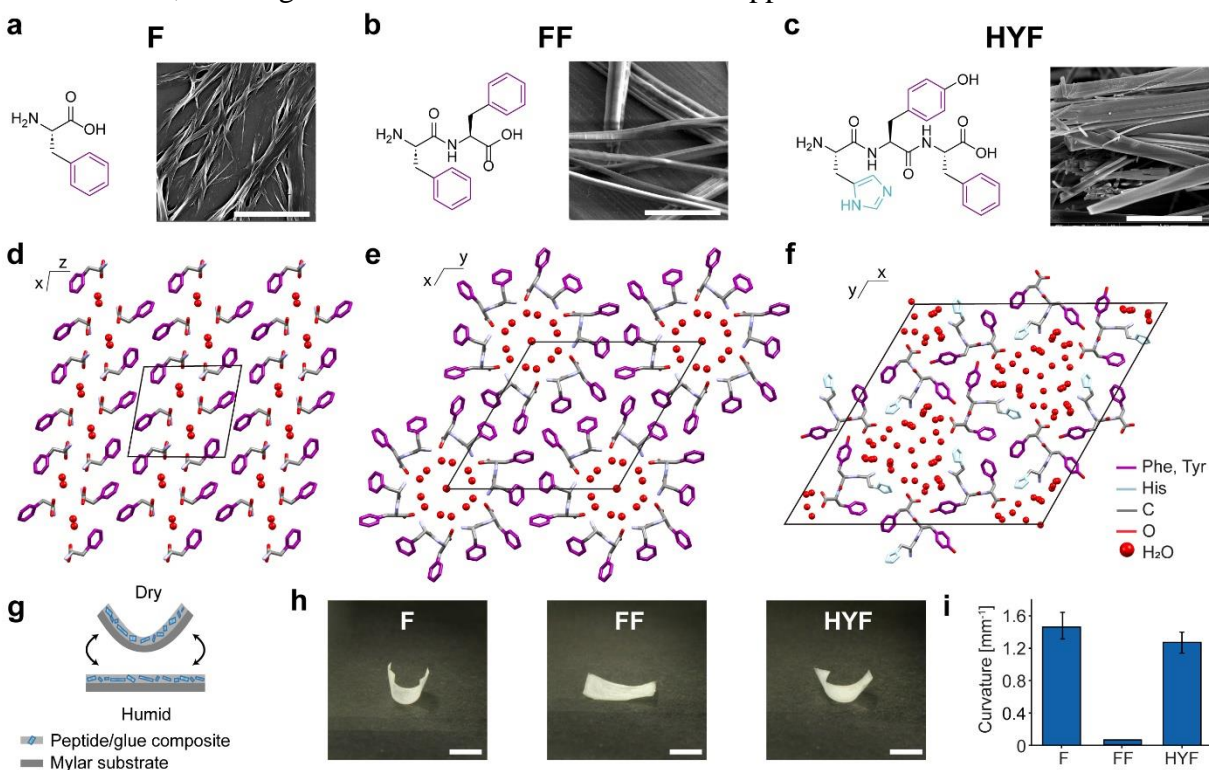




Water-responsive (WR) materials that reversibly deform in response to relative humidity (RH) changes are gaining increasing interest for their potential in energy harvesting and soft robotics applications. Despite progress, there are significant gaps in the understanding of how supramolecular structure underpins the reconfiguration and performance of WR materials. In addition, low-cost and high-performance candidates are needed. Here, we compare three crystals based on the amino acid phenylalanine (F) that contain water channels and F packing domains that are either layered (F), continuously connected (phenylalanyl-phenylalanine, FF), or isolated (histidyl-tyrosyl-phenylalanine, HYF). We analyze hydration-induced reconfiguration through changes in hydrogen-bond interactions and aromatic zipper topology through FTIR and PXRD. F crystals show the greatest RH-induced deformation (WR energy density of 19.8 MJ m^{-3}) followed by HYF (6.5 MJ m^{-3}), while FF exhibits no observable response. The difference in water-responsiveness strongly correlates to the deformability of aromatic regions, with FF crystals being too stiff to deform, whereas HYF is too soft to efficiently transfer water tension to external loads. The water sorption is also highly variable, with F adsorbing 7.4% compared to FF at 220% and HYF at 148%, suggesting sorption capacity is not correlated with water-responsiveness. Collectively, these findings reveal aromatic topology design rules for WR crystals and provide insight into general mechanisms of high-performance WR actuation. Moreover, the best performing candidate identified here, F emerges as an efficient WR material for applications at scale and low cost.



Sheehan, F. K., Wang, H., Podbevšek, D., Naranjo, E., Rivera-Cancel, J., Moran, C., Ulijn, R. V., Chen, X., Aromatic Zipper Topology Dictates Water-Responsive Actuation in Phenylalanine-Based Crystals. *Small* 2023, 2207773. <https://doi.org/10.1002/sml.202207773>