
Supplementary information

An elastic metal–organic crystal with a densely catenated backbone

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Supplementary Information for
An elastic metal–organic crystal with a densely catenated backbone

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1. General and materials

General:

^1H (500 MHz) and ^{13}C (126 MHz) NMR spectra were recorded using a JEOL model JNM-ECA 500II spectrometer. Chemical shifts (δ) are reported in ppm relative to the solvent signal of DMSO ($\delta = 2.50$ ppm, ^1H NMR; $\delta = 39.52$ ppm, ^{13}C NMR) and CHCl_3 ($\delta = 7.26$ ppm, ^1H NMR; $\delta = 77.16$ ppm, ^{13}C NMR).

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurements were carried out using a Bruker Daltonics autoflexTM speed MALDI-TOF/TOF spectrometer utilizing α -cyano-4-hydroxy cinnamic acid (CCA) as the matrix.

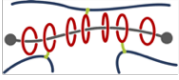
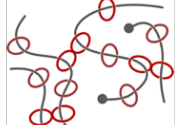
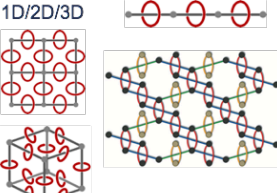
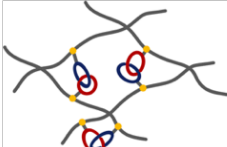
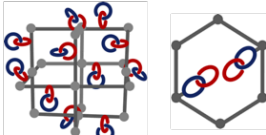
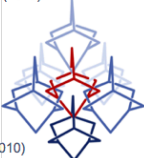
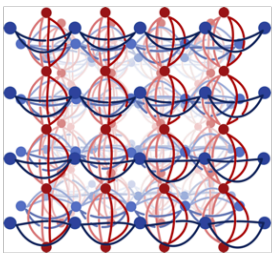
Infrared spectroscopy was performed using a JASCO FT/IR-6600 spectrometer.

Nanoindentation experiments were carried out using an ENT-NEXUS (ELIONIX Inc.) instrument that is capable of performing nanoindentation tests in both dry and liquid environments. Nanoindentations were performed under the load-control mode at 30 °C. The crystals of $^{\text{CTN}}\text{MOF}$, HKUST-1 and $\text{Zn}_2(\text{NO}_2\text{-BDC})_2(\text{DABCO})\cdot\text{DMF}$ (Zn-MOF) were fixed onto a glass plate using a Bi-based fusible alloy (Osaka Asahi Co., Ltd. U-47) to rigidly fix the specimens even in DMF. A diamond indenter tip with a Berkovich geometry was used in the nanoindentation experiments. A maximum load value of 15 mN (except for Zn-MOF where a maximum load of 8 mN^{45(main text reference)} was applied) and a loading/unloading rate of 1.5 mN/s was used for all of the experiments. The holding time at the maximum load was set to 5 s. For $\text{Me}_4^{\text{CTN}}\text{L}$, the measurement was performed using an ENT-1100a (ELIONIX INC.) instrument. The maximum load value was 10 mN, and the loading/unloading rate was 1 mN/s. The holding time at the maximum load was set to 1 s. A value of 0.433¹ was used for Poisson's ratio of the specimen.

Thermogravimetry/mass spectrometry (TG/MS) was performed with a Rigaku Thermo Plus EVO II equipped with ThermoMass Photo/S by using the photoionization (PI) method.

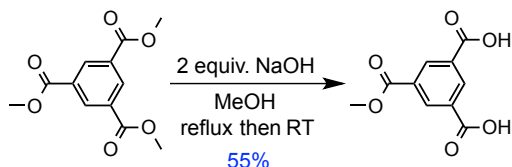
Materials: All reagents were purchased from Aldrich, Tokyo Chemical Industry (TCI) or Wako Pure Chemical Industries and used as received without further purification. A low-melting point (47 °C) alloy was purchased from Osaka Asahi Co., Ltd.

Supplementary Table 1. Comparison between b, this work and a, related works for mechanically interlocked molecule (MIM)-based materials reported previously.

a	Motif	Examples	Features
Rotaxane 	Polymer glass (Polymer binder)	 <i>Science</i> 357 , 279 (2017)	Mechanical bonds are randomly arranged
	Gel	 <i>Polym. J.</i> 44 , 38 (2012)	
	Crystalline solid (Coordination polymer)	1D/2D/3D  <i>Chem. Soc. Rev.</i> 41 , 5896 (2012)	Mechanical bonds are periodically arranged, but no study on the mechanical properties is reported.
Catenane 	Polymer glass	 <i>Chem. Rev.</i> 109 , 6024 (2009), <i>Science</i> 358 , 1434 (2017)	Topological bonds are periodically arranged but randomly oriented
	Gel	 <i>Macromol. Rapid Commun.</i> 39 , 1700361 (2018)	
	Crystalline solid (Coordination polymer)	1D bridged poly[2]catenanes <i>Org. Biomol. Chem.</i> 17 , 2442 (2019)  [2]catenane as an auxiliary <i>Chem. Eur. J.</i> 19 , 8457 (2013) <i>JACS</i> 138 , 14242 (2016) Polycatenated 3D network  <i>Nature Chem.</i> 2 , 461 (2010)	Report on the synthesis only Motions at mechanical bond are independent Difficult to design, relied on serendipitous discovery
b	This work		Features
	[2]catenane  		Topological bonds are arranged and oriented in order Collective motion of mechanical bonds realized Designed formation of polycatenated 3D network Most elastic crystalline metal-organic framework

2. Synthesis

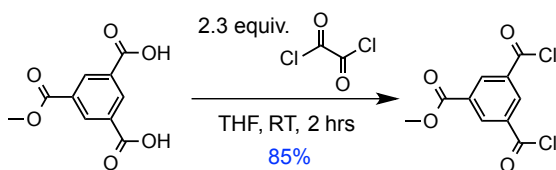
2.1. Synthesis of the ligand



The synthesis of compound 5-(methoxycarbonyl)isophthalic acid was adapted from a literature procedure³:

Trimethyl benzene-1,3,5-tricarboxylate (25.4 g, 0.10 mol, 1 equiv.) and NaOH solution (0.5 M in MeOH, 400 mL, 0.2 mol, 2 equiv.) were mixed in a 500 mL round-bottomed flask. The resulting mixture was heated under reflux at 80 °C for 1 hour and then stirred at 20 °C overnight. Then, the solvent was removed; the residue was dissolved in water and acidified by 1 M HCl first to pH 6. The resulting solution was extracted with EtOAc to remove the mono-acid byproduct. The remaining aqueous solution was subsequently acidified to pH 4 and extracted with EtOAc five times. The organics were combined, dried over MgSO₄ and concentrated. The solid precipitate was filtered and dried under reduced pressure to afford the desired product as a white solid (12.6 g, 55%).

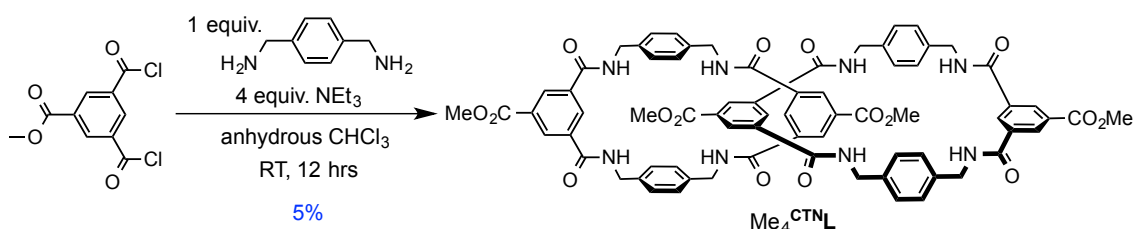
¹H NMR (500 MHz, DMSO-*d*₆): δ (ppm) 8.65 (t, J = 1.0 Hz, 1H, Ph-*H* *para* to CO₂Me), 8.63 (d, J = 2.0 Hz, 1H, Ph-*H* *ortho* to CO₂Me), 3.92 (s, 3H, CH₃). ¹³C NMR (126 MHz, DMSO): δ (ppm) 165.75, 164.86, 133.91, 133.37, 132.07, 130.67, 52.70.



5-(Methoxycarbonyl)isophthalic acid (4 g, 17.8 mmol, 1 equiv.) was dissolved in anhydrous THF (15 mL) in a preoven-dried two-necked 50 mL round-bottomed flask. Ten drops of anhydrous DMF were added to the resulting mixture. Separately, oxalyl chloride (3.5 mL, 41.0 mmol, 2.3 equiv.) was mixed with anhydrous THF (5 mL) in a preoven-dried two-necked 10 mL round-bottomed flask. The mixture containing oxalyl chloride was added dropwise *via* a syringe to the THF solution of 5-

(methoxycarbonyl)isophthalic acid prepared as described above. The reaction mixture was stirred at 20 °C for 1 hour before removing the volatile content under reduced pressure. The residue was washed with a small amount of anhydrous toluene and then anhydrous DCM to afford the desired product, methyl 3,5-bis(chlorocarbonyl)benzoate, (3.98 g, 85%) as an off-white solid. The product was used for the next step without further purification immediately after isolation.

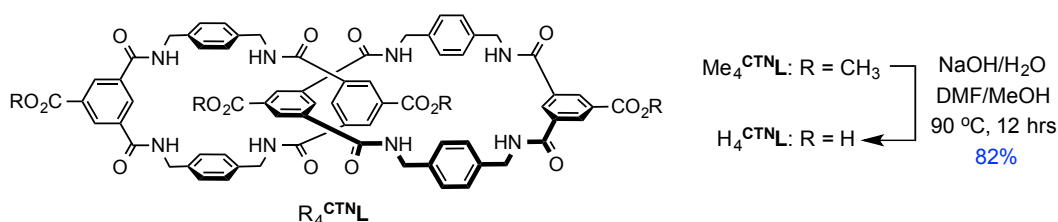
^1H NMR (500 MHz, CDCl_3): δ (ppm) 9.02 (d, $J = 1.5$ Hz, 1H, Ph-*H* *ortho* to CO_2Me), 8.98 (t, $J = 2.0$ Hz, 1H, Ph-*H* *para* to CO_2Me), 4.03 (s, 3H, CH_3). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 166.76, 164.16, 137.58, 136.77, 135.08, 132.76, 53.33.



The synthesis of $\text{Me}_4^{\text{CTNL}}$ was adapted from a literature procedure^{4,5}:

A solution of methyl 3,5-bis(chlorocarbonyl)benzoate in anhydrous CHCl_3 (amylene added 150 ppm, 230 mL, 33 mM) and a solution of 1,4-phenylenedimethanamine in anhydrous CHCl_3 (amylene added 150 ppm, 230 mL, 33 mM, 1 equiv.) were added to a solution of freshly distilled triethylamine in anhydrous CHCl_3 (amylene added 150 ppm, 4.2 mL in 230 mL CHCl_3 , 4 equiv.) *via* a syringe pump over 1 hour. The reaction mixture was stirred at 20 °C for 12 hours. The resulting mixture was then filtered, and the filtrate was concentrated and subjected to silica gel column chromatography (1% to 4% v/v MeOH in CH_2Cl_2 as the eluent). The fractions containing the product were combined and evaporated to dryness. The residue was suspended in DCM, filtered and dried *in vacuo* to afford the product as a white solid (130 mg, 5%) (Supplementary Figs. 2–8 and 16). Single crystals were obtained by layering MeOH on top of a DMF solution of $\text{Me}_4^{\text{CTNL}}$ at room temperature for a few days (Supplementary Fig. 19 and Supplementary Table 4). ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ (ppm) 9.19 (t, 4H, NH), 8.35 (s, 4H, Ph-*H* *ortho* to CO_2Me), 8.20 (t, 4H, NH), 8.10 (s, 4H, Ph-*H* *ortho* to CO_2Me), 7.55 (s, 4H, Ph-*H* *para* to CO_2Me), 7.43 (s, 8H, Ph-*H*), 6.11 (s, 8H, Ph-*H*), 4.38 (d, $J = 5.0$, 8H, CH_2), 3.89 (s, 12H, CH_3), 3.60 (d, $J = 5.0$, 8H, CH_2). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$): δ (ppm) 165.17,

164.62, 138.49, 136.56, 134.94, 134.88, 131.46, 129.72, 129.43, 129.25, 128.78, 127.78, 52.51, 43.37, 42.98. MALDI-TOF-MS: m/z found: 1319.433 ($[M + Na^+]$ calcd: 1319.434).



The synthesis of H_4^{CTNL} :

Me_4^{CTNL} (123 mg, 0.099 mmol, 1 equiv.) was dissolved in DMF (3 mL) and diluted with MeOH (3 mL), and aqueous NaOH solution (5% w/v 1.5 mL, 19 equiv.) was added to the resulting mixture. The resulting reaction mixture was placed above a $90\text{ }^\circ\text{C}$ oil bath and stirred for 12 hours. The volatile content was removed under reduced pressure; the residue was dissolved in water and acidified to pH 2 with 1 M HCl. The precipitate was filtered, washed with water, and dried in vacuo to afford the product as a white solid (117 mg, 82%) (Supplementary Figs. 9–15 and 17). Crystals suitable for single crystal X-ray analysis were obtained by diffusion of water vapor into a DMF solution of H_4^{CTNL} (Supplementary Fig. 18 and Supplementary Table 3).

[Note] When NaOH is used, if the temperature is too high, the compound will decompose. An alternative method can be used based on the reported procedure⁶: Me_4^{CTNL} (65 mg, 0.05 mmol, 1 equiv.) was dissolved in DMF (1.5 mL) in a 30 mL round bottom flask. The mixture was then diluted with THF (3 mL). $LiOH \cdot H_2O$ (42 mg, 1 mmol, 20 equiv.) was added followed by the addition of water (0.5 mL). The reaction mixture was heated at $65\text{ }^\circ\text{C}$ for 24 hours before being concentrated using a rotary evaporator. The residue was diluted with a small amount of water and then the mixture was acidified using diluted HCl to pH 1. The precipitate was collected by filtration, dried at $70\text{ }^\circ\text{C}$ for 1 hour to afford the desired product H_4^{CTNL} as a white solid (47 mg, 76%).

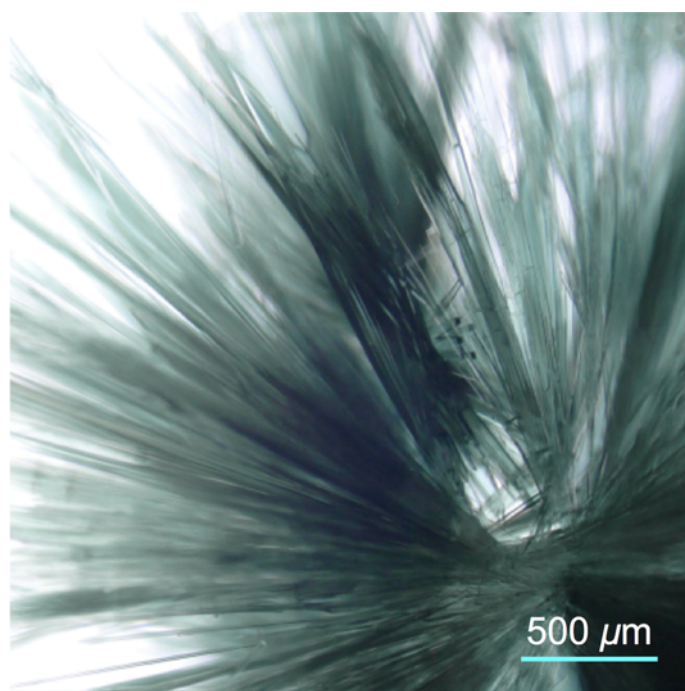
1H NMR (500 MHz, $DMSO-d_6$): δ (ppm) 9.28 (t, 4H, NH), 8.43 (s, 4H, Ph-H *ortho* to CO_2Me), 8.27 (t, 4H, NH), 8.14 (s, 4H, Ph-H *ortho* to CO_2Me), 7.90 (s, 4H, Ph-H *para* to CO_2Me), 7.37 (s, 8H, Ph-H), 5.99 (s, 8H, Ph-H), 4.38 (d, $J = 5.0$, 8H, CH_2), 3.48 (d, J

= 5.0, 8H, CH₂). ¹³C NMR (126 MHz, DMSO-*d*₆): δ (ppm) 166.28, 165.15, 164.98, 138.38, 136.38, 134.72, 134.67, 130.96, 130.84, 130.22, 130.00, 128.95, 127.51, 43.33, 42.62. MALDI-TOF-MS: *m/z* found: 1263.369 ([M + Na⁺] calcd: 1263.371). Elemental analysis: Found: C, 61.56; H, 5.09; N, 8.38%. Calcd. for C₆₈H₅₆N₈O₁₆·5H₂O: C, 61.35; H, 5.00; N, 8.42%.

2.2. Synthesis of ^{CTN}MOF

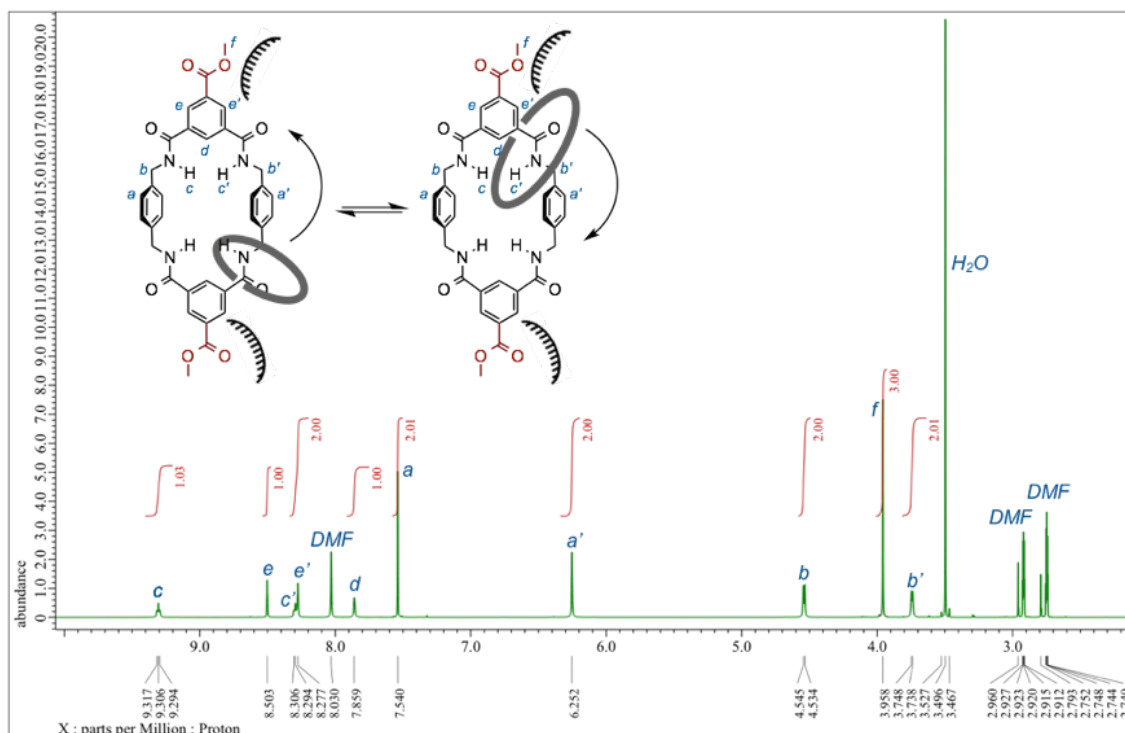
Equal volumes of a solution of H₄^{CTN}L (50 mM in DMF, 100 μL) and a solution of Co(NO₃)₂·6H₂O (400 mM in DMF, 100 μL) were mixed in a glass tube. The resulting mixture was heated at 90 °C for 18 hours. Dark-emerald-green needle-shaped crystals were formed, which were subsequently isolated by filtration (8 mg, 90% based on the formula obtained in the elemental analysis). The green crystal quickly turned pink in the air, which is attributed to the absorption of water. Elemental analysis for the sample dried under vacuum at room temperature for 2 hours: Found: C, 54.32; H, 5.48; N, 9.53%. Calc. for C₆₈H₅₂Co₂N₈O₁₆·7H₂O·4DMF(C₃H₇NO): C, 54.18; H, 5.34; N, 9.48%.

Note on the colour change of ^{CTN}MOF: If exposed to air for a while, as-synthesized ^{CTN}MOF crystals will become pink. A colour change from green to pink will also occur when as-synthesized crystals are immersed in a solvent such as acetonitrile and hexane. When as-synthesized ^{CTN}MOF crystals are dried under vacuum, they become purple.

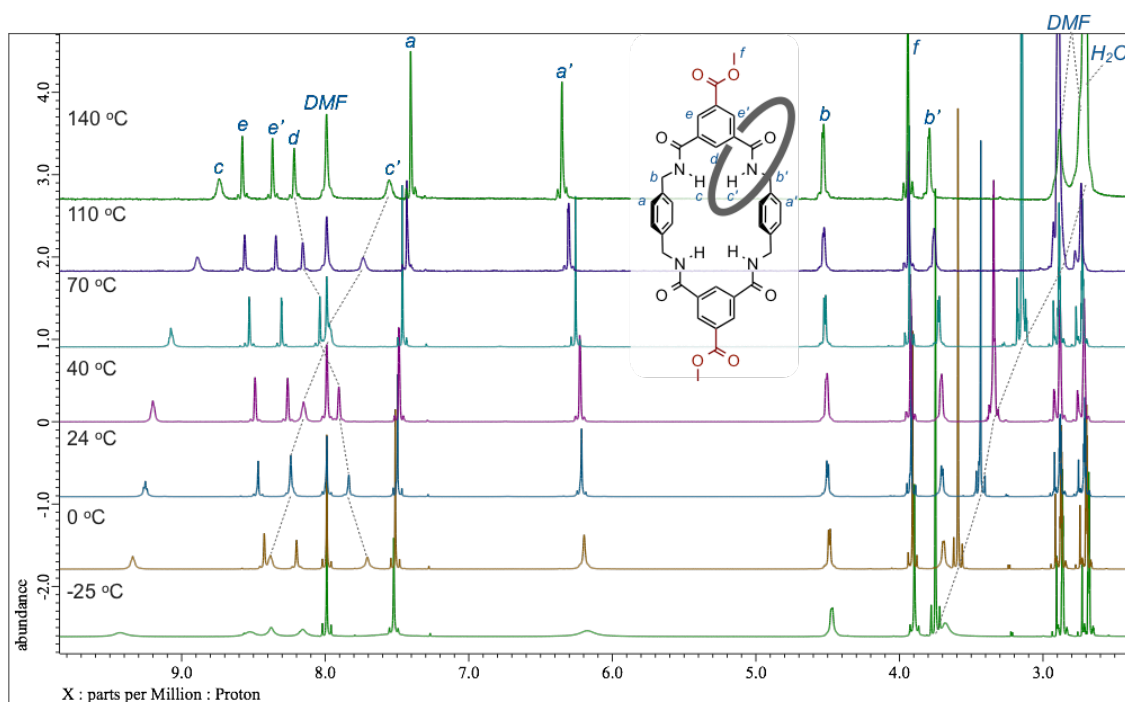


Supplementary Fig. 1. As-synthesized ^{CTN}MOF crystal soaked in DMF.

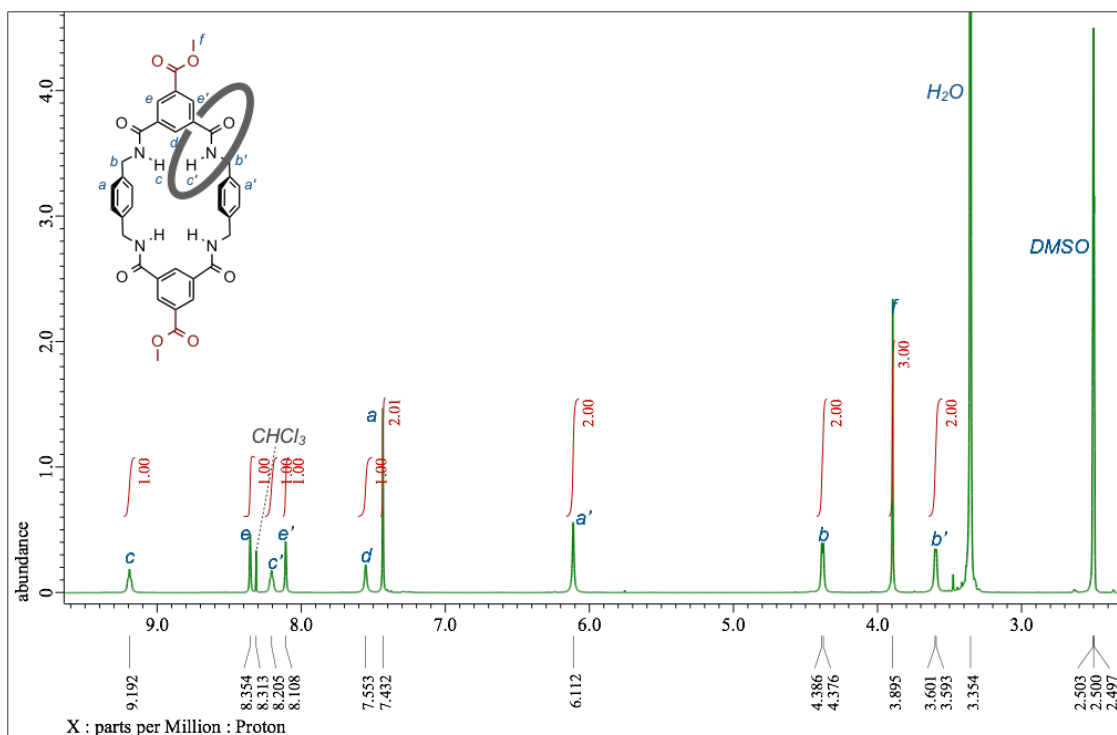
3. NMR spectra



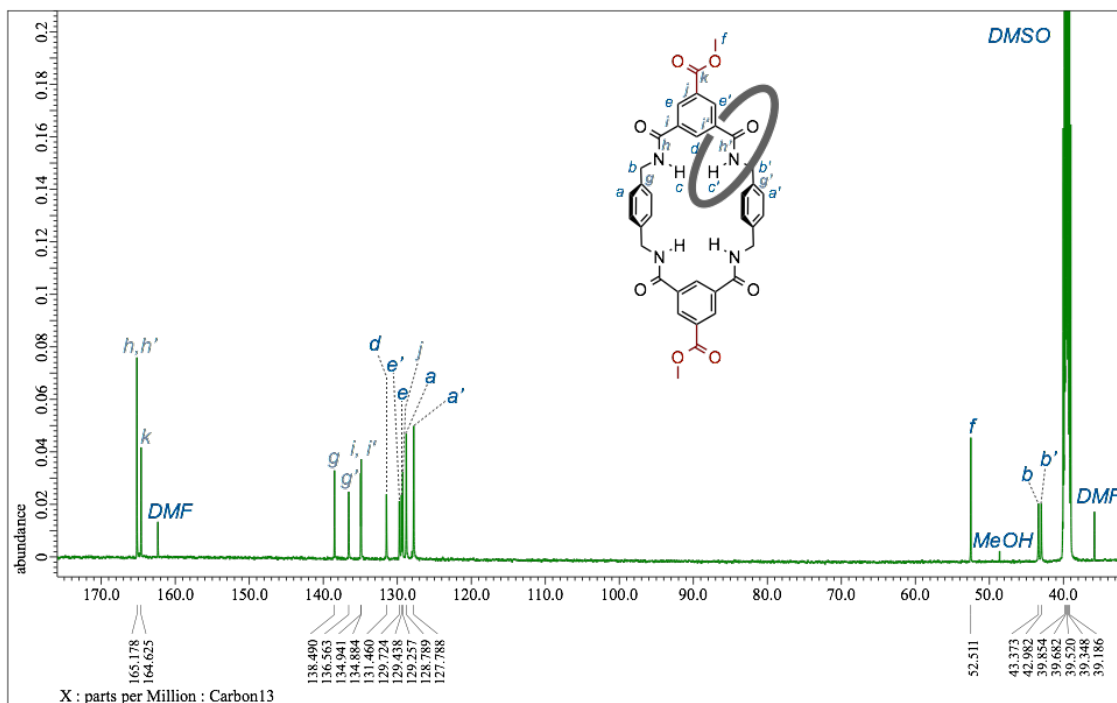
Supplementary Fig. 2. ^1H NMR spectrum of $\text{Me}_4^{\text{CTNL}}$ in DMF-d_7 at 22 °C.



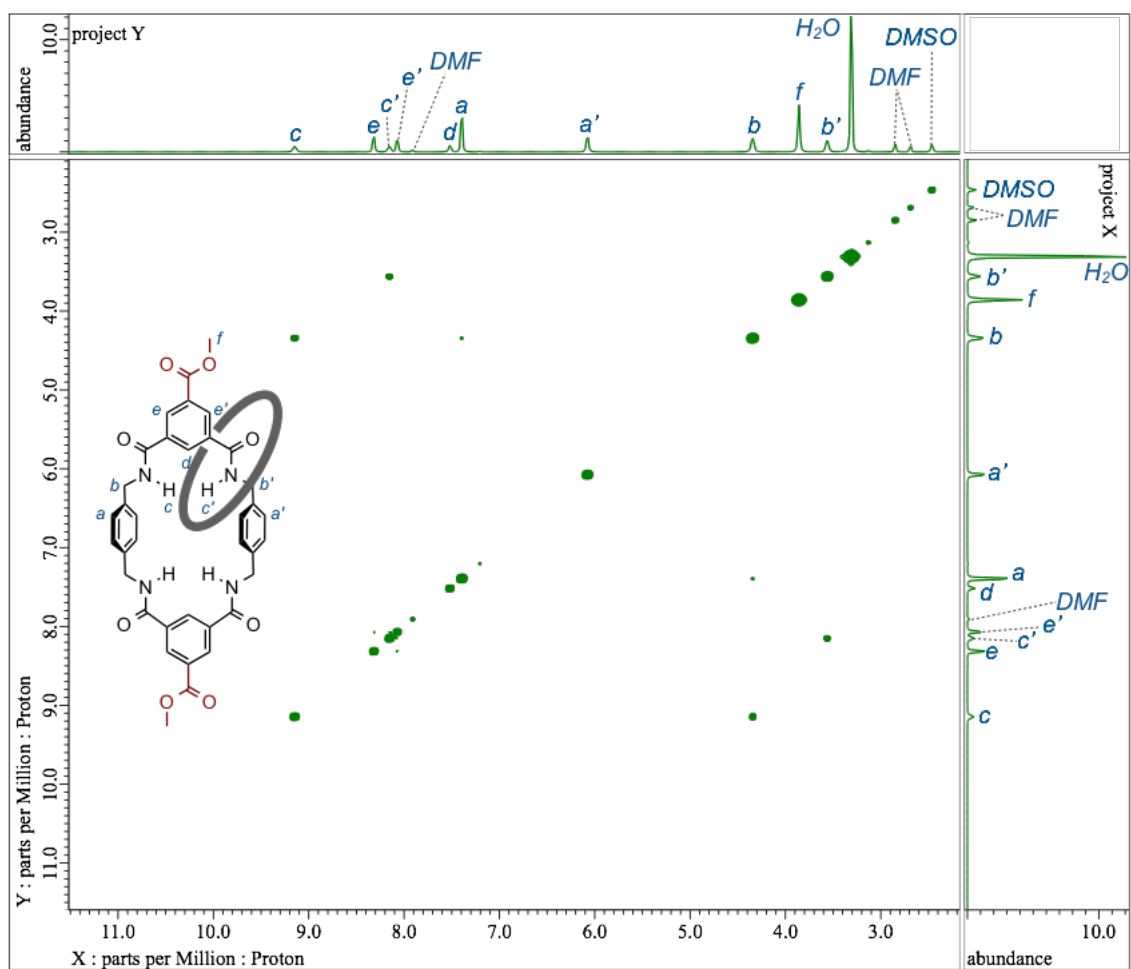
Supplementary Fig. 3. Variable temperature ^1H NMR spectra of $\text{Me}_4^{\text{CTNL}}$ in DMF-d_7 .



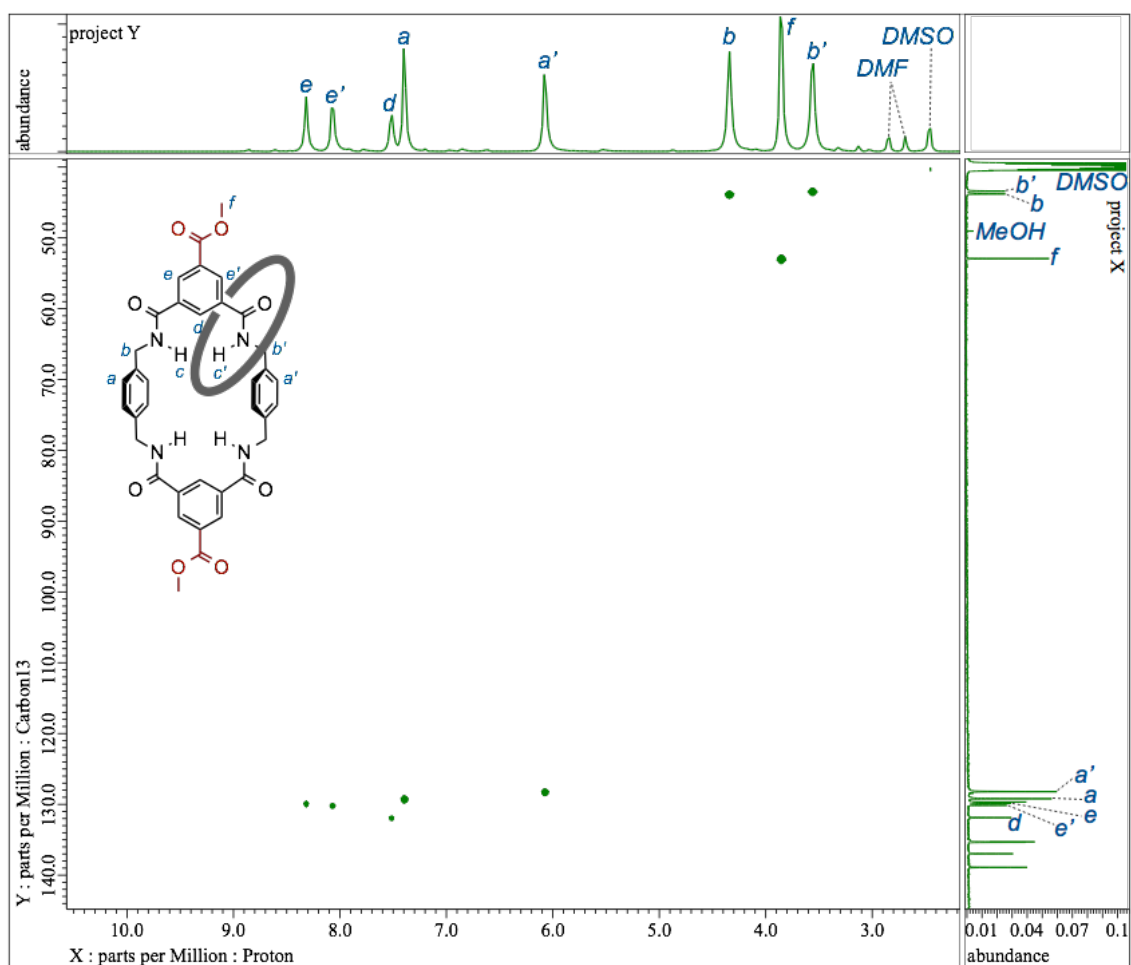
Supplementary Fig. 4. ¹H NMR spectrum of Me₄^{CTN}L in DMSO-*d*₆ at 22 °C.



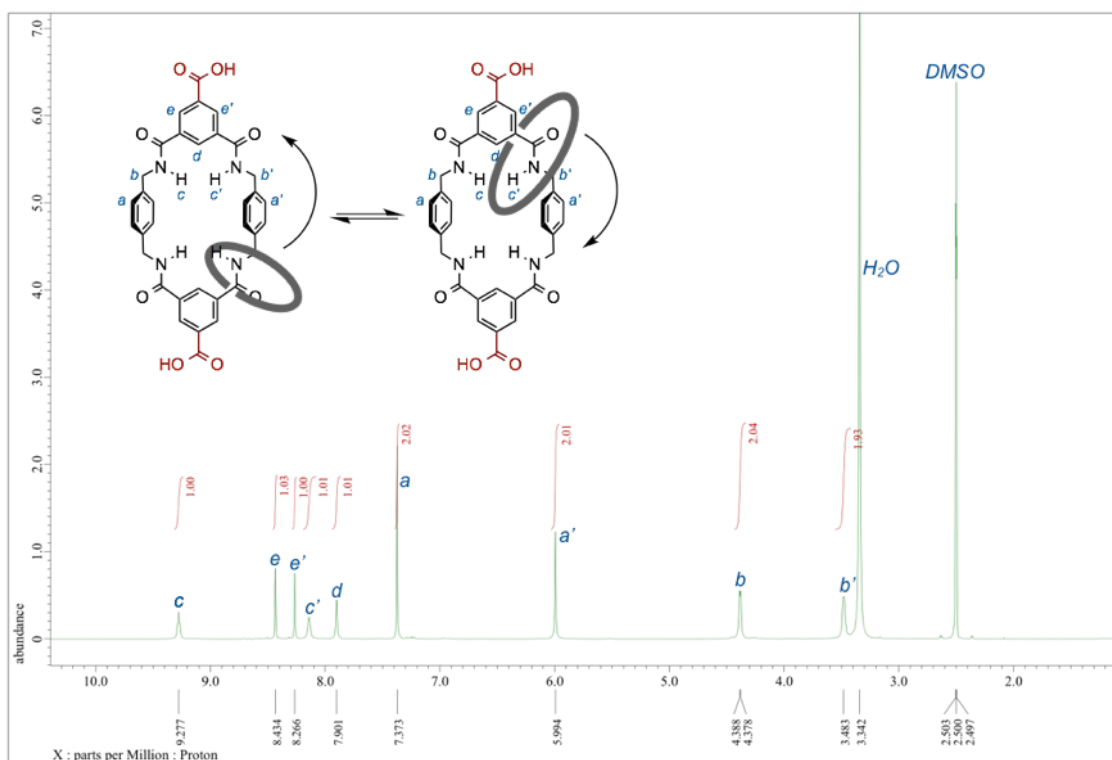
Supplementary Fig. 5. ¹³C NMR spectrum of Me₄^{CTN}L in DMSO-*d*₆ at 22 °C.



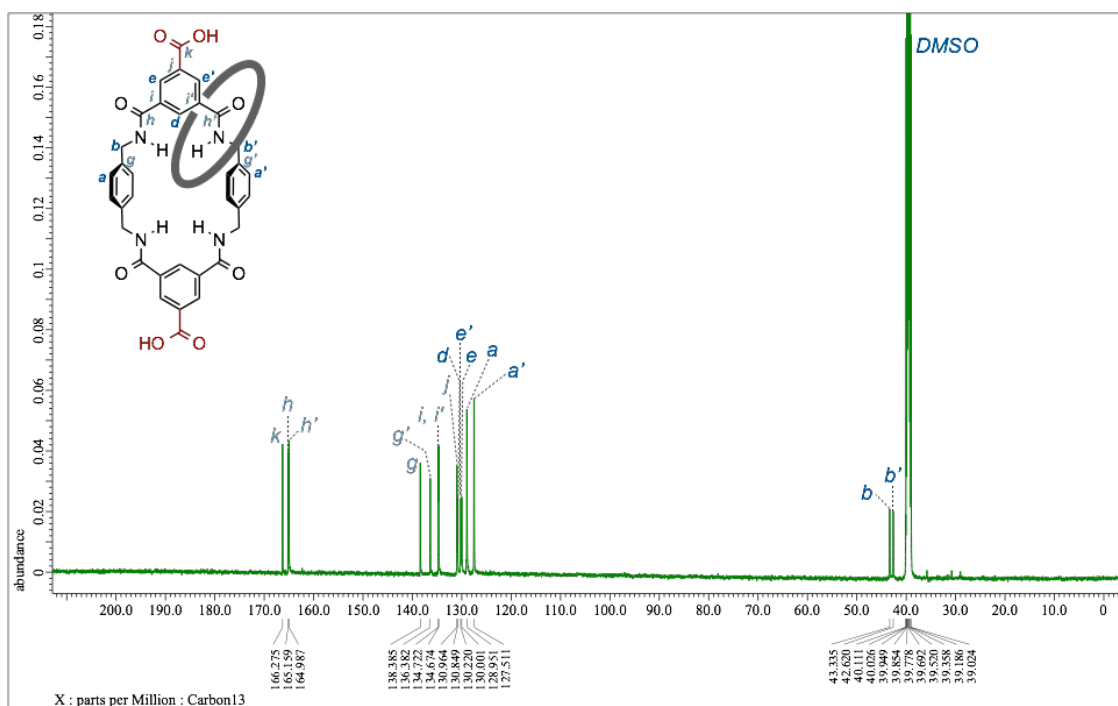
Supplementary Fig. 6. ^1H - ^1H COSY NMR spectrum of $\text{Me}_4^{\text{CTN}}\text{L}$ in $\text{DMSO}-d_6$ at 22°C .



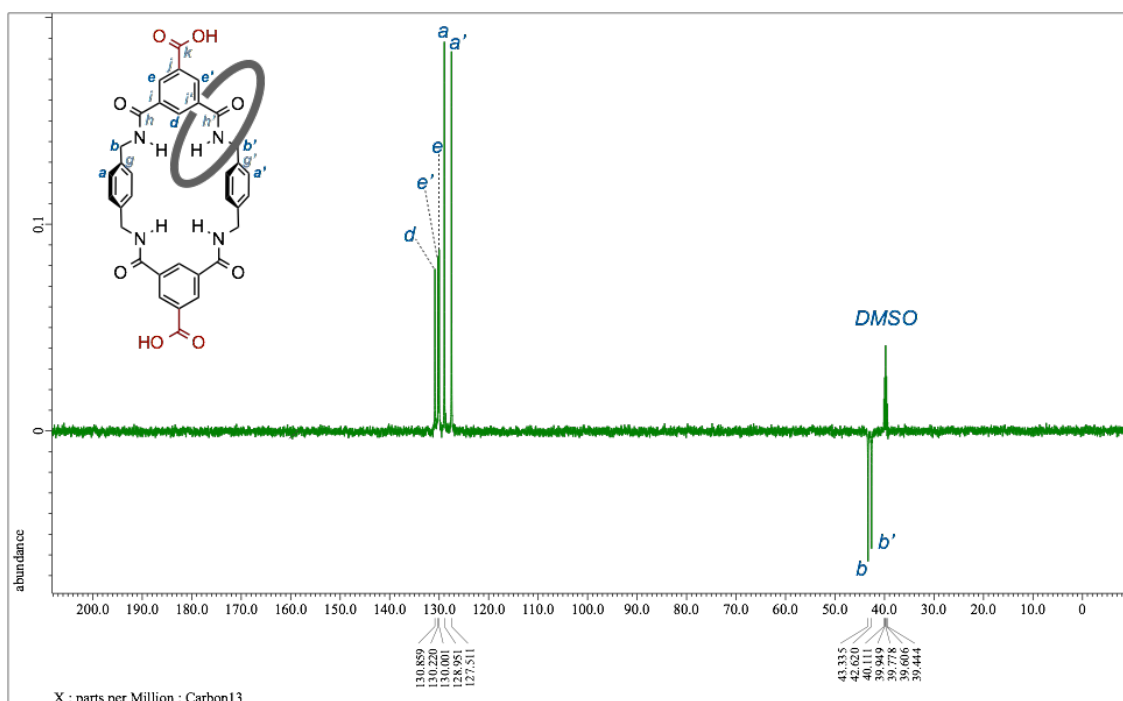
Supplementary Fig. 7. ^1H - ^{13}C HSQC NMR spectrum of $\text{Me}_4^{\text{CTN}}\text{L}$ in $\text{DMSO-}d_6$ at 22 °C.



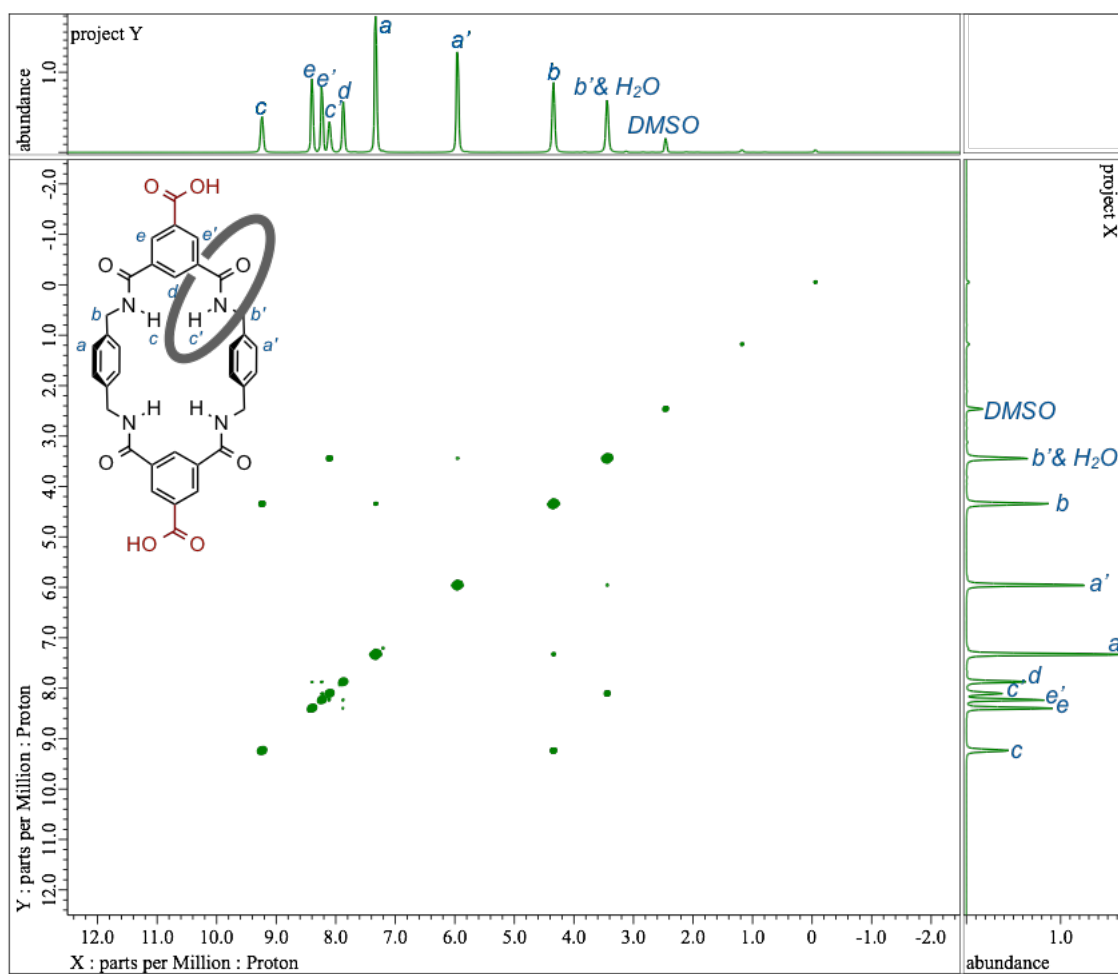
Supplementary Fig. 9. 1H NMR spectrum of $H_4^{CTN}L$ in $DMSO-d_6$ at 22 °C.



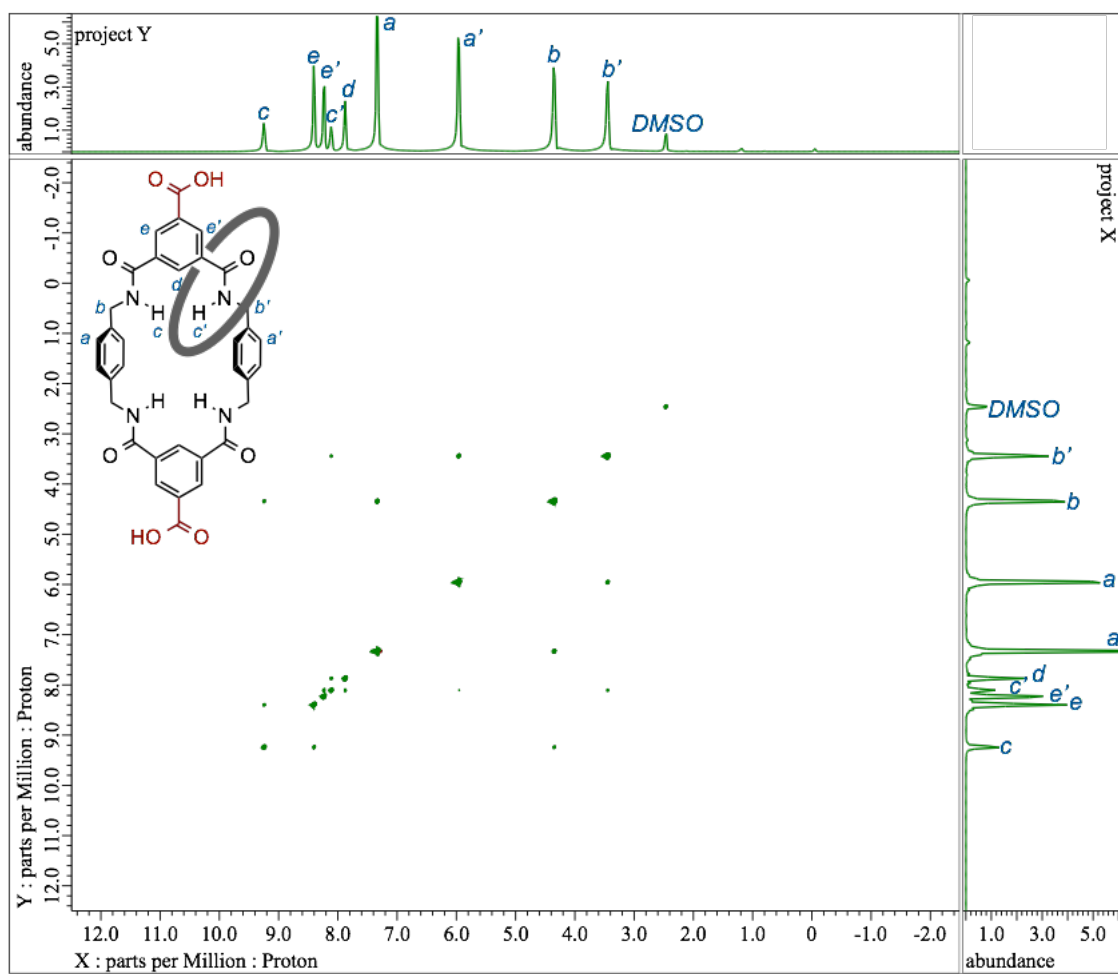
Supplementary Fig. 10. ^{13}C NMR spectrum of $H_4^{CTN}L$ in $DMSO-d_6$ at 22 °C.



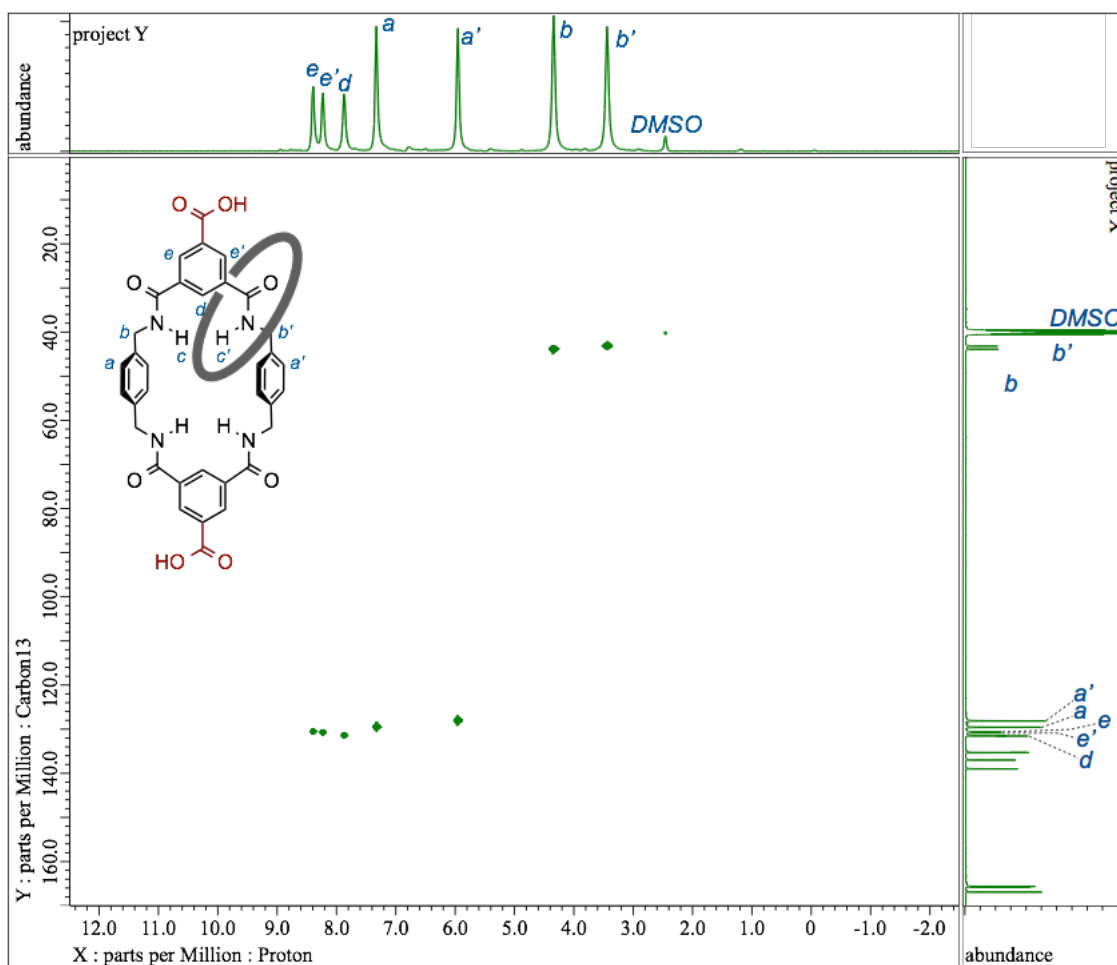
Supplementary Fig. 11. DEPT-135 NMR spectrum of $H_4^{CTN}L$ in $DMSO-d_6$ at 22 °C.



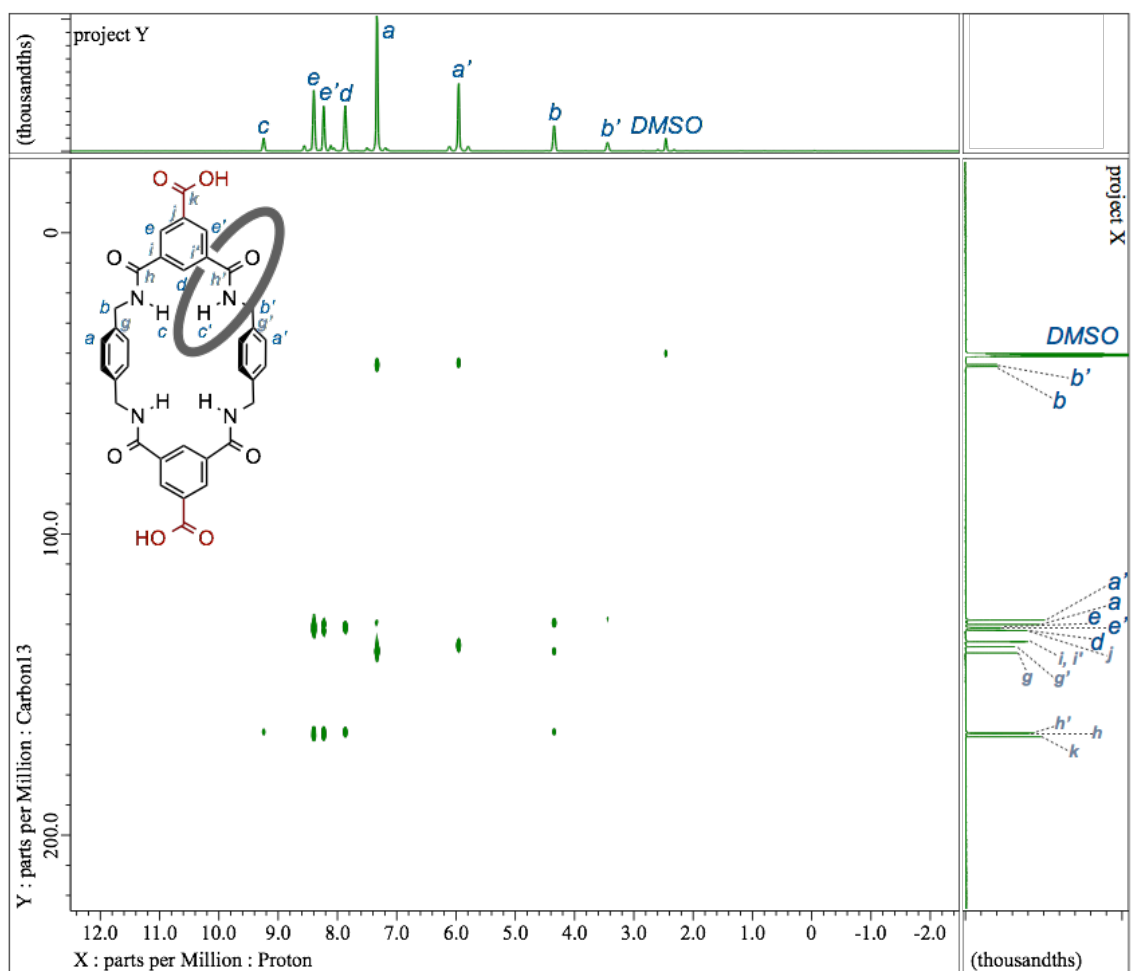
Supplementary Fig. 12. ^1H - ^1H COSY NMR spectrum of H_4^{CTNL} in $\text{DMSO}-d_6$ at 22°C .



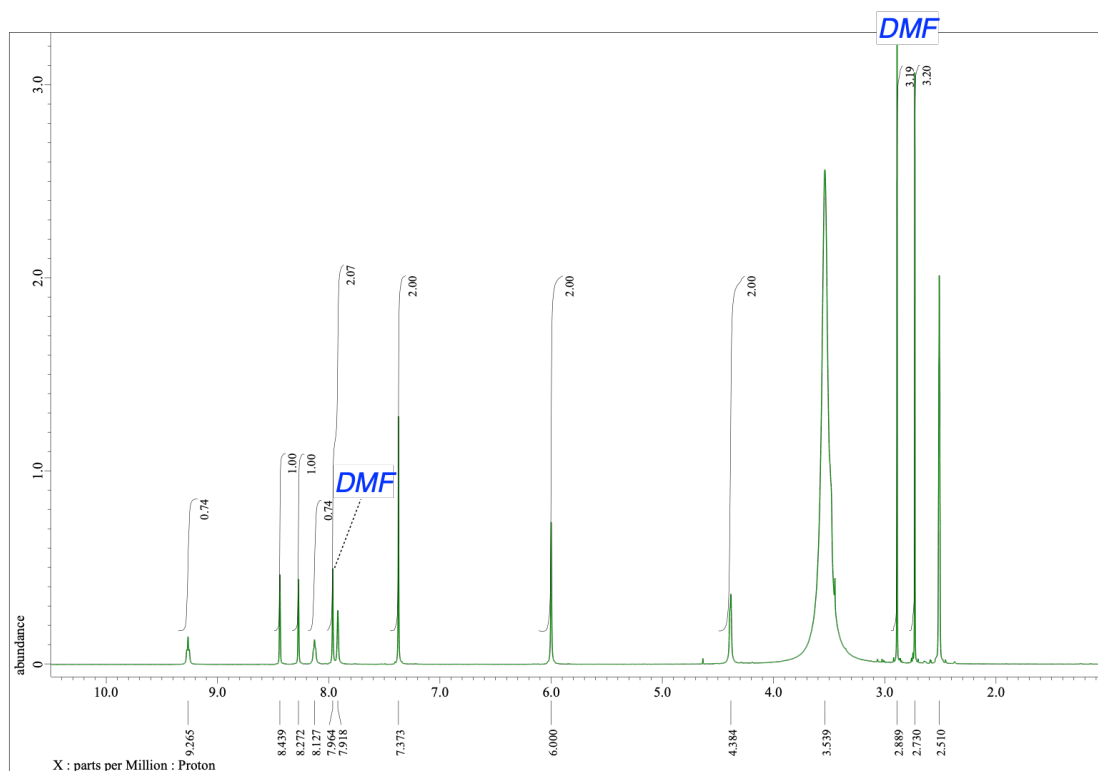
Supplementary Fig. 13. ^1H - ^1H NOESY NMR spectrum of $\text{H}_4^{\text{CTN}}\text{L}$ in $\text{DMSO}-d_6$ at 22°C .



Supplementary Fig. 14. 1H - ^{13}C HSQC NMR spectrum of $H_4^{CTN}L$ in $DMSO-d_6$ at 22 °C.

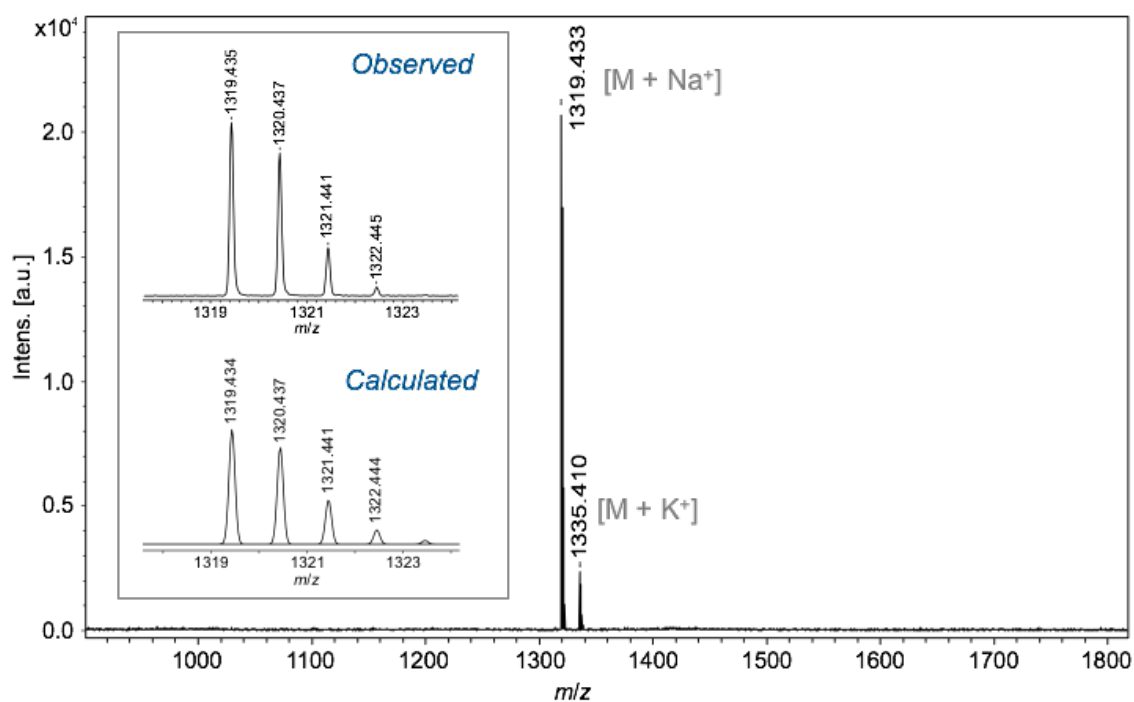


Supplementary Fig. 15. ^1H - ^{13}C HMBC NMR spectrum of $\text{H}_4^{\text{CTN}}\text{L}$ in $\text{DMSO}-d_6$ at 22°C .

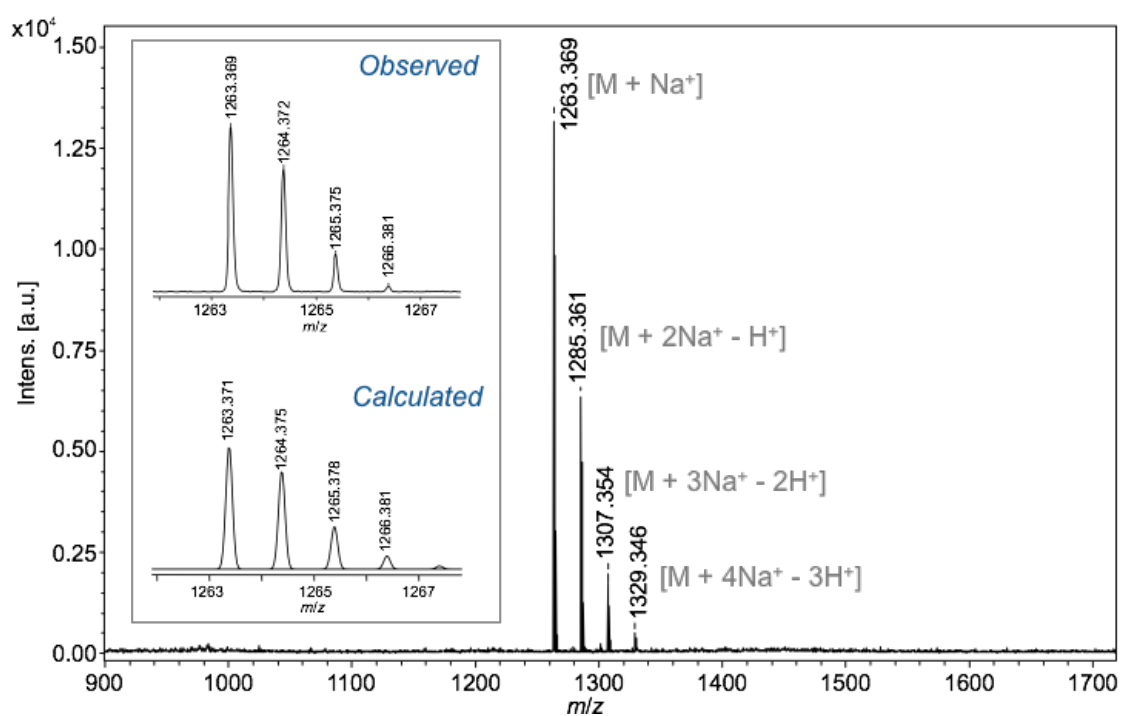


Supplementary Fig. 16. ^1H NMR spectrum of air-dried CTNMOF digested in $\text{DMSO-}d_6/\text{DCI}$ at 22 °C. The integration ratio indicates that there is one molecule of DMF per one ligand molecule.

4. MALDI-TOF-MS spectra



Supplementary Fig. 17. MALDI-MS spectrum of Me₄^{CTN}L.

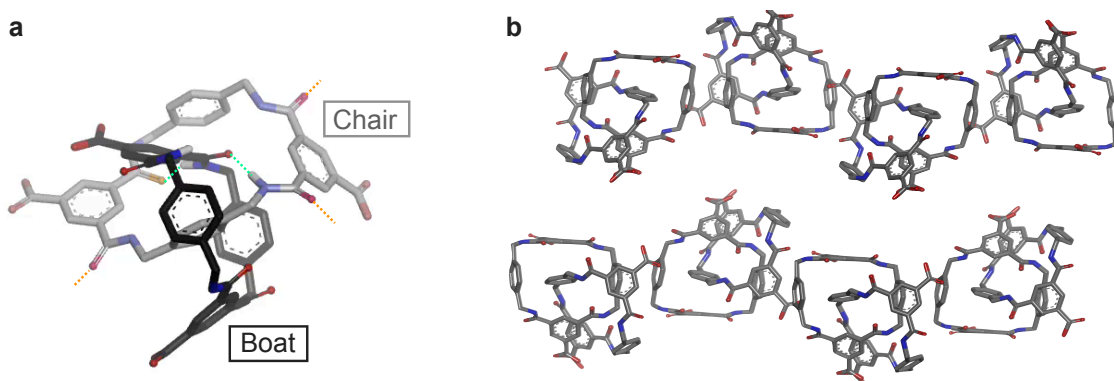


Supplementary Fig. 18. MALDI-MS spectrum of H₄^{CTN}L.

5. Single crystal X-ray crystallography

Supplementary Table 2. Summary of CCDC numbers and the corresponding samples (DAC abbreviates Diamond Anvil Cell).

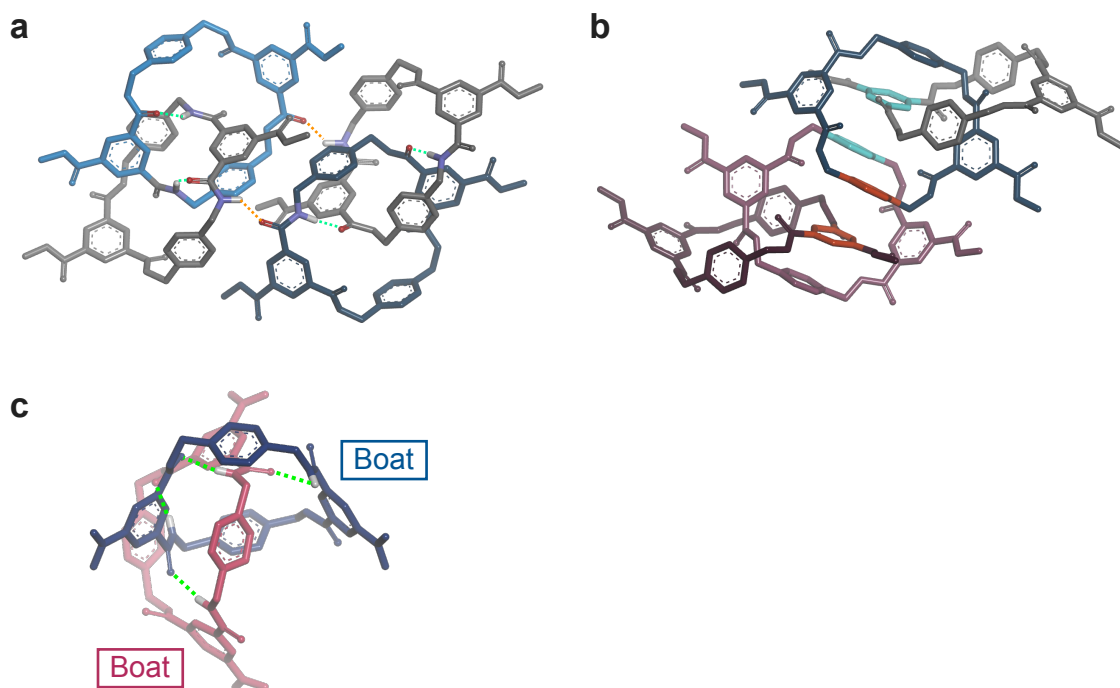
Sample	CCDC number
Me ₄ ^{CTN} L at –180 °C	2080332
H ₄ ^{CTN} L at –180 °C	2080333
^{CTN} MOF at 26 °C in DMF (capillary)	2080334
^{CTN} MOF at –52 °C in DMF	2080245
^{CTN} MOF at –58 °C in DMF	2080246
^{CTN} MOF at –80 °C in DMF	2080247
^{CTN} MOF at –130 °C in DMF	2080336
^{CTN} MOF at –180 °C in DMF	2080335
^{CTN} MOF at –180 °C in EtOH	2080330
^{CTN} MOF DAC 0.28 GPa in DMF	2080270
^{CTN} MOF DAC 0.46 GPa in DMF	2080331



Supplementary Fig. 19. Crystal structure of H₄^{CTN}L. **a**, Boat and chair conformations in the catenane unit. The green and orange dotted lines indicate intramolecular and intermolecular hydrogen bonds, respectively, observed in the solid state. **b**, Layered packing of the catenane molecules in the solid.

Supplementary Table 3. Crystal data for H₄^{CTN}L obtained at –180 °C.

Empirical Formula	C ₃₄ H ₂₈ N ₄ O ₈
Formula Weight	620.62
Temperature	93 K
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.200 × 0.200 × 0.200 mm
Crystal System	monoclinic
Space Group	<i>P</i> 2 ₁ /n (#14)
Lattice Parameters	$a = 9.539(3) \text{ \AA}$ $b = 33.830(10) \text{ \AA}$ $c = 25.724(7) \text{ \AA}$ $\alpha = \gamma = 90^\circ, \beta = 97.220(5)^\circ$
Volume	$V = 8235 (4) \text{ \AA}^3$
Z value	8
$\mu(\text{MoK}\alpha)$	0.725 cm^{-1}
D_{calc}	1.001 g/cm^3
$F(000)$	2592
Transmission factors _{min, max}	0.796, 0.986
$2\theta_{\text{max}}$	56.3
hkl_{max}	12, 44, 32
R_{int}	0.1446
No. Observations (All reflections)	18823
No. Variables	833
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.1342
Residuals: R (All reflections)	0.2016
Residuals: wR_2 (All reflections)	0.3632
Goodness of Fit Indicator	1.148
Data completeness	0.981
$\Delta\rho_{\text{min, max}}$	$-0.34, 0.37 \text{ e}^-/\text{\AA}^3$



Supplementary Fig. 20. Crystal structure of $\text{Me}_4^{\text{CTN}}\text{L}$. The two macrocycles in one catenane unit are crystallographically equivalent. **a**, Top view, where the green and orange dotted lines indicate intramolecular and intermolecular hydrogen bonds, respectively, observed in the solid state. **b**, Side view showing that the macrocycle adopts a chair conformation and also the π - π interactions between the two neighboring catenane units. The distance between stacking benzene rings is approximately 3.1 Å. **c**, Catenane unit observed in CTNMOF with the intramolecular hydrogen bonds shown as dotted lines. Hydrogen atoms except those involved in hydrogen bonds shown in (**a**) are omitted for clarity.

Supplementary Table 4. Crystal data for Me₄^{CTN}L obtained at –180 °C.

Empirical Formula	C ₃₆ H ₃₂ N ₄ O ₈
Formula Weight	648.67
Temperature	93 K
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.100 × 0.060 × 0.050 mm
Crystal System	monoclinic
Space Group	<i>C</i> 2/ <i>c</i> (#15)
Lattice Parameters	$a = 28.1390(0) \text{ \AA}$ $b = 15.5212(0) \text{ \AA}$ $c = 18.8716(0) \text{ \AA}$ $\alpha = \gamma = 90^\circ, \beta = 124.4550(0)^\circ$
Volume	$V = 6796.269(70) \text{ \AA}^3$
Z value	8
$\mu(\text{MoK}\alpha)$	0.908 cm ^{–1}
D_{calc}	1.268 g/cm ³
$F(000)$	2720
Transmission factors _{min, max}	0.826, 0.995
$2\theta_{\text{max}}$	54.9
hkl_{max}	36, 20, 24
R_{int}	0.0675
No. Observations (All reflections)	7708
No. Variables	442
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0522
Residuals: R (All reflections)	0.0776
Residuals: wR_2 (All reflections)	0.1429
Goodness of Fit Indicator	0.973
Data completeness	0.989
$\Delta\rho_{\text{min, max}}$	–0.31, 0.33 e [–] /Å ³

***CTN*MOF:**

Supplementary Table 5. Crystal data for *CTN*MOF *P4*₁22 obtained at 26 °C in a capillary.

Empirical Formula	C ₃₄ H ₂₆ CoN ₄ O ₉
Formula Weight	693.53
Temperature	299 K
Crystal Color, Habit	green, prism
Crystal Dimensions	1.200 × 0.250 × 0.150 mm
Crystal System	tetragonal
Space Group	<i>P4</i> ₁ 22 (#91)
Lattice Parameters	$a = 17.5111(2) \text{ \AA}$ $c = 40.0267(8) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume	$V = 12273.7 (3) \text{ \AA}^3$
Z value	8
$\mu(\text{MoK}\alpha)$	3.122 cm ⁻¹
D_{calc}	0.751 g/cm ³
$F(000)$	2856
Transmission factors _{min, max}	0.687, 0.954
$2\theta_{\text{max}}$	57.6
hkl_{max}	22, 23, 54
R_{int}	0.0298
No. Observations (All reflections)	14388
No. Variables	433
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0526
Residuals: R (All reflections)	0.0648
Residuals: wR_2 (All reflections)	0.1609
Goodness of Fit Indicator	1.009
Data completeness	0.988
$\Delta\rho_{\text{min, max}}$	-0.24, 0.85 e ⁻ /Å ³

Supplementary Table 6. Crystal data for ^{CTN}MOF C222₁ obtained at –180 °C.

Empirical Formula	C ₇₁ H ₅₉ Co ₂ N ₉ O ₁₈
Formula Weight	1444.16
Temperature	93 K
Crystal Color, Habit	green, needle
Crystal Dimensions	0.200 × 0.150 × 0.060 mm
Crystal System	orthorhombic
Space Group	C222 ₁ (#20)
Lattice Parameters	$a = 24.1033(0) \text{ \AA}$ $b = 25.5285(0) \text{ \AA}$ $c = 40.1075(0) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume	$V = 24678.99078 \text{ \AA}^3$
Z value	8
$\mu(\text{MoK}\alpha)$	3.124 cm ⁻¹
D_{calc}	0.777 g/cm ³
$F(000)$	5968
Transmission factors _{Smin, max}	0.808, 0.978
$2\theta_{\text{max}}$	54.5
hkl_{max}	30, 32, 51
R_{int}	0.1247
No. Observations (All reflections)	27339
No. Variables	902
Residuals: R_1 ($I > 2.00s(I)$)	0.1031
Residuals: R (All reflections)	0.1387
Residuals: wR_2 (All reflections)	0.2909
Goodness of Fit Indicator	1.046
Data completeness	0.993
$\Delta\rho_{\text{min, max}}$	–0.41, 0.68 e ⁻ /Å ³

Supplementary Table 7. Crystal data for ^{CTN}MOF C222₁ collected at –130 °C after the measurement at –180 °C.

Empirical Formula	C ₆₈ H ₅₉ Co ₂ N ₈ O ₁₈
Formula Weight	1387.07
Temperature	143 K
Crystal Color, Habit	green, needle
Crystal Dimensions	0.250 × 0.120 × 0.080 mm
Crystal System	orthorhombic
Space Group	C222 ₁ (#20)
Lattice Parameters	$a = 23.712(2) \text{ \AA}$ $b = 25.301(2) \text{ \AA}$ $c = 39.735(4) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume	$V = 23839(4) \text{ \AA}^3$
Z value	8
$\mu(\text{MoK}\alpha)$	3.214 cm ^{–1}
D_{calc}	0.773 g/cm ³
$F(000)$	5712
Transmission factors _{Smin, max}	0.707, 0.975
$2\theta_{\text{max}}$	54.7
hkl_{max}	30, 32, 51
R_{int}	0.1609
No. Observations (All reflections)	26780
No. Variables	866
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.1036
Residuals: R (All reflections)	0.1365
Residuals: wR_2 (All reflections)	0.2773
Goodness of Fit Indicator	1.074
Data completeness	0.995
$\Delta\rho_{\text{min, max}}$	–0.49, 0.77 e [–] /Å ³

Supplementary Table 8. Crystal data for ^{CTN}MOF *P4₁2₁2* obtained at –80 °C.

Empirical Formula	C ₈₃ H ₈₇ Co ₂ N ₁₃ O ₂₂
Formula Weight	1736.54
Temperature	193 K
Crystal Color, Habit	green, needle
Crystal Dimensions	0.200 × 0.100 × 0.060 mm
Crystal System	tetragonal
Space Group	<i>P4₁2₁2</i> (#92)
Lattice Parameters	$a = 24.9280(13) \text{ \AA}$ $c = 39.247(2) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume	$V = 24388 (2) \text{ \AA}^3$
Z value	8
$\mu(\text{MoK}\alpha)$	3.280 cm ^{–1}
D_{calc}	0.946 g/cm ³
$F(000)$	7248
Transmission factors _{min, max}	0.829, 0.981
$2\theta_{\text{max}}$	54.8
hkl_{max}	32, 32, 50
R_{int}	0.1213
No. Observations (All reflections)	27612
No. Variables	1082
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.1029
Residuals: R (All reflections)	0.1152
Residuals: wR_2 (All reflections)	0.2447
Goodness of Fit Indicator	1.202
Data completeness	0.995
$\Delta\rho_{\text{min, max}}$	–0.46, 1.29 e [–] /Å ³

Supplementary Table 9. Crystal data for ^{CTN}MOF *P4*₁22 obtained at –58 °C.

Empirical Formula	C ₃₇ H ₃₃ Co ₂ N ₅ O ₉
Formula Weight	750.63
Temperature	215 K
Crystal Color, Habit	green, needle
Crystal Dimensions	0.200 × 0.100 × 0.060 mm
Crystal System	tetragonal
Space Group	<i>P4</i> ₁ 22 (#91)
Lattice Parameters	$a = 17.707(9) \text{ \AA}$ $c = 40.18(2) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume	$V = 12598 (12) \text{ \AA}^3$
Z value	8
$\mu(\text{MoK}\alpha)$	3.078 cm ^{–1}
D_{calc}	0.791 g/cm ³
$F(000)$	3112
Transmission factors _{min, max}	0.852, 0.979
$2\theta_{\text{max}}$	54.6
hkl_{max}	22, 22, 51
R_{int}	0.1288
No. Observations (All reflections)	14156
No. Variables	470
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.1193
Residuals: R (All reflections)	0.1423
Residuals: wR_2 (All reflections)	0.3321
Goodness of Fit Indicator	1.112
Data completeness	0.997
$\Delta\rho_{\text{min, max}}$	–0.48, 0.97 e [–] /Å ³

Supplementary Table 10. Crystal data for ^{CTN}MOF *P2₁2₁2₁* obtained at –52 °C.

Empirical Formula	C ₁₅₄ H ₁₄₆ Co ₄ N ₂₂ O ₃₉
Formula Weight	3164.70
Temperature	221 K
Crystal Color, Habit	green, needle
Crystal Dimensions	0.180 × 0.150 × 0.080 mm
Crystal System	orthorhombic
Space Group	<i>P2₁2₁2₁</i> (#19)
Lattice Parameters	$a = 24.021(9) \text{ \AA}$ $b = 25.336(9) \text{ \AA}$ $c = 39.231(14) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume	$V = 23875 (15) \text{ \AA}^3$
Z value	4
$\mu(\text{MoK}\alpha)$	3.284 cm ^{–1}
D_{calc}	0.880 g/cm ³
$F(000)$	6576
Transmission factors _{Smin, max}	0.660, 0.974
$2\theta_{\text{max}}$	55.0
hkl_{max}	31, 32, 49
R_{int}	0.1358
No. Observations (All reflections)	53043
No. Variables	1973
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.1148
Residuals: R (All reflections)	0.1644
Residuals: wR_2 (All reflections)	0.3294
Goodness of Fit Indicator	1.011
Data completeness	0.989
$\Delta\rho_{\text{min, max}}$	–0.51, 0.84 e [–] /Å ³

Supplementary Table 11. Crystal data for ^{CTN}MOF *P4*₁ obtained at –180 °C.

Empirical Formula	C ₆₈ H ₅₂ Co ₂ N ₈ O ₁₈ •C ₂ H ₆ O
Formula Weight	1433.14
Temperature	93 K
Crystal Color, Habit	green, needle
Crystal Dimensions	0.20 × 0.20 × 0.20 mm
Crystal System	tetragonal
Space Group	<i>P4</i> ₁ (#76)
Lattice Parameters	$a = 16.87060 \text{ \AA}$ $c = 40.02360 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume	$V = 11391.40274 \text{ \AA}^3$
Z value	4
$\mu(\text{MoK}\alpha)$	3.384 cm^{-1}
D_{calc}	0.836 g/cm^3
$F(000)$	2960
Transmission factors _{min, max}	0.686, 0.935
$2\theta_{\text{max}}$	54.9
hkl_{max}	21, 21, 51
R_{int}	0.1448
No. Observations (All reflections)	25273
No. Variables	897
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.1353
Residuals: R (All reflections)	0.1543
Residuals: wR_2 (All reflections)	0.3538
Goodness of Fit Indicator	1.184
Data completeness	0.987
$\Delta\rho_{\text{min, max}}$	$-0.83, 0.79 \text{ e}^-/\text{\AA}^3$

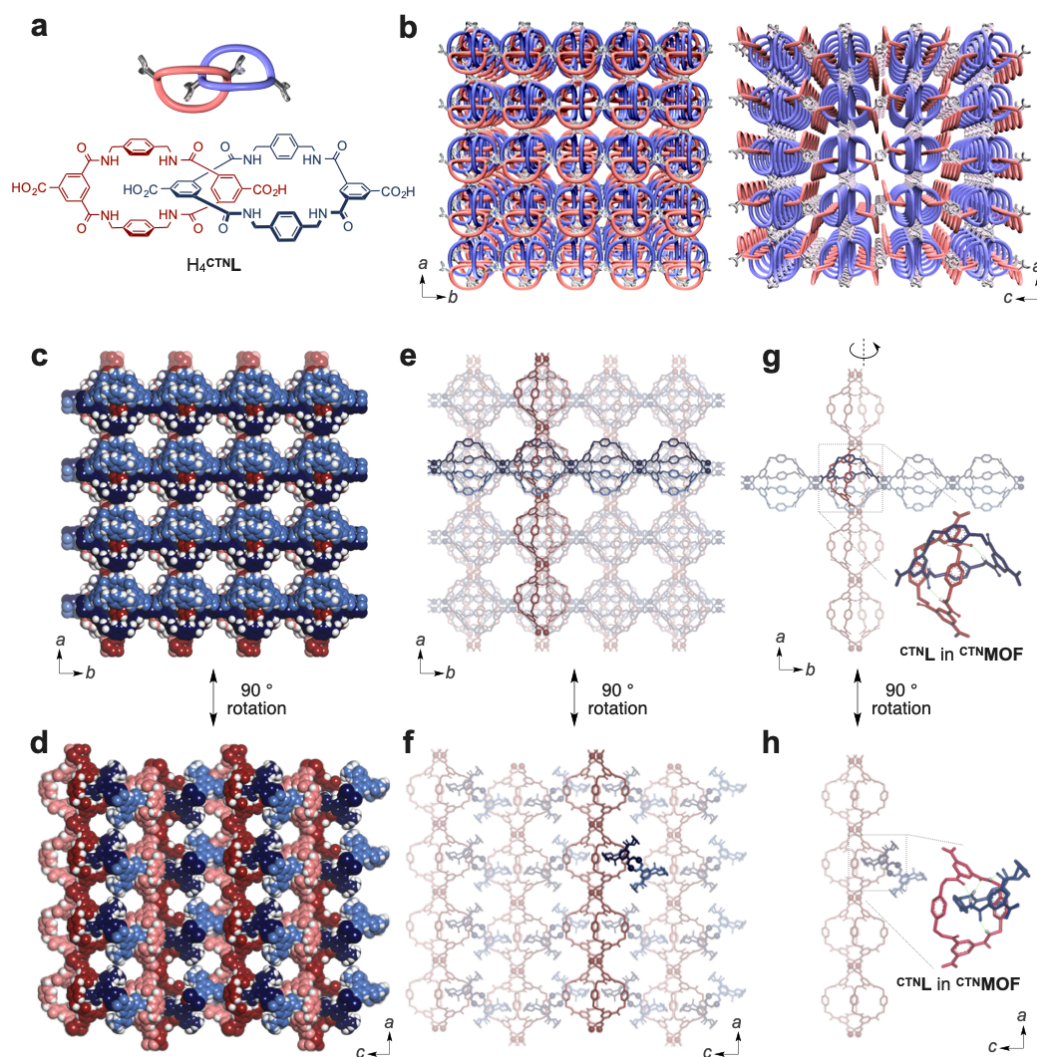
Supplementary Table 12. Comparison of the parameters for different polymorphs.

Temperature	−180 °C	−180 °C	−80 °C	−58 °C	−52 °C
Solvent	EtOH	DMF	DMF	DMF	DMF
Empirical Formula	$C_{68}H_{52}Co_2N_8O_{18} \cdot EtOH$	$C_{68}H_{52}Co_2N_8O_{18}$	$C_{68}H_{52}Co_2N_8O_{17} \cdot 5DMF$	$C_{34}H_{26}CoN_4O_9 \cdot DMF$	$C_{136}H_{104}Co_4N_{16}O_{33} \cdot 6DMF$
Crystal System	tetragonal	orthorhombic	tetragonal	tetragonal	orthorhombic
Lattice Parameter	$a = 16.87060 \text{ \AA}$ $c = 40.02360 \text{ \AA}$ $V = 11391.40274 \text{ \AA}^3$	$a = 24.29(2) \text{ \AA}$ $b = 25.83(2) \text{ \AA}$ $c = 40.70(4) \text{ \AA}$ $V = 25537(42) \text{ \AA}^3$	$a = 24.9280(13) \text{ \AA}$ $c = 39.247(2) \text{ \AA}$ $V = 24388(2) \text{ \AA}^3$	$a = 17.707(9) \text{ \AA}$ $c = 40.18(2) \text{ \AA}$ $V = 12598(12) \text{ \AA}^3$	$a = 24.021(9) \text{ \AA}$ $b = 25.336(9) \text{ \AA}$ $c = 39.231(14) \text{ \AA}$ $V = 23875(15) \text{ \AA}^3$
Space Group	$P4_1$ (#76)	$C222_1$ (#20)	$P4_12_12$ (#92)	$P4_122$ (#91)	$P2_12_12_1$ (#19)
Z	4	8	8	8	4
D_{calc}	0.836 g/cm ³	0.672 g/cm ³	0.946 g/cm ³	0.791 g/cm ³	0.880 g/cm ³
Free volume*	23.3%	26.9%	25.3%	25.0%	23.3%
Asymmetric unit**	$2 \times Co^{2+}$, $2 \times$ macrocycle (from a single catenane)	$2 \times Co^{2+}$, $2 \times$ macrocycle (from two different catenanes)	$2 \times Co^{2+}$, $2 \times$ macrocycle (from a single catenane)	$1 \times Co^{2+}$, $1 \times$ macrocycle	$4 \times Co^{2+}$, $4 \times$ macrocycle (from two different catenanes)

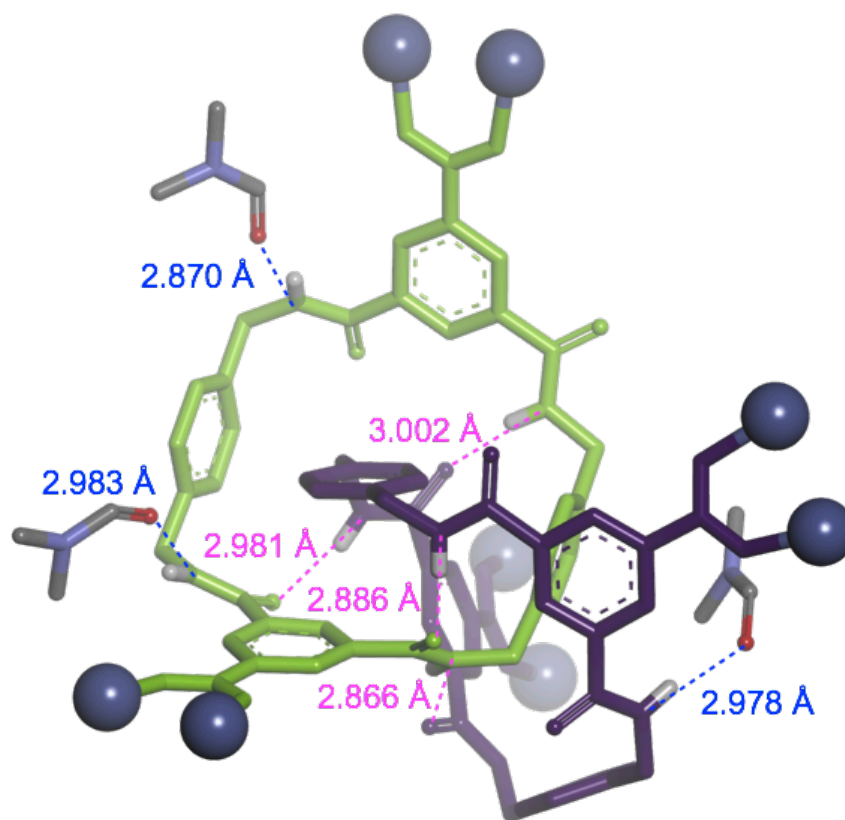
[Note] *The free volume was calculated using a probe with a radius of 1.4 Å in Mercury.

**Asymmetric unit: the smallest part that can be used to generate the entire crystal.

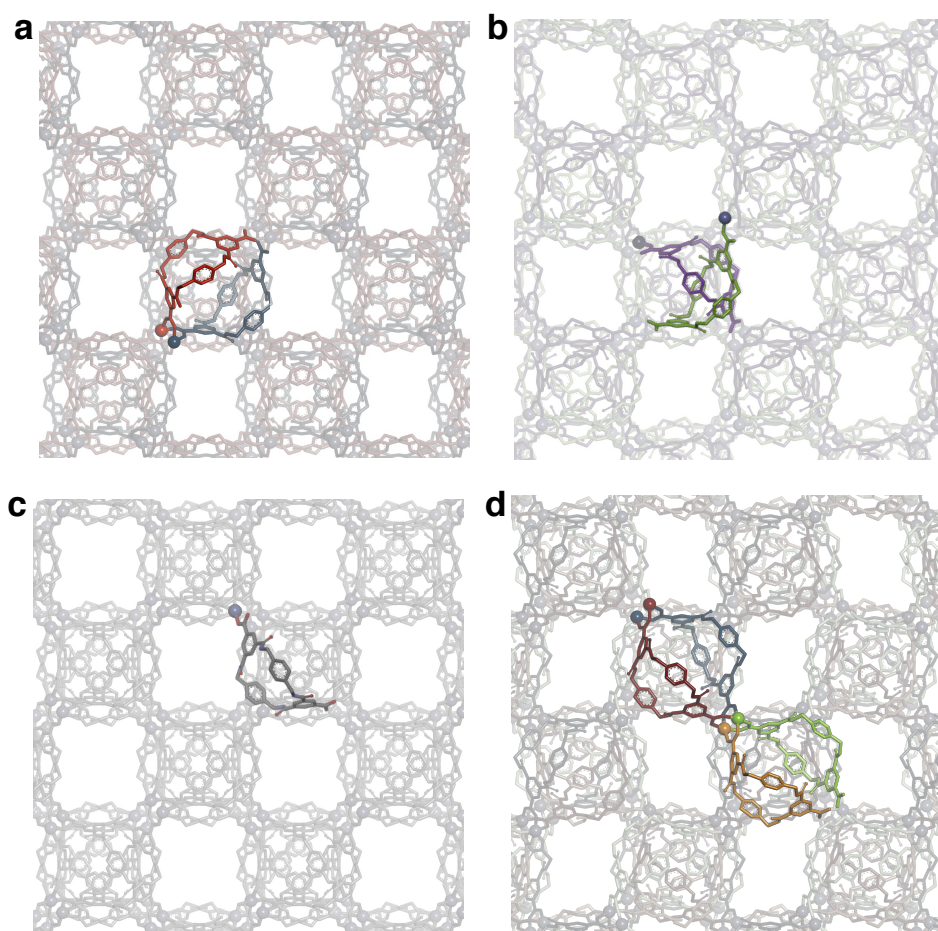
When DMF was used as the solvent, data obtained at −180 °C, −80 °C and −58 °C are from the same crystal through a set of consecutive experiments. The data obtained at −52 °C is from an as-synthesized crystal cooled from RT.



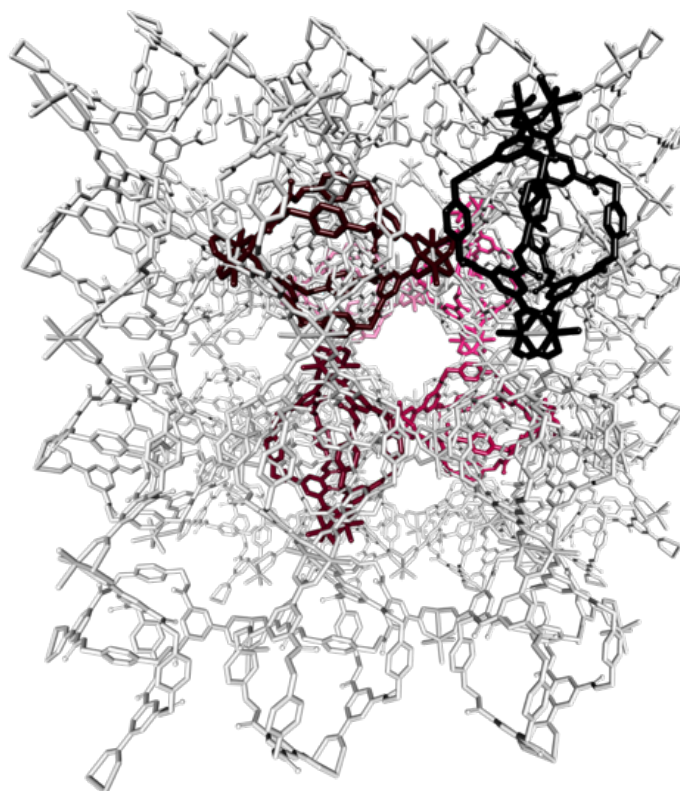
Supplementary Fig. 21. **a**, Chemical structure of the [2]catenane-based ligand H_4^{CTNL} . **b**, Schematic representations of CTNMOF , whose warps and wefts are mechanically interlocked by catenation, viewed along the c -axis (left) and b -axis (right). **c**, **d**, Space-filling representations of CTNMOF viewed along the c - and b -axes, respectively. **e**, **f**, Wireframe representations of CTNMOF viewed along the c - and b -axes, respectively. A pair of orthogonally arranged 1D metal–organic chains is highlighted in each panel. **g**, **h**, Wireframe representations of two orthogonally arranged 1D metal–organic chains viewed along the c - and b -axes, respectively. Each of the stick representations shows a pair of catenated macrocycles of CTNL in CTNMOF , where dashed green lines represent hydrogen bonds. Except for those involved in the hydrogen bonds in **g** and **h**, axial ligands of the Co^{2+} -paddle-wheel units, solvent molecules and hydrogen atoms are omitted for clarity.



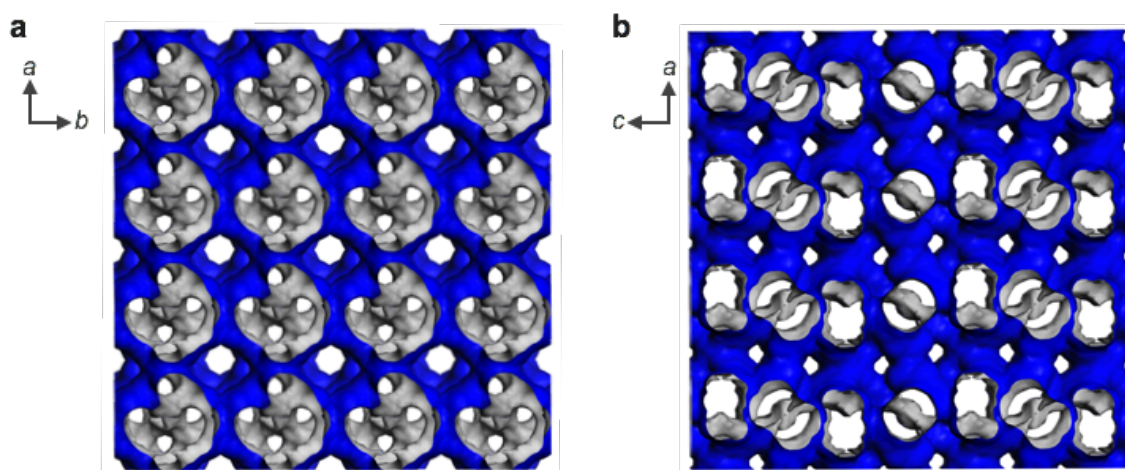
Supplementary Fig. 22. Interactions between DMF molecules and macrocycles of the catenane ligands in the crystal structure of ^{CTN}MOF observed at $-80\text{ }^{\circ}C$. [Note] Hydrogen atoms and solvent molecules, except those involved in hydrogen bonds are omitted for clarity. N-O distances in the hydrogen bonds are highlighted in blue (H-bonds between the amide moieties and DMF) and pink (H-bonds between the macrocycles in ^{CTN}L) broken lines.



Supplementary Fig. 23. Asymmetric unit for polymorphs with space groups $C222_1$ (**a**), $P4_12_12$ (**b**), $P4_122$ (**c**), and $P2_12_12_1$ (**d**), superimposed onto the bulk structure viewed along the *c* axis of the unit cell. (N.B. In the case of (**a**), a catenane contains two identical rings. In the case of (**d**), the red ring forms a catenane with the yellow ring, and the blue ring interlocks with the green ring.)



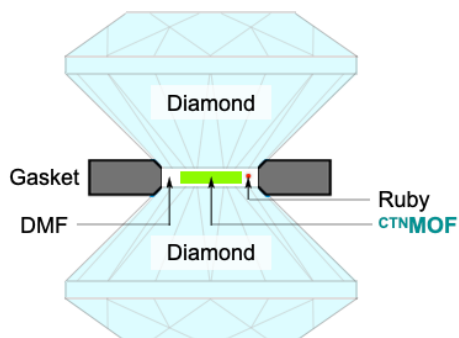
Supplementary Fig. 24. Highlights of a chiral channel of ^{CTN}MOF ($P4_122$) with *M*-helicity.



Supplementary Fig. 25. Solvent accessible surface (blue) of ^{CTN}MOF . **a**, viewed along the *c*-axis. **b**, viewed along the *b*-axis. N.B. The calculation was performed in Material Studio using a probe with a radius of 1.2 Å.

High pressure study of ^{CTN}MOF in a diamond anvil cell at room temperature:

N.B. Substantial number of reflections are unobservable due to the geometrical restriction of diamond anvil cells. As a result, data completeness is low. Data shown in **Supplementary Table 13** and **14** are obtained from the same crystal.



Supplementary Fig. 26. Schematic representation of the setup for high-pressure experiments in solvents.

Supplementary Table 13. Crystal data for ^{CTN}MOF *P4₁2₁2* obtained at 0.28 GPa.

Empirical Formula	C ₆₈ H ₅₂ Co ₂ N ₈ O ₁₈
Formula Weight	1387.06
Temperature	293 K
Crystal Color, Habit	green, block
Crystal Dimensions	0.20 × 0.20 × 0.40 mm
Crystal System	tetragonal
Space Group	<i>P4₁2₁2</i> (#92)
Lattice Parameters	$a = 24.7507(6) \text{ \AA}$ $c = 39.2898(11) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume	$V = 24068.8(13) \text{ \AA}^3$
Z value	8
$\mu(\text{MoK}\alpha)$	0.318 mm ⁻¹
D_{calc}	0.761 g/cm ³
$F(000)$	5640.0
Transmission factors _{min, max}	0.852, 1.000
$2\theta_{\text{max}}$	49.286
hkl_{max}	24, 22, 44
R_{int}	0.0393
No. Observations (All reflections)	43995
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0499
Residuals: R (All reflections)	0.0904
Residuals: wR_2 (All reflections)	0.1587
Goodness of Fit Indicator	0.969
Data completeness	0.51
$\Delta\rho_{\text{min, max}}$	-0.23, 0.25 e ⁻ /Å ³

Supplementary Table 14. Crystal data for ^{CTN}MOF *P4₁22* obtained at 0.46 GPa.

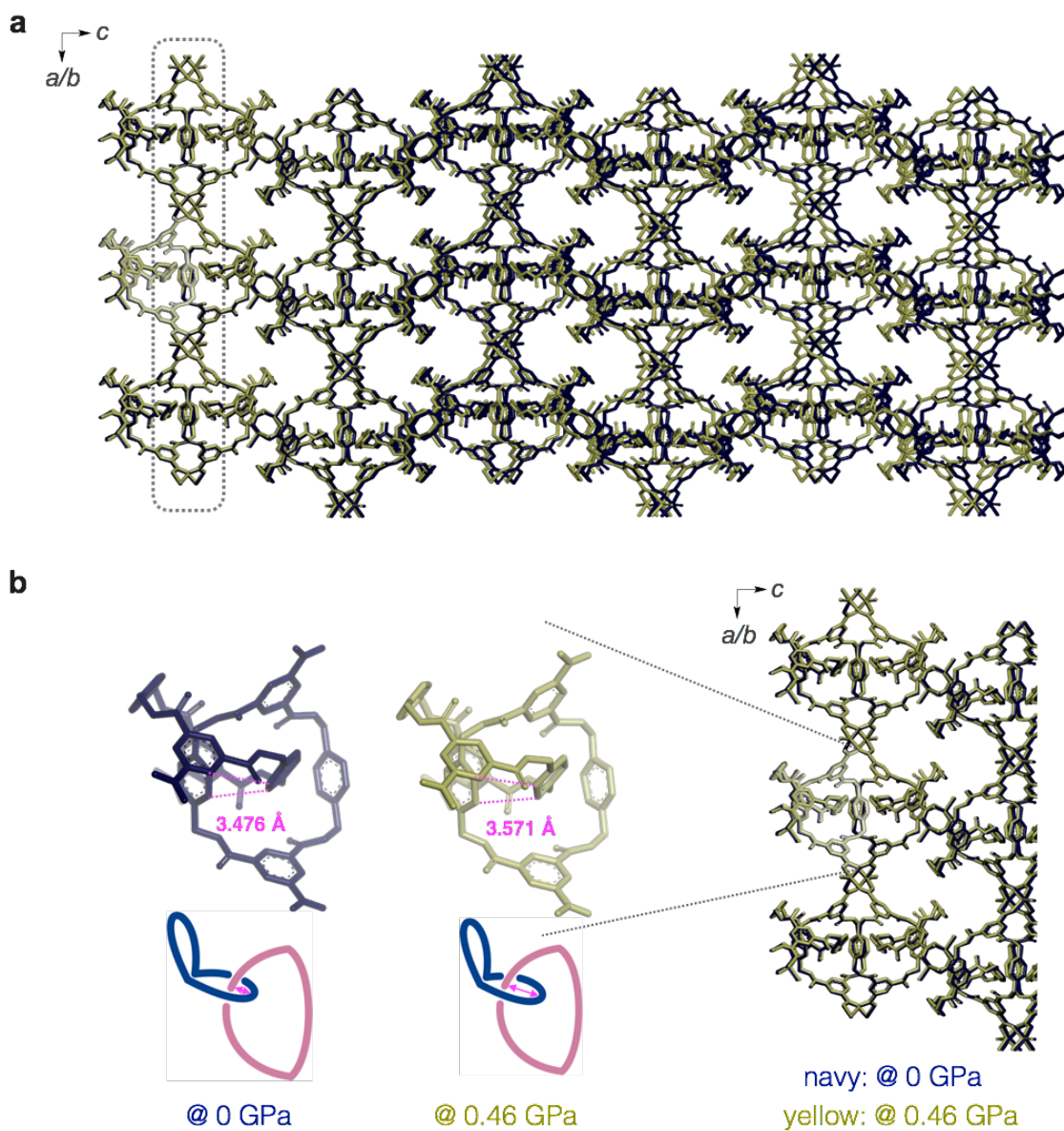
Empirical Formula	C ₃₄ H ₂₆ CoN ₄ O ₉
Formula Weight	1377.96
Temperature	293 K
Crystal Color, Habit	green, block
Crystal Dimensions	0.20 × 0.20 × 0.40 mm
Crystal System	tetragonal
Space Group	<i>P4₁22</i> (#91)
Lattice Parameters	$a = 17.4863(4) \text{ \AA}$ $c = 39.1704(10) \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume	$V = 11977.2(6) \text{ \AA}^3$
Z value	8
$\mu(\text{MoK}\alpha)$	0.320 mm ⁻¹
D_{calc}	0.769 g/cm ³
$F(000)$	2856.0
Transmission factors _{min, max}	0.881, 1.000
$2\theta_{\text{max}}$	49.214
hkl_{max}	5, 20, 44
R_{int}	0.0335
No. Observations (All reflections)	31888
Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0458
Residuals: R (All reflections)	0.0643
Residuals: wR_2 (All reflections)	0.1395
Goodness of Fit Indicator	1.046
Data completeness	0.54
$\Delta\rho_{\text{min, max}}$	-0.16, 0.17 e ⁻ /Å ³

Supplementary Table 15. Summary of the cell parameters of DMF-containing ^{CTN}MOF at various pressures.

P / GPa	$a / \text{\AA}$	$c / \text{\AA}$	$V / \text{\AA}^3$
0.00	17.470(3)	39.909(6)	12180(3)
0.28	17.5053(9)	39.302(2)	12044(1)
0.46	17.4863(4)	39.1704(10)	11977.2(6)
0.55	17.462(2)	38.812(8)	11835(3)
0.59	17.409(5)	38.679(14)	11723(6)
0.77	17.449(3)	37.862(8)	11527(4)
0.88	17.459(5)	37.878(12)	11546(6)

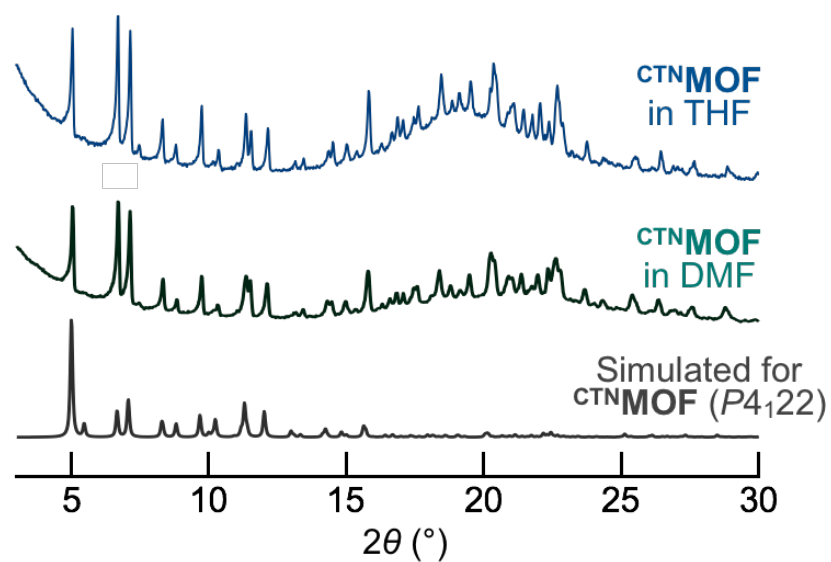
Supplementary Table 16. Summary of the cell parameters of THF-containing ^{CTN}MOF at various pressures.

P / GPa	$a / \text{\AA}$	$c / \text{\AA}$	$V / \text{\AA}^3$
0.0	17.4568(1)	40.039 (2)	12201(1)
0.12	17.3609(7)	39.6061(18)	11948.4(9)
0.34	17.3709(13)	39.625(3)	11957(2)
0.44	17.2948(12)	39.445(3)	11803(1)
0.70	17.2142(3)	39.2325(8)	11625.8(4)
0.91	17.1576(12)	39.051(3)	11496(1)



Supplementary Fig. 27. Superimposed views of crystal structures of CTNMOF at ambient (blue) and high pressure (yellow) conditions. (a) CTNMOF shrinks its structure along the c -axis when pressure is applied, and (b) the extension of the distance between the interlocked arms of the macrocycles.

6. PXRD patterns



Supplementary Fig. 28. PXRD pattern of ^{CTN}MOF soaked in THF (top), in DMF (middle) and its simulated pattern obtained from the crystal structure observed at 26 °C.

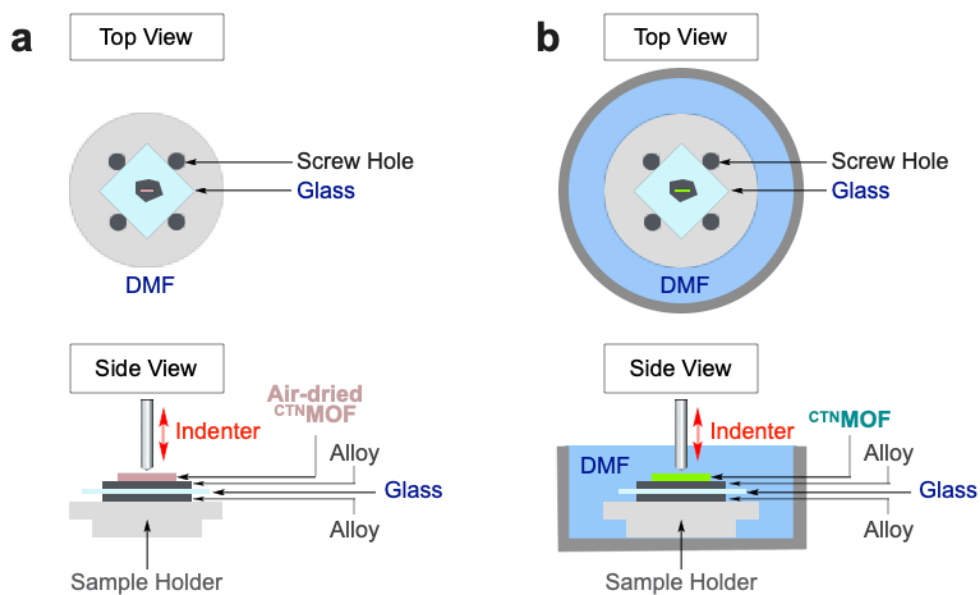
7. Nanoindentation

For nanoindentation experiments, a flat, smooth crystal surface is necessary. The single crystallinity of metal–organic crystals with guest-filling pores is highly sensitive to guest (solvent) exchange. ^{CTN}MOF is highly porous and tends to crack upon solvent exchange. Therefore, it is highly challenging to conduct nanoindentation experiments in different solvents. After many trials with 17 different solvents (i.e. DMF, acetone, acetonitrile, acetyl acetone, ethyl acetate, *n*-hexane, toluene, 1,4-dioxane, 1,2-dichloroethane, 2-butanone, cyclohexanone, methylcyclohexane, chloroform, dichloromethane, dimethylacetamide, nitromethane, and THF), we found that, in only DMF and THF, ^{CTN}MOF was able to maintain its single crystallinity; therefore, the crystals immersed in DMF or THF were subjected to nanoindentation.

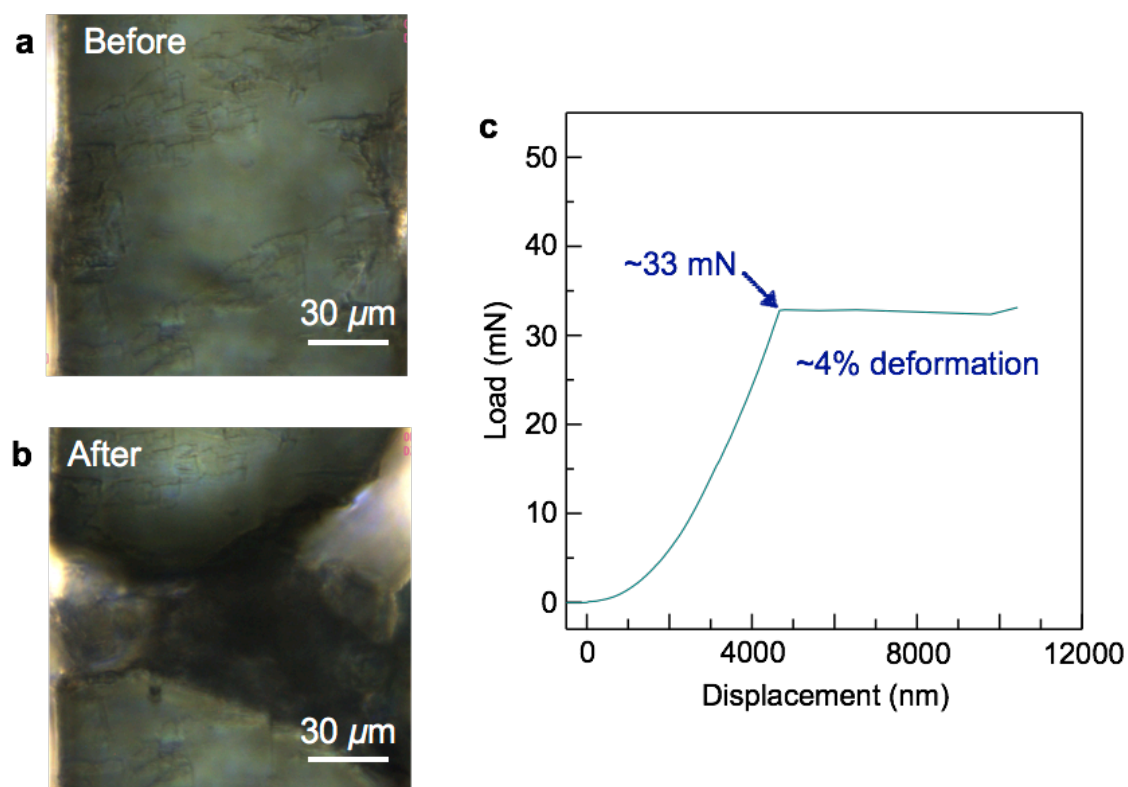
Air-dried ^{CTN}MOF was prepared by placing freshly prepared ^{CTN}MOF onto a watch glass that was covered by another watch glass inside a fume hood for several days until all the crystals turned pink. Crystals without cracks on their surface are selected for the experiment. N.B. Crystals are easily cracked during the drying process; therefore, slow evaporation of the solvent could be helpful to maintain their quality.

Crystals of as-synthesized ^{CTN}MOF were used for the experiments performed in DMF.

For the experiments performed in THF, as-synthesized ^{CTN}MOF was fixed on to a glass plate using a Bi-based fusible alloy (Osaka Asahi Co., Ltd. U-47), and then it was soaked in THF for 24 hours before the measurement.



Supplementary Fig. 29. Schematic representation of the experimental setup for nanoindentation in (a) air and (b) DMF. Nanoindentation in air was conducted using the same setup except that there was no solvent in the setup.



Supplementary Fig. 30. Fracture test for CTNMOF in DMF by nanoindentation. **a**, the sample before test. **b**, the sample after test. **c**, load-displacement curve for the test.

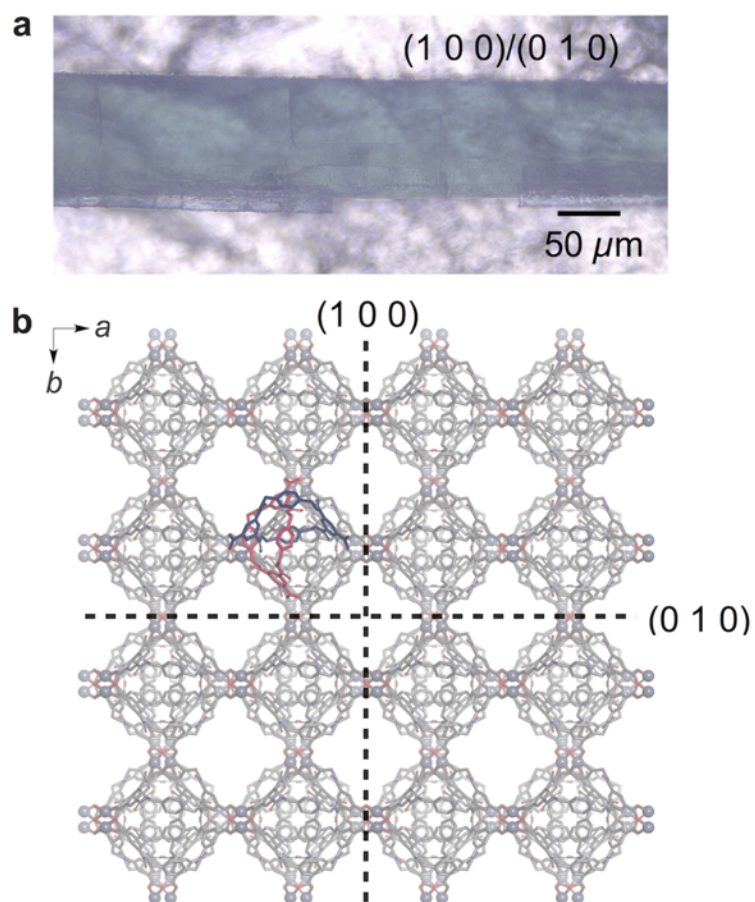
Supplementary Table 17. Summary of the average Young's moduli. a, for ^{CTN}MOF soaked in DMF. **b,** for air-dried ^{CTN}MOF. Nanoindentation experiments were performed several times for multiple crystals.

a

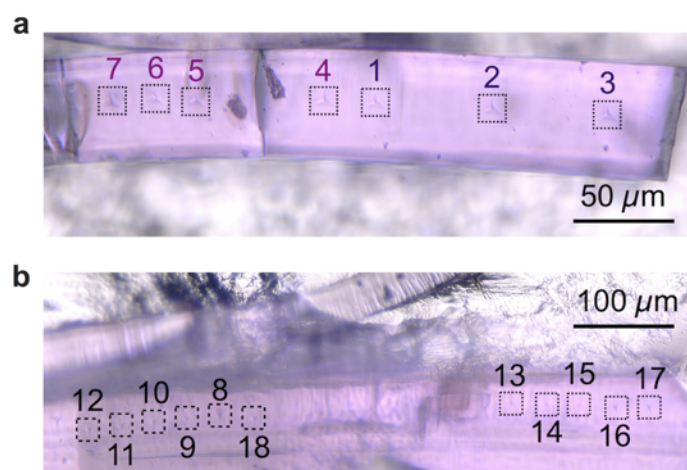
Entry	<i>E</i> / GPa
1	1.67
2	1.62
3	1.64
4	1.68
5	1.88
6	1.95
7	1.98
Average	1.77
σ	0.16

b

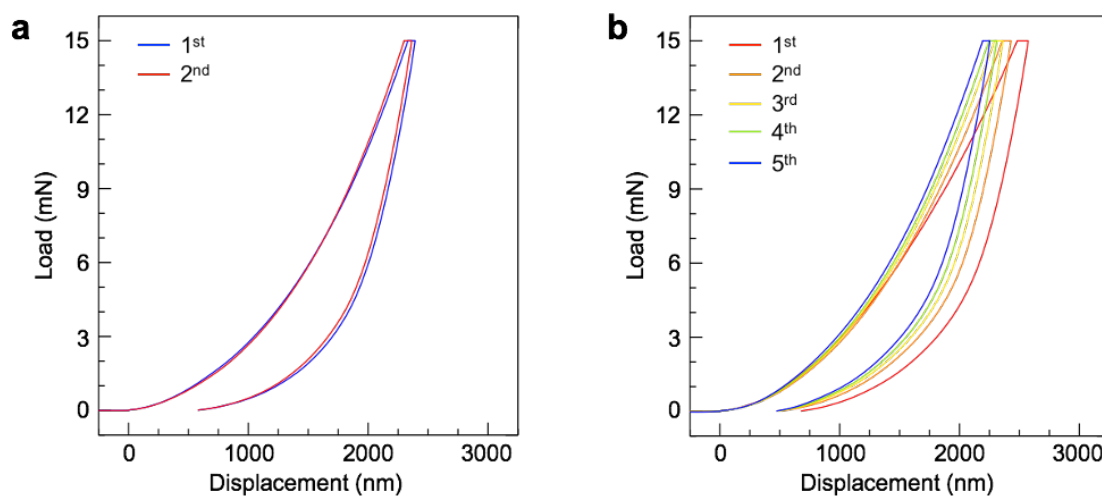
Entry	<i>E</i> / GPa
1	6.21
2	6.21
3	6.22
4	6.25
5	6.06
6	6.24
7	6.08
8	6.24
9	6.49
10	6.52
11	6.49
12	6.38
13	6.33
14	6.44
15	6.38
16	6.27
17	6.26
18	6.54
Average	6.31
σ	0.14



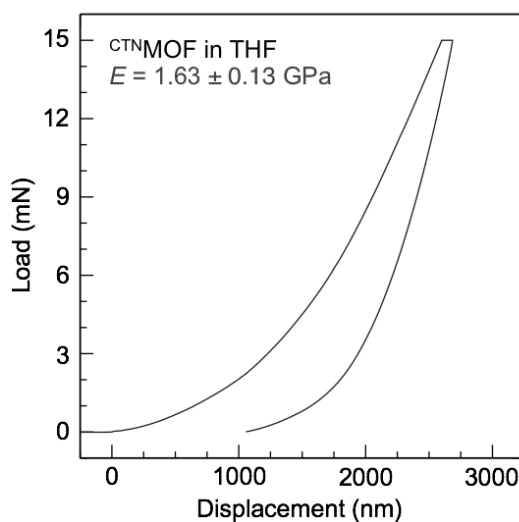
Supplementary Fig. 31. Miller index for the indenting face of $^{\text{CTN}}\text{MOF}$ in DMF. **a**, A postindentation photo of the top face of $^{\text{CTN}}\text{MOF}$ used in the experiments in DMF. **b**, Crystal structure of $^{\text{CTN}}\text{MOF}$ ($P4_122$) viewed along the c -axis of the unit cell. The $(1\ 0\ 0)$ and $(0\ 1\ 0)$ planes are indicated by dotted lines.



Supplementary Fig. 32. Photos of the air-dried ^{CTN}MOF crystals used after nanoindentation experiments. Indentation marks are labeled with numbers corresponding to the entry numbers shown in Supplementary Table 17b. **a**, Crystal used for indentation entries 1-7. **b**, Crystal used for indentation entries 8–18.



Supplementary Fig. 33. Cycle tests of load-displacement curves for ^{CTN}MOF in DMF by nanoindentation (a) with and (b) without 10 min interval. The nanoindentation experiments were repeatedly conducted at the same positions on the crystal surfaces.



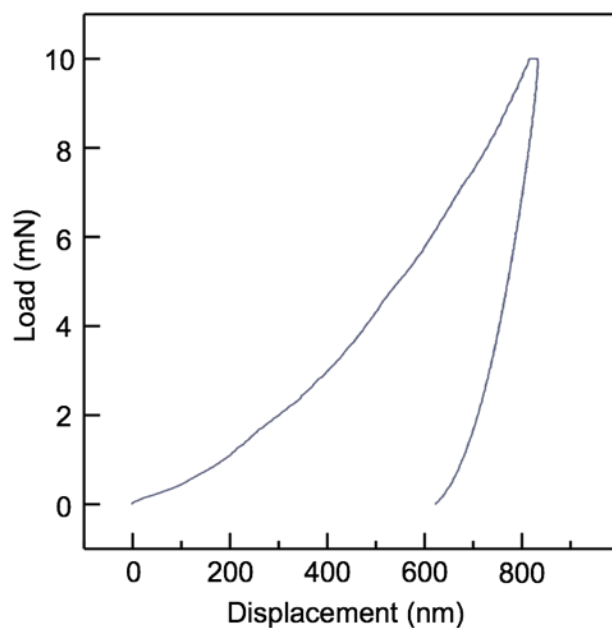
Supplementary Fig. 34. An example of a load-displacement curve obtained for ^{CTN}MOF crystals in THF by nanoindentation. The Young's modulus is shown as the average value.

$\text{Me}_4^{\text{CTN}}\text{L}$:

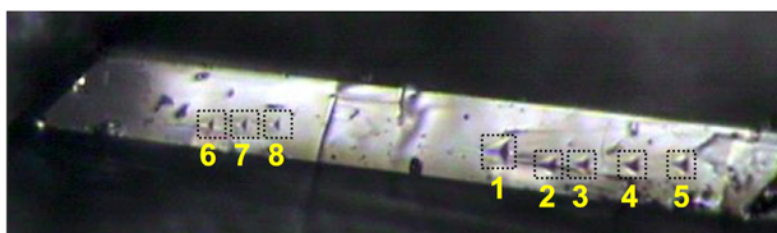
The $\text{Me}_4^{\text{CTN}}\text{L}$ crystal was prepared by layering MeOH on top of a DMF solution of $\text{Me}_4^{\text{CTN}}\text{L}$ at 25 °C.

Supplementary Table 18. Summary of the average Young's modulus of $\text{Me}_4^{\text{CTN}}\text{L}$ obtained from each indentation.

Entry	E / GPa
1	8.29
2	8.13
3	8.43
4	8.64
5	7.67
6	8.05
7	8.44
8	7.97
Average	8.20
σ	0.31



Supplementary Fig. 35. An example of a load-displacement curve obtained for $\text{Me}_4^{\text{CTNL}}$ by nanoindentation experiments.



Supplementary Fig. 36. A photograph of the $\text{Me}_4^{\text{CTNL}}$ crystal used in the nanoindentation experiments. Indentation marks are labeled with numbers corresponding to the entry number shown in Supplementary Table 18.

Supplementary Table 19. Comparison between the Young's moduli obtained for **a**, some common materials⁷ and **b**, for other MOFs reported in the literature^{1,8–11}.

a

Material	<i>E</i> / GPa
Rubber, small strain	0.01–0.1
Polytetrafluoroethylene (PTFE)	0.5
Polyethylene HDPE (high density)	0.8
Polypropylene, PP	1.5–2
^{CTN}MOF in DMF	1.8
Polystyrene, PS	3–3.5
slow dried ^{CTN}MOF	6.3
Me ₄ ^{CTN} L	8.2
Oak Wood (along grain)	11
Concrete	17
Magnesium metal (Mg)	45
Glass	50–90
Iron	210
Diamond (C)	1220

b

Material	<i>E</i> / GPa
^{CTN}MOF in DMF	1.8
Zn ₂ (NO ₂ -BDC) ₂ (DABCO)⊃DMF {110} orientation ⁸	2.1
IRMOF-1 (MOF-5) ⁹	2.7
slow dried ^{CTN}MOF	6.3
ZIFs ¹⁰	3–10
HKUST-1 ¹	9.3
[(CH ₂) ₃ NH ₂][Mn(HCOO) ₃] ¹¹	11–13
[C(NH ₂) ₃][Mn(HCOO) ₃] ¹¹	23–29

HKUST-1:

HKUST-1 was prepared following a literature procedure¹²:

Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 0.49 g, 2.0 mmol) was dissolved in deionized water (3 mL). Benzene-1,3,5-tricarboxylic acid (H_3BTC , 0.24 g, 1.1 mmol) was dissolved in ethanol (3 mL, heating was needed to fully dissolve this organic linker). The $\text{Cu}(\text{NO}_3)_2$ solution was first mixed with DMF (3 mL) in a 20 mL microwave vial, and then the H_3BTC solution and glacial acetic acid (12 mL) were added. The reaction mixture was heated at 55 °C for 3 days in an oven.

To store the as-synthesized crystal, the mother liquor was replaced by DMF and the reaction vial was kept at 4 °C. A square surface (i.e. along the [100] direction¹²) of the selected crystal was used for the measurement.

A nanoindentation experiment was first performed with the crystal immersed in DMF, then DMF was removed (the residual solvent surrounding the crystal was removed using tissue paper), and the sample was allowed to dry in air for 1 hour. The second set of measurements was conducted using the same crystal in air. Next, the crystal was soaked in DMF again, and the third set of data was taken.

Supplementary Table 20. Summary of the average Young's moduli of HKUST-1.

in DMF		in the air		back in DMF	
Entry	E / GPa	Entry	E / GPa	Entry	E / GPa
1	10.13	1	10.53	1	10.39
2	9.96	2	10.71	2	10.06
3	9.99	3	10.80	3	10.29
4	10.47	4	10.61	4	10.17
5	10.80	5	10.58	5	10.07
6	10.47	Average	10.65	Average	10.19
7	9.80	σ	0.11	σ	0.13
8	10.31				
Average	10.24				
σ	0.33				

As shown in Supplementary Table 20, in DMF, HKUST-1 showed a slightly smaller Young's modulus than the value obtained in the absence of the bulk solvent. The similarity of the values obtained in air and in DMF suggests that there is no significant influence of the solvent on the elasticity of HKUST-1. The Young's modulus obtained in our experiments is approximately 10 GPa, which is consistent with the reported values (in-the-air nanoindentation) of 9.3 GPa¹ and 10.03 GPa¹ (a theoretical value obtained from the computational method).

$Zn_2(NO_2-BDC)_2(DABCO) \supset DMF$:

$Zn_2(NO_2-BDC)_2(DABCO) \supset DMF$ (NO_2-BDC = 2-nitro-1,4-benzenedicarboxylate) was prepared following a literature procedure⁸:

$Zn(NO_3)_2 \cdot 6H_2O$ (250 mg, 0.84 mmol), 2-nitroterephthalic acid (178 mg, 0.84 mmol), and 1,4-diazabicyclo[2.2.2]octane (DABCO, 49 mg, 0.44 mmol) were suspended in DMF (20 mL). After stirring for 15 min, the suspension was filtered, and part of the obtained clear solution was transferred into a Teflon lined steel autoclave (volume of 7 mL) and heated to 125 °C for 48 h. Brownish-yellow cuboid crystals were obtained with each dimension approximately 100 μm in size. Facet {110} has a smoother surface than facet {001}.

Nanoindentation experiments were first performed with the crystal soaked in DMF. Then, DMF was removed, and the crystal was dried in air for 15 min before the measurement in air.

Supplementary Table 21. Summary of the average Young's moduli of $\text{Zn}_2(\text{NO}_2\text{-BDC})_2(\text{DABCO}) \supset \text{DMF}$.

facet {110} in DMF		facet {110} in the air		facet {001} in DMF	
Entry	E / GPa	Entry	E / GPa	Entry	E / GPa
1	2.88	1	1.85	1	9.44
2	2.53	2	1.97	2	8.04
3	3.06	3	2.10	3	10.10
4	3.47	4	1.81	4	9.28
5	3.19	5	2.45	5	8.96
Average	3.03	Average	2.04	6	9.45
σ	0.35	σ	0.26	7	7.65
				8	8.53
				9	9.29
				10	8.50
				Average	8.92
				σ	0.73

For facet {110}, the crystal became less deformable when soaked in DMF. The average Young's modulus obtained in our experiment performed in air is 2.04 ± 0.24 GPa, which is in excellent agreement with the reported value of 2.08 GPa⁸. For facet {001}, the Young's modulus obtained with the crystal in DMF is 8.92 ± 0.73 GPa, which is slightly smaller than the reported value of 9.26 GPa⁸ obtained in the absence of the bulk solvent.

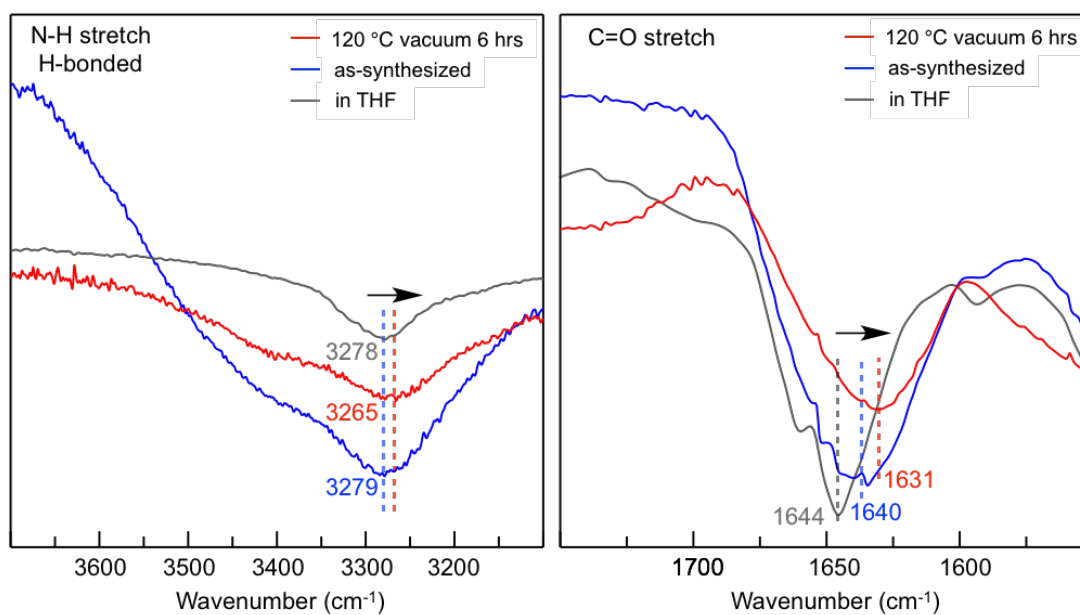
Supplementary Table 22. Summary of the average Young's moduli of MOFs measured in DMF and in air.

MOF	<i>E</i> / GPa	
	in DMF	in Air
CTN^{MOF}	1.77 ± 0.16	6.31 ± 0.14
Zn ₂ (NO ₂ -BDC) ₂ (DABCO)⊃DMF {110} orientation	3.03 ± 0.35	2.04 ± 0.26
Zn ₂ (NO ₂ -BDC) ₂ (DABCO)⊃DMF {001} orientation	8.92 ± 0.73	N/A
HKUST-1	10.24 ± 0.33	10.65 ± 0.11

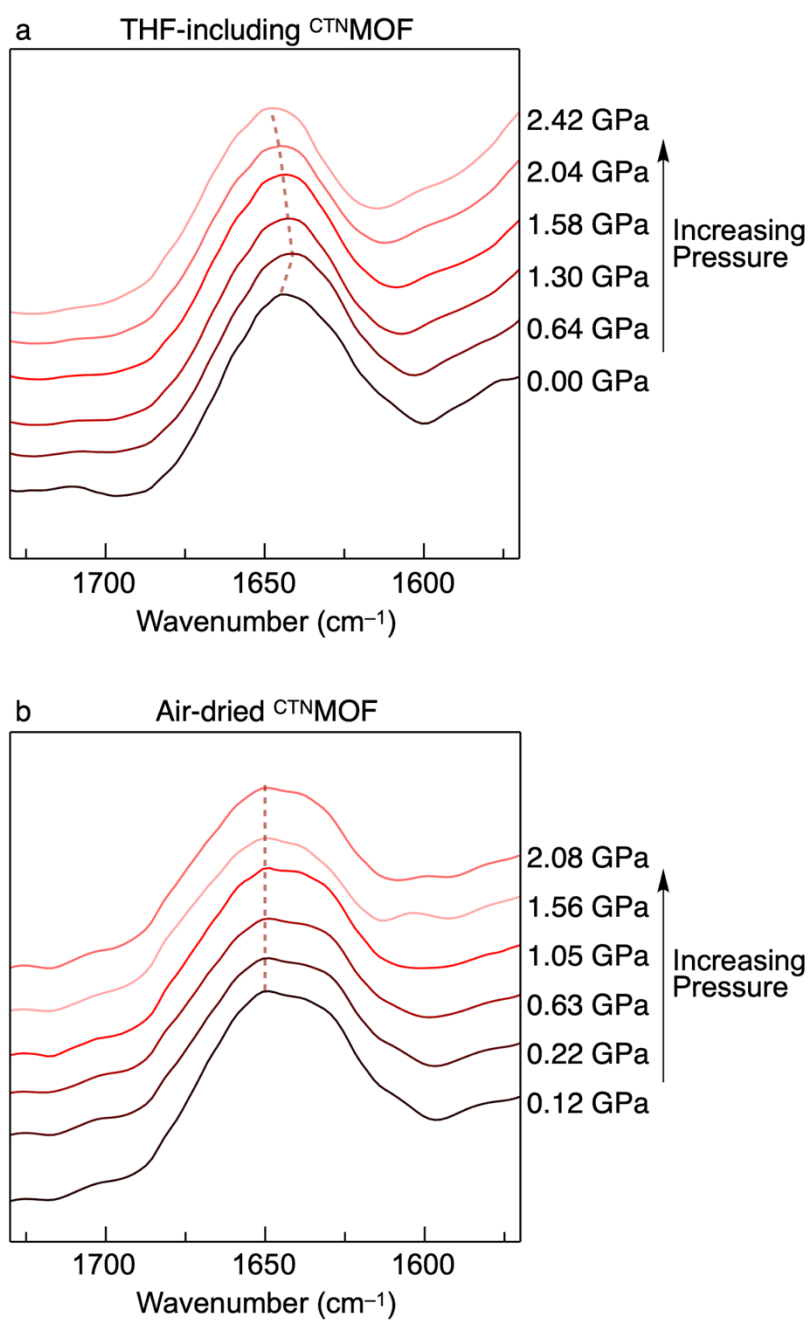
Supplementary Table 23. Summary of the average hardness of MOFs.

MOF	<i>H</i> / GPa	
	in DMF	in Air
CTN^{MOF}	0.138 ± 0.013	0.340 ± 0.012
Zn ₂ (NO ₂ -BDC) ₂ (DABCO)⊃DMF {110} orientation	0.253 ± 0.069	0.205 ± 0.031
HKUST-1	0.556 ± 0.029	0.532 ± 0.008

8. Infrared spectra

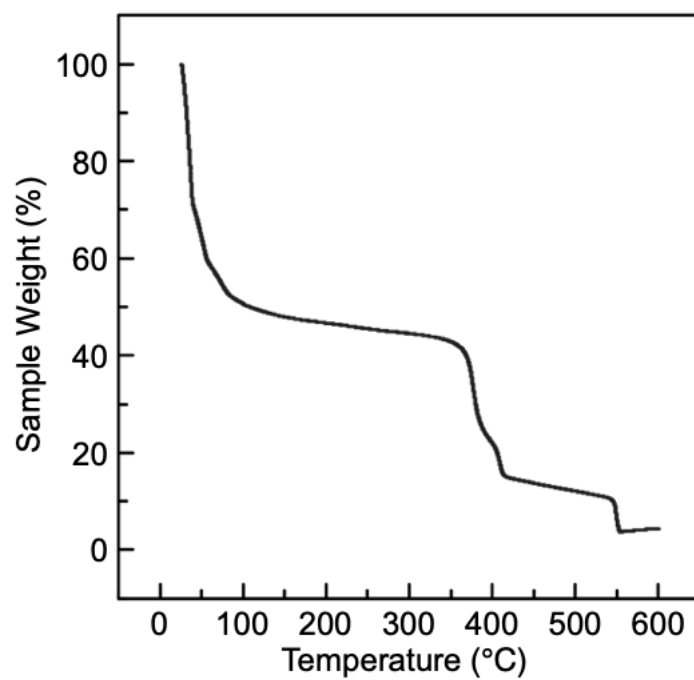


Supplementary Fig. 37. IR spectra of DMF-including, THF-including and dried ^{CTN}MOF at 25 °C. These spectra were collected using an ATR (attenuated total reflectance) unit.



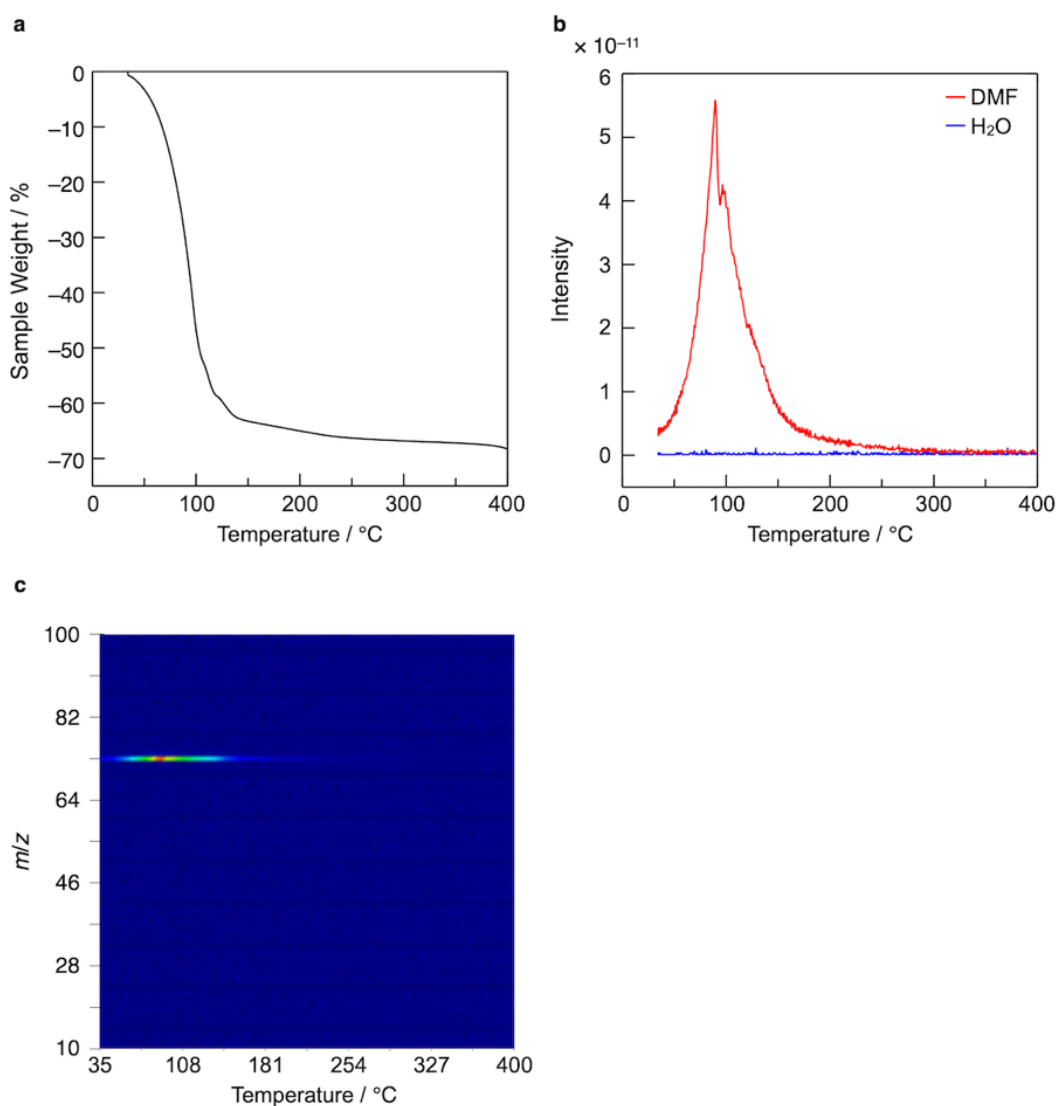
Supplementary Fig. 38. Variable-pressure IR spectra of C=O stretching bands for (a) THF-including and (b) air-dried CTNMOF at 25 °C. These spectra were collected for CTNMOF suspended in KBr upon increasing the applied pressure using a diamond anvil cell.

9. Thermogravimetry



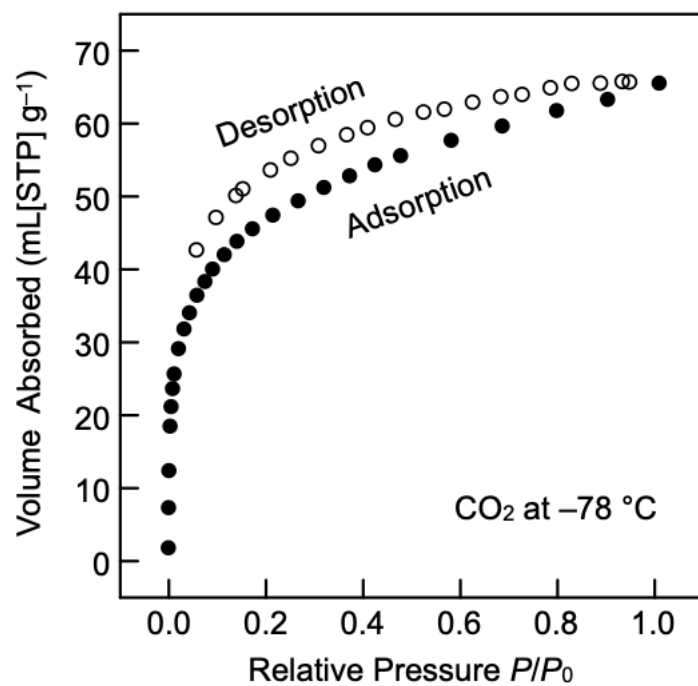
Supplementary Fig. 39. Thermogravimetric analysis (TGA) profile of ^{CTN}MOF as-synthesized in DMF.

10. Thermogravimetry/mass spectrometry



Supplementary Fig. 40. Thermogravimetry/mass spectrometry (TG/MS) profile of as-synthesized CTNMOF . (a) TG profile of as-synthesized CTNMOF . (b) DMF (red) and water (blue) release profile from as-synthesized CTNMOF in DMF. (c) 2D MS profile of as-synthesized CTNMOF . These profiles were recorded for as-synthesized CTNMOF freshly prepared in DMF.

11. CO₂ sorption



Supplementary Fig. 41. CO₂ adsorption and desorption isotherms ($-78\text{ }^{\circ}\text{C}$, $P_0 = 101.3\text{ kPa}$) for ^{CTN}MOF after heated at $80\text{ }^{\circ}\text{C}$ for 6 h under a reduced pressure.

12. Computational studies

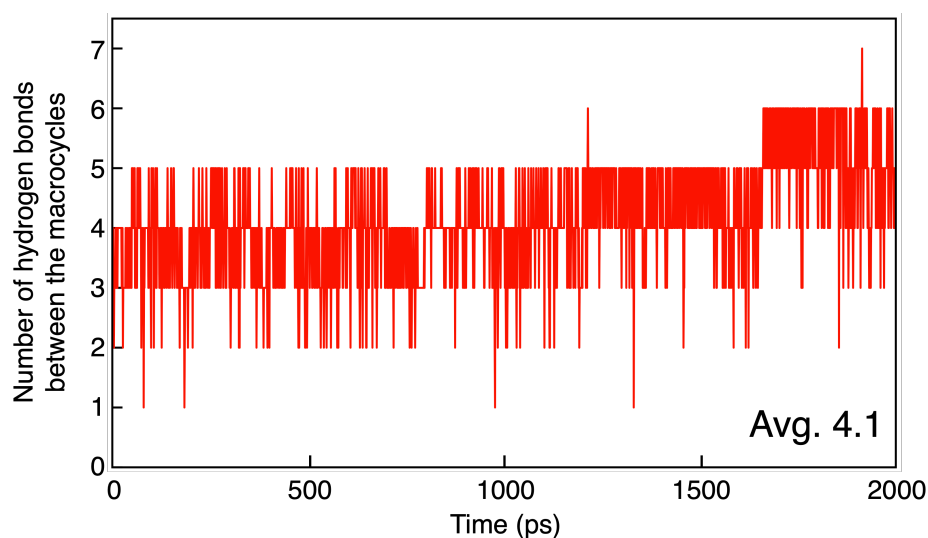
1. Model construction for molecular dynamics (MD) simulations

For MD simulation, we constructed the model structure consisting of catenane moiety, where the four carboxylate groups originally coordinated to the cobalt atoms in the MOF were replaced with methyl groups. Three systems were prepared to perform MD simulation in gas phase, in hexane, and in DMF. The model was placed at the center of 8 Å cubic box for gas phase simulation, while the model was solvated by 1693 hexane molecules or 3997 DMF molecules in the cases of simulation in solutions.

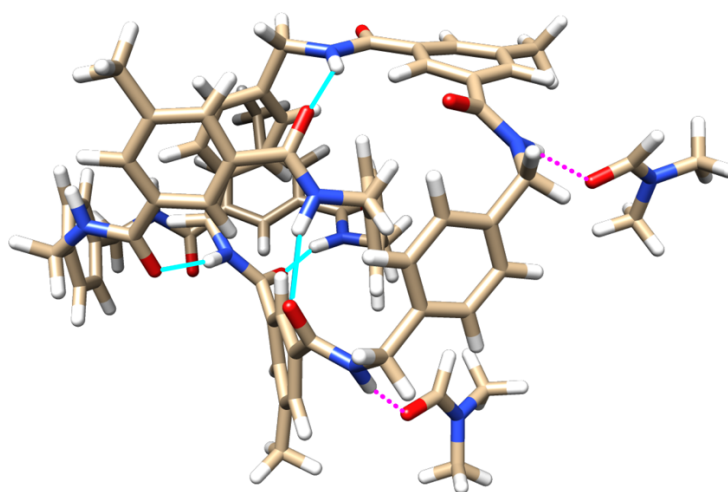
2. Details of MD simulations

First, we performed quantum mechanical calculations at HF/6-31G* level of theory by Gaussian 16 Rev. C.0¹³ software to obtain atomic charges. The topology files of the model and solvent were generated by the antechamber package¹⁴ with GAFF¹⁵ force field. Amber topology files generated by the package were converted into a GROMACS format using the python script, Acpype¹⁶. Second, equilibration of the systems in gas phase and in the solvents was conducted by following procedure. Energy minimization of the systems was performed based on the conjugate gradient algorithm with the threshold of the maximum force, 10.0 kJ/mol/nm. Next, NVT equilibration for 100 ps at 300 K followed by NPT ensemble equilibration for 100 ps at 1 bar pressure were carried out for relaxation of solvent molecules, while the atomic positions of the model are restrained with a harmonic potential. Third, the final MD simulations were performed without any restraints and NPT ensemble. The temperature and pressure are kept constant (300K and 1 bar) by using the velocity rescale thermostat¹⁷ and the Parrinello-Rahman barostat¹⁸, respectively. The cutoff value of 14 Å was assigned for non-bonded interactions. Long-range electrostatic interactions were treated using a particle-mesh Ewald scheme¹⁹. Dynamics were propagated with a leapfrog integrator using a time step of 0.2 fs, while preserving bond lengths using LINCS²⁰. All simulations were carried out under periodic boundary conditions using GROMACS software version 2020.5²¹. To analyze the results, we used GROMACS inbuilt tools, where we defined that the hydrogen bond has shorter N-O distance than 3.5 Å and smaller angle of N-H-O than 30°. The MD simulation for 2000 ps was conducted, and the snapshots every 1ps were collected. Then, the analysis of the hydrogen bonds in each structure the series of the snapshots were analyzed to

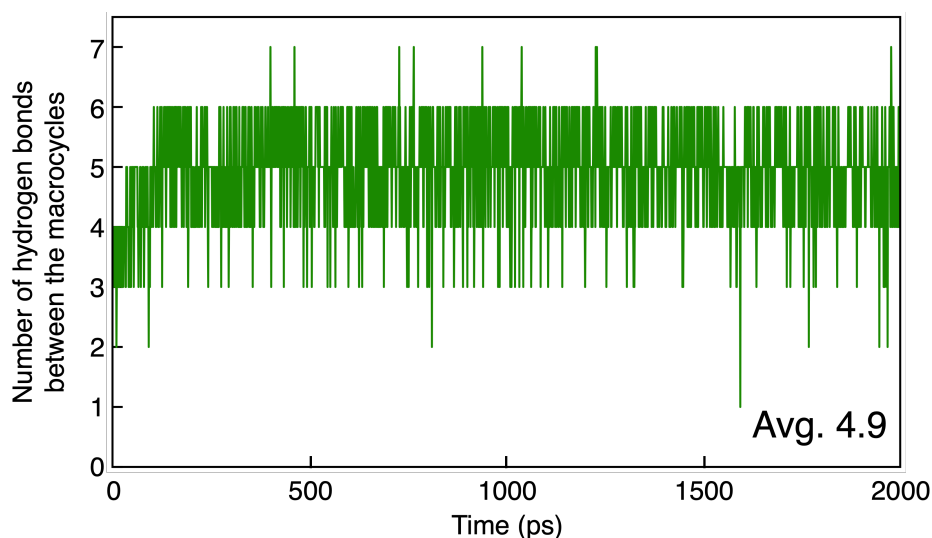
summarize the number of the hydrogen bonds between the macrocycles (Supplementary Figs. 42, 44 and 46). Typical snapshots of the simulations in gas phase, in hexane and in DMF are shown as Supplementary Figs. 43, 45 and 47.



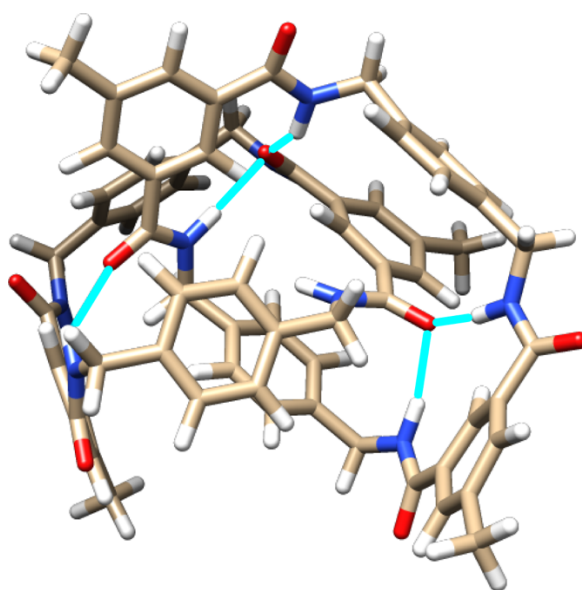
Supplementary Fig. 42. The counted number of hydrogen bonds in the series of the snapshots collected every 1 ps during the MD simulation for 2000 ps at 300 K in DMF. The average number of the hydrogen bonds in the catenane molecule is 4.142, and that between the catenane molecule and DMF is 2.269.



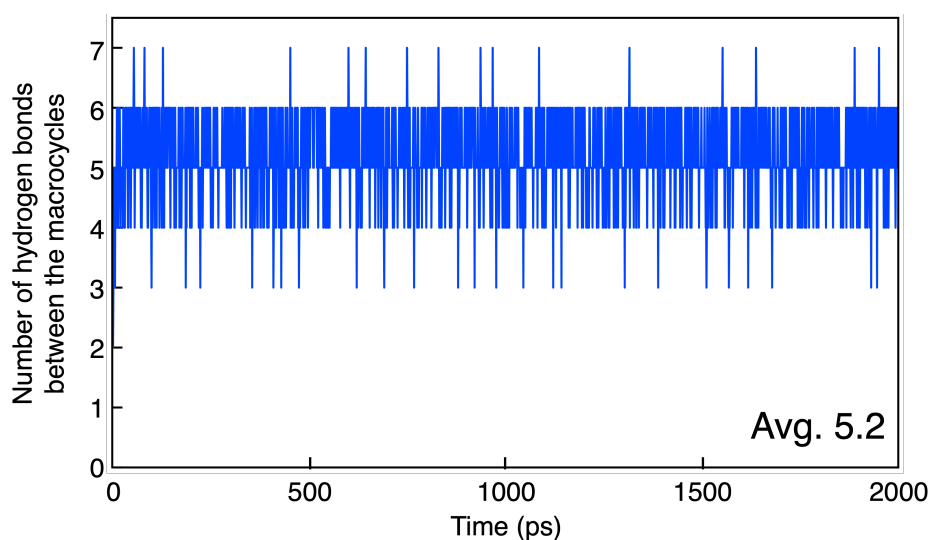
Supplementary Fig. 43. The snapshot of the model at 15 ps during the simulation, where we found 4 hydrogen bonds in the catenane molecule and 2 hydrogen bonding with DMF. Ocher, red, blue, and white indicate carbon, oxygen, nitrogen, hydrogen atoms, respectively. Light blue solid lines show hydrogen bonds between the macrocycles. Broken lines represent hydrogen bonds between the macrocycle and DMF. Solvent molecules are omitted for clarity, except for two DMF molecules interacting with the catenane molecule via hydrogen bond.



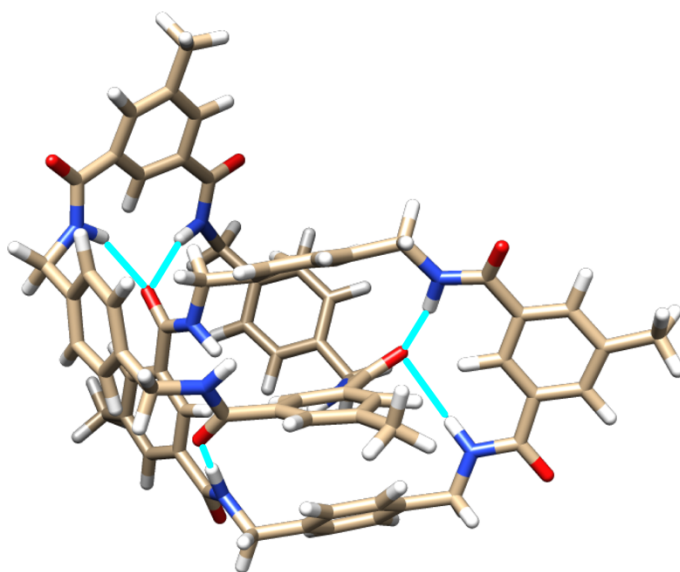
Supplementary Fig. 44. The counted number of hydrogen bonds in the series of the snapshots collected every 1 ps during the MD simulation for 2000 ps at 300 K in hexane solution. The average number of the hydrogen bonds in the catenane molecule is 4.926.



Supplementary Fig. 45. The snapshot of the model at 57 ps during the simulation, where we found 5 hydrogen bonds. Ocher, red, blue, and white indicate carbon, oxygen, nitrogen, hydrogen atoms, respectively. Light blue solid lines show hydrogen bonds between the macrocycles. Solvent molecules are omitted for clarity.



Supplementary Fig. 46. The counted number of hydrogen bonds in the series of the snapshots collected every 1 ps during the MD simulation for 2000 ps at 300 K in gas phase. The average number of the hydrogen bonds in the catenane molecule is 5.201.



Supplementary Fig. 47. The snapshot of the model at 10 ps during the simulation, where we found 5 hydrogen bonds. Ocher, red, blue, and white indicate carbon, oxygen, nitrogen, hydrogen atoms, respectively. Light blue solid lines show hydrogen bonds between the macrocycles.

References

1. Bundschuh, S. *et al.* Mechanical properties of metal–organic frameworks: an indentation study on epitaxial thin films. *Appl. Phys. Lett.* **101**, 101910 (2012).
2. Oliver, W. C. & Pharr, G. M. Measurement of hardness and elastic modulus by instrumented indentation: advances in understanding and refinements to methodology. *J. Mater. Res.* **19**, 3–20 (2004).
3. Kim, J.-H., Lee, E., Jeong, Y.-H. & Jang, W.-D. Unique photoluminescence of diacetylene containing dendrimer self-assemblies: application in positive and negative luminescence patterning. *Chem. Mater.* **24**, 2356–2363 (2012).
4. Johnston, A. G., Leigh, D. A., Nezhat, L., Smart, J. P. & Deegan, M. D. Structurally diverse and dynamically versatile benzylic amide [2]catenanes assembled directly from commercially available precursors. *Angew. Chem. Int. Ed. Engl.* **34**, 1212–1216 (1995).
5. Johnston, A. G., Leigh, D. A., Pritchard, R. J. & Deegan, M. D. Facile synthesis and solid-state structure of a benzylic amide [2]catenane. *Angew. Chem. Int. Ed. Engl.* **34**, 1209–1212 (1995).
6. Saura-Sanmartin, A., Martinez-Cuezva, A., Marin-Luna, M., Bautista, D. & JBerna, J. Effective Encapsulation of C₆₀ by Metal–Organic Frameworks with Polyamide Macrocyclic Linkers. *Angew. Chem. Int. Ed.* **60**, 10814–10819 (2021).
7. Young's modulus - tensile and yield strength for common materials. https://www.engineeringtoolbox.com/young-modulus-d_417.html
8. Henke, S., Li, W. & Cheetham, A. K. Guest-dependent mechanical anisotropy in pillared-layered soft porous crystals – a nanoindentation study. *Chem. Sci.* **5**, 2392–2397 (2014).
9. Bahr, D. F. *et al.* Mechanical properties of cubic zinc carboxylate IRMOF-1 metal–organic framework crystals. *Phys. Rev. B* **76**, 184106 (2007).
10. Tan, J. C., Bennett, T. D. & Cheetham, A. K. Chemical structure, network topology, and porosity effects on the mechanical properties of Zeolitic Imidazolate Frameworks. *Proc. Natl. Acad. Sci. U.S.A.* **107**, 9938–9943 (2010).
11. Li, W. *et al.* Mechanical tunability via hydrogen bonding in metal–organic frameworks with the perovskite architecture. *J. Am. Chem. Soc.* **136**, 7801–7804 (2014).

12. Tovar, T. M. et al. Diffusion of CO₂ in large crystals of Cu-BTC MOF. *J. Am. Chem. Soc.* **138**, 11449–11452 (2016).
13. Frisch, M. J. et al. Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford CT (2016).
14. Wang, J., Wang, W., Kollman P. A. & Case, D. A. Automatic atom type and bond type perception in molecular mechanical calculations. *J. Mol. Graph. Model.* **25**, 247260 (2006).
15. Wang, J., Wolf, R. M., Caldwell, J. W., Kollman, P. A. & Case, D. A. Development and testing of a general AMBER force field. *J. Comput. Chem.* **25**, 1157-1174 (2004).
16. Sousa da Silva, A. W. & Vranken, W. F. ACPYPE - AnteChamber PYthon Parser interfacE. *BMC Res. Notes* **5**, 367 (2012).
17. Bussi, G., Donadio, D. & Parrinello, M. Canonical sampling through velocity rescaling. *J. Chem. Phys.* **126**, 014101 (2007).
18. Parrinello, M. & Rahman, A. Polymorphic transitions in single crystals: a new molecular dynamics method, *J. Appl. Phys.* **52**, 7182–7190 (1981).
19. Darden, T., York, D. & Pedersen, L. Particle mesh Ewald - an N.Log(N) method for Ewald sums in large systems. *J. Chem. Phys.* **98**, 10089–10092 (1993).
20. Hess, B., Bekker, H., Berendsen, H. J. C. & Fraaije, J. G. E. M. LINCS: A linear constraint solver for molecular simulations. *J. Comput. Chem.* **18**, 1463–1472 (1997).
21. Abraham, M. J. et al. GROMACS: High performance molecular simulations through multi-level parallelism from laptops to supercomputers. *SoftwareX* **1**, 19–25 (2015).