nature portfolio

Peer Review File

Solid–Vapor Synthesis of Dynamic Crystalline One-Dimensional Supramolecular Polymers from Amorphous Macrocycles

Corresponding Author: Professor Kecheng Jie

This manuscript has been previously reviewed at another journal. This document only contains information relating to versions considered at Nature Communications.

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I have carefully read the revised manuscript together with the authors' detailed point-by-point responses to all of the reviewers' comments. The authors have addressed the concerns raised during the initial review in a thorough and convincing manner, and I appreciate the care with which they have revised the manuscript. In my assessment, all of the major issues have been satisfactorily resolved, and the revisions have substantially improved the quality and clarity of the work. I have no further comments and believe that the manuscript is suitable for publication in *Nature Communications*. I therefore recommend acceptance in its present form.

Reviewer #2

(Remarks to the Author)
I appreciate the authors' serious and transparent efforts in addressing my previous comments. They have made substantial revisions that truly improve the manuscript.

In particular, removing the AFM data and the claims about vapor-controlled mechanical properties was a wise decision. It avoids the risk of overinterpretation and the structural contradictions I pointed out in my previous comment. Also, stepping back from the claim that the solid-vapor route is the "only" way to make CSP-1, and redefining the thermal recovery simply as a "thermodynamically driven solid-state polymorphic phase transition," makes the physical chemistry of the system much more rigorous and believable.

By dropping the mechanical application part, the paper has shifted to a purely fundamental study on dynamic crystalline supramolecular polymers. It is now a very solid piece of crystal engineering work. Whether this fundamental focus still carries the broad impact expected for Nature Communications is ultimately up to the Editor. However, from a technical standpoint, I am satisfied with the robustness of the revised manuscript and can recommend its publication, with just a few minor suggestions below.

Minor Comment
(1) Macroscopic observation of the crystals (POM): In response to my previous Comment 5 regarding Polarized Optical Microscopy (POM), the authors explained that since the mechanical analysis was removed, there is no longer a need to show the macroscopic crystal quality to justify the hardness differences.
I understand their logic regarding the mechanical part. However, seeing is believing. In a paper heavily focused on "bulk crystalline phase transformations," simply showing optical or POM images of the crystals before and after the vapor/thermal treatments would serve as great visual proof of the material's dynamic nature and bulk homogeneity. It is a very basic characterization in solid-state chemistry. I still think it would be beneficial to include these images in the Supplementary Information to complement the PXRD data, though I will leave it to the authors to decide whether to add them at this stage.

(2) Quantitative proof of reversibility and cycling data: The manuscript highlights the "highly dynamic" nature and "reversible" solid-state transformations of this system (e.g., CSP-1 ↔ P5PA-2C4N). However, in a closed vessel, a 100% complete reverse exchange is thermodynamically difficult to achieve without removing the displaced guests. To further strengthen the claim of reversibility, it would be highly beneficial to provide PXRD and 1H NMR data for at least 2–3 full cycles to demonstrate the material's fatigue resistance. Additionally, I suggest quantifying the residual amine ratio by dissolving the sample and running 1H NMR after the reverse exchange. If the conversion is not 100%, slightly softening the wording (e.g., "predominantly transformed back" instead of "ultimately transformed into original CSP-1") would make the discussion more rigorous.

(3) Reconsidering the nomenclature of "NonCSP": The authors have nicely reframed the thermal recovery process as a "solid-state polymorphic phase transition" between two crystalline states. Given this new thermodynamic context, continuing to refer to the metastable crystal as "NonCSP" might be slightly confusing to readers, as the prefix "Non-" often implies an amorphous or non-crystalline state. I would suggest renaming this metastable phase to something more crystallographically intuitive, such as "Guest-Free Phase," "Discrete Phase," or "Polymorph B."

(4) Presentation of NMR data in the SI: For better readability, I suggest stacking the 1H NMR spectra of the starting precursors and the resulting solid-vapor products in single comparative figures. Currently, these spectra are scattered across different individual figures in the Supplementary Information, making it a bit tedious for readers to visually track the peak shifts and evaluate the conversion efficiency at a glance.

Reviewer #3

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The revised manuscript reports a solid–vapor route to a dynamic crystalline one-dimensional supramolecular polymer, CSP-1, from amorphous macrocycle precursors. The authors have addressed the major conceptual and evidentiary concerns from the previous review round by clarifying that CSP-1 can also be obtained by conventional solution-phase crystallization, adding DOSY and DLS data to support concentration-dependent supramolecular assembly in noncompetitive solvents, removing unsupported nanomechanical claims, and reframing the thermal recovery of CSP-1 from NonCSP as a thermally activated solid-state phase transition rather than a fundamentally new polymerization mechanism. Overall, the revision is substantially improved and the main conclusions are now largely supported by the experimental evidence.

The authors have adequately addressed the concern that the solid–vapor route was overemphasized as uniquely enabling CSP-1. The manuscript now explicitly states that CSP-1 can also be prepared by conventional solution-phase synthesis followed by crystallization, and more appropriately presents the solid–vapor method as a one-step, solvent-free platform that couples monomer formation, host–guest supramolecular polymerization, crystallization, and response studies.

The new solution-state characterization is a meaningful improvement. DOSY shows a clear concentration-dependent decrease in diffusion coefficient, and DLS shows an increase in hydrodynamic diameter with concentration, supporting formation of larger supramolecular assemblies in noncompetitive solvent. The authors should, however, retain cautious language and avoid implying that DOSY/DLS alone unambiguously prove exclusively long, 1D CSP-like chains in solution.

The most important remaining issues are textual and interpretive rather than experimental. The revised thermodynamic section is much improved, with VT-PXRD/DSC evidence supporting a NonCSP-to-CSP-1 phase transition and a metastable-to-stable polymorph interpretation, but phrases such as “thermally induced polymerization,” “annealing-like,” “unprecedented,” and “scalable” should be further softened or qualified. In addition, several typographical/wording errors remain, including “severs” instead of “serves,” “continues” instead of “continuous,” “straightly,” “donated” instead of “denoted,” and “broaden size distributions.”

Reviewer #1 (Remarks for the Author):

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We sincerely thank the reviewer for the positive evaluation of our revised manuscript and for the recommendation to accept our work for publication in *Nature Communications*. We greatly appreciate the reviewer's time, constructive comments, and recognition of our efforts in revising the manuscript.

Reviewer #2 (Remarks to the Author):

I appreciate the authors' serious and transparent efforts in addressing my previous comments. They have made substantial revisions that truly improve the manuscript.
In particular, removing the AFM data and the claims about vapor-controlled mechanical properties was a wise decision. It avoids the risk of overinterpretation and the structural contradictions I pointed out in my previous comment. Also, stepping back from the claim that the solid-vapor route is the "only" way to make CSP-1, and redefining the thermal recovery simply as a "thermodynamically driven solid-state polymorphic phase transition," makes the physical chemistry of the system much more rigorous and believable.
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We sincerely thank the reviewer for the careful re-evaluation of our revised manuscript and for the positive and encouraging comments. We greatly appreciate the reviewer's constructive suggestions throughout the review process, which have helped us improve the rigor and clarity of the manuscript. We are grateful for the reviewer's recognition of our revisions. Our responses to the minor comments are provided below.

Minor Comment
(1) Macroscopic observation of the crystals (POM): In response to my previous Comment 5 regarding Polarized Optical Microscopy (POM), the authors explained that since the mechanical analysis was removed, there is no longer a need to show the macroscopic crystal quality to justify the hardness differences.
I understand their logic regarding the mechanical part. However, seeing is believing. In a paper heavily focused on "bulk crystalline phase transformations," simply showing optical or POM images of the crystals before and after the vapor/thermal treatments would serve as great visual proof of the material's dynamic nature and bulk homogeneity. It is a very basic characterization in solid-state chemistry. I still think it would be beneficial to include these images in the Supplementary Information to complement the PXRD data, though I will leave it to the authors to decide whether to add them at this stage.

We sincerely thank the reviewer for this suggestion. We agree that optical microscopy or polarized optical microscopy (POM) images can provide intuitive information on the macroscopic morphology of crystals. However, the materials investigated in this work are crystalline powders rather than relatively large single crystals. Their structures have been determined by PXRD comparison with corresponding SC-XRD structures. The morphological information provided by optical microscopy or POM is insufficient to distinguish the differences in crystal structure. In addition, the conclusions of this work are based on the structure-dependent thermodynamic differences rather than macroscopic morphology. These differences have been demonstrated by VT-PXRD, DSC, and theoretical calculations. We therefore consider the current data sufficient to support the conclusions of this work.

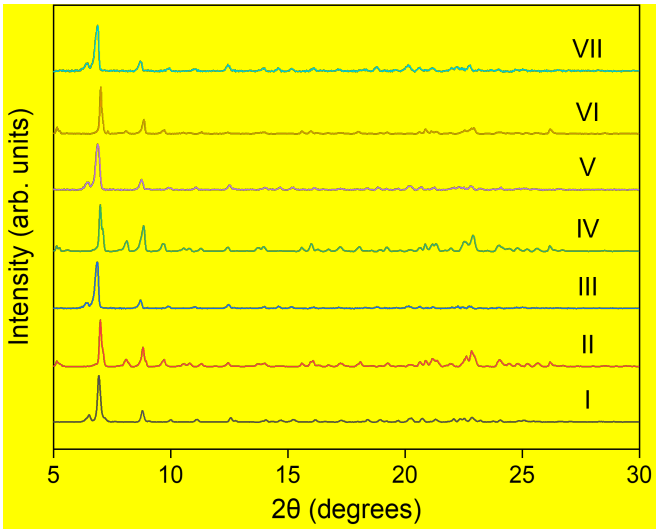
(2) Quantitative proof of reversibility and cycling data: The manuscript highlights the "highly dynamic" nature and "reversible" solid-state transformations of this system (e.g., CSP-1 ↔ P5PA-2C4N). However, in a closed vessel, a 100% complete reverse exchange is thermodynamically difficult to achieve without removing the displaced guests. To further strengthen the claim of reversibility, it would be highly beneficial to provide PXRD and 1H NMR data for at least 2–3 full cycles to demonstrate the material's fatigue resistance. Additionally, I suggest quantifying the residual amine ratio by dissolving the sample and running 1H NMR after the reverse exchange. If the conversion is not 100%, slightly softening the wording (e.g., "predominantly transformed back" instead of "ultimately transformed into original CSP-1") would make the discussion more rigorous.

We sincerely thank the reviewer for this suggestion. We agree that cycling experiments are important to further demonstrate the reversibility of the solid-state structural transformation. Following the reviewer's suggestion, we have added PXRD data over three transformation cycles. Regarding the analysis of residual amines by ^{1}H NMR, we agree that such analysis can provide quantitative information when the guest signals can be reliably distinguished. However, the signals of C_4N and C_6N largely overlap, making it difficult to accurately quantify residual guests by ^{1}H NMR. Therefore, ^{1}H NMR cannot provide a reliable estimation of the conversion ratio in this case. Accordingly, we have revised the related descriptions in the manuscript to make the discussion more rigorous.

Corresponding revisions in page 7 of the main text:

After 24 hours of exposure, these crystals predominantly transformed back to CSP-1, indicating the recovery of SP chains. This reversible transformation could be repeated over three consecutive vapor-treatment cycles (Supplementary Fig. 60).

Corresponding revisions in page S54 of the Supplementary Information:



Supplementary Figure 60. Reversible transformations between CSP-1 and C_4N@P5PA-2C_4N over three vapor-treatment cycles: (I) experimental CSP-1; (II) crystals of I after exposure to C_4N vapor for 12 hours; (III) crystals of II after exposure to C_6N vapor for 24 hours; (IV) crystals of III after exposure to C_4N vapor for 12 hours; (V) crystals of IV after exposure to C_6N vapor for 24 hours; (VI) crystals of V after exposure to C_4N vapor for 12 hours; (VII) crystals of VI after exposure to C_6N vapor for 24 hours.

(3) Reconsidering the nomenclature of "NonCSP": The authors have nicely reframed the thermal

recovery process as a "solid-state polymorphic phase transition" between two crystalline states. Given this new thermodynamic context, continuing to refer to the metastable crystal as "NonCSP" might be slightly confusing to readers, as the prefix "Non-" often implies an amorphous or non-crystalline state. I would suggest renaming this metastable phase to something more crystallographically intuitive, such as "Guest-Free Phase," "Discrete Phase," or "Polymorph B."

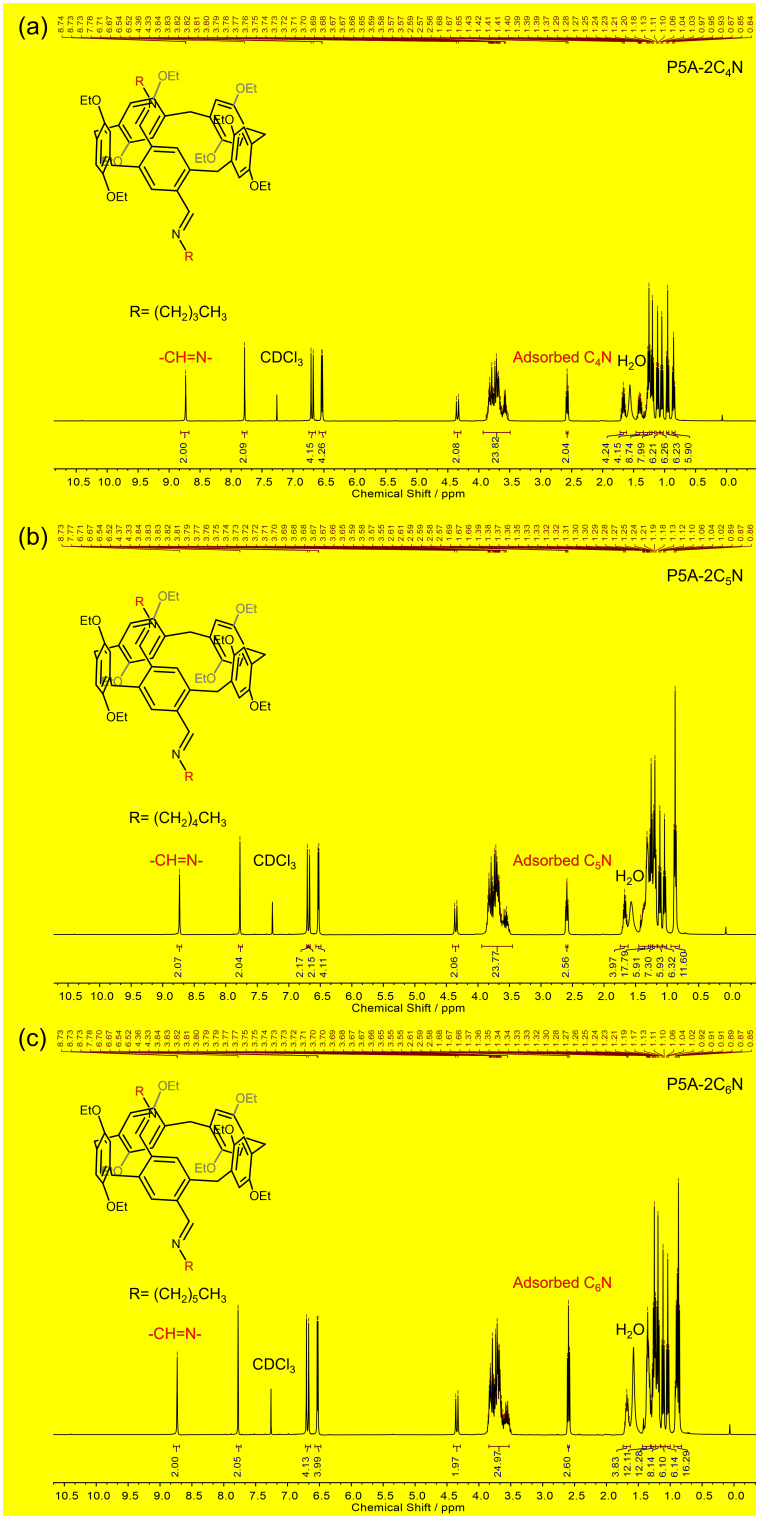
We sincerely thank the reviewer for this suggestion. We agree that the term "NonCSP" may be misleading, as it could imply a non-crystalline state. Following the reviewer's suggestion, we have renamed "NonCSP" to "DisCSP" (disassembled phase) throughout the manuscript to avoid possible confusion.

Corresponding revisions in page 8 of the main text:
The aforementioned results reveal the existence of contrasting phases of P5PA-2C_6N, including CSP-1 with SP chains and DisCSP with disassembled monomers (Fig. 6a).

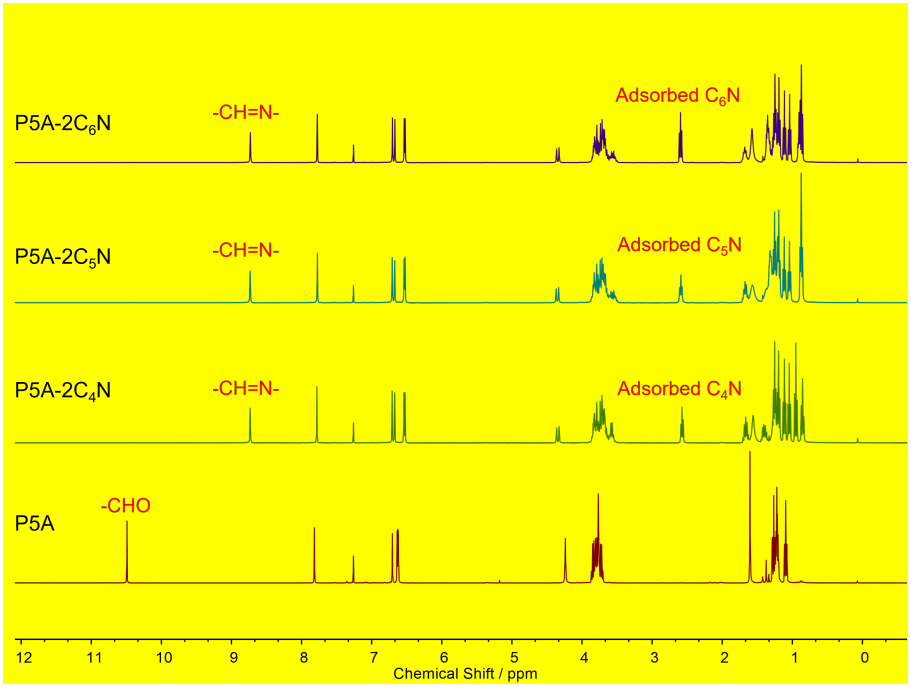
(4) Presentation of NMR data in the SI: For better readability, I suggest stacking the 1H NMR spectra of the starting precursors and the resulting solid-vapor products in single comparative figures. Currently, these spectra are scattered across different individual figures in the Supplementary Information, making it a bit tedious for readers to visually track the peak shifts and evaluate the conversion efficiency at a glance.

We sincerely thank the reviewer for this helpful suggestion. Following the reviewer's recommendation, we have reorganized the ^{1}H NMR spectra in the Supplementary Information to facilitate direct comparison between the precursors and the solid–vapor products. We believe that the revisions can improve the readability of the Supplementary Information.

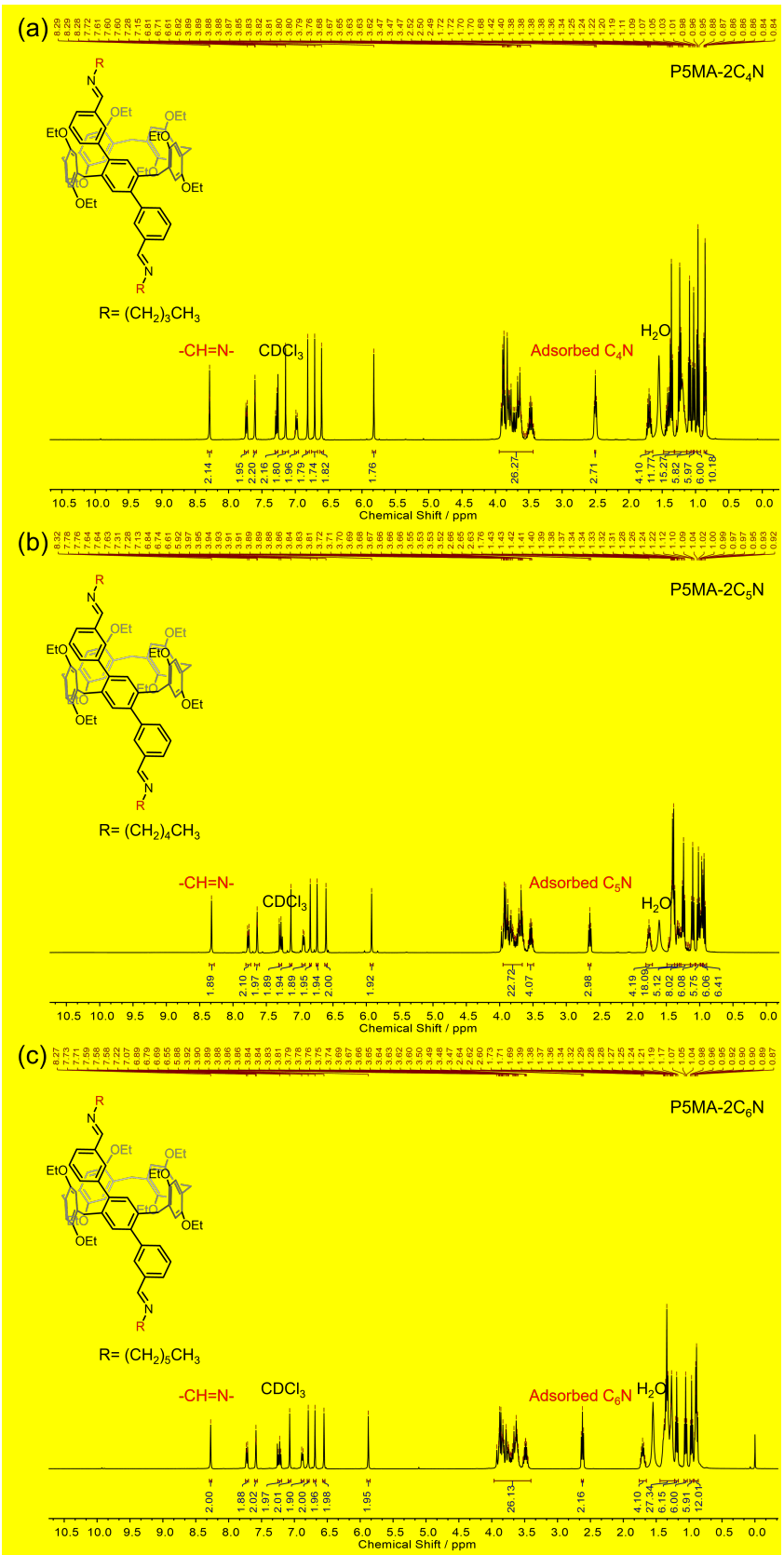
Corresponding revisions in page S22 of the Supplementary Information:



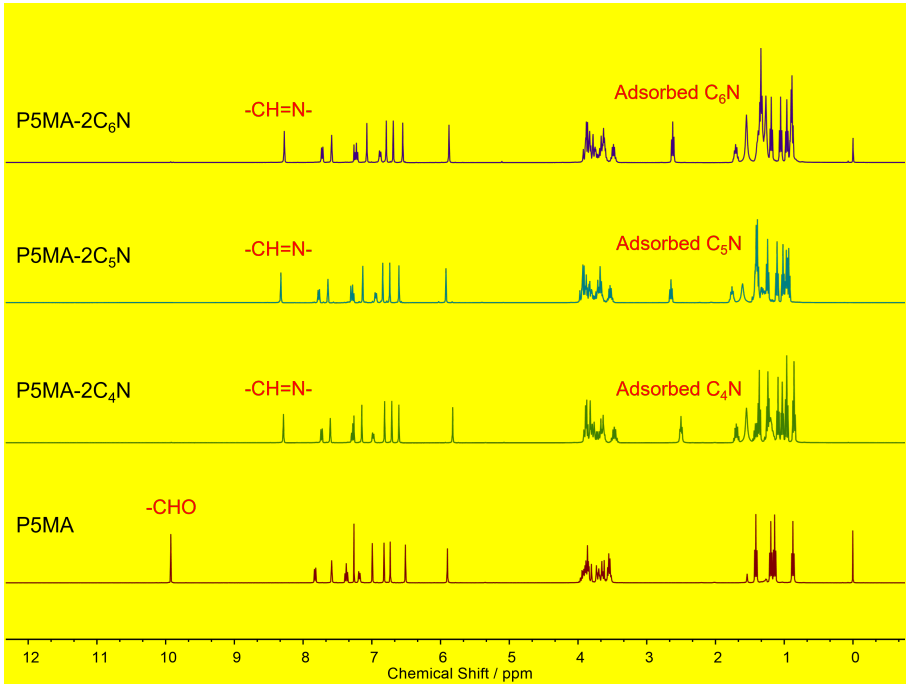
Supplementary Figure 23. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of P5A after exposure to aliphatic amine vapors: (a) C_4N, (b) C_5N and (c) C_6N.



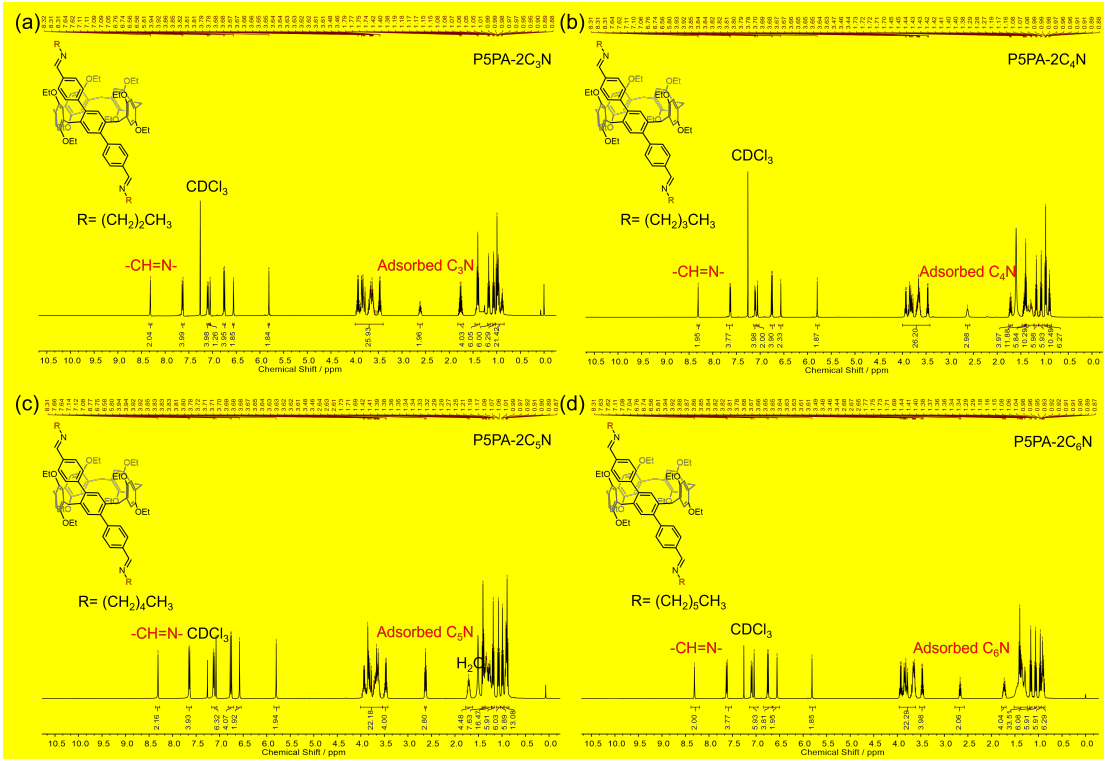
Supplementary Figure 24. Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of P5A and the corresponding solid–vapor products after exposure to C_4N, C_5N and C_6N vapors (from bottom to top).



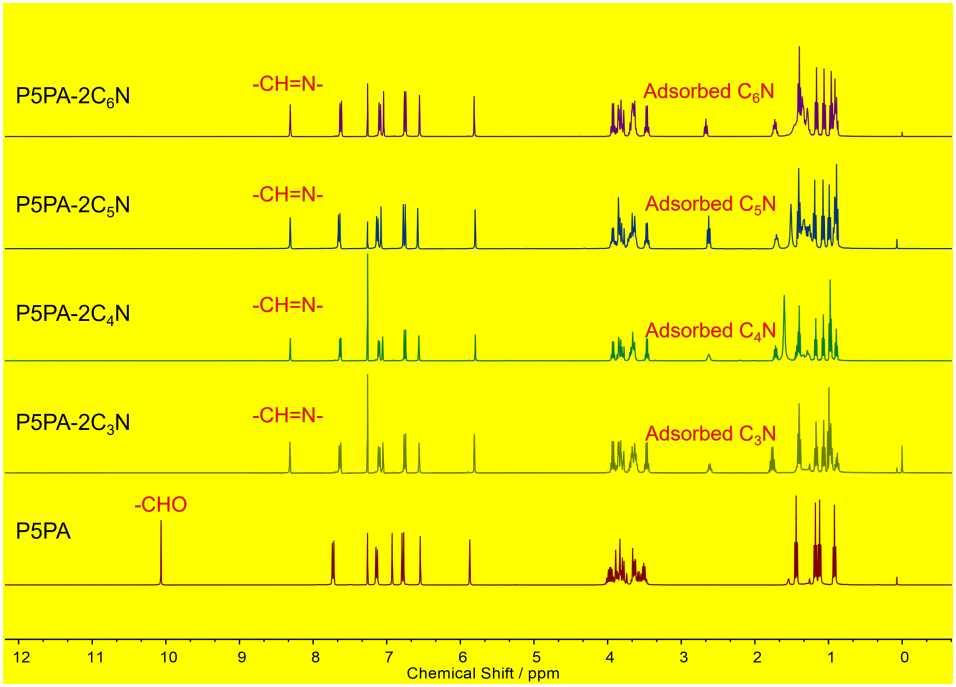
Supplementary Figure 25. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of P5MA after exposure to aliphatic amine vapors: (a) C_4N, (b) C_5N and (c) C_6N.



Supplementary Figure 26. Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of P5MA and the corresponding solid–vapor products after exposure to C_4N, C_5N and C_6N vapors (from bottom to top).



Supplementary Figure 27. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of P5PA after exposure to aliphatic amine vapors: (a) C_3N, (b) C_4N, (c) C_5N and (d) C_6N.



Supplementary Figure 28. Stacked ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of P5PA and the corresponding solid–vapor products after exposure to C_3N, C_4N, C_5N and C_6N vapors (from bottom to top).

Reviewer #3 (Remarks to the Author):

The revised manuscript reports a solid–vapor route to a dynamic crystalline one-dimensional supramolecular polymer, CSP-1, from amorphous macrocycle precursors. The authors have addressed the major conceptual and evidentiary concerns from the previous review round by clarifying that CSP-1 can also be obtained by conventional solution-phase crystallization, adding DOSY and DLS data to support concentration-dependent supramolecular assembly in noncompetitive solvents, removing unsupported nanomechanical claims, and reframing the thermal recovery of CSP-1 from NonCSP as a thermally activated solid-state phase transition rather than a fundamentally new polymerization mechanism. Overall, the revision is substantially improved and the main conclusions are now largely supported by the experimental evidence.

The authors have adequately addressed the concern that the solid–vapor route was overemphasized as uniquely enabling CSP-1. The manuscript now explicitly states that CSP-1 can also be prepared by conventional solution-phase synthesis followed by crystallization, and more appropriately presents the solid–vapor method as a one-step, solvent-free platform that couples monomer formation, host–guest supramolecular polymerization, crystallization, and response studies.

The new solution-state characterization is a meaningful improvement. DOSY shows a clear concentration-dependent decrease in diffusion coefficient, and DLS shows an increase in hydrodynamic diameter with concentration, supporting formation of larger supramolecular assemblies in noncompetitive solvent. The authors should, however, retain cautious language and avoid implying that DOSY/DLS alone unambiguously prove exclusively long, 1D CSP-like chains in solution.

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We sincerely thank the reviewer for the positive evaluation of our revised manuscript and for the helpful suggestions. Following the reviewer's recommendation, we have removed the descriptions of "unprecedented" and "scalable" and revised the interpretation of solution-state supramolecular polymerization. We have also corrected the typographical and wording errors identified by the reviewer.

Corresponding revisions in page 3 of the main text:

We anticipated that the *n*-alkyl chains introduced by imine condensation may thread into adjacent macrocycle cavities to form continuous host–guest complexes, leading to long-range SPs.

In page 4 of the main text:

In the resulting SC-XRD structure, one *n*-hexyl chain appended on the monomer (denoted as P5PA-2C_6N) penetrates directly into the adjacent cavity, forming continuous head–to–tail 1-D SP chains driven by host–guest complexation (Fig. 2e).

In page 5 of the main text:

As such, this solid–vapor process differs fundamentally from vapor-phase COF synthesis, in which

reversible imine formation is independent of reactant size and primarily serves as an error-correction mechanism during framework construction[46–48].

In page 6 of the main text:

Therefore, unlike conventional molecular crystals, CSP-1 retains polymeric assemblies upon dissolution at relatively high monomer concentrations rather than completely dissociating into monomers.

At lower concentrations, the DLS profiles exhibited a sharp peak, whereas large aggregates with broad size distributions formed at 72 and 96 mM.

In page 7 of the main text:

The depolymerization of CSP-1 after DCE treatment (denoted as DCE@P5PA-2C_6N) was validated by SC-XRD analysis, in which DCE molecules replace the threading *n*-hexyl chains and form discrete host–guest complexes with P5PA-2C_6N (Fig. 5d).

In page 8 of the main text:

This represents a new phase of P5PA-2C_6N (denoted as DisCSP) that is completely different from CSP-1, with P5PA-2C_6N existing as discrete units within the crystal lattice (Fig. 5g).

We hope that the revised version of the work should be suitable for publication in *Nature Communications.*

Yours Sincerely,