Buckling of Two-Dimensional Covalent Organic Frameworks Under Thermal Stress

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Two-dimensional Covalent organic frameworks (2D COFs) are periodic, permanently porous, and lightweight solids that are polymerized from topologically designed monomers. The predictable design and structural modularity of these materials make them promising candidates for applications including catalysis, environmental remediation, chemical separations, and organic electronics, many of which will require stability to mechanical and thermal stress. Based on their reinforced structures and high degradation temperatures as determined by thermal gravimetric analysis (TGA), many reports have claimed that COFs have excellent thermal stability. However, their stability to heat and pressure has not been probed using methods that report on structural changes rather than the loss of volatile compounds. Here we explore two structurally analogous 2D COFs with different polymerization chemistries using in operando X-ray diffraction, which demonstrates the loss of crystallinity at lower temperatures than the degradation temperatures measured by TGA. Density functional theory calculations suggest that an asymmetric buckling of the COF lattice is responsible for the observed loss of crystallinity. In addition to their thermal stability, x-ray diffraction of the 2D COFs under gas pressures up to 100 bar showed no loss in crystallinity or structural changes, indicating that these materials are robust to mechanical stress by applied pressure. We expect that these results will encourage further exploration of COF stability as a function of framework design and isolated form, which will guide the design of frameworks that withstand demanding application-relevant conditions.
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ABSTRACT: Two-dimensional Covalent organic frameworks (2D COFs) are periodic, permanently porous, and lightweight solids that are polymerized from topologically designed monomers. The predictable design and structural modularity of these materials make them promising candidates for applications including catalysis, environmental remediation, chemical separations, and organic electronics, many of which will require stability to mechanical and thermal stress. Based on their reinforced structures and high degradation temperatures as determined by thermal gravimetric analysis (TGA), many reports have claimed that COFs have excellent thermal stability. However, their stability to heat and pressure has not been probed using methods that report on structural changes rather than the loss of volatile compounds. Here we explore two structurally analogous 2D COFs with different polymerization chemistries using in operando X-ray diffraction, which demonstrates the loss of crystallinity at lower temperatures than the degradation temperatures measured by TGA. Density functional theory calculations suggest that an asymmetric buckling of the COF lattice is responsible for the observed loss of crystallinity. In addition to their thermal stability, x-ray diffraction of the 2D COFs under gas pressures up to 100 bar showed no loss in crystallinity or structural changes, indicating that these materials are robust to mechanical stress by applied pressure. We expect that these results will encourage further exploration of COF stability as a function of framework design and isolated form, which will guide the design of frameworks that withstand demanding application-relevant conditions.

INTRODUCTION: New classes of structurally regular, porous materials are approaching a level of maturity where they are being considered for industrial use.¹ Covalent organic frameworks (COFs) are an emerging class of highly stable, structurally precise, permanently porous macromolecules.²³ These properties make them attractive candidates for applications such as electrochemical energy storage,⁴⁻⁵ catalysis,⁶⁻⁸ gas storage and separations,⁹¹⁰ optoelectronics,¹¹⁻¹² and chemical sensing.¹³ The realization of these applications will often require stability of the nanoscale COF structure to thermal and mechanical stresses. The high thermal stability of COFs has been touted based on thermogravimetric analysis (TGA), which indicates no loss of volatile products to temperatures as high as 800 °C.¹⁴ Therefore TGA indicating high thermal stability has fueled hypotheses that COFs might be ideal candidates for applications requiring demanding thermal or mechanical stability.¹⁵⁻¹⁶ However, the thermal and pressure-induced degradation of the COF crystalline structure has not been studied. Because many emergent properties of COFs arise from their atomically precise structures; it is essential to investigate how thermal and mechanical stress affect their crystallinity and porosity. Here we perform the first structural deformation
study of structurally similar but chemically distinct two-dimensional (2D) COFs by in operando synchrotron x-ray diffraction (XRD). During this study, we found that a crystalline-to-amorphous transition occurs at temperatures lower than degradation temperatures determined by TGA. Furthermore, a lattice contraction was observed for these COF systems as they were heated. The magnitudes of these in-plane contractions were among the highest values observed for porous, crystalline systems.\(^{17}\) Density functional theory (DFT) calculations support that the lattice contraction could be attributed to a buckling of the 2D COF lattice. In addition to their thermal stability, we also explored the stability of these COFs to high-pressure gasses using in operando XRD. We found that the COF structure was unaffected by gas pressures up to 100 bar, which supports their promise as useful materials for gas storage and separations.\(^{9-10,18}\)

RESULTS AND DISCUSSIONS: An imine-linked 2D COF (BND-TFB COF) was prepared through the transimination of 1,3,5-triformylbenzene and \(N\)-benzidine benzophenone imine, an approach that was recently shown to provide high-quality COF materials.\(^{19}\) A chemically distinct but structurally similar 2D COF (BND-TFP), featuring the same benzidine groups linked by \(\beta\)-ketoenamines, was prepared through a monomer exchange reaction between BND-TFB COF and 2,4,6-triformylphloroglucinol (TFP). This monomer exchange process provides \(\beta\)-ketoenamine-linked COFs with superior crystallinity and BET surface areas than those prepared from the direct condensation of diamines and TFP.\(^{20}\) Brunauer-Emmett-Teller (BET) surface area analysis, Fourier-transform infrared spectroscopy (FTIR), x-ray diffraction, and solid-state \(^{13}\)C NMR confirmed the formation of each COF (see Supplementary Information). Based on their BET surface areas (>2000 m\(^2\) g\(^{-1}\)) and broadening of the XRD features due to finite grain size effects (see Supplementary Information), we were able to assign that the BND-TFB and BND-TFP COFs were of similar and high quality.

The thermal stability of each 2D COF was probed using variable-temperature XRD measurements performed at Sector 17 of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). Under a constant flow of helium, powder samples of BND-TFB and BND-TFP COF were heated at a rate of 5 °C min\(^{-1}\). XRD patterns of the microcrystalline powders were recorded continuously on a 2D Pilatus detector, which were radially integrated to produce 1D patterns. It was noted that at a threshold temperature the <100> Bragg feature of the COF materials dropped in intensity. We define a degradation temperature \(T_{\text{XRD}}\) at which the integrated 100 Bragg feature decreased below 80% of
its original intensity. This temperature was then compared to the TGA degradation temperature ($T_{TGA}$) which was assigned at the local minimum of the first derivative of the mass with respect to temperature.\textsuperscript{21}

The imine-linked COF, BND-TFB, underwent a gradual degradation with a $T_{XRD}$ of approximately 430 °C (Figure 2C), after which the residual diffraction signal quickly and irreversibly dissipated (Figure 2A). The attenuation of the diffraction signal indicates the layered hexagonal structure of the COF degrades at this temperature. However, TGA showed that the primary mass loss event occurred at approximately 540 °C (Figure 2C), 110 °C higher than $T_{XRD}$. For the structurally analogous \( \beta \)-ketoenamine-linked COF, BND-TFP, the <100> intensity increased, and the peak shape sharpened until approximately 300 °C. We attribute this phenomenon to the liberation of volatile species, likely trace residual solvent molecules, intercalated into the COF network, whose removal decreased the overall network disorder and increased the electron density contrast of the vacant COF pores and the COF structure. After this minor initial increase in intensity, the COF structure underwent a sharp degradation at a $T_{XRD}$ of 540 °C (Figure 2C). In contrast, the BND-TFP COF underwent a significant mass loss event at a $T_{TGA}$ of 600 °C. The observation of two degradation temperatures, one related to the loss of crystallinity and the other related to the loss of mass, indicates that the COF forms an amorphous phase that subsequently degrades to volatile small molecules at higher temperatures. In this study, the temperature differential between $T_{XRD}$ and $T_{TGA}$ was found to be approximately 110 °C for both COFs. However, it is possible that other COFs may exhibit either larger or smaller differences between $T_{TGA}$ and $T_{XRD}$ as a function of other linkage chemistries, topologies, or monomer structures.

The \( \beta \)-ketoenamine-linked BND-TFP COF is considerably more stable than the structurally analogous imine-linked BND-TFB COF as judged by the 100 °C increase in both its $T_{TGA}$ and $T_{XRD}$. Because BND-TFP and BND-TFB share the same structural morphology (P6 tiled hexagons), pore size (29 Å pore diameter), and approximate crystallite size (100 nm), this stability difference to their different linkage chemistries. \( \beta \)-ketoenamine-linked COFs are also notably more hydrolytically stable than their imine-linked counterparts, although it is unclear if their increased thermal stability arise from the same phenomenon.\textsuperscript{22-23}

In examining the response of the crystalline network over the thermal ramp, we noted that the relative intensities and peak locations of the COF diffraction features were not constant, which provides insight into the mechanism of the crystalline-to-amorphous transition. In Figure 3A, the in-plane diffraction features (<100>, <110>, <200>, <210>)
decrease in intensity when compared to the interlayer features \(<001>, <111>\). This decrease indicates a loss of in-plane crystallinity, even as the layered structure of the material is retained. During heating, the BND-TFB \(<100>\) Bragg diffraction feature trended to shorter real space distance, which is indicative of a lattice contraction. Analysis of the BND-TFP COF revealed a similar behavior, in which the in-plane features decreased relative to the out-of-plane features and the lattice contracted upon heating. Lattice contractions for metal-organic frameworks and zeolites have been attributed to the unusual physiochemical process of negative thermal expansion (NTE).\(^{17, 24}\) However, the degree of in-plane lattice contractions of these 2D COFs, 5% and 9% for BND-TFB and BND-TFP, respectively, were among the highest lattice contraction values reported for porous materials.

DFT calculations provide insight into the thermal contraction of these materials by examining the framework structure upon compression. The computational results confirmed the framework stiffens upon compression with the bulk modulus increasing as a function of pressure (Figure S13). This effect is commonly associated with materials that have positive thermal expansion and soften and expand as a function of temperature. The results also showed a structural instability to lattice compression, likely due to a change in the phase of the 2D layers. The geometry of the structure was relaxed to a volumetrically contracted phase, which agreed with the dynamic position of the \(<100>\) diffraction corresponding to a buckling of the 2D planar layers. The buckled phase of BND-TFP is shown in Figure 4, along with the expected shift in the XRD pattern (Figure 4C).

**Figure 3.** X-ray line plots over the course of thermal profile. Normalized x-ray intensities over the course of thermal heating demonstrating the change in relative peak intensities over the course of the heated experiment for A) BND-TFB COF and B) BND-TFP COF. Insets show the position of the 100 Bragg reflection (normalized intensities) over the course of the same thermal profile.

**Figure 4.** Proposed Buckling of BND-TFP COF. A) Initial BND-TFP structure transforming to the buckled phase under compressive strain. B) Experimental change in diffraction peak location over the course of a thermal ramp. C) Computational changes in diffraction peak under compressive buckling.

The asymmetry of the peaks in the buckled phase arises from the reduction in the symmetry of the COF as the \(a\) and
b lattice parameters are no longer equivalent. This analysis is consistent with the structure undergoing a thermally-induced phase transition to a volumetrically contracted geometry and not, stiffening as a function of temperature like materials described as possessing NTE.

In contrast to the structural changes observed at elevated temperatures, both COFs showed exceptional stability to mechanical stress introduced from high-pressure gasses. In operando mechanical stresses are frequently applied to porous materials either under the weight of the supports packed into a column or by the high pressures of gasses used in industrial processes.25-26 Capillaries filled with BND-TFB and BND-TFP COF powder were pressurized to 100 bar under a He atmosphere. No structural changes were observed in the XRD patterns of either COF up to 100 bar, at which point the capillary failed (Figure 5). These results demonstrate the robust mechanical stability of COFs under high gas pressures, and so augments previous studies of COF powders under mechanical pressures.9-10 Moreover, this indicates the stability of these 2D COFs is seemingly congruent with the pressure regimes required by the chemical industry.

CONCLUSIONS: COFs are an emerging class of permanently porous, synthetically modular, crystalline materials that have potential applications ranging from catalytic supports to energy storage materials. Much of the promise of these materials hinges on their ability to maintain their crystalline structure under operating conditions, which includes thermal and mechanical stresses. In this study, we have shown that COFs maintain their crystalline morphology under in operando conditions including temperatures of up to 500 °C and pressures of up to 100 bar. However, the thermal stability is lower than originally assumed by TGA measurements, which we have shown may be attributed to a buckling of the 2D COF layers. We anticipate that these studies will inform and guide COF design for future applications that require highly stable, porous materials.

ASSOCIATED CONTENT
Detailed information regarding monomer and materials synthesis, materials characterization, and computational results are available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interests.

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ABBREVIATIONS
BET, Brunauer-Emmett-Teller; COF, Covalent Organic Framework; DFT, Density-Functional Theory; MOF, Metal-Organic Frameworks; NTE, Negative Thermal Expansion; XRD, X-Ray Diffraction

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I. Materials and Instrumentation

Materials
Dry dichloromethane (DCM) was obtained by passing previously degassed solvents through activated alumina columns. All other reagents were purchased from commercial sources and used without further purification, or prepared from them. Reactions were monitored by thin layer chromatography (TLC) carried out on EMD 250μm silica gel 60-F254 plates. Visualization was performed by UV light irradiation and potassium permanganate stain and heat.

Instrumentation

Nuclear Magnetic Resonance. $^1$H and $^{13}$C NMR spectra were acquired on Bruker AvanceIII-500 MHz equipped with a DHC CryoProbe and recorded at 25 °C. The spectra were calibrated using residual solvent as internal reference (CDCl$_3$: 7.26 ppm for $^1$H NMR, 77.00 for $^{13}$C NMR). Solid state $^{13}$C CP/MAS NMR spectra of covalent organic frameworks were recorded on a Varian 400 MHz at a spin rate of 10,000 Hz and calibrated using Adamantane as an external standard.

Infrared Spectroscopy. Infrared spectra were recorded on a Nicolet iS10 FT-IR spectrometer equipped with a diamond ATR attachment and are uncorrected.

High Resolution Mass Spectrometry. High-resolution mass spectra were acquired on Agilent 6210A LC-TOF Mass Spectrometer, with Atmospheric Pressure Photoionization (APPI) as an ionization source. The instrument is equipped with an Agilent Series 1200 HPLC binary pump, and Autosampler, using Mass Hunter software. The samples were run using direct injection.

Microwave Reactor. Microwave reactions were performed on a CEM Discover SP unit, operating at 110 V, with a microwave irradiation of 2.45 GHz, and a maximum microwave output of 300 W in 10 mL capacity Teflon-capped tubes. All reactions were performed using the “standard” method, where only the temperature point and run times were controlled.
Gas Adsorption. Gas adsorption isotherms were conducted on a Micromeritics ASAP 2420 Accelerated Surface Area and Porosity Analyzer. Typically, 20-50 mg samples were transferred to dried and tared analysis tubes equipped with filler rods and capped with a Transeal. The samples were heated to 40 °C at a rate of 1 °C/min and evacuated at 40 °C for 20 min, then heated to 100 °C at a rate of 1 °C/min heat, and evacuated at 100 °C until the outgas rate was ≤0.3 μmHg/min (holding the samples at 100 °C for 5 hours was sufficient), at which point the tube was weighed again to determine the mass of the activated sample. The tube was then transferred to the analysis port of the instrument. UHP-grade (99.999% purity) N₂ was used for all adsorption measurements. N₂ isotherms were generated by incremental exposure to nitrogen up to 760 mmHg (1 atm) in a liquid nitrogen (77 K) bath. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements. Brunauer-Emmett-Teller (BET) surface areas were calculated from the linear region of the N₂ isotherm at 77 K within the pressure range $P/P_0$ of 0.05 – 0.10.

In Operando X-ray Diffraction Studies. In operando x-ray diffraction was performed at sector 17 of the Advanced Photon Source Argonne National Laboratory. Samples were prepared by packing ~25 mg of COF sample into a thick-walled Kapton capillary and mounted into a sample holder available at the Sector 17. A thermocouple was then mounted in the center of the powder sample, inside of the Kapton capillary. The sample was then placed under a constant stream of helium and heated at a rate of 10 °C min⁻¹ under a helium atmosphere. X-ray patterns were collected over the course of this heating on a 2D Pilatus detector approximately every minute by collecting ten frames per minute and averaging the counts of these ten frames. These frames were then radially integrated to produce a 1D diffraction pattern which were then analyzed.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was performed on a Netzch Simultaneous Thermal Analysis (STA) system using approximately 5 mg of sample. The samples were heated to designated temperature at a rate of 10 °C min⁻¹ under a helium atmosphere.

Sonication. Sonication was performed with a Branson 3510 ultrasonic cleaner with a power output of 100W and a frequency of 42 kHz.
II. Experimental Procedures and Characterization of COF Monomers

Benzophenoneimine of benzidine (BND-Benzophenone).\(^1\) To a 500mL flame-dried round-bottom flask, benzidine (5.10 g, 27.75 mmol, 1.0 equiv), benzophenone (10.11 g, 55.50 mmol, 2.0 equiv), 1,4-diazobicyclo[2.2.2]octane (DABCO) (18.69 g, 166.50 mmol, 6.0 equiv), and chlorobenzene (300 mL) were added and the contents were stirred at room temperature under a nitrogen atmosphere. Titanium(IV) chloride (4.56 mL, 41.64 mmol, 1.5 equiv) was syringed in portions over 15 min (1/4 of the portion at times 0 min, 5 min, 10 min, and 15 min). After the addition was complete, the reaction mixture was stirred for another 20 min at room temperature, then the flask was equipped with a reflux condenser, and the reaction stirred at 125 °C overnight (12 h). The reaction mixture was then cooled to about 40 °C, and filtered while warm through a Buchner funnel equipped with a filter paper. The filtrate was then concentrated in vacuo. The crude product was purified by stirring in hot absolute ethanol / chloroform mixture (~3:1, ~1200 mL), performing a hot filtration through a cotton-plugged plastic funnel, and allowing the filtrate to slowly cool to room temperature, at which point the product starts crystallizing. The flask is then further cooled in a fridge overnight. The solid was then collected and dried to give the product as a yellow/orange solid (8.22 g, 58% yield).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.76 - 7.70\) (m, 4H), 7.47 – 7.41 (m, 2H), 7.38 (dd, \(J = 8.3, 6.7\) Hz, 4H), 7.33 – 7.29 (m, 4H), 7.28 – 7.20 (m, 6H), 7.15 – 7.08 (m, 4H), 6.78 – 6.68 (m, 4H).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 168.11, 150.02, 139.71, 136.25, 135.39, 130.66, 129.50, 129.30, 128.58, 128.16, 128.02, 127.97, 126.55, 121.45.\)

Triformylphloroglucinol is a previously reported compound and was prepared according to the reported procedure, and the NMR data is consistent with those reported.\(^2\)
Figure S1. $^1$H NMR spectra of BND-Benzophenone.
Figure S2. $^{13}$C NMR spectra of BND-Benzophenone.
III. Experimental Procedures for COF Syntheses

**BND-TFB COF**: To a flame-dried 250 mL high-pressure flask with vacuum valve, 1,3,5-triformylbenzene (0.97 g, 6.0 mmol, 1.5 equiv) and benzidine-benzophenone (4.61 g, 9.0 mmol, 1.5 equiv) were added, followed by mesitylene:dioxane (1:1, 60.0 mL) along the walls of the flask (to push down any remaining solids remaining atop of the flask). The flask was sealed and sonicated at room temperature for 10 min, and then 6M acetic acid (10 mL) was added, and the flask was sealed again. The reaction mixture was then degassed through three freeze-pump-thaw cycles (vacuum <50 mTorr), after which the vacuum valve was switched to N₂, and the flask was charged with N₂ and sealed under positive N₂ pressure. The flask was then placed (no stirring) in a 120 °C pre-heated oil bath for three days. The flask was removed from the oil bath, allowed to cool, and filtered through a Buchner funnel equipped with a filter paper. Acetone was used to ensure all of the material is filtered from the flask to the Buchner funnel. The solid was collected and stirred in an Erlenmeyer flask in hot DMF (600 mL at 90 °C for 30min), and filtered while hot. This procedure was repeated two more times in DMF (600 mL at 90 °C for 30min), once in absolute ethanol (600 mL at 80 °C for 30min), and lastly once in acetone (600 mL at 60 °C). The material was then filtered, collected, placed in a vacuum chamber and dried at 120 °C for 24 h under vacuum to give an orange solid (1.98 g, 86%).

**BND-TFP COF**: To a flame-dried 150 mL high-pressure flask with vacuum valve, triformylphloroglucinol (0.63 g, 3.0 mmol, 1.0 equiv) and BND-TFB COF (1.15 g, 3.0 mmol, 1.0 equiv) were added, followed by mesitylene:dioxane (1:1, 30.0 mL) along the walls of the flask (to push down any remaining solids remaining atop of the flask). The flask was sealed and sonicated at room temperature for 10 min, and then 6M acetic acid (5 mL) was added, and the flask was sealed again. The reaction mixture was then degassed through three freeze-pump-thaw cycles (vacuum <50 mTorr), after which the vacuum valve was switched to N₂, and the flask was charged with N₂ and sealed under positive N₂ pressure. The flask was then placed (no stirring) in a 120 °C pre-heated oil bath for three days. The flask was removed from the oil bath, allowed to cool, and filtered through a Buchner funnel equipped with a filter paper. Acetone was used to ensure all of the material is filtered from the flask to the Buchner funnel. The solid was collected and stirred in
an Erlenmeyer flask in hot DMF (600 mL at 90 °C for 30min), and filtered while hot. This procedure was repeated two more times in DMF (600 mL at 90 °C for 30min), once in absolute ethanol (600 mL at 80 °C for 30min), and lastly once in acetone (600 mL at 60 °C). The material was then filtered, collected, placed in a vacuum chamber and dried at 120 °C for 24 h under vacuum to give a red solid (1.25 g, 97%).
IV. FT-IR Spectra of Covalent Organic Frameworks

Figure S3. FT-IR spectra of BND-TFB COF

Figure S4. FT-IR spectra of BND-TFP COF
V. CP-MAS $^{13}$C NMR Spectra of COFs

**Figure S5.** CP-MAS $^{13}$C NMR spectra of BND-TFB COF
Figure S5. CP-MAS $^{13}$C NMR spectra of BND-TFP COF
VI. X-ray Diffraction of Covalent Organic Frameworks

Figure S6. Room temperature x-ray diffraction pattern of BND-TFP COF
Figure S7. Room temperature x-ray diffraction pattern of BND-TFB COF
VII. Nitrogen Isotherms of Covalent Organic Frameworks

Figure S7. Nitrogen Isotherm of BND-TFP COF
Figure S8. Nitrogen Isotherm of BND-TFB COF
VIII. Pore Size Distributions of Covalent Organic Frameworks

Figure S9. Pore Size Distribution of BND-TFP COF
Figure S10. Pore Size Distribution of BND-TFB COF
IX. Density Functional Theory (DFT) Calculations

Density functional theory (DFT) calculations were performed using the periodic ab initio code CRYSTAL17. The PBE exchange-correlation functional was used with a semi-classical dispersion correction (PBE-D3) to better account for the noncovalent interactions present in the 2D COF structures. The dispersion correction includes a BJ damped pairwise and three-body term to the DFT energies. Each of the DFT calculations was performed with all-electron atom-centered Gaussian-type basis sets of double-zeta quality, similar to previous work on the electronic properties and dielectric response of other porous materials.

The all-electron basis sets contained a total of 1,128 basis functions, corresponding to 450 electrons spread over 378 shells per unit cell for BND-TFP. The lattice parameters and atomic coordinates were optimized while maintaining the space group symmetry (P6) via a quasi-Newtonian algorithm. The optimization was considered to have converged when the maximum and root-mean-square (RMS) gradient, and the maximum and RMS atomic displacements were simultaneously below $1.5 \times 10^{-5}$, $1.0 \times 10^{-5}$, $3.0 \times 10^{-5}$ and $2.0 \times 10^{-5}$ a.u., respectively.

Table S1. Summary of the calculated lattice parameters for BND-TFP.

| Phase     | Lattice parameters (Å) | BND-TFP |
|-----------|------------------------|---------|
|           | $a$        | $b$        | $c$        | $\beta$ |
| Planar    | 30.03      | 30.03      | 3.61       | 120.0   |
| Buckled   | 29.97      | 29.54      | 3.60       | 122.2   |

The planar and buckled geometries have hexagonal and monoclinic symmetry respectively.

The structural stability of BND-TFP upon compression was investigated using a similar procedure to that recently reported for MOF-5 by computing the energy at various optimized volumetrically constrained geometries and fitting the curve to an equation of state (EOS). The bulk modulus values reported in the main text (Figure S13) were obtained from fitting the curve to a third-order isothermal Birch-Murnaghan EOS. A series of volumetrically contracted and expanded geometries were investigated ranging from -10% to +4% and the resultant energy curve is shown in Figure S#. Within the experimental symmetry confinements of the initial structure (P6), the optimized equilibrium geometry was the most energetically favorable (minimum energy).
However, upon further analysis of the volumetrically constrained geometries, the low-energy phonon modes were seen to soften as a function of compression and became imaginary indicating the possibility of a symmetry-reduced phase transition. To obtain structural insight into the new phase of BND-TFP, we analyzed the geometrical changes along the trajectory of the imaginary phonon mode and allowing for the associated symmetry reduction relaxed the resultant structure to optimize to the ‘buckled’ phase. The infrared (IR) absorption spectra of both the planar and buckled phases of BND-TFP are reported in Figure S12. The IR intensities were computed through the Berry Phase approach, by evaluating the Born atomic tensors as polarization differences between the original and the distorted geometries. In the range of 650-3500 cm$^{-1}$ the spectral features did not change significantly in either position or intensity, in good agreement with experiment (Figure S12). Therefore, the slight shift in the experimental signal around 1600 cm$^{-1}$ is likely due to thermal expansion of the lattice which is omitted from the computed spectra. Therefore, the vibrational modes involved do not appear to be significantly affected by the change from the planar to the buckled phase. The presence of multiple phases made analyzing the linear thermal response of the crystalline lattice over a broad range challenging and will be investigated further in a more in-depth computational study.

Figure S11. Change in energy upon compression an expansion with constant symmetry ($P6$).
**Figure S12.** IR spectra of the planar and buckled phase of BND-TFP.

**Figure S13.** Bulk modulus as a function of pressure. Structural stiffening of BND-TFP occurs upon compression.
X. References

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