

Peer Review File

Manuscript Title: An elastic metal–organic crystal with a densely catenated backbone

Editorial Notes:

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referee #1 (Remarks to the Author):

The manuscript by Meng et al. describes the synthesis of a metal organic crystal in which the organic fragments are all [2]catenanes. The authors have also managed to vacate the pores of the crystal and present some preliminary data on guest release, uptake and exchange. Finally, they also present mechanical characterization of the crystal using nanoindentation, reporting a low Young's modulus of 1.77 GPa.

Design/chemical structure: This is, in fact, the first MOF with a fully catenated backbone, as far as I know and have been able to find. As such, it is an interesting and beautiful structure, mostly characterized through crystallography. I am not a crystallographer, so I cannot judge the quality of the data and the refinement, but I could not access the original cif files through the CCDC numbers described in the Methods section (page 3), which instead correspond to structures described in a paper by Nitschke (Nature Chemistry, 2017, 9, 1276).

With regards of the extent to which it makes full use of the mechanically interlocked structures, I believe it is clear that it falls behind the work by other groups (refs. 27-34) since in the catenated structures the circumrotation of one ring about the other is not possible because the ends are coordinated to the metal centers.

With regards to the porosity and host-guest chemistry, I think it is also apparent that it falls behind most other MOFs in terms of pore size and chemical tunability.

Mechanical properties: I have some technical comments with regards to this section (see below) but let me first present a qualitative evaluation. The authors use nanoindentation to characterize the mechanical properties of the crystal and consider it highly elastic because it has a low Young's modulus when it is soaked in DMF (1.77 GPa, compared to 6.31 GPa when dry). The authors write that this Young's modulus is comparable to that of PP, which is true. I understand that polymers and MOFs are very different materials and that "highly" is not a quantitative adjective, and therefore it is difficult to evaluate objectively if it is or it isn't used correctly. By definition, an elastic material does not only present a low Young's modulus (takes little energy to deform reversibly) but can also be deformed significantly. This is difficult to evaluate from the nanoindentation data presented, but from the compression experiments the authors find that the crystal can be contracted by 5% at 0.88GPa...it does not look like the crystal can be called "highly elastic" without pushing the definition of elasticity a bit.

Manuscript: The manuscript is very well written and adequately referenced, although in my opinion, the novelty and relevance of the results is overstated, particularly in the title and abstract. To name just one example, I believe that the last phrase "...squeezable porous crystals that may address an essential difficulty in realizing both high abilities of guest uptake and release are on the horizon." Overstates the squeezability (just 5% at very high pressure), and the porosity and therefore the potential for guest uptake and release (significantly lower than state-of-the-art MOFs).

Overall, my opinion is that the present work is a very worthy contribution to materials featuring mechanically interlocked fragments, the experimental work is correctly carried out and presented (except comments below), and the manuscript is well written and referenced. However, the considerations detailed above make me think that it does not meet the stringent criteria for publication in Nature, and I honestly do not think it could reach that level with extra experiments or characterization, so I am very sorry to have to recommend rejection.

Technical comments on the mechanical characterization:

1. In the methods section on nanoindentation (pg 14, lines 9-13), the author claims 'A maximum load value of 15mN... was used for all samples' However, according Fig. 4f, the maximum load indented into the Zn-MOF samples was 8mN.
2. On pg. 7 and supplementary fig. 10, the author describes a 'fracture test' of the air dried MOF sample where the crystal fractures at a load of 33mN. However, there is no discussion of the significance of this measurement or comparison to any expected or relative value.
3. References to the measured moduli from indentation should included standard deviation values, to denote they are indeed average values. For example, on pg 7 line 19, the author should write, 'From the unloading curve, the Young's modulus of MOF was determined to be 6.31 +/- 0.14 GPa...' Additionally, the standard deviation should also be included on the plots in Fig. 4 b,d,f
4. Figs 4c,e,g need a scale bar. In addition, the caption doesn't clarify if these are the indents after the tests in air or DMF.
5. Supplementary Table 17. I think 0.01c0.1 should be 0.01 – 0.1.
6. In the discussion around supplementary table 19. The author states that the Zn-MOF crystal 'becomes harder' when soaked in DMF when describing the change in Young's modulus. It is very important to remember that indentation, hardness and modulus are two distinct measurements, and, given the fact that the author doesn't report the indentation hardness values of all the samples (given by Max Force divided by contact area), they should refer to the change in properties as an 'increase in modulus' and not hardness. The author is welcome to report the hardness values as well, as the trends in hardness and modulus are likely pretty similar in these systems.
7. Supplementary Table 20. Should list standard deviation values for each of the average Modulus values, as well as state that the listed Young's Modulus are averages, for instance, change the table description to 'Summary of the average Young's modulus of MOFs measured in DMF. A similar plot of the average modulus measurements and st. deviation for the measurements in Air may also be useful to summarize the data.

Referee #2 (Remarks to the Author):

This manuscript reports the synthesis and characterization of a MOF in which catenanes are the organic struts between cobalt metal ions. The MOF is prepared by reacting a [2]catenane with carboxylic acid moieties on the catenane ring with cobalt ions. The [2]catenanes are the well-known amide based catenanes, which becomes important later as they are well known to have hydrogen bonding within the catenane structure that reduces the mobility of the ring. The MOF was characterized by X-ray crystallography and shows some interesting changes in structure with solvent and temperature. However, what I think is most interesting and unique about this work are the mechanical properties of these crystals. The researchers nicely show that these MOF crystals, when swollen in a hydrogen-bond competing solvent, DMF, are elastic through a series of nanoindentation studies. When not swollen (in DMF) they show less elasticity.

Overall, I like this paper and think it has the potential to be published in Nature. I have two comments

- I do think it is misleading to say that this system has a fully catenated backbone (in the title and in numerous places in the text) as the metal ions should also be considered part of the backbone and they are not catenated. This is maybe better called a poly[2]catenane MOF or a MOF-consisting of catenated struts. I even think it is fine for it be called a highly catenated backbone. A fully catenated backbone implies polymer backbone made only of interlocked rings i.e., a poly[n]catenane-like structure more akin to what was reported in ref 18.

- It would have been good to see the nano-indentation studies on a crystal swollen in a non-hydrogen bond competing solvent. The hypothesis of the researchers is it is the mobility of the non-hydrogen bonded rings that impart the elasticity to the crystal, and they may be right, but it could also be that the solvent plays an important role helping to "plasticize" the rings and that some elasticity would be seen in the crystal even if the

catenanes were still had internal hydrogen bonded (and therefore less mobile). It would also be good to better characterize the mobility of the rings in the [2]catenane monomer in different solvents and compare/contrast this with the mechanical properties of a crystal swollen in those different solvents. This way it should be possible to more definitively link the ring mobility with the crystal elasticity.

Referee #3 (Remarks to the Author):

The manuscript by Aida, Sato and co-workers describes the synthesis of a metal-organic framework (MOF) in which the ligand components are mechanically interlocked [2]catenanes. This is a rare example of a crystalline coordination network in which the mechanical bond plays a key structural role as part of the “main chain” and, to the best of my knowledge, the first example of a crystalline coordination polymer constructed from catenane ligands that extends in three dimensions.

Solvent filling the voids of the MOF were able to be exchanged through heating and subsequently soaking in the new solvent. In the case of DMF and EtOH this allowed a single-crystal-to-single-crystal transformation with a change in the free volume of the MOF. Some structural adaptations were observed with changing temperature, most noticeably with a change in the shape of the porous channels at -52 °C. Perhaps most interestingly the elasticity of the MOF crystals could be attenuated upon soaking the guest-evacuated form in DMF, reasoned to arise from disruption of inter-component H-bonds within the catenane ligand. Single-crystal X-ray diffraction data obtained from crystals placed under pressure revealed a slight change in the co-conformation of the catenane ligands, suggesting that systems based on this design could be used for mechanically-responsive porous materials.

This is a truly fantastic piece of work that I am sure will be of very wide-ranging interest to the scientific community. Although the structural changes observed under the various conditions examined are rather limited, they are nonetheless remarkable given the novelty of the material being investigated. The characterisation data for the catenane ligand and its precursors are adequate, although I think the full gamut of NMR spectra (including 2D NMR that were presumably collected to aid in the assignment of the 1D spectra) and the MALDI-MS (including full MS, and a comparison of the observed and calculated isotopic patterns, particularly as the values deviate somewhat) should be included in the supporting information. The manuscript is well written and enjoyable to read.

This work represents the realisation of a new type of metal-organic system that would be of substantial interest purely for its structural features alone. In addition to this the authors have conducted a raft of experiments to exhaustively probe the structurally adaptive behaviour engendered by the mechanically interlocked components. Given the high novelty of the work and the intense interest I am sure it will generate across multiple scientific disciplines, combined with the exemplary manner in which the work has been undertaken, I must absolutely recommend that this can be published in Nature, with only a few relatively minor comments, discussed below, to address.

[1] Page 3 Line 20: “metal-organic crystals fully composed of MIM-based backbones have not been reported to date.”

I think the authors need to clarify this statement as Loeb and co-workers have published several reports of rotaxane ligands in MOFs with donor groups on both the axle and macrocycle components that could be viewed as fulfilling this criterion (Chem. Eur. J., 2013, 19, 14076; Eur. J. Inorg. Chem., 2016, 4524; Dalton Trans., 2017, 46, 2462) and Lewis has reported a crystalline coordination polymer using a [2]catenane ligand (Org. Biomol. Chem., 2019, 17, 2442 – noted in the supporting information) where the metal nodes are linked across the mechanical bond.

[2] Page 4 Line 9-10: “these catenated macrocycles are connected by a pair of two hydrogen bonds.”

This makes it sounds as though it is the H-bonds that are holding the catenane together, rather than the mechanical bond. Suggest re-wording to indicate that these are inter-component interactions.

[3] Page 6: a single-crystal-to-single-crystal transformation is observed upon changing from the DMF-loaded MOF to the EtOH-loaded one. Did the authors observe any changes in the co-conformation of the catenanes from this change?

[4] Soaking the MOF crystals in DMF is suggested to attenuate the intramolecular H-bonds between interlocked catenanes – do the authors observe any H-bonding interactions between DMF molecules and the catenane amide bonds in the crystal structures that might support this?

[5] Reference 10: no authors listed.

[6] In the supporting information on page 5 the chemical diagram of the catenane structure is not correct – the R group is given as CH₃/H, whereas it should be CO₂CH₃/CO₂H.

Author Rebuttals to Initial Comments:

[3] Point-to-Point Answers to the Reviewers’ Comments

Referee #1

Design/chemical structure: This is, in fact, the first MOF with a fully catenated backbone, as far as I know and have been able to find. As such, it is an interesting and beautiful structure, mostly characterized through crystallography. I am not a crystallographer, so I cannot judge the quality of the data and the refinement, but I could not access the original cif files through the CCDC numbers described in the Methods section (page 3), which instead correspond to structures described in a paper by Nitschke (*Nature Chemistry*, **2017**, 9, 1276).

=> [We revised the CCDC numbers in the Methods section and in the revised Supplementary Information \(Supplementary Table 2\).](#)

With regards of the extent to which it makes full use of the mechanically interlocked structures, I believe it is clear that it falls behind the work by other groups (refs. 27-34) since in the catenated structures the circumrotation of one ring about the other is not possible because the ends are coordinated to the metal centers. With regards to the porosity and host-guest chemistry, I think it is also apparent that it falls behind most other MOFs in terms of pore size and chemical tunability.

=> [Our main focus is to explore what mechanical properties would emerge if the backbone of a MOF is densely catenated, because such a MOF was unprecedented in the past.](#)

=> [We believe that our finding that the mechanical properties of our MOF correlate with the solvent uptake and release \(Supplementary Fig. 28\) is a new insight for the host-guest chemistry in materials science.](#)

Mechanical properties: I have some technical comments with regards to this section (see below) but let me first present a qualitative evaluation. The authors use nanoindentation to characterize the mechanical properties of the crystal and consider it highly elastic because it has a low Young’s modulus when it is soaked in DMF (1.77 GPa, compared to 6.31 GPa when dry). The authors write that this Young’s modulus is comparable to that of PP, which is true. I understand that polymers and MOFs are very different materials and that “highly” is not a quantitative adjective, and therefore it is difficult to evaluate objectively if it is or it isn’t used correctly. By definition, an elastic material does not only present a low Young’s modulus (takes little energy to deform

reversibly) but can also be deformed significantly. This is difficult to evaluate from the nanoindentation data presented, but from the compression experiments the authors find that the crystal can be contracted by 5% at 0.88 GPa...it does not look like the crystal can be called “highly elastic” without pushing the definition of elasticity a bit.

=> We appreciate this comment and removed the word “highly” from the manuscript.

=> As for the experimental evidence for the elastic nature, please note that the indentation test did not leave any footprint on the **CTN^NMOF** surface (Fig. 4c). This phenomenon is very special, and did not occur for other MOFs (Figs. 4e and 4g).

Manuscript: The manuscript is very well written and adequately referenced, although in my opinion, the novelty and relevance of the results is overstated, particularly in the title and abstract. To name just one example, I believe that the last phrase “...squeezable porous crystals that may address an essential difficulty in realizing both high abilities of guest uptake and release are on the horizon.” Overstates the squeezability (just 5% at very high pressure), and the porosity and therefore the potential for guest uptake and release (significantly lower than state-of-the-art MOFs).

=> We removed the word "highly" from the manuscript.

=> We removed the last sentence from the abstract.

Overall, my opinion is that the present work is a very worthy contribution to materials featuring mechanically interlocked fragments, the experimental work is correctly carried out and presented (except comments below), and the manuscript is well written and referenced.

=> We highly appreciate this encouraging comment.

However, the considerations detailed above make me think that it does not meet the stringent criteria for publication in Nature, and I honestly do not think it could reach that level with extra experiments or characterization, so I am very sorry to have to recommend rejection.

=> We believe that this reviewer may be satisfied with our revised manuscript.

In the methods section on nanoindentation (pg 14, lines 9-13), the author claims ‘A maximum load value of 15 mN... was used for all samples’ However, according Fig. 4f, the maximum load indented into the Zn-MOF samples was 8 mN.

=> We appreciate this suggestion and revised the manuscript and Supplementary Information in regard to this issue. We set the maximum load of 8 mN for Zn-MOF by following a precedented paper (ref. 44).

On pg. 7 and supplementary fig. 10, the author describes a ‘fracture test’ of the air-dried MOF sample where the crystal fractures at a load of 33 mN. However, there is no discussion of the significance of this measurement or comparison to any expected or relative value.

=> The main purpose of the fracture test was to confirm the maximum load that can be applied to the crystal for the nanoindentation test. We clarified the purpose of this test in the revised manuscript (page 7, lines 14–15).

=> Another reason to perform the fracture test was to confirm whether the indenter properly pressed the specimen surface or not, since indentation marks, which are usually observed after an indentation test, were not found on the crystalline surface of our catenated MOF.

References to the measured moduli from indentation should include standard deviation values, to denote they are indeed average values. For example, on pg 7 line 19, the author should write, ‘From the unloading curve, the Young’s modulus of MOF was determined to be 6.31 +/-

0.14 GPa...’ Additionally, the standard deviation should also be included on the plots in Fig. 4b, d, f.

=> As suggested by this reviewer, we added the standard deviation values to the revised version of the main text and figures.

Figs 4c, e, g need a scale bar. In addition, the caption doesn’t clarify if these are the indents after the tests in air or DMF.

=> We added the scale bars to the corresponding figures and also revised the caption to clarify that the indents were observed after the experiments in DMF.

Supplementary Table 17. I think 0.01c0.1 should be 0.01 – 0.1.

=> We revised the table (Supplementary Table 18) in the revised Supplementary Information.

In the discussion around supplementary table 19. The author states that the Zn-MOF crystal ‘becomes harder’ when soaked in DMF when describing the change in Young’s modulus. It is very important to remember that indentation, hardness and modulus are two distinct measurements, and, given the fact that the author doesn’t report the indentation hardness values of all the samples (given by Max Force divided by contact area), they should refer to the change in properties as an ‘increase in modulus’ and not hardness. The author is welcome to report the hardness values as well, as the trends in hardness and modulus are likely pretty similar in these systems.

=> Considering these comments, we revised the phrase ‘becomes harder’ to ‘becomes less deformable’ in the Supplementary Information. We also added the summary of hardness for the MOFs to the Supplementary Information (Supplementary Table 22).

Supplementary Table 20. Should list standard deviation values for each of the average Modulus values, as well as state that the listed Young’s Modulus are averages, for instance, change the table description to ‘Summary of the average Young’s modulus of MOFs measured in DMF. A similar plot of the average modulus measurements and st. deviation for the measurements in air may also be useful to summarize the data.

=> Following these suggestions, we revised the Supplementary Information (Supplementary Tables 16, 17, 19–21).

Referee #2

This manuscript reports the synthesis and characterization of a MOF in which catenanes are the organic struts between cobalt metal ions. The MOF is prepared by reacting a [2]catenane with carboxylic acid moieties on the catenane ring with cobalt ions. The [2]catenanes are the well-known amide based catenanes, which becomes important later as they are well known to have hydrogen bonding within the catenane structure that reduces the mobility of the ring. The MOF was characterized by X-ray crystallography and shows some interesting changes in structure with solvent and temperature. However, what I think is most interesting and unique about this work are the mechanical properties of these crystals. The researchers nicely show that these MOF crystals, when swollen in a hydrogen-bond competing solvent, DMF, are elastic through a series of nanoindentation studies. When not swollen (in DMF) they show less elasticity. Overall, I like this paper and think it has the potential to be published in Nature.

=> We highly appreciate these encouraging comments.

I do think it is misleading to say that this system has a fully catenated backbone (in the title and in numerous places in the text) as the metal ions should also be considered part of the backbone and they are not catenated. This is maybe better called a poly[2]catenane MOF or a MOF- consisting of catenated struts. I even think it is fine for it be called a highly catenated backbone. A fully catenated backbone implies polymer backbone made only of interlocked rings i.e., a poly[n]catenane-like structure more akin to what was reported in ref 18.

=> According to this reviewer's concern, we changed the phrase "fully-catenated" to "densely catenated" and would like to propose a new title of "An elastic metal-organic crystal with a densely catenated backbone".

It would have been good to see the nano-indentation studies on a crystal swollen in a non- hydrogen bond competing solvent. The hypothesis of the researchers is it is the mobility of the non-hydrogen bonded rings that impart the elasticity to the crystal, and they may be right, but it could also be that the solvent plays an important role helping to "plasticize" the rings and that some elasticity would be seen in the crystal even if the catenanes were still had internal hydrogen bonded (and therefore less mobile). It would also be good to better characterize the mobility of the rings in the [2]catenane monomer in different solvents and compare/contrast this with the mechanical properties of a crystal swollen in those different solvents. This way it should be possible to more definitively link the ring mobility with the crystal elasticity.

=> We appreciate these important suggestions.

=> For nanoindentation experiments, a flat crystal surface with single crystallinity is necessary as shown in Supplementary Fig. 26. In general, the single crystallinity of metal-organic crystals with guest-filling pores is highly sensitive to guest (solvent) exchange. Our material is highly porous (DMF-included **CTN^{MOF}** has a 59% void volume) and tends to crack upon solvent exchange. Therefore, it is highly challenging to conduct nanoindentation experiments in different solvents. After many trials with 16 different solvents (acetone, acetyl acetone, ethyl acetate, *n*-hexane, toluene, 1,4-dioxane, 1,2-dichloroethane, 2-butanone, THF, cyclohexanone, methylcyclohexane, chloroform, dichloromethane, dimethylacetamide,

nitromethane and acetonitrile), we found that, in only THF that acts as a hydrogen bond acceptor,

CTN^{MOF} was able to maintain its single crystallinity. Interestingly, THF-included **CTN^{MOF}**

showed a small Young's modulus (Supplementary Fig. 29, 1.63 ± 0.13 GPa). As expected, FT-IR spectroscopy of **CTN^{MOF}** in THF (Supplementary Fig. 32) showed a 13 cm^{-1} shift from 1631 cm^{-1} in air to 1644 cm^{-1} in THF for the amide moieties of **CTN^{MOF}**. Unfortunately, **CTN^{MOF}** cracked in all of the non-hydrogen bond competing solvents tested.

=> Instead, we performed molecular dynamics simulations for a [2]catenane in hexane (Supplementary Figs. 35 and 36) as a representative of non-hydrogen bond competing solvents as well as in DMF (Supplementary Figs. 33 and 34) and gas phase (Supplementary Figs. 37 and 38), to explore how the hydrogen bonds between the catenated macrocycles in gas phase are modulated by solvation. The results clearly indicated that the hydrogen bonds are not attenuated in hexane but partially cleaved in DMF. We newly added one paragraph to the revised manuscript for the computational studies (page 9, lines 1–12).

=> We tried to analyze the mobilities of the catenated ligand $\text{H}_4^{\text{CTN}}\text{L}$ in different solvents. However, beyond our expectation, not only $\text{H}_4^{\text{CTN}}\text{L}$ but also its methyl ester version was sparingly soluble in common organic solvents except DMF. Even THF, their solubilities were very low. So, we conducted VT- ^1H NMR spectroscopy of $\text{Me}_4^{\text{CTN}}\text{L}$ in DMF-*d*₇ (Supplementary Fig. 3) and confirmed its high dynamic nature over a wide temperature range from -25 to 140°C .

The manuscript by Aida, Sato and co-workers describes the synthesis of a metal-organic framework (MOF) in which the ligand components are mechanically interlocked [2]catenanes. This is a rare example of a crystalline coordination network in which the mechanical bond plays a key structural role as part of the "main chain" and, to the best of my knowledge, the first example of a crystalline coordination polymer constructed from catenane ligands that extends in three dimensions. Solvent filling the voids of the MOF were able to be exchanged through heating and subsequently soaking in the new solvent. In the case of DMF and EtOH this allowed a single-crystal-to-single-crystal transformation with a change in the free volume of the MOF. Some structural adaptations were observed with changing temperature, most noticeably with a change in the shape of the porous channels at -52°C . Perhaps most interestingly the elasticity of the MOF crystals could be attenuated upon soaking the guest-evacuated form in DMF, reasoned to arise from disruption of inter-component H-bonds within the catenane ligand. Single-crystal X-ray diffraction data obtained from crystals placed under pressure revealed a slight change in the co-conformation of the catenane ligands, suggesting that systems based on this design could be used for mechanically-responsive porous materials. This is a truly fantastic piece of work that I am sure will be of very wide-ranging interest to the scientific community. Although the structural changes observed under the various conditions examined are rather limited, they are nonetheless remarkable given the novelty of the material being investigated.

=> We highly appreciate these encouraging comments.

The characterisation data for the catenane ligand and its precursors are adequate, although I think the full gamut of NMR spectra (including 2D NMR that were presumably collected to aid in the assignment of the 1D spectra) and the MALDI-MS (including full MS, and a comparison of the observed and calculated isotopic patterns, particularly as the values deviate somewhat) should be included in the supporting information.

=> We conducted additional 1D/2D NMR and MALDI-TOF-MS measurements for the ligand ($\text{H}_4^{\text{CTN}}\text{L}$) and its precursor ($\text{Me}_4^{\text{CTN}}\text{L}$), and added the obtained spectra to the revised Supplementary Information (1D NMR: Supplementary Figs. 5, 10 and 11, 2D NMR: Supplementary Figs. 6–8 and 12–15, MALDI-TOF-MS: Supplementary Figs. 16 and 17).

The manuscript is well written and enjoyable to read. This work represents the realisation of a new type of metal-organic system that would be of substantial interest purely for its structural features alone. In addition to this the authors have conducted a raft of experiments to exhaustively probe the structurally adaptive behaviour engendered by the mechanically interlocked components. Given the high novelty of the work and the intense interest I am sure it will generate across multiple scientific disciplines, combined with the exemplary manner in which the work has been undertaken, I must absolutely recommend that this can be published in Nature, with only a few relatively minor comments, discussed below, to address.

=> We highly appreciate these encouraging comments.

Page 3 Line 20: "metal-organic crystals fully composed of MIM-based backbones have not

been reported to date." I think the authors need to clarify this statement as Loeb and co-workers have published several reports of rotaxane ligands in MOFs with donor groups on both the axle and macrocycle components that could be viewed as fulfilling this criterion (*Chem. Eur. J.*, 2013, 19, 14076; *Eur. J. Inorg. Chem.*, 2016, 4524; *Dalton Trans.*, 2017, 46, 2462) and

Lewis has reported a crystalline coordination polymer using a [2]catenane ligand (*Org. Biomol. Chem.*, 2019, 17, 2442 – noted in the supporting information) where the metal nodes are linked across the mechanical bond.

=> We appreciate these suggestions. We cited the suggested papers and revised the corresponding part (page 3, lines 19–21) as follows:

However, as for metal-organic crystals composed of MIM-based backbones, only a few examples have been reported without exploration of their mechanical properties^{35–38}.

Page 4 Line 9-10: "these catenated macrocycles are connected by a pair of two hydrogen bonds." This makes it sounds as though it is the H-bonds that are holding the catenane together, rather than the mechanical bond.

Suggest re-wording to indicate that these are inter-component interactions.

=> We revised the corresponding part (page 4, lines 11–13) as follows:

In its crystalline state, these catenated macrocycles are geometrically fixed by an inter- component hydrogen bonding interaction and adopt either a chair or boat conformation.

Page 6: a single-crystal-to-single-crystal transformation is observed upon changing from the DMF-loaded MOF to the EtOH-loaded one. Did the authors observe any changes in the co- conformation of the catenanes from this change?

=> As shown in Figs. 3a and 3f, two MOFs, including the catenated parts, are geometrically very similar to each other.

Soaking the MOF crystals in DMF is suggested to attenuate the intramolecular H-bonds between interlocked catenanes – do the authors observe any H-bonding interactions between DMF molecules and the catenane amide bonds in the crystal structures that might support this?

=> In the crystal structure (CCDC 2080247) obtained at –80 °C, we successfully confirmed that three out of eight amide moieties in two catenated macrocycles are hydrogen-bonded with DMF. We added a graphical representation of this structural characteristics to the revised Supplementary Information (Supplementary Fig. 20).

Reference 10: no authors listed.

=> This is the special issue featuring 119 authors. Because of the request by this reviewer, we included only the name of the guest editor in the revised Reference section.

In the supporting information on page 5 the chemical diagram of the catenane structure is not correct – the R group is given as CH₃/H, whereas it should be CO₂CH₃/CO₂H.

=> We appreciate this suggestion and corrected the chemical diagram on page 5 in the revised Supplementary Information.

Reviewer Reports on the First Revision:

Referee #1 (Remarks to the Author):

I read the new version of the manuscript by Meng et al. with interest. I see the authors have done some extra experiments and improved on the statistical presentation of their data, which was clearly sub-par in the original version. I also see that they have included some calculations. However, I have to stand by my opinion as expressed in my previous review report: "it does not meet the stringent criteria for publication in Nature, and I honestly do not think it could reach that level with extra experiments or characterization". This is exactly what the authors have done, and I appreciate the efforts, but I do not think any of the extra experiments (or theory) make the conceptual advance worthy of publication in Nature. I am aware that this is just my opinion, but it was, I believe, solidly based on analysis of the different aspects of the findings, and comparison with previous results in the literature. If anything, my opinion has been reinforced by reading the reports from other reviewers, highlighting even more examples of similar results, which are now included in the reference section.

I am therefore sorry to recommend rejection again. I believe this manuscript could very well be published as is in Nature Communications or a premier chemistry journal.

Referee #2 (Remarks to the Author):

The authors have done a good job addressing the comments from the three reviewers. This includes carrying out additional experiments and adding in a computational study to help support their claims. It is unfortunate that the crystals cracked in the other solvents, but the authors added computation work to support their hypothesis that it is the disruption of the hydrogen bonds and therefore mobility of catenane that plays a role in the properties of these materials. One aspect that was added which is important is the error on the mechanical data which certainly helps to put this data in better context. I feel that this work can now be published.

Referee #3 (Remarks to the Author):

The authors have satisfactorily addressed the minor comments I posed about the original manuscript, which were simply related to clarification of some statements.

A number of modifications have been made to the text in line with the other referees' comments that I think have clarified a few points.

Attempts were made to perform nano-indentation studies on the MOF soaked in a variety of solvents. For all additional solvents investigated, with the exception of THF, the studies could not be undertaken due to crystal cracking. As a surrogate, MD simulations of a model catenane in DMF and hexane were conducted and the results contrasted, showing an increased average number of inter-component H-bonds in hexane. I am not sure that too much can really be inferred from this given that these are purely calculations and were performed on a discrete catenane model, rather than system incorporated into polymeric frameworks. I do not request any additional experiments to be run, however, and am happy for this section to remain as is.

I was impressed with this manuscript before and I think it is even better now! Given the changes made to the manuscript I recommend publication of the article as it currently stands.

Referee #4 (Remarks to the Author):

The authors of this paper state that their motivation behind their work was to explore the mechanical properties of MOFs with densely catenated backbones. However, the paper is lacking in its analysis of how the catenation impacts the mechanical properties of the material. As CTN-MOF is a flexible material, it is clear that it possesses an open and closed form, with the closed one appearing upon the evacuation of the framework. Based on the decrease in void space of closed structures, it is reasonable that the evacuated MOF had a higher Young's modulus compared to the solvated structures. While the differences in mechanical properties based on solvent are interesting, are the authors certain that this is due to hydrogen bonding attenuation from the catenated backbone rather than due to guest-dependent differences in unit cell? Finally, It would great to see DAC experiments of the unsolvated material.

Author Rebuttals to First Revision:

Point-to-Point Answers to the Reviewers' Comments

Referee #1

I read the new version of the manuscript by Meng *et al.* with interest. I see the authors have done some extra experiments and improved on the statistical presentation of their data, which was clearly sub-par in the original version. I also see that they have included some calculations.

=> We appreciate these encouraging comments.

However, I have to stand by my opinion as expressed in my previous review report: "it does not meet the stringent criteria for publication in Nature, and I honestly do not think it could reach that level with extra experiments or characterization". This is exactly what the authors have done, and I appreciate the efforts, but I do not think any of the extra experiments (or theory) make the conceptual advance worthy of publication in Nature. I am aware that this is just my opinion, but it was, I believe, solidly based on analysis of the different aspects of the findings, and comparison with previous results in the literature. If anything, my opinion has been reinforced by reading the reports from other reviewers, highlighting even more examples of similar results, which are now included in the reference section. I am therefore sorry to recommend rejection again. I believe this manuscript could very well be published as is in Nature Communications or a premier chemistry journal.

=> We carefully checked the papers (1)–(3), which were newly added to the list of references. We gave brief summaries of these works in the following. **First of all, no mechanical properties were investigated in these works.** In contrast with our three dimensional porous metal–organic crystal, which is unprecedented in that its warps and wefts are connected only by catenation, the MOFs reported in these papers were not strategically

designed to show unique mechanical properties.

(1) *Chem. Eur. J.* **19**, 14076–14080 (2013).

An interwoven MOF combining mechanically interlocked linkers and highly interpenetrated networks was reported, where the mechanically interlocked parts have only a limited freedom.

(2) *Eur. J. Inorg. Chem.* 4524–4529 (2016).

The reported MOF did not show any detectable change in its XRD profile over a wide temperature range. On the basis of this observation, the authors concluded that their MOF is rigid.

(3) *Dalton Trans.* **46**, 2462–2470 (2017).

The reported MOFs are composed of stacked 2D layers where the constitutional mechanically interlocked parts have only a limited freedom.

We believe that our current version is now worthy of publication in *Nature*.

Referee #2

1. The authors have done a good job addressing the comments from the three reviewers. This includes carrying out additional experiments and adding in a computational study to help support their claims. It is unfortunate that the crystals cracked in the other solvents, but the authors added computation work to support their hypothesis that it is the disruption of the hydrogen bonds and therefore mobility of catenane that plays a role in the properties of these materials. One aspect that was added which is important is the error on the mechanical data which certainly helps to put this data in better context. If feel that this work can now be published.

=> We highly appreciate these encouraging comments.

Referee #3

The authors have satisfactorily addressed the minor comments I posed about the original manuscript, which were simply related to clarification of some statements. A number of modifications have been made to the text in line with the other referees' comments that I think have clarified a few points. Attempts were made to perform nano-indentation studies on the MOF soaked in a variety of solvents. For all additional solvents investigated, with the exception of THF, the studies could not be undertaken due to crystal cracking. As a surrogate, MD simulations of a model catenane in DMF and hexane were conducted and the results contrasted, showing an increased average number of inter-component H-bonds in hexane. I am not sure that too much can really be inferred from this given that these are purely calculations and were performed on a discrete catenane model, rather than system incorporated into polymeric frameworks. I do not request any additional experiments to be run, however, and am happy for this section to remain as is.

=> Thank you for acknowledging the additional experiments we have done.

I was impressed with this manuscript before and I think it is even better now! Given the changes made to the manuscript I recommend publication of the article as it currently stands.

=> We highly appreciate these encouraging comments.

Referee #4

1. The authors of this paper state that their motivation behind their work was to explore the mechanical properties of MOFs with densely catenated backbones. However, the paper is lacking in its analysis of how the catenation impacts the mechanical properties of the material. As CTN-MOF is a flexible material, it is clear that it possesses an open and closed form, with the closed one appearing upon the evacuation of the framework. Based on the decrease in void space of closed structures, it is reasonable that the evacuated MOF had a higher Young's modulus compared to the solvated structures. While the differences in mechanical properties

based on solvent are interesting, are the authors certain that this is due to hydrogen bonding attenuation from the catenated backbone rather than due to guest-dependent differences in unit cell? Finally, it would great to see DAC experiments of the unsolvated material.

=> We appreciate this reviewer's advice on DAC experiments on **CTN^NMOF**.

=> We newly conducted *in situ* FTIR spectroscopy of THF-including **CTN^NMOF** (0–2.4 GPa) and dried **CTN^NMOF** (0–2.1 GPa) under different applied pressures in a diamond anvil cell (Supplementary Fig. 34) [Note: DMF-including **CTN^NMOF** was not appropriate due to the spectral interference by included DMF]. We also added a new cartoon (Supplementary Fig. 24) to show the structural change of DMF-including **CTN^NMOF** upon increasing the applied pressure to 0.46 GPa. The results in these two figures clearly support our claim that the mechanical properties of **CTN^NMOF** depend on whether its NHCO H-bonds are in a solvent-attenuated state or not: Upon increasing the applied pressure to 2.4 GPa, THF- including **CTN^NMOF** showed an expected shift for the NHCO vibrational band toward a higher wavenumber region (Supplementary Fig. 34a), while its crystal structure showed a contraction along the *c*-axis (Supplementary Fig. 24). In contrast, dried **CTN^NMOF**, upon being pressurized up to 2.1 GPa, did not show any shift for the NHCO vibrational band (Supplementary Fig. 34b). We newly added the description about these results to the revised manuscript (page 10, lines 5–13). Please note that we could not obtain the information about the void space in dried **CTN^NMOF** because its XRD profile was very broad, as reported in the previous version.

Reviewer Reports on the Second Revision:

Referee #4 (Remarks to the Author):

The authors included a few more experiments that have improved the revised manuscript. However, more edits and experiments need to be performed for the publication to be published in Nature, particularly for the mechanical stability studies.

Minor comments:

- There are many reports of flexible MOFs used for the adsorption and desorption of different compounds; the authors should make sure to cite relevant literature about flexible porous materials.
- The authors state that the mass loss at 100 C from their TGA data corresponds to the loss of DMF; however, this is most likely water as loss of physisorbed DMF should occur closer to 150 C. Was the crystal that TGA was performed on taken out of the DMF solution immediately prior to the analysis? 50% mass loss from water is a considerable amount. Were the experiments on the DMF-soaked MOFs used from this same solvent? If so, then how can the authors conclude that the results are due to DMF and not water?
- For the single crystal to single crystal transition that takes place, could the authors add 1-2 sentences to rationalize why that is occurring?

Mechanical stability studies:

- For the nanoindentation experiments, the authors compare an air-dried sample with a DMF-soaked sample. In the SI, the authors state that air-drying the sample results in a color change, which based on their experimental section, indicates that water has been removed from the framework. As the crystals have not been thermally activated, would DMF still not be present in the crystal, especially since heating is required to remove the DMF? In this case, what would be the difference between the air-dried material and the DMF-soaked one?
- Could the authors list the 15 hydrogen bond competing and non-competing used solvents in the SI? Additionally, why did these particular solvents result in crystal fracture? If using a non-competing solvent, would one not expect a more robust framework (and no crystal breakage) based on the hydrogen-bonding attenuation rationale?
- The authors still do not have DAC experiments of the unsolvated crystal. It is well known that a penetrating pressure-transmitting medium will result in a higher bulk modulus due to the pressure-induced filling of the pores of the material. Therefore, a non-penetration PTM should be used to obtain a better understanding of the intrinsic framework. Finally, an additional DAC experiment with THF to compare with the DMF-soaked MOF would make the DAC results more meaningful.

Author Rebuttals to Second Revision:

[3] Point-to-Point Answers to the Reviewers' Comments

Referee #4

1. The authors included a few more experiments that have improved the revised manuscript. However, more edits and experiments need to be performed for the publication to be published in Nature, particularly for the mechanical stability studies.

=> According to the referee's suggestions, we performed additional analytical studies using TG/MS, ^1H NMR and XRD/DAC, and revised the manuscript and Supplementary Information.

2. There are many reports of flexible MOFs used for the adsorption and desorption of different compounds; the authors should make sure to cite relevant literature about flexible porous materials.

=> Although the present work focuses attention on the elastic mechanical properties of MOFs, there have been reported many MOFs that change their structures upon sorption, as pointed out by this referee. According to the request by the referee, we added the following review paper on flexible MOFs to the revised reference list.

42. Schneemann A. *et al.* Flexible metal–organic frameworks. *Chem. Soc. Rev.* **43**, 6062–6096 (2014).

3. The authors state that the mass loss at 100 °C from their TGA data corresponds to the loss of DMF; however, this is most likely water as loss of physisorbed DMF should occur closer to 150 °C. Was the crystal that TGA was performed on taken out of the DMF solution immediately prior to the analysis? 50% mass loss from water is a considerable amount. Were the experiments on the DMF-soaked MOFs used from this same solvent? If so, then how can the authors conclude that the results are due to DMF and not water?

=> We carried out thermogravimetry/mass spectrometry (TG/MS) analysis of a crystalline sample of DMF-including CTN^{MOF} , which was taken out from its DMF suspension just before the TG/MS analysis in order to avoid the volatilization of included DMF. The result clearly showed the release of DMF in a temperature range from 25 °C to 150 °C (Supplementary Fig. 37), whereas no release of water was detected over a wide temperature range. We also conducted ^1H NMR spectroscopy of a DCl-digested sample of "air-dried CTN^{MOF} (air-dried for 4 h under dry air flow at 25 °C)" in $\text{DMSO-}d_6$ (Supplementary Fig. 16), where only one molecule of DMF per ligand was detected. Such residual DMF in CTN^{MOF} most likely coordinates to the axial position of the coordination-unsaturated Co^{2+} and therefore cannot attenuate the H-bonds between the catenated macrocycles. In the previous version, we carried out in situ FTIR spectroscopy of air-dried CTN^{MOF} and substantiated the presence of these H-bonds by means of in situ FTIR spectroscopy. The TG/MS result (release of DMF at lower temperatures than its boiling point of 153 °C) is not surprising, as there are many similar examples.

4. For the single crystal to single crystal transition that takes place, could the authors add 1-2 sentences to rationalize why that is occurring?

=> Because of an editorial request for shortening the main text, we added the following message to the caption for Fig. 3.

Since the above crystal structures are analogous to each other, the energy barriers required for their transitions are likely small, so that they can be smoothly interconverted without any structural deterioration.

5. For the nanoindentation experiments, the authors compare an air-dried sample with a DMF-soaked sample. In the SI, the authors state that air-drying the sample results in a color change, which based on their experimental section, indicates that water has been removed from the framework. As the crystals have not been thermally activated, would DMF still not be present in the crystal, especially since heating is required to remove the DMF? In this case, what would be the difference between the air-dried material and the DMF-soaked one?

=> As described for Comment #3, the TG/MS analysis revealed that DMF-soaked **CTN^{MOF}** includes DMF (rather than water). However, upon being air-dried for 4 h at 25 °C, this DMF-including **CTN^{MOF}** (the H-bonds between the catenated macrocycles are attenuated) releases the majority of DMF (80%) and recovers the H-bonds between the catenated macrocycles.

6. Could the authors list the 15 hydrogen bond competing and non-competing used solvents in the SI? Additionally, why did these particular solvents result in crystal fracture? If using a non-competing solvent, would one not expect a more robust framework (and no crystal breakage) based on the hydrogen-bonding attenuation rationale?

=> We added the list of solvents tested for the solvent exchange to the revised Supporting Information. Considering the Young's modulus, we assume that air-dried **CTN^{MOF}** with H-bonded catenated macrocycles is not flexible and adaptive enough for solvent uptake.

7. The authors still do not have DAC experiments of the unsolvated crystal. It is well known that a penetrating pressure-transmitting medium will result in a higher bulk modulus due to the pressure-induced filling of the pores of the material. Therefore, a non-penetration PTM should be used to obtain a better understanding of the intrinsic framework. Finally, an additional DAC experiment with THF to compare with the DMF-soaked MOF would make the DAC results more meaningful.

=> We appreciate these comments. Indeed, if non-penetrating PTM that could attenuate the H-bonds between the catenated macrocycles in **CTN^{MOF}** is available, **CTN^{MOF}** must be more elastic. However, in reality, such a PTM is unavailable.

=> In the XRD/DAC analysis in THF, we found that THF-including **CTN^{MOF}** showed a pressure-dependent anisotropic deformation analogous to DMF-including **CTN^{MOF}** in DMF (Supplementary Table 16) despite a smaller level of deformation than that of DMF-including **CTN^{MOF}** in DMF.

=> We also attempted XRD/DAC analysis of DMF-including **CTN^{MOF}** in Dephne oil and

fluorinert, which are common non-penetrating pressure transmitting media. However, CTN_{MOF} cracked in these media, and we were unable to conduct a similar evaluation in DAC.

Reviewer Reports on the Third Revision:

Referee #4 (Remarks to the Author):

The authors attempted to answer the questions, I believe to the best of their ability, and therefore this reviewer is satisfied