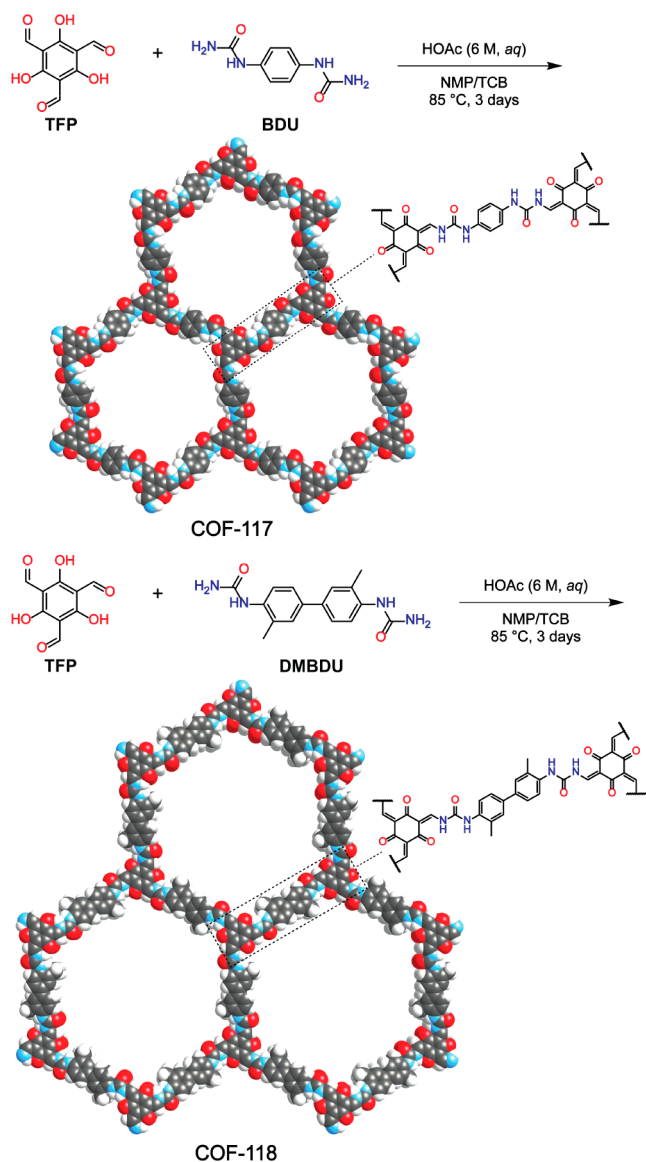
In the chemistry of covalent organic frameworks (COFs), the linkage between the building blocks impacts the physical and chemical properties of the material.^{1,2} For example, the chemical stability,³ adsorption behavior,⁴ and catalytic activity⁵ of this family of frameworks are profoundly affected by the nature of the linkages employed. New linkage chemistry has also allowed for the employment of diverse building units that otherwise would not be capable of reticulating COFs.⁶ However, developing new linkage chemistries is challenging because conditions for obtaining crystalline COF products, without compromising the integrity of the building units, have to be explored. Furthermore, most known COFs are based on rigid linkages and building blocks because increased molecular flexibility adds to the significant challenge of obtaining crystalline products.⁷ Here, we report the use of urea as linkages for 2D COFs. Condensation of 1,3,5-triformylphloroglucinol (TFP) and 1,4-phenylenediurea (BDU) or 1,1'-(3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diyl)diurea (DMBDU) yields crystalline COF-117 and COF-118, respectively (Scheme 1). Because this new urea linkage is flexible around the C–N bonds, the two frameworks exhibit reversible structural dynamics within their layers upon guest inclusion and removal, which is the first evidence of such behavior in 2D COFs.

A major challenge in making urea-linked COFs is the flexibility of such linkages: Various conformations in molecules are known depending on the specific steric, hydrogen-bonding, and π – π stacking environments.⁸ The rotational barriers of urea C–N bonds are typically lower than that of amides.⁹ It is therefore anticipated that phenylenediurea unit might adopt

various conformations during the COF synthesis under solvothermal conditions, resulting in varied linker lengths and directionalities (Figure 1). This linkage flexibility increases the potential for crystallographic defects and undermines the process of dynamic error correction required for growth of crystalline COFs. We studied the condensation between TFP and phenylurea as a model reaction for COF synthesis. X-ray crystallographic analysis indicates the product undergoes tautomerization to the keto form, therefore each urea group possesses two N–H bonds rather than an imine moiety (Supporting Information (SI), Section S10).^{10,11} The corresponding urea-linked COF (termed COF-117) was synthesized by solvothermal reaction between TFP and BDU in a mixed solvent of *N*-methyl-2-pyrrolidinone (NMP) and 1,2,4-trichlorobenzene (TCB) catalyzed by 6 M aqueous acetic acid (Scheme 1, top). The molecular connectivity of the urea linkage in the resulting COF was ascertained by Fourier-transform infrared (FT-IR) and ¹³C cross-polarization magic angle spinning (CP-MAS) NMR spectroscopies. Data were collected on the starting materials, model compound, and the COF (SI, Sections S3 and S4). As a result of an increased double-bond character, the urea C=O stretching band undergoes a blueshift from 1650 cm⁻¹ in the starting material, BDU, to 1713 cm⁻¹ in the framework (Figures S2 and S5).¹² The disappearance of the characteristic aldehyde stretching peak at 1633 cm⁻¹ was also noted, indicating a complete reaction. The ¹³C CP-MAS NMR spectrum of the COF has the characteristic resonance of the newly formed ketone, which matches well with the model compound (Figure S16). The newly formed ketone functionality is observed at 184.4 ppm. The peak at 149.1 ppm results from overlapped carbon signals of both the urea and its α -methine groups, as corroborated by the solution spectrum of the model compound.

We observed that crystalline COF-117 was rendered amorphous upon desolvation, possibly due to the flexible nature of the urea linkages. Nevertheless, it readily regains crystallinity when treated with solvents such as methanol, acetonitrile, and tetrahydrofuran (Figure 2a,b).¹³ Pawley refinement of a structural model based on conformation 1 was performed against the experimental powder X-ray diffraction (PXRD) pattern of a sample solvated with

Scheme 1. Synthesis of Urea-Linked COFs^a



^aColor code for space-filling diagrams: H, white; C, gray; N, blue; and O, red.

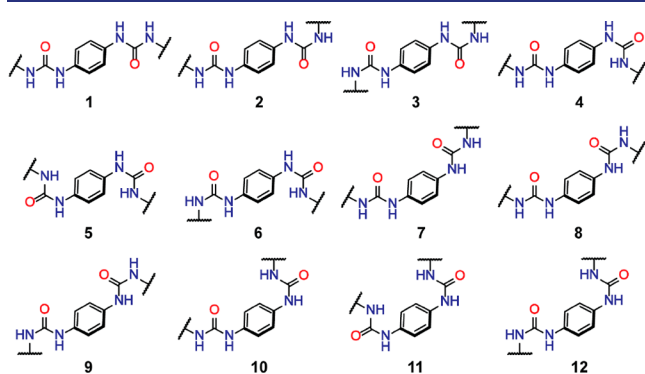


Figure 1. Selected possible conformations of the diurea linker.

acetonitrile. The unit cell parameters ($a = b = 29.0$ Å and $c = 3.4$ Å) were obtained with good agreement factors ($R_p = 1.21\%$, $R_{wp} = 2.11\%$) in the trigonal space group $P\bar{3}$ (No. 147). It is noteworthy that some linker conformations other than 1

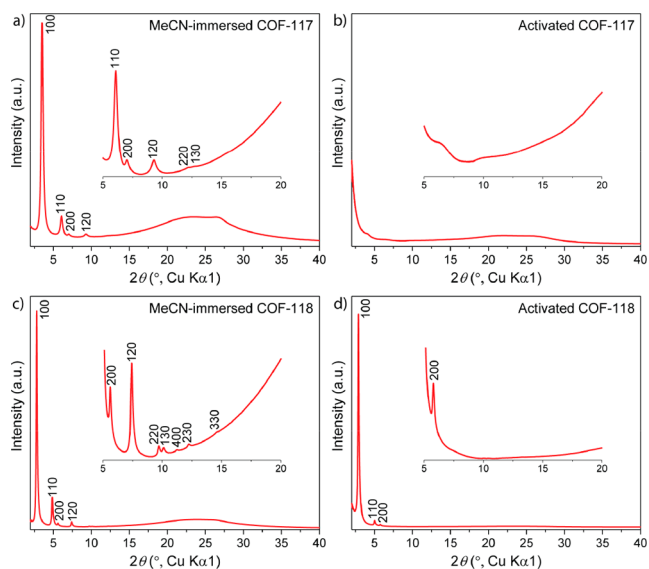


Figure 2. (a) PXRD pattern of COF-117 immersed with MeCN. (b) PXRD pattern of activated COF-117. (c) PXRD pattern of COF-118 immersed with MeCN. (d) PXRD pattern of activated COF-118.

can also provide reasonable structures in good agreement with the observed PXRD pattern, but current data cannot determine their distribution in the COF (SI, Section S5). The nitrogen adsorption isotherm measured on the activated sample at 77 K gives a Brunauer–Emmett–Teller (BET) surface area of 114 m²/g (Figures S25 and S26). This low value is likely due to the observed pore deformation upon activation as a result of framework flexibility.

An extended framework termed COF-118 was synthesized and characterized in a similar fashion (Scheme 1, bottom). In stark contrast to COF-117, this material remains crystalline upon activation, though a contraction of the unit cell and a decrease in the number of Bragg diffractions were observed when compared to the solvated sample (Figure 2c,d). Structure modeling and Pawley refinement based on conformation 1 in the trigonal space group $P\bar{3}$ (No. 143) yielded unit cell parameters in good agreement with the acetonitrile solvated sample ($a = b = 36.1$ Å, $c = 3.4$ Å, $R_p = 3.86\%$, $R_{wp} = 6.83\%$) and the activated sample ($a = b = 35.3$ Å, $c = 3.8$ Å, $R_p = 6.55\%$, $R_{wp} = 8.80\%$). The observed structural change from activated phases for both COFs can be induced by exposure to methanol vapor under ambient conditions. In the case of COF-118, vapor exposure over time resulted in continuous change between the two phases as evidenced by the change in the PXRD pattern (Figure 3), confirming the Bragg diffractions at 2.90°, 5.02°, and 5.78° of the guest-free sample gradually shift to 2.81°, 4.86°, and 5.60° in the solvated phase. The nitrogen adsorption isotherm at 77 K revealed the mesoporous nature of activated COF-118, and yielded a BET surface area of 1524 m²/g (Figures S27 and S28). The markedly higher crystallinity and surface area of activated COF-118 compared to COF-117 can be partly attributed to an interlayer stabilizing effect¹⁴ resulting from the biphenylene linker used in the COF-118 synthesis, which constrains the contraction process during activation. Urea is well-known to aggregate due to favorable hydrogen-bonding interactions.¹⁵ Compared with COF-118, COF-117 is more inclined to undergo structural deformation caused by hydrogen bonding due to its higher weight percentage of urea groups.¹⁶

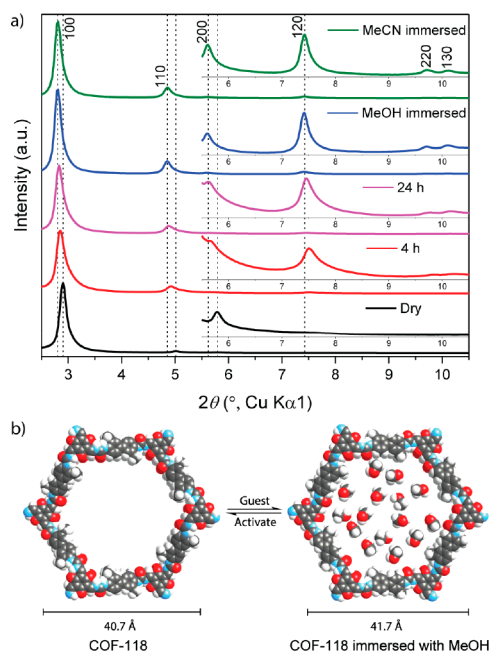


Figure 3. (a) Comparison of PXRD patterns of activated COF-118, material exposed to vapor of methanol for 4 or 24 h, and COF fully immersed with methanol and acetonitrile. (b) Space-filling illustration of the pores of activated and methanol immersed COF-118. Methanol molecules were drawn arbitrarily. Scale indicates the maximal diameter of the hexagon. Color code: H, white; C, gray; N, blue; and O, red.

To explore the origin of framework flexibility in response to guest molecules, FT-IR studies were performed on acetonitrile treated COFs. Compared with the guest-free samples, the presence of acetonitrile resulted in blueshifts of the urea C=O and N–H stretching peaks for both COFs while no significant shift was observed for the other bands (Figures S7 and S8). The observed changes in the positions of C=O stretching peaks can be attributed to diminished hydrogen-bonding interactions that contribute to urea–urea aggregation.¹⁷ Specifically, upon guest removal, urea groups can potentially engage in interlayer N–H···O hydrogen-bonding interactions with disordered conformations due to facile C–N bond rotation and slight layer offset. The addition of acetonitrile disrupts such intraframework interactions and therefore restores or augments the materials’ crystallinity. In contrast, if acetonitrile merely interacted with free urea N–H bonds through hydrogen bonding, then a redshift should be observed for the N–H stretching frequencies instead.

As noted above, exposure of both COFs to methanol vapor under ambient conditions can induce structural deviations from their activated phases. Methanol vapor adsorption isotherms were performed at 288 K on activated samples and found to exhibit a moderate step for COF-118 ($P/P_0 = 0.2–0.3$) and no step for COF-117 (Figure S34). This suggests that structural responses to methanol dosing are gradual for both COFs.

The high crystallinity and surface area of COF-118 allow for detection of potential structural degradation under various conditions. This material displayed excellent stability toward 12 M HCl (aq), boiling water, and saturated NaHCO₃ (aq) for 24 h, with retained crystallinity and only minor decrease in surface area (Figure 4). On the other hand, no COF material

was recovered after treatment with 1 M NaOH (aq) for the same duration.

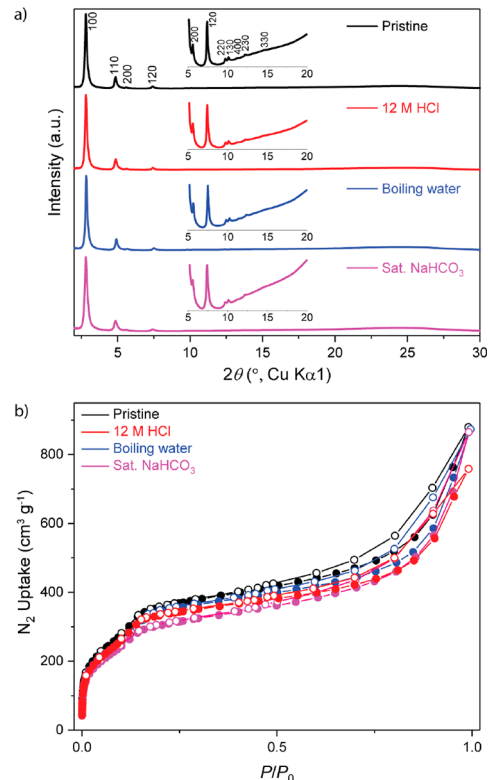


Figure 4. Stability test of COF-118. (a) Comparison of PXRD patterns of methanol-immersed samples. (b) Comparison of N₂ isotherms at 77 K.

On a fundamental level, this report identifies and illustrates the conditions under which urea-linked COFs can be crystallized. These materials undergo reversible structural dynamics upon addition and removal of guest molecules. The observed framework dynamics are attributed to facile urea linkage rotation and interlayer hydrogen-bonding interactions. This work also provides an approach to extend COF dynamics from 3D frameworks to layered structures.

■ AUTHOR INFORMATION

Corresponding Author

*yaghi@berkeley.edu

ORCID

Chenfei Zhao: 0000-0003-3960-3047

Christian S. Diercks: 0000-0002-7813-0302

Omar M. Yaghi: 0000-0002-5611-3325

Notes

The authors declare no competing financial interest.

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