Growing and Shaping Metal–Organic Framework Single Crystals at the Millimeter Scale

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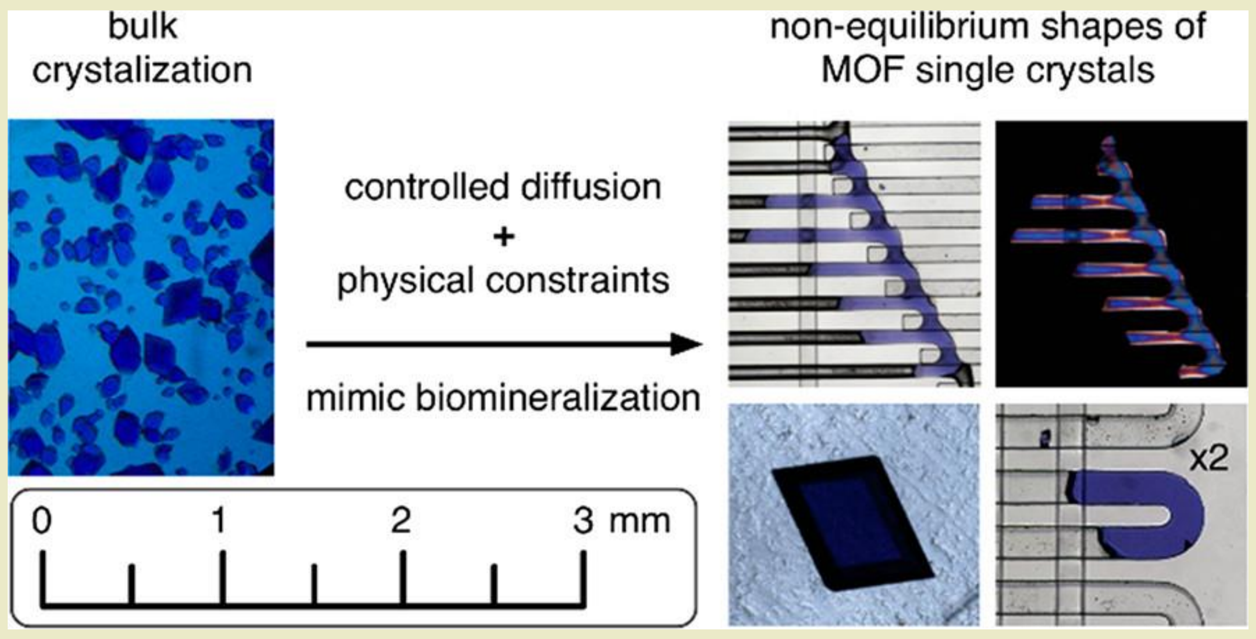
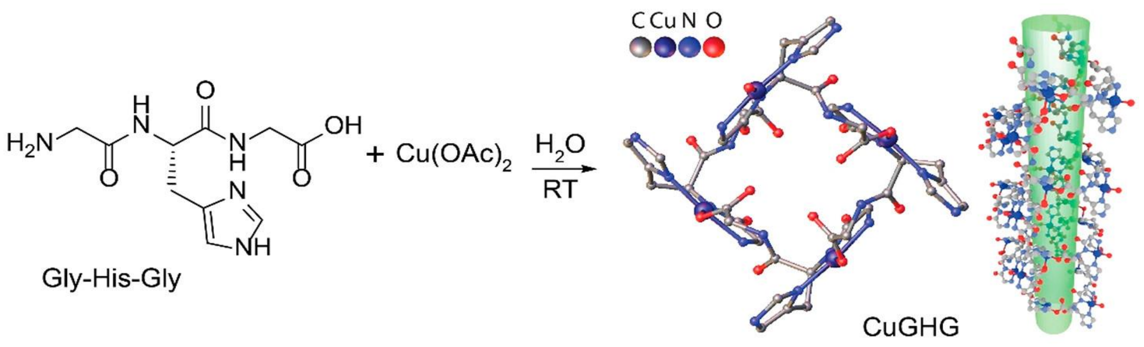
1. INTRODUCTION

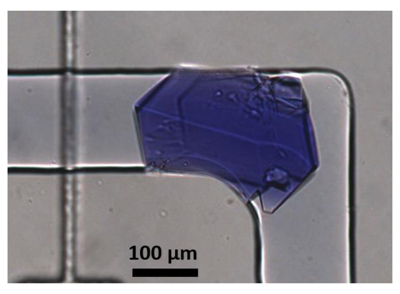
- **Morphological control of crystals** is utterly important in reticular chemistry, especially as a fundamental strategy toward preparing functional materials of superior properties[1,2].
- In the realm of metal-organic frameworks (MOFs), previous endeavors primarily focus on shape manipulation at the nano- and microscale during bulk synthesis and subsequent processing at the mesoscale (e.g., incorporation into polycrystalline films, patterns, and composites) [3,4]
- A notable challenge persists in attaining a meticulous control over both the shape and size of macroscopic single crystals**.**
- Here we successfully demonstrated the spatial and morphological control of crystal growth from a **non-equilibrium state** through the utilization of a **microfluidic device**.
- Due to **low Grashof number condition** in microchannels, **homogenous growth** of peptide-based MOF - CuGHG was greatly promoted, resulting in formation of **well-shaped single crystal at millimeter scale.**



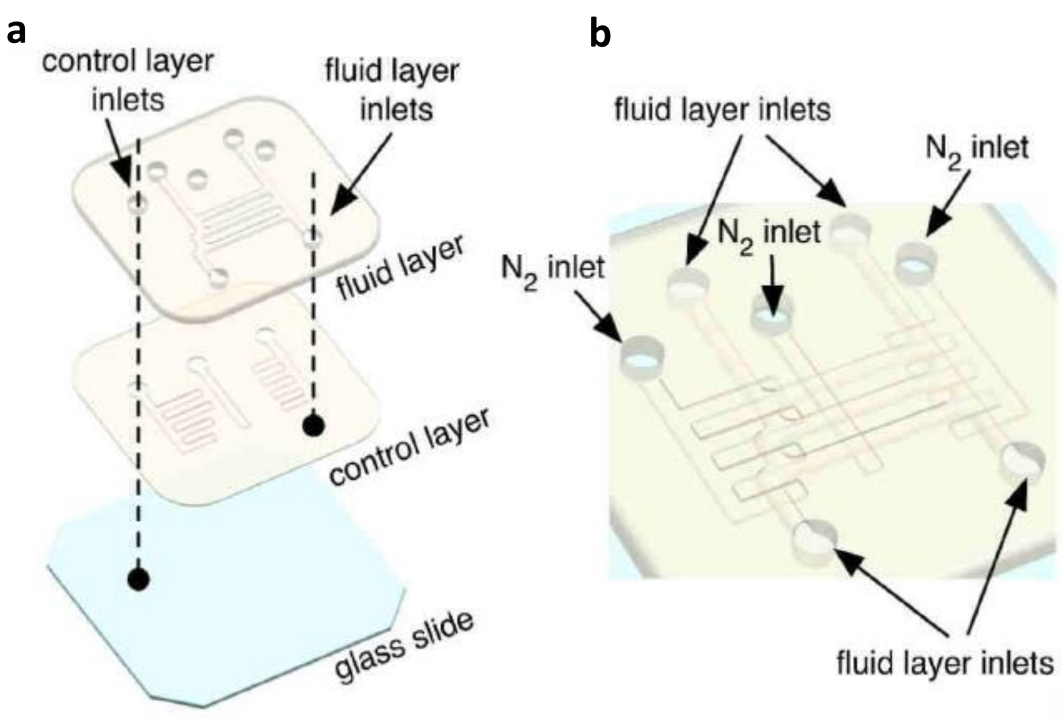
2. METHODOLOGY

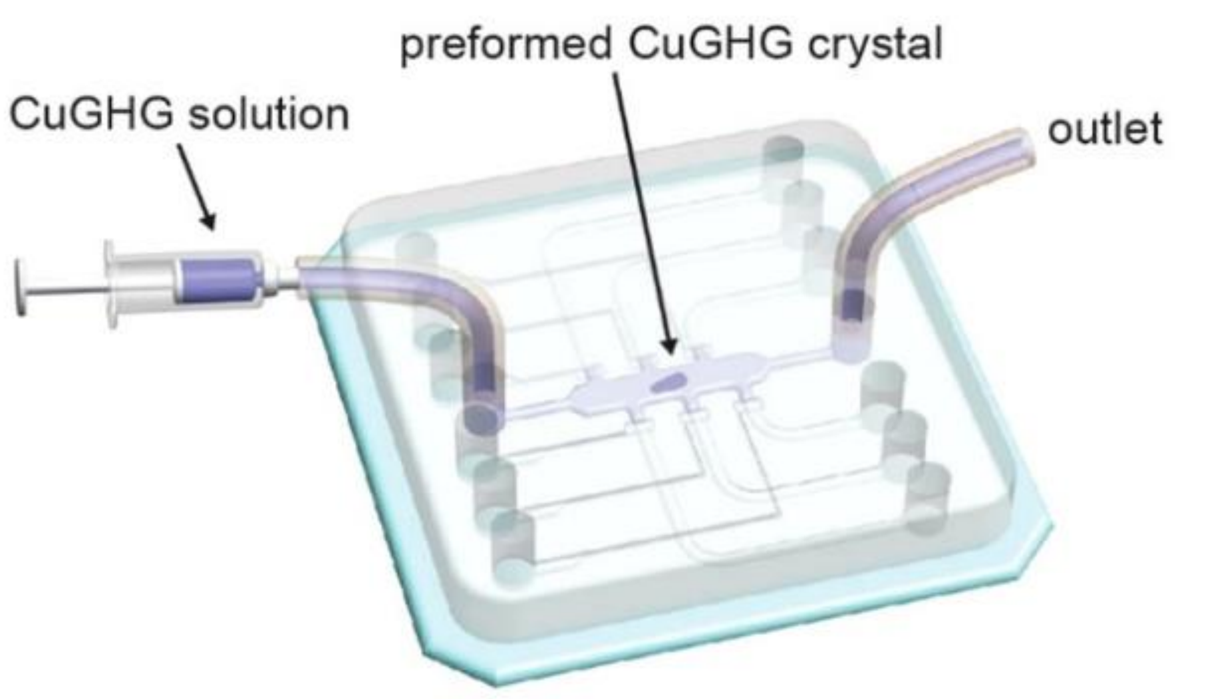
A. Preparing CuGHG solution





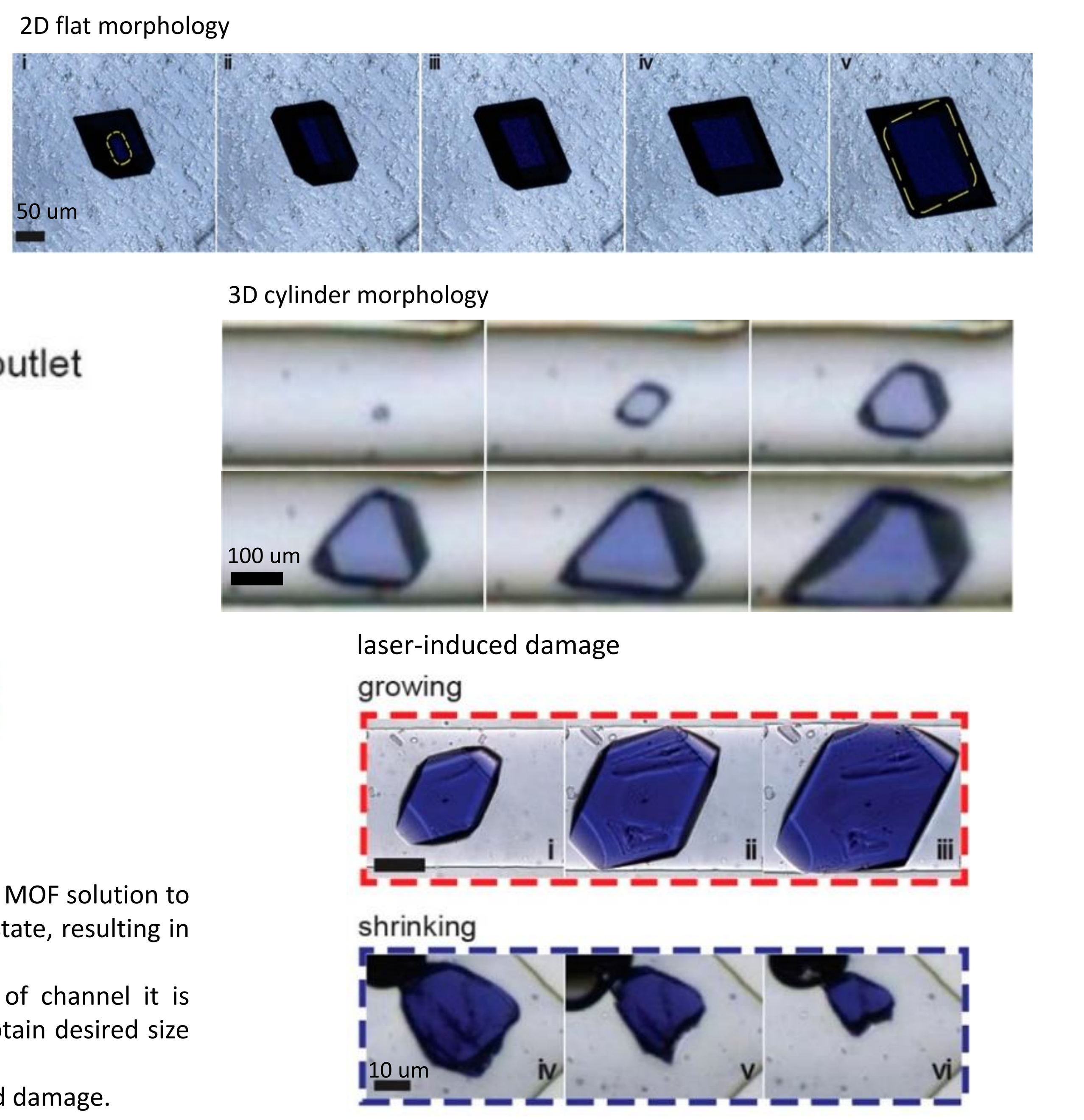
B. Fabrication of PDMS microfluidic chip





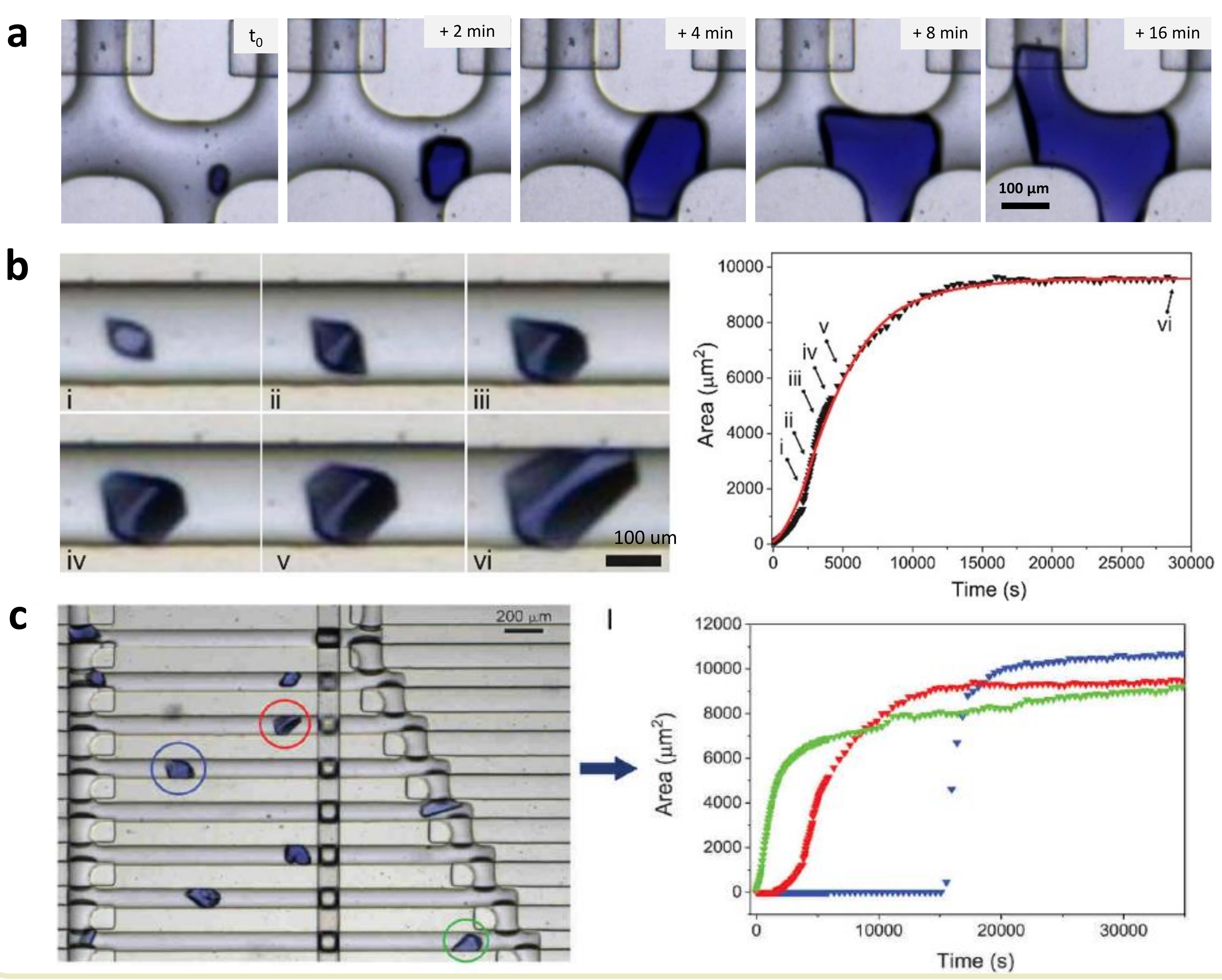
- Micro scale dimension enables **advection to be minimized** and allow the MOF solution to be stabilized and slowly transition from non-equilibrium to equilibrium state, resulting in homogeneous crystal growth.
- Due to **template effect** of microchannel, CuGHG crystal takes shape of channel it is confined in. We can tailor the size and shape of the microchannel to obtain desired size and shape of the crystal.
- CuGHG single crystals can **shrink and regrow** in response to laser-induced damage.

C. Confined growth of CuGHG crystal in microchamber



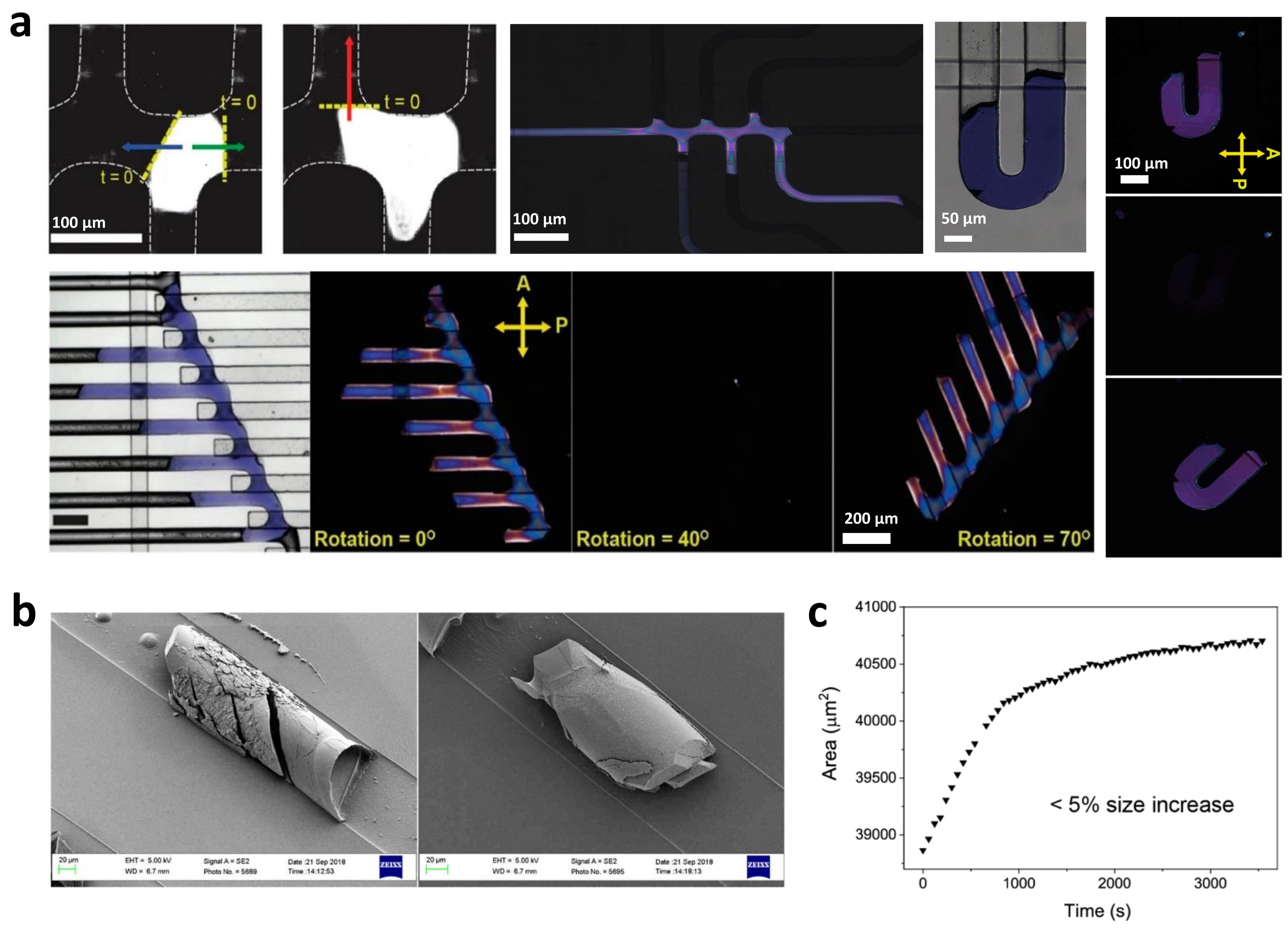
3. RESULT

CuGHG crystal were grown and shaped using different microchambers



4. CHARACTERIZATION

CuGHG crystal were grown and shaped using different microchambers



a) CuGHG crystals grown from microchambers are confirmed to be single crystals under cross polarizer. b) SEM images of selected CuGHG crystals c) In absence of flow, CuGHG crystal shows a non-linear growth profile approaching a plateau, which corresponds to a percentage increase of size as small as 5%

References

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5. CONCLUSION

- Here we successfully demonstrated the **spatial and morphological control** of crystal growth at **the millimeter scale from a non-equilibrium state** through the utilization of a **microfluidic device**.
- Within an advection-free microenvironment of microchamber, peptide-based MOF – CuGHG can be grown homogeneously and continuously as a consequence of a diffusion-controlled supply of precursors.
- We can tailor the size and shape of the microchannel to obtain the size and shape of the crystal.
- Regrowth or shrinkage of the crystals after laser-induced damage demonstrated the stability and mechanical strength of the crystal.
- This work helps expanding the precise control over tailoring shape and size of different material classes for specific applications

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