ABSTRACT: Understanding polymorphism in metal–organic frameworks (MOFs) provides opportunities to unravel the process of MOF crystallization, and it enables the elucidation of structure–property relationships of compositionally identical crystals. Here, we present the modulator- and temperature-mediated polymorphic transformation of the kinetic product from Zr$_6$-based MOF synthesis, EHU-30, to the thermodynamic product, UiO-66. The partial dissolution–recrystallization process was demonstrated by a combination of in situ powder X-ray diffraction (PXRD) and in situ $^1$H NMR spectroscopy where EHU-30 was heated in the presence of a monotopic acid modulator, acetic acid. Density functional theory (DFT) calculations show that the EHU-30 polymorph is less stable because the bent linkers have higher Gibbs free energy compared to linear linkers in the thermodynamic product, UiO-66.
UiO-66, first reported in 2008, is one of the most studied MOFs due to its ease of synthesis, exceptional stability, and its ability to be both pre- and postsynthetically functionalized. While there are many reports of defect engineering in UiO-66, resulting in different topologies with different nominal stoichiometries, there is only one reported polymorph of UiO-66, EHU-30. Similar to UiO-66, EHU-30 has 12-connected Zr nodes but rather crystallizes in a hex topology as opposed to a fcu topology. The structural dissimilarity arises from three distorted linkers per formula unit, shown schematically in Figure 1.

Fig. 1. Schematic reaction energy profile and structure of kinetic product EHU-30 and thermodynamic product UiO-66 (C, black; H, pink; O, red; Zr, green).

Herein, we monitor in situ powder X-ray diffraction (PXRD) and in situ ¹H NMR spectroscopy to determine the structural conversion process of the modulator- and temperature-mediated polymorphic transformation from a kinetic product, EHU-30, to the thermodynamic product, UiO-66’ (where UiO-66’ is transformed EHU-30) (Figure 1). Scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and gas adsorption isotherms complement the in situ measurements to reveal the necessity of both heat and acetic acid to convert EHU-30 to UiO-66’. Furthermore, density functional theory (DFT) is applied to identify the driving force of this transformation by comparing the linkers in UiO-66’ and the distorted linkers of EHU-30.

EHU-30 was synthesized based on the original reported scheme (see the Supporting Information for details). Unlike the synthetic conditions for UiO-66 formation where concentration of the reaction solution is kept low, EHU-30 was synthesized from a concentrated solution of methacrylic acid modulator; kinetic access to the first known metastable polymorph of UiO-66 was gained through an excess of modulator, which encourages prenucleation of the zirconia motif of BDC. An activation barrier must be overcome for the conversion process to occur (Figure S6). The transformation begins in the second region, from 2 to 6 h, during which three major EHU-30 peaks (2θ = 7.4°, 6.9°, and 9.4°) decrease, and two major peaks for the targeted, fcu topology of UiO-66’ was observed. PXRD patterns of each product suggest that higher temperatures and lower reaction concentrations favor UiO-66’ formation (Figure S1–S3), consistent with the typical UiO-66 synthetic conditions. Complete conversion of EHU-30 to UiO-66’ was achieved at 100 °C in DMF:acetic acid = 5:1 v:v (Figure 2).

Unincorporated starting materials were removed by soaking the as-synthesized EHU-30 material in new batches of DMF for 3 days, until no further methacrylic acid or BDC was detected in the supernatant fluid by ¹H NMR (Figure S4a). The composition of each species was analyzed by ¹H NMR spectra of the digested parent EHU-30 and UiO-66’ in 1 M NaOD solution. The EHU-30 spectrum showed that approximately 17% of coordinated species were the methacrylic acid modulator rather than the BDC linker (Figure S5a). No methacrylate peaks were observed in the ¹H NMR of digested UiO-66’, indicating complete exchange of methacrylate for acetate during the transformation (Figure S5b). Acetate peaks, however, were observed. In either case, the presence of a modulator indicates missing linker type defects in both structures.

Analysis of ground state materials provides ample structural information; however, we sought to explore the relationship between polymorphs by examining intermediate species as well. PXRD experiments were therefore performed in situ. The reaction conditions from the oven were mimicked in a sealed capillary, and time-resolved in situ PXRD patterns were collected to follow the reaction; measurements were taken every 5 min for 12 h. The PXRD data showed the gradual disappearance of EHU-30 peaks (2θ = 5.4°, 6.9°, and 9.4°), with a concomitant increase in UiO-66’ peaks (2θ = 7.4° and 8.5°). Upon further analysis, the transformation process can be divided into three regions. The first region is the induction period; in the first 2 h no noticeable changes occur in the PXRD patterns. Both UiO-66 and EHU-30 feature strong bonds between Zr(IV) ions in the cluster and the carboxylate motif of BDC. An activation barrier must be overcome for the conversion process to occur (Figure S6). The transformation begins in the second region, from 2 to 6 h, during which three major EHU-30 peaks (2θ = 5.4°, 6.9°, and 9.4°) decrease, and two major peaks for the targeted, fcu topology of UiO-66'
emerge ($2\theta = 7.4^\circ$ and $8.5^\circ$). In the third region, after 6 h, EHU-30 peaks in the PXRD pattern are nearly absent, while the intensity of UiO-66$'$ peaks continues to gradually increase. At the end of 12 h, the final PXRD pattern is in good agreement with simulated UiO-66, indicating the successful polymorphic transformation of EHU-30 to its thermodynamic minimum (Figure 3c). The scanning electron microscopy (SEM) images of EHU-30 and UiO-66$'$ showed a similar morphology with a similar particle size (Figure S8).

In order to differentiate between the dissolution-recrystallization process and a single crystal transformation, in situ $^1$H NMR spectra were collected under the same reaction conditions. The initial $^1$H NMR of EHU-30 (6 mg) suspended in DMF- $d_7$ (0.5 mL) did not show signals from BDC or methacrylic acid, supporting the complete removal of unreacted species from our modified washing procedure. A small amount ($\mu$L) of N-methyl-2-pyrrolidone (NMP) was added as an internal standard along with acetic acid- $d_4$ (0.1 mL). The reaction was allowed to proceed at 100 °C, and in situ $^1$H NMR spectra were collected every 10 min for 12 h (Figure 4b). Ex situ $^1$H NMR spectra were then collected until the system equilibrated, every 3 h up to 36 h (Figure 4c). Both BDC and methacrylic acid were observed in the first spectrum after acetic acid- $d_4$ addition (Figure S4b), which can be attributed to the displacement of dangling species on the crystal surface. Importantly, this also shows that acetic acid is involved in the decoordination of both BDC and methacrylate from the node. The relative concentrations of methacrylic acid and BDC (Figure 4c) showed a steep initial increase of methacrylic acid that reached equilibrium in $\sim$3 h. The facile removal of coordinated methacrylates indicates that they are replaced by acetic acid, and the plateau in final concentration shows that dissolved methacrylic acid neither participates in building the UiO-66$'$ phase nor is included in the thermodynamic product; this is supported by the absence of methacrylic acid peaks in the $^1$H NMR spectra of digested UiO-66$'$ product after the reaction.

The concentration of dissolved BDC, however, initially increased in concentration, for $\sim$6 h, and then decreased in concentration as the reaction proceeded. The correlation between methacrylic acid and BDC signals indicates dissolution of linkers in EHU-30, followed by consumption of the free BDC linkers in solution and formation of UiO-66$'$, confirming that dissolution-recrystallization is an active component of the transformation. Coupled with the PXRD and incomplete dissolution of EHU-30, this result indicates a partial dissolution and recrystallization. The rate of methacrylate release is expected to be faster than BDC$^{2-}$ because of the different energetic contribution of entropy when removing a mononotic or ditopic ligand. Notably, the BDC concentration in the equilibrated system is higher after the transformation is complete. The UiO-66$'$ phase, which incorporates acetic acid rather than methacrylic acid, is therefore more defective than the parent EHU-30 phase. Polymorphic transformations may provide a strategy to increase the concentration of missing linker defects, i.e., coordinatively unsaturated metal sites.

Importantly, both samples demonstrated permanent porosity; thus, the structural integrity of the crystal was maintained. N$_2$ physisorption isotherms were collected at 77 K (Figure S7). EHU-30 and UiO-66$'$ both exhibited steep initial uptake at low pressures, which indicates microporosity, consistent with the expected topology. Surface areas were calculated with the BET equation; EHU-30 and UiO-66$'$ were found to have apparent BET surface areas of 920 and 1070 m$^2$/g, respectively. Despite a higher geometric surface area that was estimated for EHU-30, $^{50}$ the observed higher surface area in UiO-66$'$ can be attributed to the defects present in the structure. Notably, we did not observe complete dissolution of EHU-30; complete disassembly of the parent framework may not be necessary to assemble UiO-66$'$. Both EHU-30 and UiO-66$'$ have six, coplanar linkers oriented in the same hexagonal net. The polymorphs differ in both the conformation and connectivity of the other six linkers. In UiO-66, they are connected to six different nodes such that all 12 linkers are equivalent at a pristine node. In the case of EHU-30, however, the other six linkers are split between only two nodes resulting in a significant amount of strain.

To assess the relative conformational stability of linkers in each MOF, density functional theory (DFT) was employed to determine the energetic penalty for linker distortion in EHU-30. The difference in energy between the bent and linear conformations was found through linker models extracted from the bulk optimized structures of EHU-30 and UiO-66$'$. The difference in Gibbs free energy, a measure of strain, was found to be $\sim$3.0 kcal/mol. In conjunction with the incomplete dissolution of EHU-30 observed in situ, we hypothesized that
the population of disconnected linkers observed by NMR was dominated by the formerly bent linkers, which disconnect from the node and reorganize to form the more stable UiO-66 topology. The computed densities of states are further presented for each polymorph, to demonstrate that both polymorphs are expected to have similar photophysical properties, with their optical gap governed by a ligand-to-ligand transitions occurring in the UV.

As mentioned earlier, in EHU-30 about 17% of BDC\textsuperscript{2−} positions are occupied by methacrylate, which is completely leached into the solution during the phase transformation. With knowledge of the final methacrylic acid concentration in the solution, we estimated the amount of BDC in the solution to be \( \sim 12\% \) after 6 h (Figure 4c). However, this does not necessarily mean that only 12% of the linkers are involved in phase transformation, since this 12% only represents free BDC in solution. Mono-coordinated BDC linkers still will not show up in solution NMR. Additionally, the bond breaking/forming time scale can also be faster than the NMR spectra collection time. These results were in line with the in situ PXRD results, since it showed the coexistence of both phases.

In summary, we showed the modulator- and temperature-mediated polymorphic transformation of a kinetic MOF product, EHU-30, into its thermodynamic form, UiO-66. The rate of EHU-30 conversion showed a positive correlation with temperature and an inverse correlation with reaction concentration; the conversion conditions are closely related to the synthetic conditions of UiO-66. By monitoring reaction progress with in situ PXRD and \textsuperscript{1}H NMR, and probing the energetic relationship between EHU-30 and UiO-66 with DFT, it was found that EHU-30 undergoes a partial dissolution-recrystallization process driven by the rearrangement of linkers to release strain. Therefore, efforts to understand the relationship between kinetic and thermodynamic MOF products and characterizing the intermediate phases of transitions between them will inform the general design of synthetic parameters to target certain phases, which includes the formation of intrinsic defects as well as connectivity.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.0c00012.

Detailed description of synthesis, characterization, and modeling; and additional experimental results of PXRD, \textsuperscript{1}H NMR, TGA, \textsuperscript{15}N isotherms, and SEM images (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

Christopher H. Hendon — Department of Chemistry and Biochemistry, University of Oregon, Eugene, Oregon 97403, United States; orcid.org/0000-0002-7132-768X; Email: chendon@uoregon.edu

Timur Islamoglu — Department of Chemistry and International Institute of Nanotechnology, Northwestern University, Evanston,
Illinois 60208, United States; orcid.org/0000-0003-3688-9158; Email: timur.islamoglu@northwestern.edu

Omar K. Farha — Department of Chemistry and International Institute of Nanotechnology, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-9904-9845; Email: o-farha@northwestern.edu

Seung-Joon Lee — Department of Chemistry and International Institute of Nanotechnology, Northwestern University, Evanston, Illinois 60208, United States; Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 03722, Republic of Korea

Jenna L. Mancuso — Department of Chemistry and Biochemistry, University of Oregon, Eugene, Oregon 97403, United States

Khoa N. Le — Department of Chemistry and Biochemistry, University of Oregon, Eugene, Oregon 97403, United States

Christos D. Malliakas — Department of Chemistry and International Institute of Nanotechnology, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0003-4416-638X

Youn-Sang Bae — Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 03722, Republic of Korea; orcid.org/0000-0002-3447-4058

Complete contact information is available at: https://pubs.acs.org/10.1021/acsmaterialslett.0c00012

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
O.K.F. gratefully acknowledges support from the Defense Threat Reduction Agency (HDTRA1-19-1-0007). This research was supported in part by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2018R1A6A3A01011909). This work was also supported in part by the Yonsei University Research Fund (Yonsei Frontier Lab, Young Researcher Supporting Program) of 2018. PXRD and NMR studies made use of the IMSERC at Northwestern University, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205), the State of Illinois, and the International Institute for Nanotechnology (IIN); SEM study made use of EPIC facility of Northwestern University’s NUANCE Center, which has received support from the SHyNE, the MRSEC program (NSF DMR-1720139) at the Materials Research Center, IIN, and the Keck Foundation. Computational works were performed using the High-Performance Computing cluster at the University of Oregon (Talapas), the Extreme Science and Engineering Discovery Environment (XSEDE) which is supported by National Science Foundation grant number ACI-1548562, and the Portland State University machine, Coeus, which is supported by the NSF (DMS1624776).

REFERENCES
(21) Gong, X.; Noh, H.; Gianneschi, N. C.; Farha, O. K. Interrogating Kinetic Versus Thermodynamic Topologies of Metal-Organic Frameworks via Combined Transmission Electron Micros-


