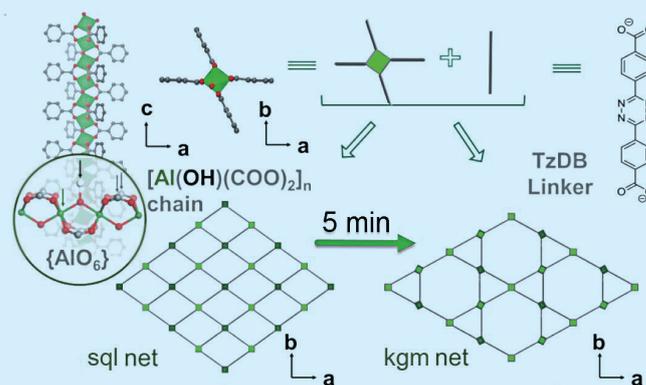


# A Crystalline Open-Framework Transformation within Minutes

*A rapid defect- and desolvation-triggered lattice rearrangement in a mesoporous metal-organic framework material was revealed by powder X-ray diffraction structural analysis.*

Topological transitions between significantly different phases typically require extreme conditions to break chemical bonds collectively and to overcome the stress caused to the original structure on altering its correlated bond environment. Metal-organic frameworks (MOF) are nanoporous solids of a new class that have attracted much attention owing to their prospective applications. The tunable rigidity and dynamics have resulted in the development of extensive applications in areas such as gas storage and separation, catalysis and drug delivery. Many flexible MOF typically undergo only volume and bond-angle changes while the topology and connectivity between clusters and linkers are maintained. In some cases, flexible behaviors of MOF typified by the coordination changes, such as ligand migration, can be observed after solvent adsorption or desorption or cluster metalation inside the structures. In these examples, the slippage degree and the distance of coordinating linkers have, however, been limited mostly to a small range within particular crystal features, resulting in only a slight change of pore size or shape. Larger changes to the crystal structures reported so far, *i.e.* notable topology and porosity variation, have been mostly irreversible.

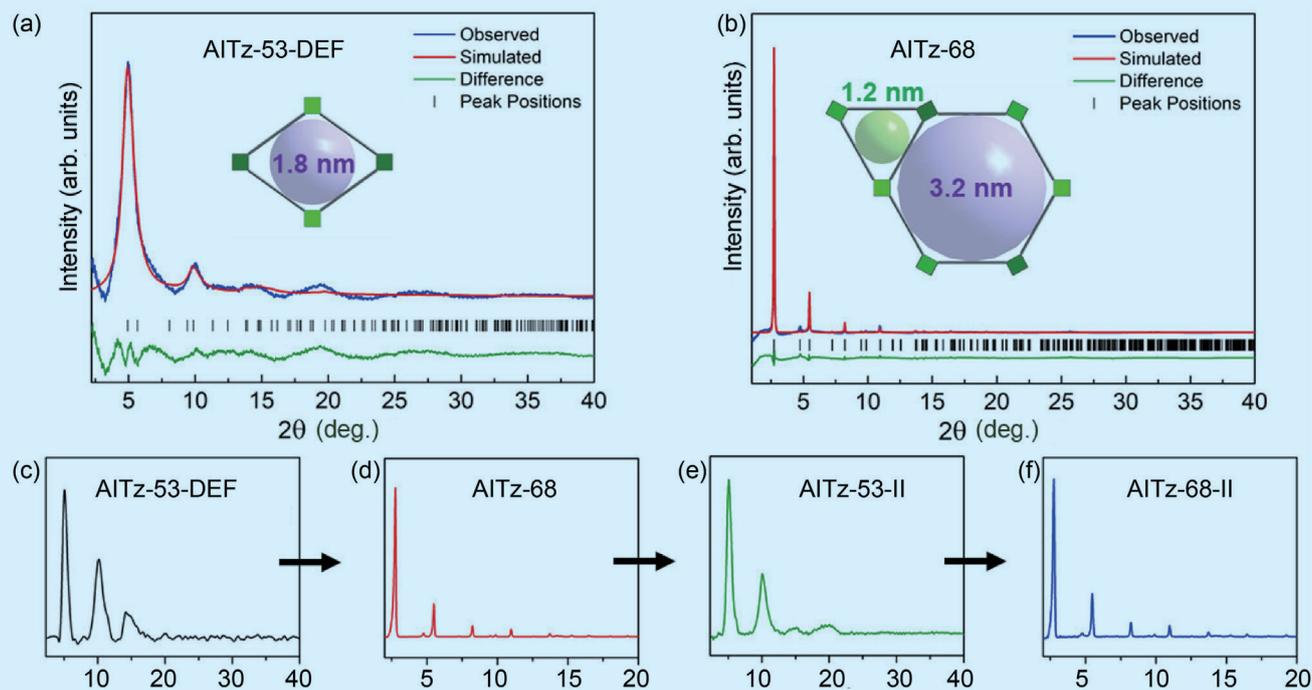
Sue-Lein Wang (National Tsing Hua University), Kuang-Lieh Lu (Academia Sinica) and Chia-Her Lin (National Taiwan Normal University) have recently made a remarkable discovery, successfully developing a structural transform from a disordered and less crystalline MOF (AlTz-53) with low porosity to a highly crystalline and porous isomer (AlTz-68) within few minutes upon activation (through solvent exchange and desorption), resulting in a significantly increased framework crystallinity and surface area, from about 700 to 2700 m<sup>2</sup>/g.<sup>1</sup> Spectrometric measurements show that this counter-intuitive lattice rearrangement involves a metastable intermediate with defect frameworks that results from solvent removal on coordinately unsaturated metal sites. After the lattice rearrangement, the resulting AlTz-68 shows sharper powder X-ray diffraction (PXRD) features at **TPS 09A** and **TLS 01C2**, indicative of enhanced crystallinity. This switch between less crystalline and more crystalline conditions between two topologically distinct MOF is shown to be reversible over a few cycles through activation and re-immersion in polar solvents (Fig. 1).



**Fig. 1:** Lattice rearrangement in aluminium metal-organic frameworks within minutes. From a topological view, the three-dimensional net of sra topology in AlTz-53 can be interpreted as consisting of interconnected sql nets, whereas the triply periodic AlTz-68 can be viewed as consisting of interconnected kgm nets. [Reproduced from Ref. 1]

The transformation of AlTz-68 was achieved on placing the samples within these solvents at 75 °C for 3 h, yielding defective AlTz-53. The transformation occurred also when the sample was left in these solvents at room temperature, but the conversion was much slower in this case, with the transformation to defective AlTz-53 at room temperature complete after one month in DMF. The cyclability of this atypical reversible rearrangement phenomenon was investigated. The AlTz-53-DEF as synthesized was washed with toluene three times and then immersed in toluene (3 mL) at room temperature. The sample was dried overnight under vacuum at 125 °C and labelled as AlTz-68. This AlTz-68 was then placed in DMF that was preheated to 75 °C for 3 h followed by centrifuging and filtering. The resulting powder was dried in an oven at 90 °C overnight and labeled as AlTz-53-II. This AlTz-53-II was washed with toluene three times and immersed in toluene (3 mL) at room temperature. The sample was dried under vacuum at 125 °C and labelled as AlTz-68-II. As observed by PXRD, the materials underwent two desolvation-solvation cycles with no apparent loss of crystallinity (Fig. 2).

Lin and his coworkers recently also developed a bio-inspired encapsulation-rearrangement strategy to construct superhydrophobic mesoporous metal-organic framework systems by selectively modifying the external surface of an internal lattice-rearranged mesoporous MOF.<sup>2</sup> The



**Fig. 2:** Characterization of a reversible transformation between AITz-53 and AITz-68. (a-b) Rietveld refinement of PXRD patterns for AITz-53-DEF and AITz-68 from a synchrotron source ( $\lambda = 1.0332 \text{ \AA}$ , measured from TLS 01C2). (c-f) PXRD patterns ( $\lambda = 1.5418 \text{ \AA}$ ). [Reproduced from Ref. 1]

surface of a defective MOF with limited porosity named AITz-53 is initially modified with hydrophobic alkyl chains through click reactions on the tetrazine groups. The internal framework subsequently undergoes a lattice rearrangement upon solvent desorption, leading to a significantly improved internal porosity and material crystallinity. Functionalizing the surface of AITz-68 with octadecene (AITz-68-C18) induces superhydrophobicity with water contact angle  $173.6^\circ$ . AITz-68-C18 also exhibits one of the largest BET surface areas among all reported superhydrophobic framework materials.

In summary, the desorption-triggered domino rearrangement of AITz-53-DEF also exhibits a new paradigm for the design and preparation of novel copolymers, high-crystalline covalent organic frameworks and metal alloys from volatile precursors, wherein monomers or functional groups or other components could potentially enable the desorption-triggered domino rearrangement. (Reported by Chia-Her Lin, National Taiwan Normal University)

This report features the work of (1) Chia-Her Lin and his collaborators published in *Nat. Chem.* **12**, 90 (2020); and (2) Chia-Her Lin and his collaborators published in *Matter* **2**, 988 (2020).

#### TPS 09A Temporally Coherent X-ray Diffraction TLS 01C2 SWLS – X-ray Powder Diffraction

- PXRD
- Porous Materials, Inorganic Chemistry, Environmental Science

#### References

1. S. H. Lo, L. Feng, K. Tan, Z. Huang, S. Yuan, K. Y. Wang, B. H. Li, W. L. Liu, G. S. Day, S. Tao, C. C. Yang, T. T. Luo, C. H. Lin, S. L. Wang, S. J. L. Billinge, K. L. Lu, Y. J. Chabal, X. Zou, H.-C. Zhou, *Nat. Chem.* **12**, 90 (2020).
2. L. Feng, S. H. Lo, K. Tan, B. H. Li, S. Yuan, Y. F. Lin, C. H. Lin, S. L. Wang, K. L. Lu, H.-C. Zhou, *Matter* **2**, 988 (2020).