Roadmap for finding new functional porous materials

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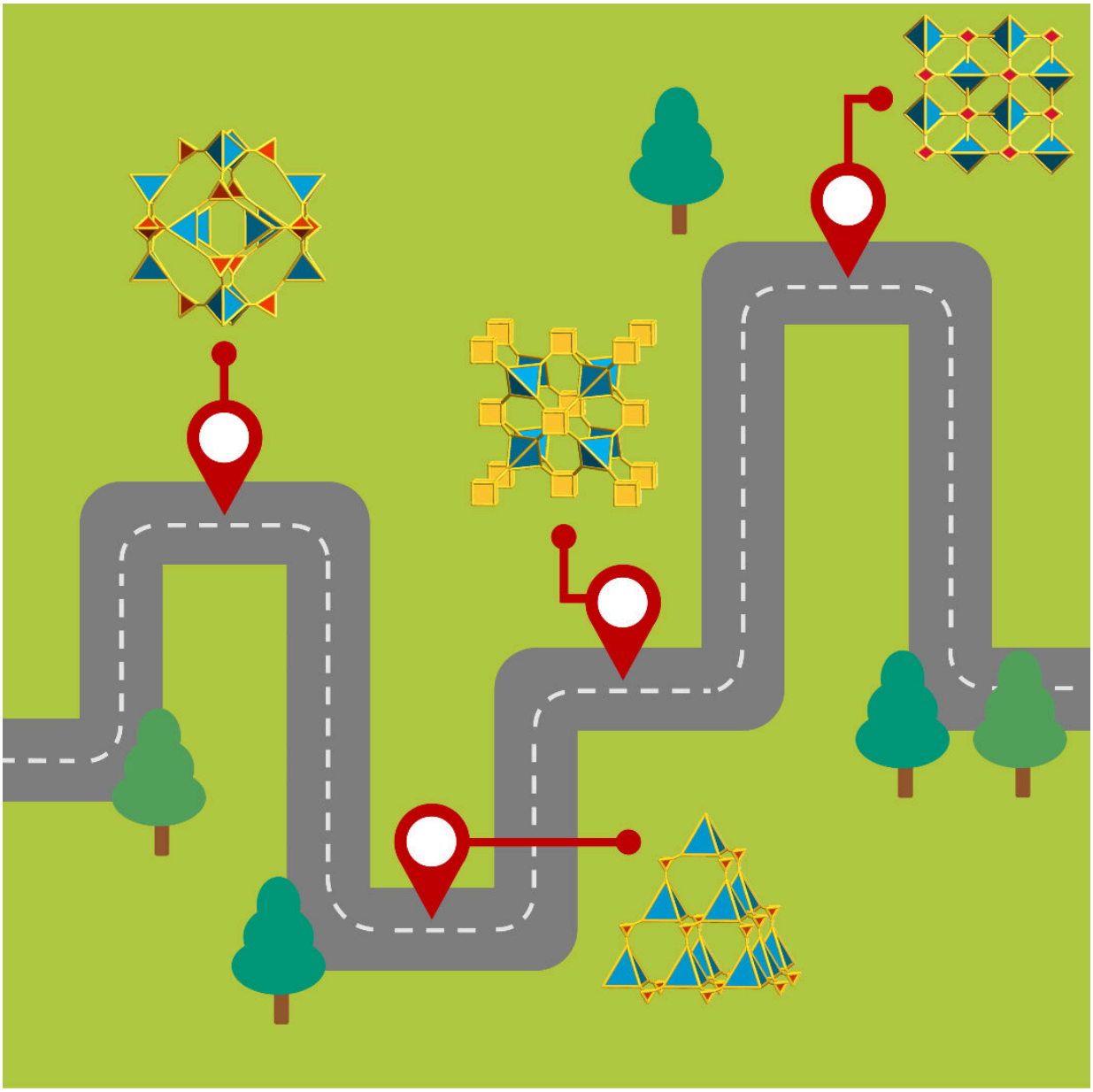

Roadmap for finding new functional porous materials. Credit: UNIST

The discovery of new structures holds tremendous promise for accessing advanced functional materials in energy and environmental applications. Although cage-based porous materials, metal-organic polyhedra (MOPs), are attracting attention as an emerging functional platform for numerous applications, hardly predictable and seemingly uncontrollable packing structures remain an open question. There is a high demand for a roadmap for discovering and rationally designing new MOP structures.

A research team, led by Professor Wonyoung Choe in the Department of Chemistry at Ulsan National Institute of Science and Technology (UNIST), South Korea, has made a major leap forward in revealing how future structures of MOPs can be predicted and designed at the molecular level. Their findings are expected to create a new paradigm for accelerating materials development and application of MOPs.

Prior to MOPs, metal-organic frameworks (MOFs), another well-known class of porous material, have developed rapidly. MOFs share compositional similarities (i.e., metal clusters and organic ligands) to MOPs. However, the molecular building blocks of MOFs are connected in an extended manner, while discrete cages consisting of metal clusters and organic ligands are packed by weak interactions in MOPs. Unlike MOPs, thousands of MOFs have been synthesized since their first discovery and now they are becoming increasingly important materials in academia and industries alike. A major driving force behind the phenomenal success of MOFs is their predictable and designable structures with a rich choice of molecular building blocks. By considering the molecular geometry of building blocks, the possible structures can be predicted and designed.

So far, it was believed that strong bonds to connect building blocks are necessary to construct structures in a predictable way. Since weak or non-directional interactions have often resulted in unpredictable structures, the rational design of MOPs has been less illuminated. In this study, the research team discovered a special type of MOPs where the design principle can be applied to molecular packing systems, despite the absence of strong bonds. The zirconium (Zr)-based MOPs are notable examples. The authors unveiled multiple weaker bonds can do a similar role to strong bonds.

Zr-based MOPs are an emerging class of MOPs with their excellent chemical stability. While the Zr-MOPs are essentially cage-based compounds, features mainly found in MOFs, such as robust framework and permanent porosity, also appear in Zr-MOPs. The authors say that such extraordinary dual features motivated them to further investigate the solid-state packing of Zr-MOPs. In this study, the authors not only provided a comprehensive study of the existing structures but also discovered future structures that have not been observed but are potentially accessible. A fundamental understanding of the nanoscale self-assembly of cages provides opportunities to control the packing structure, porosity, and properties. The authors expected that these unique dual features of Zr-MOPs can lead to many intriguing applications that are not accessible by typical MOPs or MOFs. They also encouraged to find other interesting classes of cage-based frameworks.

"The emergence of new structures would provide a new opportunity to control their properties," said Professor Wonyoung Choe. "Taking a different perspective on cage-based frameworks can lead to a new stage of functional porous materials."

The findings of this research have been published as a Perspective in *Chem*, a sister journal to *Cell*, on March 10, 2022.

More information: Wonyoung Choe, Topology-Guided Roadmap for Reticular Chemistry of Metal-Organic Polyhedra, *Chem* (2022). DOI: 10.1016/j.chempr.2022.02.008