Supporting Information

Molecular retrofitting adapts a metal-organic framework to extreme pressure

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Section S1: General Methods

Chemicals used in this work: Aluminum nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$, N,N-dimethylformamide (DMF) (purity ≥ 99.9 %), biphenyl-4,4'-dicarboxylic acid (H_2BPDC), ethanol (purity ≥ 99.5 %), methanol (purity ≥ 99.8 %) were purchased form Sigma Aldrich Co. 1,3,5-benzenetribenzoic acid (H_3BTB) was purchased from TCI America. Formic acid (99.8 %) was obtained from EMD Chemicals. Anhydrous acetone (purity ≥ 99.8 %, extra dry with AcroSeal) was purchased from Acros Organics. All chemicals obtained were used without further purification.

Analytical Techniques: Powder X-ray diffraction data were collected using a Bruker D8-advance θ-θ diffractometer in parallel beam geometry employing Cu Kα1 line focused radiation at 1600 W (40 kV, 40 mA) power and equipped with a position sensitive detector with at 6.0 mm radiation entrance slit. Samples were mounted on zero background sample holders by dropping powders from a wide-blade spatula and then leveling the sample with a razor blade. Data were collected using a 0.02˚ 2θ step scan from 2 – 35˚ with exposure time of 3 s per step. Thermogravimetric analysis (TGA) curves were recorded on a TA Q500 thermal analysis system under nitrogen flow. Elemental microanalyses (EA) were performed in the Microanalytical Laboratory of the College of Chemistry at UC Berkeley, using a Perkin Elmer 2400 Series II CHNS elemental analyzer. FT-IR spectra were collected in-house using a Bruker ALPHA Platinum ATR-FT-IR Spectrometer equipped with a single reflection diamond ATR module. Low-pressure Ar adsorption isotherms were recorded on a Quantachrome Autosorb-1 volumetric gas adsorption analyzer. A liquid argon bath was used for the N_2 measurements at 77 K. Solution ^1H NMR spectra were acquired on a Bruker Advance-500 MHz NMR spectrometer in Molecular Foundry in LBNL. Single-crystal X-ray diffraction (SXRD) data at ambient conditions was collected using synchrotron radiation in beamline 11.3.1 of the Advanced Light Source, Lawrence Berkeley National Laboratory (LBNL), equipped with a PHOTO100 CMOS detector operating in shutterless mode equipped, and the radiation is monochromated using silicon (111). Single-crystal X-ray diffraction at non-ambient pressure was collected using synchrotron radiation in beamline 12.2.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory (LBNL); details are described in Section S4.

Section S2: Synthesis of MOF-520 and MOF-520-BPDC single crystals

MOF-520, **$Al_8(OH)_8(HCOO)_4BTB_4$.** In a 20 mL scintillation vial, the mixture solution of $Al(NO_3)_3 \cdot 9H_2O$ (90.0 mg, 0.240 mmol), H_3BTB (75.0 mg, 0.170 mmol) in DMF (17 mL) was prepared. The solution was sonicated for 1 min and formic acid (1.40 mL, 0.0310 mol) was added to the solution. The vial was capped and placed in the preheated 140 °C oven. After 4 days, block shaped clear single crystals with size range 50 to 100 μm were obtained on the wall of the vial. Subtle temperature difference can affect the quality of the single crystals. The vial with the best single crystals was chosen and the single crystals were used for the inclusion of the biphenyl-4,4'-dicarboxylic acid molecules. For the characterization of MOF-520, the rest of the crystals were further processed.

MOF-520-BPDC, **$Al_8(OH)_8(BPDC)_2BTB_4$.** In a 20 mL scintillation vial, the solution of H_2BPDC (315.0 mg, 1.3 mmol) in DMF (8 mL) was prepared. MOF-520 single crystals (5.0 mg) impregnated with DMF were added to the solution. The vial was capped and placed in the preheated 100 °C oven for 5 days.

Solvent exchange and guest removal activation procedure for the full characterization: The single crystals were washed with DMF (10.0 mL) three times per day for three days to remove the unreacted reagents in the pores. DMF solvent in the pore was exchanged with anhydrous acetone by washing the crystals with anhydrous acetone (10.0 mL) three times per day for three days. For supercritical CO_2 drying (SCD) activation, the acetone was decanted and acetone in the crystals was thoroughly exchanged with liquid CO_2 in the chamber of a Tousimis Samdri PVT-3D critical point dryer. The sample was subsequently kept in a supercritical CO_2 atmosphere (typical conditions of 40 °C and 1200 psi) for 30 min and then the supercritical CO_2 was slowly vented over the course of 6 hours.

Solvent exchange for the high-pressure measurements: The single crystals were washed with DMF (10.0 mL) three times per day for three days to remove the unreacted reagents in the pores. DMF solvent in the pore was exchanged by washing the crystals with methanol/ethanol (4:1 ratio) solution (4 ml) three times per day for three days. After that, the crystals were kept in methanol/ethanol media for at least several weeks before the high-pressure SXRD measurements.

Section S3: Comparative characterization of MOF-520 and MOF-520-BPDC

Argon isotherms at 87 K: 40 mg of activated samples in 9 mm bulb gas cell was charged with Ar to avoid air contamination and the cell was mounted on the instrument. Liquid argon bath was used for the measurements at 87 K. Helium was used for the estimation of dead space for gas adsorption measurements. Ultra-high-purity grade Ar and He gases (Praxair, 99.999% purity) were used throughout the adsorption experiments. 46 adsorption and 16 desorption points were collected.

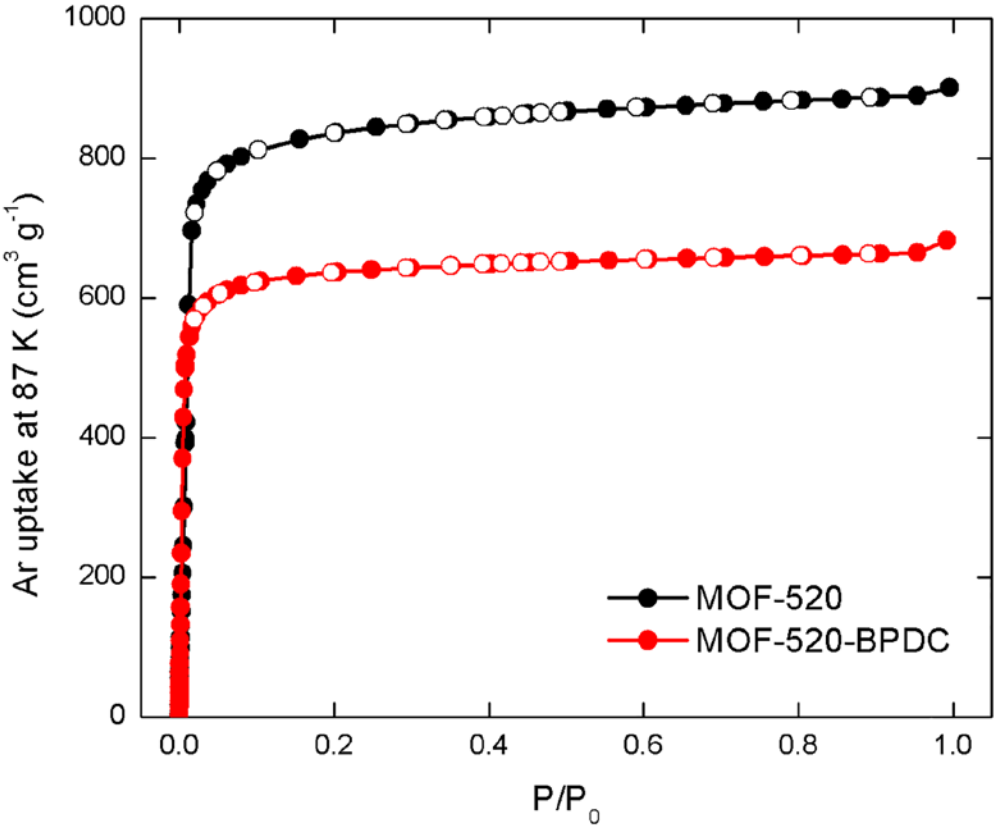

Figure S1. Comparison of MOF-520 and MOF-520-BPDC Ar isotherms at 87 K.

Thermogravimetric analysis: The activated sample was held in a platinum pan under nitrogen atmosphere with a flow rate of 40 mL/min. Temperature was controlled by the furnace heating from 25 °C up to 800 °C with a ramp rate of 5 °C/ min.

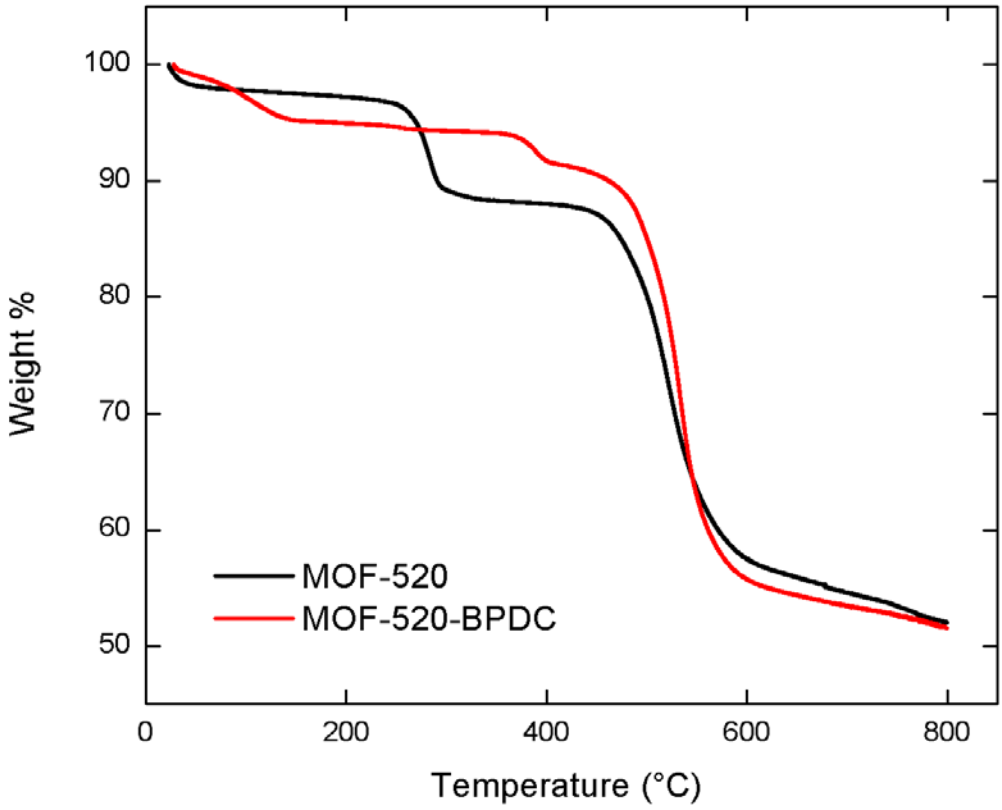

Figure S2. Comparison of activated MOF-520 and MOF-520-BPDC TGA traces under N_2 flow.

^{1}H NMR analysis: The activated sample (1 mg) was transferred to a 4 mL vial. Deuterated dimethyl sulfoxide (d_6-DMSO) (600 µL) was add to the vial followed by the addition of 20 µL of NaOH (1 M in D_2O). The solution was sonicated for 10 min to digest the crystals. The vial was capped and placed in a preheated 120 °C oven for 20 min to completely dissolve the crystals. The final clear solution was used for the ^{1}H NMR experiment. The integration ratio suggests the occupancy of BPDC linker to be about 70%. The deviation from 100% occupancy of BPDC in the single-crystalline sample used for high-pressure experiments can be explained by that the molecule incorporation in a single crystal does not represent the whole batch of the sample.

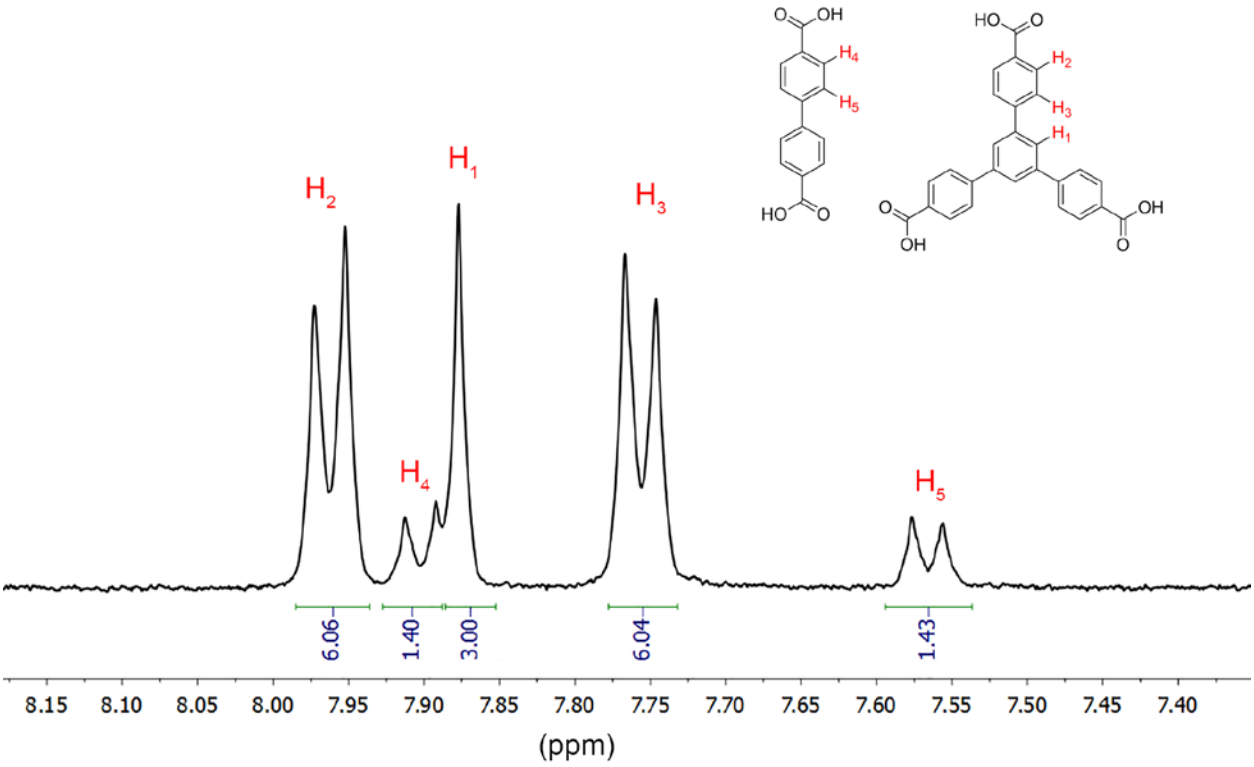

Figure S3. ^{1}H NMR data of digested activated MOF-520-BPDC in d_6-DMSO. The integration ratio suggests the occupancy of BPDC linker to be about 70%.

Powder X-ray diffraction analysis: The activated single crystals were used for PXRD experiment. Ground sample was placed on a quartz sample holder and was mounted on the diffractometer. The data was collected from 2 to 35 degrees by 0.02 step for total 60 minutes data collection time.

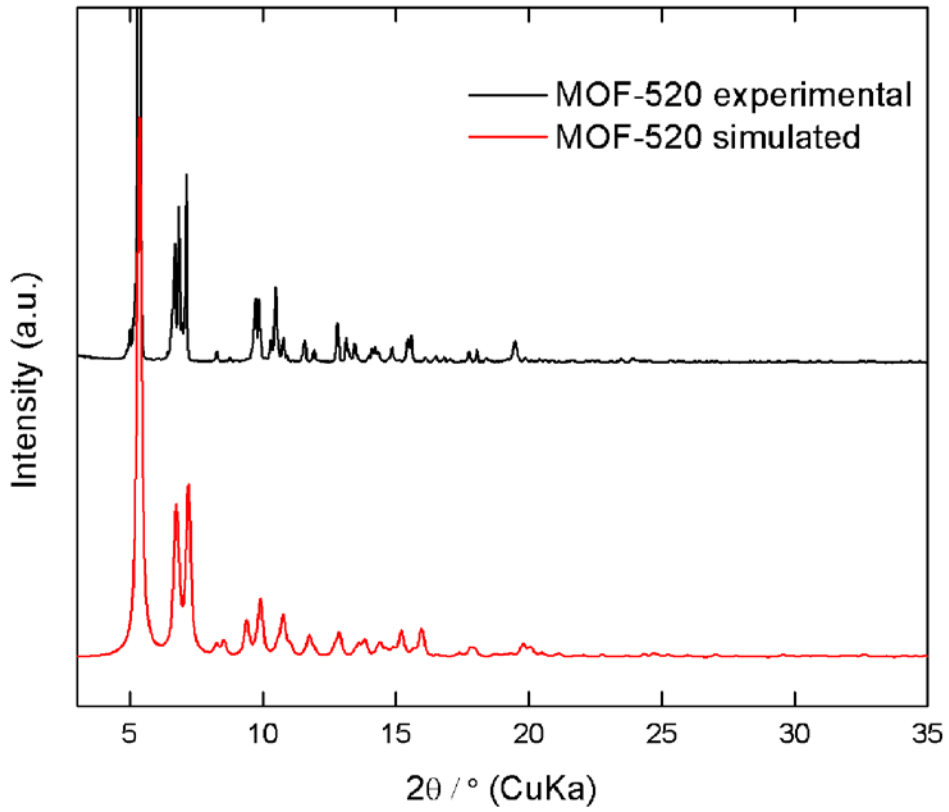

Figure S4. PXRD pattern of activated MOF-520 and the simulated pattern of MOF-520 structure from SXRD data.

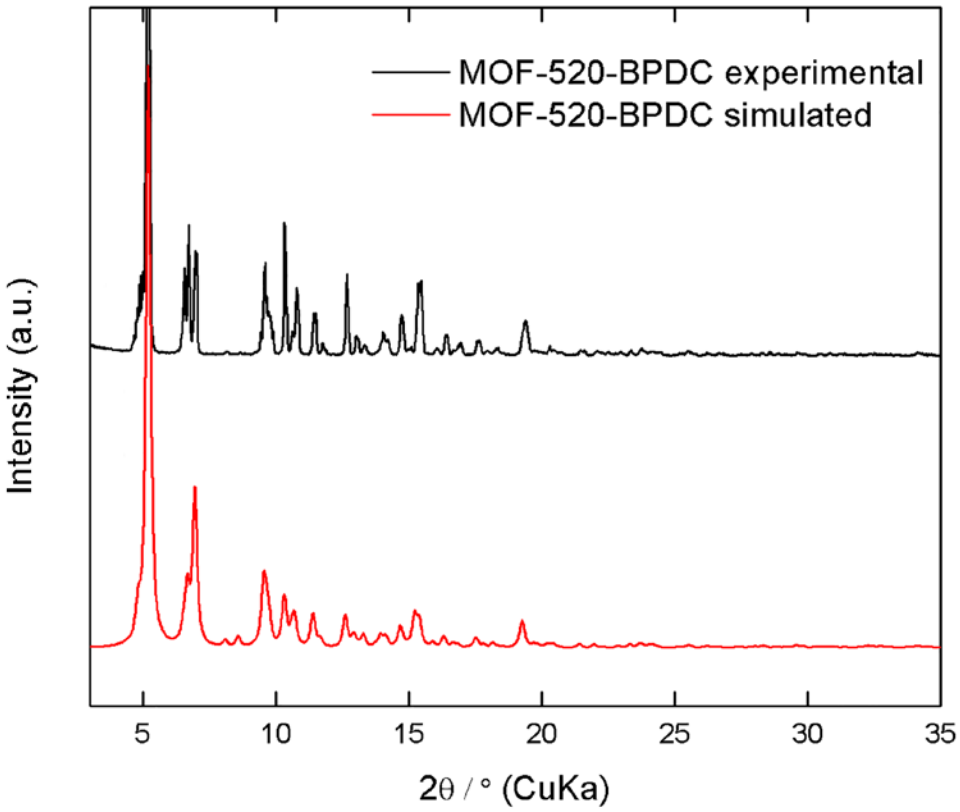

Figure S5. PXRD pattern of activated MOF-520-BPDC and the simulated pattern of MOF-520-BPDC structure from SXRD data.

Elemental analysis: MOF-520 ($Al_8C_{112}H_{72}O_{40}$) Found (wt %): C: 57.86; H: 3.24; N: < 0.2. Calculated (wt %): C: 59.17; H: 3.19; N: 0.0; MOF-520-BPDC ($Al_8C_{136}H_{84}O_{40}$) Found (wt %): C: 61.67; H: 3.36; N: < 0.2. Calculated (wt %): C: 63.46; H: 3.29; N: 0.0.

IR analysis:

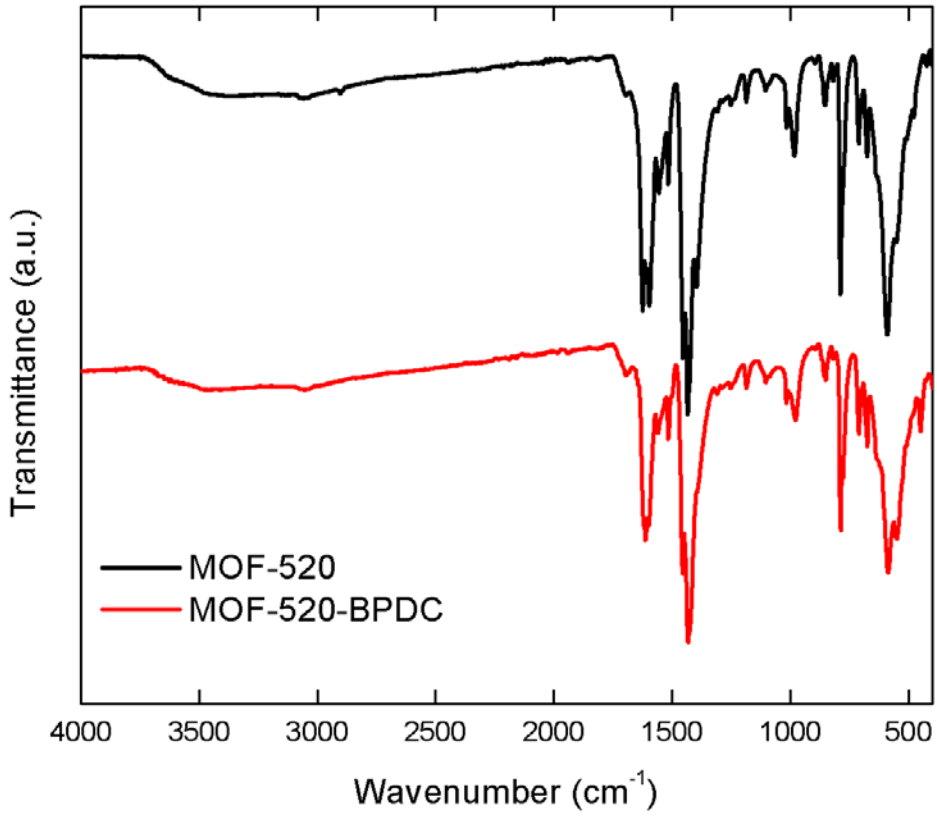

Figure S6. Comparison of activated MOF-520 and MOF-520-BPDC IR spectra.

Single crystal X-ray diffraction analysis at ambient conditions: Single-crystalline samples were mounted on MiTeGen® kapton loops in LV CryoOil®. In all cases, the raw data were processed with the Bruker APEX2 software package. The data were first integrated using the SAINT procedure and then corrected for absorption with SADABS procedure. The structures were solved by direct methods (XS-2008) and the refinement was done by full-matrix least squares on F^2 (SHELXL-2014), using the Olex2 software package (*1-2*). Mercury software was used for structure visualization (*3*).

Δ-MOF-520. A block-shaped crystal (50 x 40 x 40 μm^3) of Δ-MOF-520 a was measured at beamline 11.3.1 at the ALS with radiation of λ = 1.0332 Å. According to intensity statistics table for the whole dataset (PRP file), the resolution was cut off to 0.83 Å. Solvent masking was applied during structure refinement. Before solvent masking instruction, structure was refined anisotropically and hydrogen atoms were placed into positions calculated geometrically. The connected asymmetric unit was defined inside the unit cell: MOVE command was applied to all atoms. The void volume is estimated to be 8963 $Å^3$ with 9196 electrons removed during masking. Some reflections were omitted due to non-ideal solvent masking, beam stop clipping and the minor presence of diffuse scattering. The threshold $(I_{obs}-I_{calc})/\sigma(W)>10$ was chosen for omitting these reflections. Omission of these reflections did not affect the refinement; the fraction of omitted reflections is less than 0.1% of the whole dataset.

Table S1. Crystal data, data collection, and structure refinement parameters for Δ-MOF-520.

Name	Δ-MOF-520
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{28}\ H_{18}\ O_{10}$
Chemical formula of bound molecule	none
Formula mass	568.38
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	18.3754(6)
c, Å	37.6893(12)
V, Å^3	12726.0(9)
d, g cm^{-3}	0.593
μ, mm^{-1}	0.190
Z	8
Measured reflections	107906
Independent reflections	11720
Observed reflections	10185
θ_{min} , º	2.250
θ_{max} , º	38.603
h	-22 to 21
k	-22 to 22
l	-45 to 45
R int	0.0414
$R\ [F^2>2\sigma(F^2)]$	0.0338
$wR(F^2)$	0.01066
S	1.058
Parameters	362
Flack parameter	0.086(15)
$\Delta\rho_{max}$, e Å^{-3}	0.227
$\Delta\rho_{min}$, e Å^{-3}	-0.219
Crystal size, mm^3	0.050 x 0.040 x 0.040
Radiation, Å	1.0332
Temperature, K	100
Pressure, GPa	0.0001

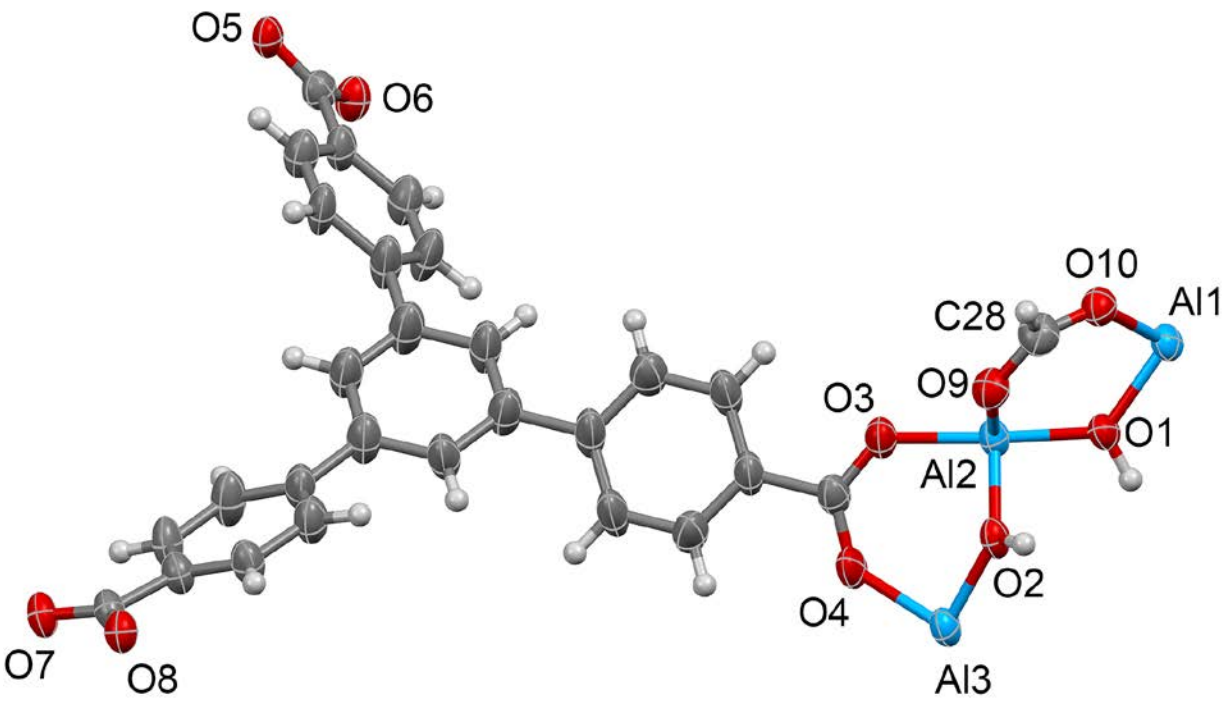

Figure S7. Asymmetric unit in the single crystal structure of Δ-MOF-520. Thermal ellipsoids are drawn with 50% probability. Same numbering scheme is used for all structures of MOF-520 under non-ambient conditions.

Δ-MOF-520-BPDC. A block-shaped crystal (80 x 60 x 60 μm^3) of as-synthesized Δ-MOF-520-BPDC was measured at beamline 11.3.1 at the ALS with radiation of λ = 1.0332 Å. According to intensity statistics table for the whole dataset (PRP file), the resolution was cut off to 0.83 Å. Solvent masking was applied during structure refinement. Before solvent masking instruction, structure was refined anisotropically and hydrogen atoms were placed into positions calculated geometrically. The occupancy of the BPDC linker is 1.0. The connected asymmetric unit was defined inside the unit cell: MOVE command was applied to all atoms. The void volume is estimated to be 9052.2 $Å^3$ with 5819.9 electrons removed during masking. Some reflections were omitted due to non-ideal solvent masking, beam stop clipping and the minor presence of diffuse scattering. The threshold $(I_{obs}-I_{calc})/\sigma(W)>10$ was chosen for omitting these reflections. Omission of these reflections did not affect the refinement; the fraction of omitted reflections is less than 0.1% of the whole dataset.

Table S2. Crystal data, data collection, and structure refinement parameters for Δ-MOF-520-BPDC.

Name	Δ-MOF-520-BPDC
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{34}\ H_{21}\ O_{10}$
Formula mass	643.47
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.1813(7)
c, Å	36.6658(13)
V, $Å^3$	13490.2(11)
d, g cm^{-3}	0.634
μ, mm^{-1}	0.190
Z	8

Measured reflections	46877
Independent reflections	11988
Observed reflections	10083
θ_{min} , º	2.183
θ_{max} , º	38.564
h	-18 to 23
k	-23 to 22
l	-43 to 37
R int	0.0335
R [F^2>2σ(F^2)]	0.0315
wR(F^2)	0.0732
S	1.045
Parameters	424
Flack parameter	0.08(2)
$\Delta\rho_{max}$, e Å^{-3}	0.174
$\Delta\rho_{min}$, e Å^{-3}	-0.179
Crystal size, mm^3	0.080 x 0.060 x 0.060
Radiation, Å	1.0332
Temperature, K	100
Pressure, GPa	0.0001

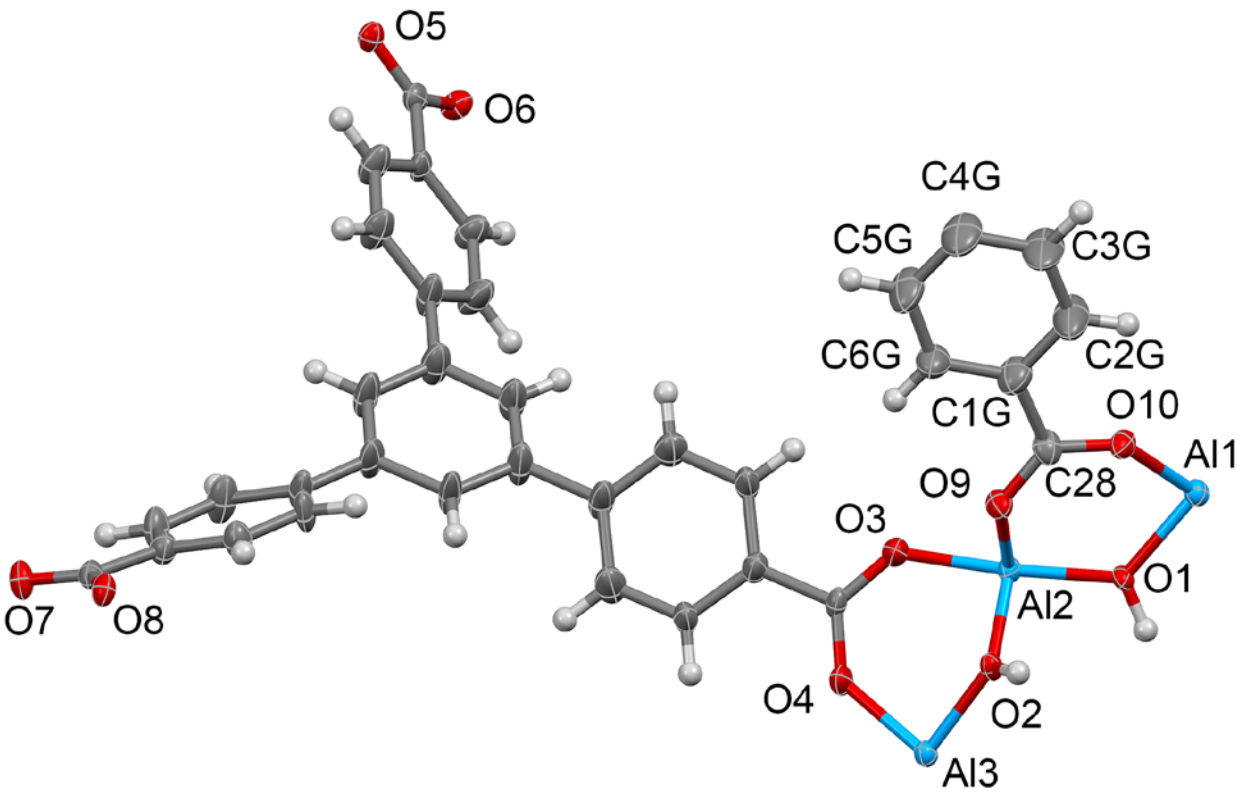

Figure S8. Asymmetric unit in the single crystal structure of Δ-MOF-520-BPDC. Thermal ellipsoids are drawn with 50% probability. Same numbering scheme is used for all structures of MOF-520-BPDC under non-ambient conditions.

Section S4: High-pressure single-crystal diffraction setup and data collection procedure. PASCal calculations procedure.

The X-ray diffraction studies of MOF-520 and MOF-520-BPDC at variable pressure were performed on a single crystal samples. The samples of 0.040 x 0.040 x 0.030 mm^3 were loaded into a Merrill-Bassett-type diamond anvil cell (DAC) with Boehler-Almax cut diamonds, with culets of 500 μm and a tungsten gasket with hole diameter of 200 μm. Gasket holes were drilled using an Oxford Lasers Laser mill. A 4:1 methanol/ethanol mixture was used as the hydrostatic pressure medium. Once the single-crystalline sample was fixed on the culet of the diamond in the gasket hole, several rubies were placed next to it, and the pressure/medium was added right before closing the DAC. The pressure calibration was done using the Ruby fluorescence method.

The high-pressure SXRD data was collected using synchrotron radiation (λ = 0.49594 Å) in beamline 12.2.2 of the Advanced Light Source. The beamline is equipped with Perkin-Elmer CMOS detector. The DAC centering procedure and the geometry setup was performed according to literature (*4*). To maximize the data collected, two datasets were collected in the typical experiment: a first ω-scan with a rotation of DAC from the front by 80 ° from -40 to 40 °, and the second ω-scan with a rotation of DAC from the front by 80 ° from 140 to 220 °. The exposure time was adjusted throughout the whole pressure range to achieve the highest possible resolution.

In all cases, the raw data were processed with the Bruker APEX2 software package. In order to find the orientation matrix of the MOF sample, all reflections from both diamonds were removed using cell_now command. The data were integrated using the SAINT procedure; the pre-determined masking procedure was applied. The shielding of the diffraction pattern by the DAC was taken into account by the generation of dynamic masks using Eclipse software (Parsons, Simon. 2010. ECLIPSE – Program for masking high pressure diffraction images and conversion between CCD image formats). The data were then corrected for absorption with SADABS multiscan procedure. The structures were solved by direct methods (XS-2008) and the refinement was done by full-matrix least squares on F^2 (SHELXL-2014), using the Olex2 software package (*2*). Mercury software was used for structure visualization (*3*). The resolution obtained for all samples was limited due to DAC-opening angle and in order to improve the refinement of the model, the resolution was cut off, according to intensity statistics table. DISP command was used to set the f′, f″, and μ values for atoms in the structures.

All geometrical restraints, applied to non-hydrogen atoms are listed in the CIF files as well as on the corresponding table of each structure.

Note that poor quality of the experimental data, including low resolution, non-ideal dynamic masking, overlap with the diamond reflections, overlap with the powder rings from the gasket, results in several alert of A and B level in CheckCif reports. In addition, because of very short wavelength ((λ = 0.49594 Å) and presence of light atoms in the structure, the flack parameter could not be estimated precisely.

A structural model refined at a previous pressure point served as a starting one for the next pressure. The atom positions. Olex2 software was used to monitor the quality of the structural models using convenient graphs. In case of severe distortion of the building units of MOF under pressure, we applied RIGU

restraints to the whole framework. All hydrogen atoms were placed into geometrically calculated positions and refined using a riding model.

The principal axis strain calculations were conducted using PASCal web tool: pascal.chem.ox.ca.uk. The unit cell parameters for MOF-520 and MOF-520-BPDC were used to plot the ellipsoid of compression and to estimate the median compressibility coefficients in TPa^{-1}. Only the regime of compression was used in case of MOF-520. The error of 0.02 or 0.05 GPa in pressure data was used as an input. No error for the unit cell parameters was considered.

The median compressibilities for each principal directions were found from these calculations.

Table S3. Crystal data, data collection, and structure refinement parameters for MOF-520 at 10^{-4} GPa.

Name	MOF-520_10-4 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{28}\ H_{18}\ O_{10}$
Formula mass	568.38
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	18.920(3)
c, Å	37.190(7)
V, Å^3	13313(5)
d, g cm^{-3}	0.567
μ, mm^{-1}	0.029
Z	8
Measured reflections	13052
Independent reflections	5124
Observed reflections	2572
θ_{min} , º	1.062
θ_{max} , º	13.660
h	-17 to 17
k	-17 to 16
l	-30 to 26
R int	0.1343
$R\ [F^2>2\sigma(F^2)]$	0.0407
$wR(F^2)$	0.0737
S	0.672
Parameters	363
Restraints	324
Flack parameter	0.70(13)
$\Delta\rho_{max}$, e Å^{-3}	0.075
$\Delta\rho_{min}$, e Å^{-3}	-0.099
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	0.0001

Table S4. Crystal data, data collection, and structure refinement parameters for MOF-520 at 0.15 GPa.

Name	MOF-520_0.15 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{28}\ H_{18}\ O_{10}$
Formula mass	568.38
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.070(3)
c, Å	36.930(7)
V, Å^3	13430(5)
d, g cm^{-3}	0.563
μ, mm^{-1}	0.029
Z	8
Measured reflections	10435
Independent reflections	4641
Observed reflections	1888
θ_{min} , º	0.839
θ_{max} , º	13.025
h	-16 to 15
k	-17 to 17
l	-32 to 29
R int	0.1067
$R\ [F^2>2\sigma(F^2)]$	0.0628
$wR(F^2)$	0.1628
S	0.922
Parameters	329
Restraints	303
Flack parameter	0.6(7)
$\Delta\rho_{max}$, e Å^{-3}	0.153
$\Delta\rho_{min}$, e Å^{-3}	-0.351
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	0.15

Table S5. Crystal data, data collection, and structure refinement parameters for MOF-520 at 0.86 GPa.

Name	MOF-520_0.86 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{28}\ H_{18}\ O_{10}$
Formula mass	568.38
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.196(3)
c, Å	36.569(7)
V, Å^3	13475(5)
d, g cm^{-3}	0.560
μ, mm^{-1}	0.029
Z	8
Measured reflections	12386
Independent reflections	4730
Observed reflections	3219
θ_{min} , º	0.836
θ_{max} , º	13.027
h	-16 to 15
k	-17 to 16
l	-31 to 30
R int	0.0826
$R\ [F^2>2\sigma(F^2)]$	0.0396
$wR(F^2)$	0.0809
S	0.883
Parameters	362
Restraints	336
Flack parameter	0.50(9)
$\Delta\rho_{max}$, e Å^{-3}	0.097
$\Delta\rho_{min}$, e Å^{-3}	-0.219
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	0.86

Table S6. Crystal data, data collection, and structure refinement parameters for MOF-520 at 1.47 GPa.

Name	MOF-520_1.47 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{28}\ H_{18}\ O_{10}$
Formula mass	568.38
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.182(3)
c, Å	36.534(7)
V, Å^3	13443(5)
d, g cm^{-3}	0.562
μ, mm^{-1}	0.029
Z	8
Measured reflections	9518
Independent reflections	3850
Observed reflections	3381
θ_{min} , º	0.837
θ_{max} , º	11.925
h	-14 to 15
k	-15 to 15
l	-26 to 28
R int	0.0491
R [$F^2>2\sigma(F^2)$]	0.0361
wR(F^2)	0.1009
S	1.062
Parameters	362
Restraints	336
Flack parameter	0.1(3)
$\Delta\rho_{max}$, e Å^{-3}	0.115
$\Delta\rho_{min}$, e Å^{-3}	-0.185
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	1.47

Table S7. Crystal data, data collection, and structure refinement parameters for MOF-520 at 2.24 GPa.

Name	MOF-520_2.24 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{28}\ H_{18}\ O_{10}$
Formula mass	568.38
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.130(3)
c, Å	36.480(7)
V, Å^3	13350(5)
d, g cm^{-3}	0.566
μ, mm^{-1}	0.029
Z	8
Measured reflections	11629
Independent reflections	4366
Observed reflections	3499
θ_{min} , º	0.839
θ_{max} , º	12.449
h	-16 to 16
k	-15 to 15
l	-30 to 28
R int	0.0567
$R\ [F^2>2\sigma(F^2)]$	0.0465
$wR(F^2)$	0.1261
S	0.981
Parameters	362
Restraints	336
Flack parameter	-0.2(3)
$\Delta\rho_{max}$, e Å^{-3}	0.146
$\Delta\rho_{min}$, e Å^{-3}	-0.254
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	2.24

Table S8. Crystal data, data collection, and structure refinement parameters for MOF-520 at 2.82 GPa.

Name	MOF-520_2.82 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{28}\ H_{18}\ O_{10}$
Formula mass	568.38
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.070(3)
c, Å	36.409(7)
V, Å^3	13241(5)
d, g cm^{-3}	0.566
μ, mm^{-1}	0.029
Z	8
Measured reflections	19178
Independent reflections	7050
Observed reflections	3723
θ_{min} , º	0.841
θ_{max} , º	15.130
h	-18 to 19
k	-18 to 18
l	-36 to 35
R int	0.1082
$R\ [F^2>2\sigma(F^2)]$	0.0495
$wR(F^2)$	0.1101
S	0.863
Parameters	362
Restraints	336
Flack parameter	0.4(5)
$\Delta\rho_{max}$, e Å^{-3}	0.155
$\Delta\rho_{min}$, e Å^{-3}	-0.232
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	2.82

Table S9. Crystal data, data collection, and structure refinement parameters for MOF-520-BPDC at 10^{-4} GPa.

Name	MOF-520-BPDC_10-4 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{34}\ H_{21}\ O_{10}$
Formula mass	643.47
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.215(4)
c, Å	36.779(4)
V, Å^3	13580(6)
d, g cm^{-3}	0.629
μ, mm^{-1}	0.031
Z	8
Measured reflections	22070
Independent reflections	7973
Observed reflections	4948
θ_{min} , º	0.834
θ_{max} , º	15.998
h	-21 to 21
k	-9 to 9
l	-40 to 40
R int	0.1141
$R\ [F^2>2\sigma(F^2)]$	0.0404
$wR(F^2)$	0.0745
S	0.763
Parameters	424
Restraints	0
Flack parameter	0.4(5)
$\Delta\rho_{max}$, e Å^{-3}	0.093
$\Delta\rho_{min}$, e Å^{-3}	-0.133
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	0.0001

Table S10. Crystal data, data collection, and structure refinement parameters for MOF-520-BPDC at 0.64 GPa.

Name	MOF-520-BPDC_0.64 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{34}\ H_{21}\ O_{10}$
Formula mass	643.47
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.1965(10)
c, Å	36.699(2)
V, Å^3	13523.9(16)
d, g cm^{-3}	0.632
μ, mm^{-1}	0.031
Z	8
Measured reflections	22120
Independent reflections	9102
Observed reflections	7042
θ_{min} , º	0.835
θ_{max} , º	15.990
h	-21 to 21
k	-19 to 14
l	-38 to 35
R int	0.0642
R [$F^2>2\sigma(F^2)$]	0.0404
wR(F^2)	0.1171
S	1.293
Parameters	424
Restraints	0
Flack parameter	1.6(2)
$\Delta\rho_{max}$, e Å^{-3}	0.925
$\Delta\rho_{min}$, e Å^{-3}	-0.793
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	0.64

Table S11. Crystal data, data collection, and structure refinement parameters for MOF-520-BPDC at 1.12 GPa.

Name	MOF-520-BPDC_1.12 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{34}\ H_{21}\ O_{10}$
Formula mass	643.47
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.185(2)
c, Å	36.720(2)
V, Å^3	13515(3)
d, g cm^{-3}	0.632
μ, mm^{-1}	0.031
Z	8
Measured reflections	21306
Independent reflections	7387
Observed reflections	5614
θ_{min} , º	0.836
θ_{max} , º	15.993
h	-9 to 7
k	-21 to 21
l	-40 to 40
R int	0.0645
R [$F^2>2\sigma(F^2)$]	0.0343
$wR(F^2)$	0.0729
S	0.983
Parameters	416
Restraints	0
Flack parameter	0.8(3)
$\Delta\rho_{max}$, e Å^{-3}	0.087
$\Delta\rho_{min}$, e Å^{-3}	-0.126
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	1.12

Table S12. Crystal data, data collection, and structure refinement parameters for MOF-520-BPDC at 1.67 GPa.

Name	MOF-520-BPDC_1.67 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{34}\ H_{21}\ O_{10}$
Formula mass	643.47
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.156(2)
c, Å	36.710(2)
V, Å^3	13471(3)
d, g cm^{-3}	0.635
μ, mm^{-1}	0.031
Z	8
Measured reflections	22317
Independent reflections	7218
Observed reflections	5599
θ_{min} , º	0.837
θ_{max} , º	15.979
h	-7 to 8
k	-21 to 21
l	-40 to 40
R int	0.0654
R [$F^2>2\sigma(F^2)$]	0.0356
wR(F^2)	0.0855
S	1.007
Parameters	416
Restraints	36
Flack parameter	0.8(3)
$\Delta\rho_{max}$, e Å^{-3}	0.115
$\Delta\rho_{min}$, e Å^{-3}	-0.136
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	1.67

Table S13. Crystal data, data collection, and structure refinement parameters for MOF-520-BPDC at 2.26 GPa.

Name	MOF-520-BPDC_2.26 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{34}\ H_{21}\ O_{10}$
Formula mass	643.47
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.123(2)
c, Å	36.648(2)
V, Å^3	13401(3)
d, g cm^{-3}	0.638
μ, mm^{-1}	0.032
Z	8
Measured reflections	19345
Independent reflections	6198
Observed reflections	4987
θ_{min} , º	0.838
θ_{max} , º	15.124
h	-8 to 7
k	-20 to 20
l	-38 to 38
R int	0.0667
$R\ [F^2>2\sigma(F^2)]$	0.0361
$wR(F^2)$	0.0880
S	0.984
Parameters	416
Restraints	378
Flack parameter	1.1(3)
$\Delta\rho_{max}$, e Å^{-3}	0.125
$\Delta\rho_{min}$, e Å^{-3}	-0.142
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	2.26

Table S14. Crystal data, data collection, and structure refinement parameters for MOF-520-BPDC at 2.86 GPa.

Name	MOF-520-BPDC_2.86 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{34}\ H_{21}\ O_{10}$
Formula mass	643.47
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.086(2)
c, Å	36.593(3)
V, Å^3	13330(3)
d, g cm^{-3}	0.641
μ, mm^{-1}	0.032
Z	8
Measured reflections	16805
Independent reflections	5361
Observed reflections	4642
θ_{min} , º	0.840
θ_{max} , º	14.352
h	-7 to 8
k	-19 to 19
l	-36 to 36
R int	0.0528
R [$F^2>2\sigma(F^2)$]	0.0379
wR(F^2)	0.1037
S	1.062
Parameters	416
Restraints	387
Flack parameter	0.7(2)
$\Delta\rho_{max}$, e Å^{-3}	0.146
$\Delta\rho_{min}$, e Å^{-3}	-0. 169
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	2.86

Table S15. Crystal data, data collection, and structure refinement parameters for MOF-520-BPDC at 4.20 GPa.

Name	MOF-520-BPDC_4.20 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{34}\ H_{21}\ O_{10}$
Formula mass	643.47
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	18.955(4)
c, Å	36.464(4)
V, Å^3	13101(5)
d, g cm^{-3}	0.652
μ, mm^{-1}	0.032
Z	8
Measured reflections	18454
Independent reflections	6609
Observed reflections	4821
θ_{min} , º	0.845
θ_{max} , º	15.134
h	-7 to 9
k	-19 to 19
l	-38 to 38
R int	0.0962
$R\ [F^2>2\sigma(F^2)]$	0.0551
$wR(F^2)$	0.1385
S	0.969
Parameters	416
Restraints	387
Flack parameter	0.3(6)
$\Delta\rho_{max}$, e Å^{-3}	0.178
$\Delta\rho_{min}$, e Å^{-3}	-0.224
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	4.20

Table S16. Crystal data, data collection, and structure refinement parameters for MOF-520-BPDC at 5.33 GPa.

Name	MOF-520-BPDC_5.33 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{34}\ H_{21}\ O_{10}$
Formula mass	643.47
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	18.857(3)
c, Å	36.302(7)
V, Å^3	12909(4)
d, g cm^{-3}	0.662
μ, mm^{-1}	0.033
Z	8
Measured reflections	11848
Independent reflections	4477
Observed reflections	2732
θ_{min} , º	0.849
θ_{max} , º	13.027
h	-17 to 17
k	-9 to 7
l	-32 to 33
R int	0.1199
R [$F^2>2\sigma(F^2)$]	0.0967
wR(F^2)	0.1275
S	0.914
Parameters	416
Restraints	387
Flack parameter	-0.2(8)
$\Delta\rho_{max}$, e Å^{-3}	0.146
$\Delta\rho_{min}$, e Å^{-3}	-0.175
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	5.33

Table S17. Crystal data, data collection, and structure refinement parameters for MOF-520-BPDC at 4.71 GPa.

Name	MOF-520-BPDC_4.71 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{34}\ H_{21}\ O_{10}$
Formula mass	643.47
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	18.933(3)
c, Å	36.424(4)
V, Å^3	13056(4)
d, g cm^{-3}	0.655
μ, mm^{-1}	0.032
Z	8
Measured reflections	18321
Independent reflections	7030
Observed reflections	4836
θ_{min} , º	0.846
θ_{max} , º	15.128
h	-12 to 9
k	-19 to 19
l	-38 to 35
R int	0.0907
R [$F^2>2\sigma(F^2)$]	0.0519
wR(F^2)	0.1226
S	0.935
Parameters	416
Restraints	387
Flack parameter	1.9(5)
$\Delta\rho_{max}$, e Å^{-3}	0.166
$\Delta\rho_{min}$, e Å^{-3}	-0.272
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	4.71

Table S18. Crystal data, data collection, and structure refinement parameters for MOF-520-BPDC at 3.32 GPa.

Name	MOF-520-BPDC_3.32 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{34}\ H_{21}\ O_{10}$
Formula mass	643.47
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.0287(13)
c, Å	36.5400(17)
V, Å^3	13230.8(19)
d, g cm^{-3}	0.646
μ, mm^{-1}	0.032
Z	8
Measured reflections	19092
Independent reflections	6997
Observed reflections	5936
θ_{min} , º	0.846
θ_{max} , º	15.128
h	-20 to 20
k	-8 to 11
l	-38 to 36
R int	0.0514
$R\ [F^2>2\sigma(F^2)]$	0.0508
$wR(F^2)$	0.1443
S	1.084
Parameters	416
Restraints	387
Flack parameter	0.9(2)
$\Delta\rho_{max}$, e Å^{-3}	0.294
$\Delta\rho_{min}$, e Å^{-3}	-0.337
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	3.32

Table S19. Crystal data, data collection, and structure refinement parameters for MOF-520-BPDC at 2.45 GPa.

Name	MOF-520-BPDC_2.45 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{34}\ H_{21}\ O_{10}$
Formula mass	643.47
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.083(4)
c, Å	36.725(7)
V, Å^3	13374(6)
d, g cm^{-3}	0.637
μ, mm^{-1}	0.032
Z	8
Measured reflections	13071
Independent reflections	5012
Observed reflections	3377
θ_{min} , º	0.839
θ_{max} , º	13.031
h	-11 to 13
k	-17 to 17
l	-30 to 33
R int	0.1277
$R\ [F^2>2\sigma(F^2)]$	0.0557
$wR(F^2)$	0.1401
S	0.791
Parameters	416
Restraints	387
Flack parameter	1.1(8)
$\Delta\rho_{max}$, e Å^{-3}	0.179
$\Delta\rho_{min}$, e Å^{-3}	-0.197
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	2.45

Table S20. Crystal data, data collection, and structure refinement parameters for MOF-520-BPDC at 0.32 GPa.

Name	MOF-520-BPDC_0.32 GPa
Chemical composition of MOF per asymmetric unit	$Al_2\ C_{34}\ H_{21}\ O_{10}$
Formula mass	643.47
Crystal system	Tetragonal
Space group	$P4_22_12$
a, Å	19.2263(19)
c, Å	36.708(3)
V, Å^3	13569(3)
d, g cm^{-3}	0.629
μ, mm^{-1}	0.031
Z	8
Measured reflections	17486
Independent reflections	6205
Observed reflections	5044
θ_{min} , º	0.834
θ_{max} , º	14.357
h	-8 to 11
k	-19 to 19
l	-35 to 36
R int	0.0592
$R\ [F^2>2\sigma(F^2)]$	0.0323
$wR(F^2)$	0.0675
S	0.965
Parameters	416
Restraints	0
Flack parameter	0.9(3)
$\Delta\rho_{max}$, e Å^{-3}	0.079
$\Delta\rho_{min}$, e Å^{-3}	-0.091
Crystal size, mm^3	0.040 x 0.040 x 0.030
Radiation, Å	0.49594
Temperature, K	298
Pressure, GPa	0.32

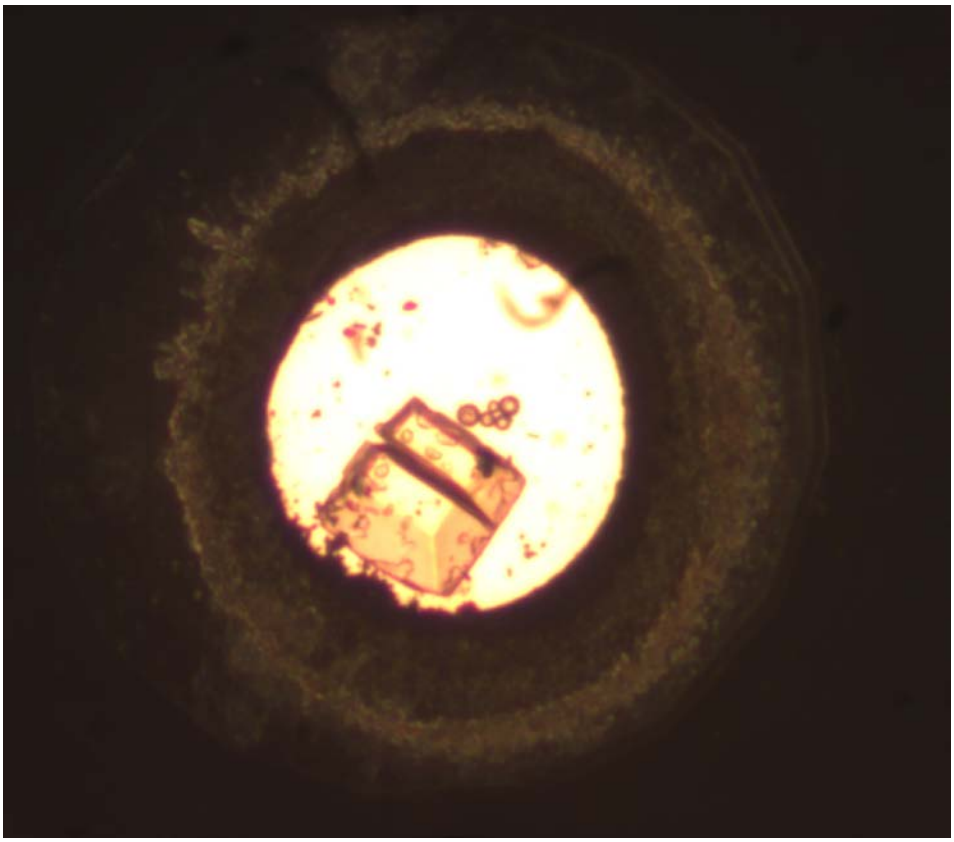

Figure S9. Degradation of pristine MOF-520 single crystal under high pressure. The cracking occurred at pressures higher than 3 GPa. At this point, the sample turned completely amorphous, preserving, however, its crystalline shape.

Section S5: Summary of geometrical parameters for MOF-520 and MOF-520-BPDC under compression

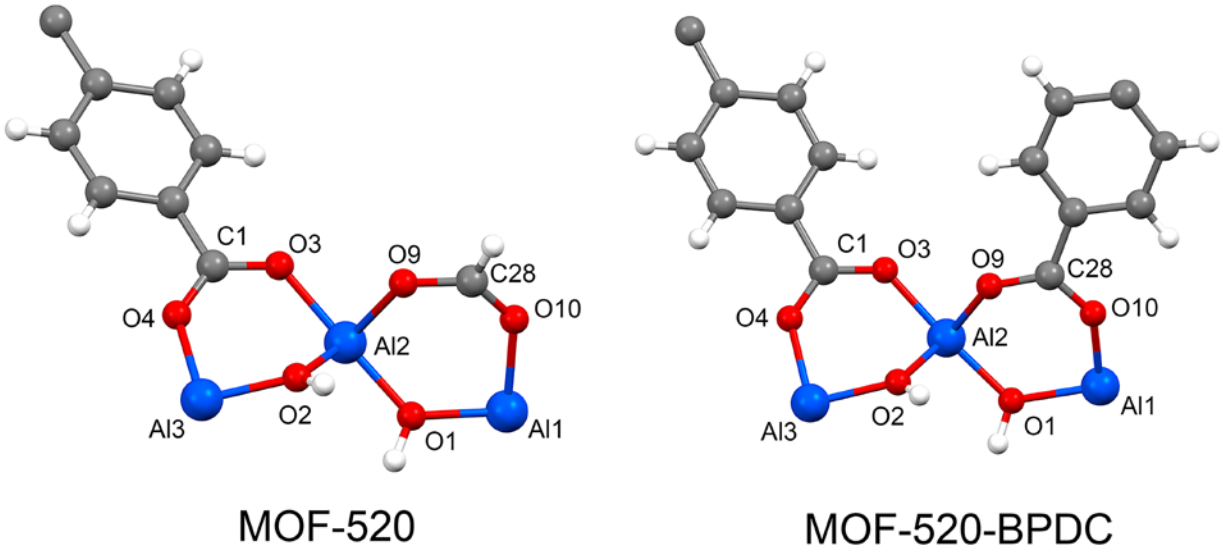

Figure S10. Crystal structures of MOF-520 and MOF-520-BPDC. Selected atoms are labeled for geometrical comparison clarity.

Table S21. List of Al-O bond lengths in the Al-based SBU in MOF-520 and MOF-520-BPDC at selected pressures.

MOF-520 Al-O bond lengths / Å					MOF-520-BPDC Al-O bond lengths / Å				
Pressure / GPa	Al3-O4	Al2-O3	Al2-O9	A1-O10	Pressure / GPa	Al3-O4	Al2-O3	Al2-O9	A1-O10
0.0001	1.907(2)	1.904(2)	1.909(2)	1.945(2)	0.0001	1.921(3)	1.909(3)	1.921(3)	1.881(3)
0.86(2)	1.893(5)	1.901(5)	1.885(4)	1.926(5)	0.64(2)	1.910(7)	1.896(7)	1.941(6)	1.875(6)
1.47(2)	1.888(5)	1.912(5)	1.857(4)	1.914(5)	1.67(2)	1.903(3)	1.920(2)	1.919(3)	1.877(3)
2.81(2)	1.860(4)	1.935(4)	1.878(4)	1.886(4)	2.86(2)	1.919(4)	1.937(3)	1.937(4)	1.878(3)

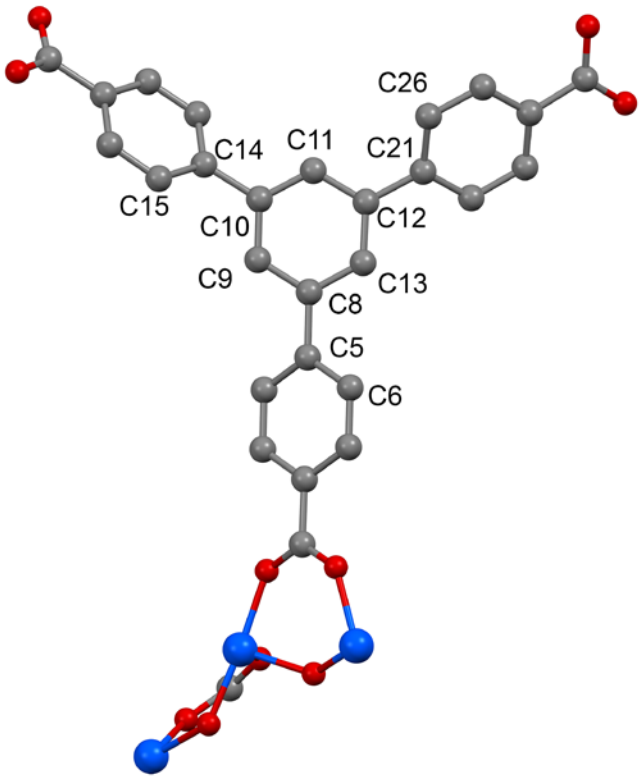

Figure S11. Crystal structures of MOF-520 and MOF-520-BPDC. Selected atoms are labeled for geometrical comparison clarity.

Table S22. List of torsion angles of BTB organic linkers in MOF-520 and MOF-520-BPDC at selected pressures.

MOF-520 BTB linker C-C-C-C torsion angle / °				MOF-520-BPDC BTB linker C-C-C-C torsion angle / °			
Pressure / GPa	6-5-8-13	11-12-21-26	9-10-14-15	Pressure / GPa	6-5-8-13	11-12-21-26	9-10-14-15
0.0001	24.9(3)	31.0(3)	28.5(3)	0.0001	35.9(4)	32.7(4)	42.3(4)
0.86(2)	20(1)	34(1)	25(1)	0.64(2)	35(1)	34(1)	41(1)
1.47(2)	21(1)	33(1)	31(1)	1.67(2)	37(1)	36(1)	33(1)
2.81(2)	27(1)	33(1)	17(1)	2.86(2)	29(1)	41(1)	32(1)

Section S6: References

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