The Active Role of Water in Artificial Water Channel Arrays

In water-induced self-assembly, water becomes an active component that regulates the supramolecular structures and functions of synthetic functional materials.

Water is known as the solvent of life in nature, because it can operate the self-assembly structures and functions of biomolecules. One example that shows the active role of water is found in the hydrophobic gate of trans-membrane proteins. Structural characterizations and theoretical calculations showed that water can open and close the hydrophobic gate by changing the self-assembly structure of the gate. In so doing, water alters also the kinetic barriers required for water and ions to pass through the gate and regulates the water and ion permeabilities of the trans-membrane protein. In contrast, the role of water in synthetic matters is passive. Although synthetic molecules such as dendritic dipeptide, carbon nanotube, pillar arenes, *etc*. have been synthesized to mimic the tube-like structure of trans-membrane proteins, the synthetic molecules are too rigid to interact dynamically with water. In this case, water is simply a liquid that passes through the tube-like supramolecular structures of synthetic molecules, but lacks the ability to operate the self-assembly structures and functions of synthetic molecules.

To make water an active component for synthetic molecules, Chien-Lung Wang (National Yang Ming Chiao Tung University) and Wei-Tsung Chuang (NSRRC) developed a flexible amphiphilic discotic molecule (ADM) and characterized the active role of water in the supramolecular chemistry of this molecule (illustrated in **Fig. 1(a)**).[1] Under polarized light in an optical microscope, they found that water induces the self-assembly of the amorphous ADM as shown in **Figs. 1(b) and 1(c)**, and use of small-angle X-ray scattering at **TLS 23A1** confirmed that this water-induced self-assembly (WISA) resulted in the formation of a hexagonal columnar (Col_h) phase of ADM, which contains bulk artificial water channels (AWC). Moreover, on letting water act as the orientation-directing agent, the directional WISA that they developed can further turn these randomly oriented bulk AWC into a well oriented AWC array.
The excellent orientation control of the bulk AWC was confirmed with grazing Incidence X-ray diffraction (GI XRD) at **TLS 01C2**, **TLS 17A1** and **TLS 23A1** as shown in **Fig. 1(d)**.
Comparing to the nearly 0 water permeability of the dehydrated ADM, the well oriented AWC array prepared by the directional WISA is salt-rejected and delivered an effective water permeability, 4.34 X 10^7 H_2O· nm· channel^{-1} ·s^{-1}, indicating that water not only induces an ordering, but also turns on the function of the ADM. AWC in the literature are tube-like molecules, which provide water transport at the length of several nanometers (~ the

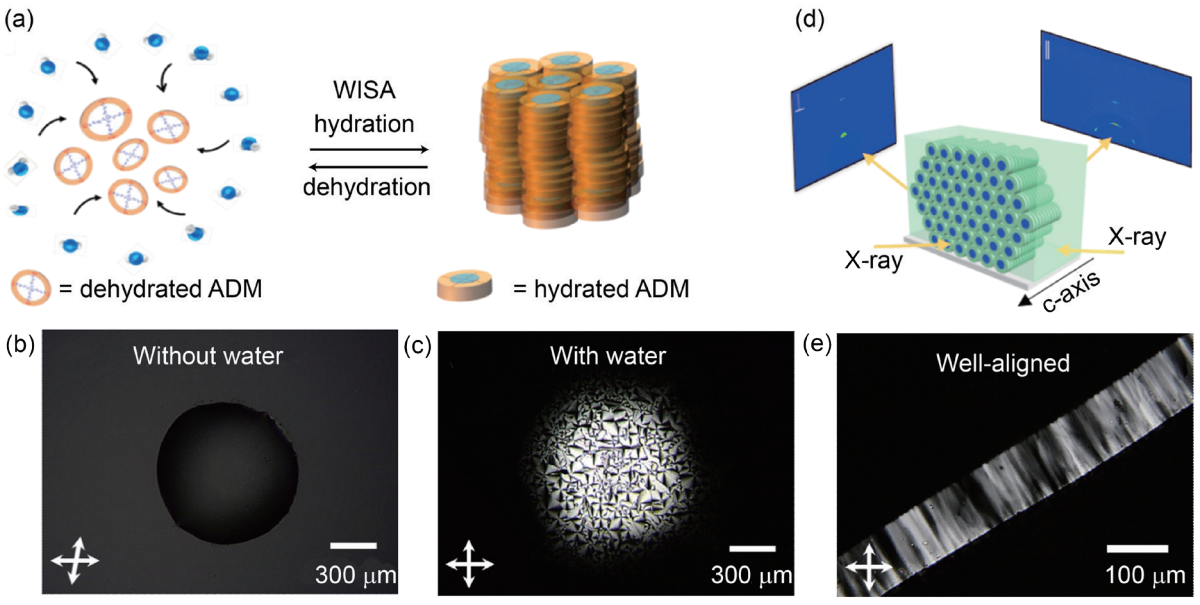

Fig. 1: (a) Illustration of the WISA process. POM images of (b) dehydrated amorphous ADM and (c) hydrated ordered phase of ADM. (d) GI XRD patterns of an oriented AWC array of ADM produced from the directional WISA. (e) POM image of the well-aligned AWC array. [Reproduced from Ref. 1]

molecular length). The bulk AWC array developed in this work provides comparable water permeability at transport length of hundreds of μm (**Fig. 1(e)**), showing that, with a great control in the mesoscale structures, the synthetic molecule is able to transfer their molecular functions hierarchically into useful material properties.

Water plays important roles in physiological functions of living matter. Through dynamically interacting with biomolecules, water assists them to switch quickly between different physical states under ambient conditions. Combining suitable molecular designs and profound structural characterizations at the NSRRC, the study turns the role of water in the supramolecular chemistry of the synthetic molecule from passive to active. The WISA process allows water to govern the self-assembly and function of the synthetic molecule as it does to biomolecules. The quick physical transformation resulting from the dynamic interaction with water is highly desirable for the development of condensed-phase soft materials and might inspire more innovation in the development of self-assembled functional materials. (Reported by Chien-Lung Wang, National Yang Ming Chiao Tung University)

This report features the work of Chien-Lung Wang, Wei-Tusng Chuang and their collaborators published in ACS Nano ***15****, 14885 (2021).*

TLS 23A1 Small/Wide Angle X-ray Scattering
TLS 01C2 X-ray Powder Diffraction
TLS 17A1 X-ray Powder Diffraction

- SAXS, WAXS, GI XRD, *In-situ* SAXS
- Supramolecular Chemistry, Artificial Water Channels, Materials Science, Condensed-matter Physics

Reference

1. H. Y. Chang, K. Y. Wu, W. C. Chen, J. T. Weng, C. Y. Chen, A. Raj, H. O. Hamaguchi, W. T. Chuang, X. Wang, C. L.Wang, ACS Nano **15**, 14885 (2021).

Application of Synchrotron Microbeam X-rays to Mechanisms of Periodic Assembly of Polymeric Ring-Banded Spherulites

Periodic patterns are commonly seen in nature, and spontaneously form on nanometer molecular to macro-cosmic scales, as illustrated in Fig. 1.

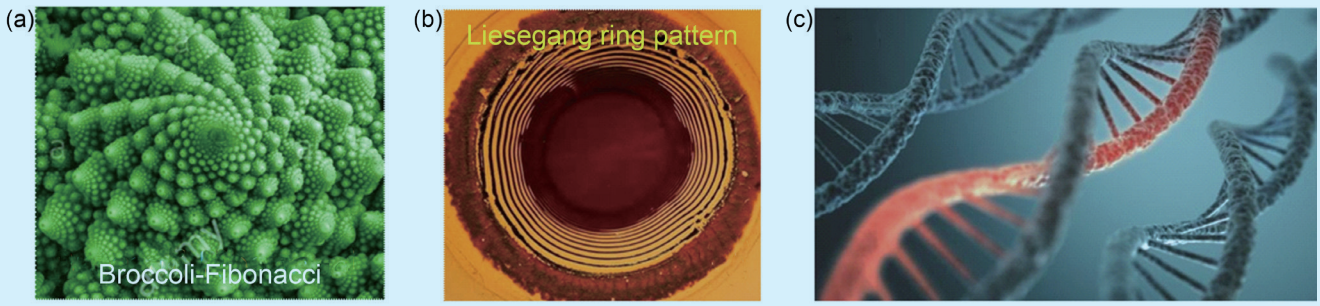

Fig. 1: (a) Broccoli flower with fractal pattern in a Fibonacci sequence, (b) Liesegan ring pattern on dropping a crystal of silver nitrate onto a thin gel layer containing potassium dichromate, and (c) DNA double-helices in genes. [Images all adapted from free sources, Wikipedia].

One of the most fascinating phenomena in crystallization is self-assembly in the periodic repetition of the same circular-ringed patterns. All crystalline spherulites, including ring-banded spherulites (RBS), of polymers or small-molecule compounds are packed in an anisotropic fashion. Polymeric spherulites are highly isotropic with lamellar crystals highly aggregates of all kinds, and a standard table-top X-ray instrument has wide X-ray beams and inherent limitations and can perform analysis results only as a cumulative average of multiple lamellae of varied morphology or orientation, *etc*. A specific location of crystal size and orientation can be precisely measured only *via* microbeam X-ray analysis. A limitation of the surface morphology is that it is unable to predict how to explore the mechanism of 3D lamellar assembly in polymeric RBS. Polymeric RBS are constructed with periodic rings with alternate valleys and ridges in 3D space, not just 2D films. Self-assembled lamellar architectures of RBS can be examined in two ways, *via* destructive and non-destructive methods. In