Supramolecular Peptide Crystals with Hydrophilic and Hydrophobic Pores for Chemo-Mechanical Actuation

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Water-responsive (WR) materials drastically change their dimensions with respect to the changes in relative humidity, and by this process generate mechanical energy.[1] We recently explored supramolecular peptide crystals with aqueous pores for a systematic understanding of water molecules induced H-bonding triggered actuation, and have demonstrated the first examples.[2] Based on these results, we hypothesized that peptides self-assembling into hydrated crystals with flexible hydrophobic and hydrophilic pores can be developed as reversibly interconvertible multi-structural chemo-mechanical actuators.

Aliphatic side chains of amino acids: leucine (Leu) and isoleucine (Ile) are known to form domains with zippers in protein. In comparison to aromatic zippers, the aliphatic Leu/Ile zippers are known to result in flexible domains facilitated by their isotropic weak van der Waals interactions. Here, we demonstrate that a peptide composed of Leu or Ile can be utilized to develop reversibly deformable crystals with tunable mechanical and optical properties, which is triggered by changes in relative humidity and temperature. The dipeptide, Leu-Ile, crystallizes from water at room temperature to form a 2.5 hydrate and under heating 0.75 hydrate. Both forms have hydrophilic and hydrophobic channels and are interconvertible, resulting in switchable porosity. Remarkably, we found that changes in heating and hydration on the 2.5 hydrate allow us to access an additional polymorph, with different properties and porosity. All three forms are interconverted reversibly by controlling relative humidity or temperature accordingly. The changes in the H-bonding pattern of the water channel in each structure influenced the porosity, mechanical and solid-state fluorescence properties. Thus, a single crystal of the dipeptide can be tuned reversibly for different properties with the aid of relative humidity and temperature.

In summary, we demonstrate that short peptide crystals are highly versatile materials with tunable porosity and responsiveness to humidity and temperature. These materials can be designed for multifunctional chemo-mechanical actuation by choosing the suitable sequence of amino acid components. These structures are based on short peptides and are therefore scalable and hold much promise as sustainable and biodegradable materials.

1. Y. Park, X. Chen, *J. Mater. Chem. A*, **2020**, 8, 15227-15244.
2. R. Piotrowska, T. Hesketh, H. Wang, A. R. G. Martin, D. Bowering, C. Zhang, C. T. Hu, S. A. McPhee, T. Wang, Y. Park, P. Singla, T. McGlone, A. Florence, T. Tuttle, R. V. Ulijn, X. Chen, *Nat. Mater.* **2021**, *20*, 403-409.