Sensing, Energy conversion, Molecular seiving

Development of multicomponent covalent organic frameworks

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Abstract

Covalent Organic Frameworks (COFs) are crystalline porous polymers formed through covalent bonds between organic building blocks. Due to their high structural order and exceptional porosity, COFs are considered for various applications including gas storage and separation, sensing, and catalysis. Multicomponent COFs, in particular, are garnering significant attention due to their remarkable design flexibility, encompassing both structural diversity and property variations. With this in mind, we are working on the design and structural control of multicomponent COFs based on a new perspective of considering them as "solid solutions." The structural depiction of solid solutions differs significantly from the conventional hypothesis that multicomponent COFs are formed as highly symmetrical and stable structures. This calls for the establishment of new design concepts and synthetic chemical methodologies.

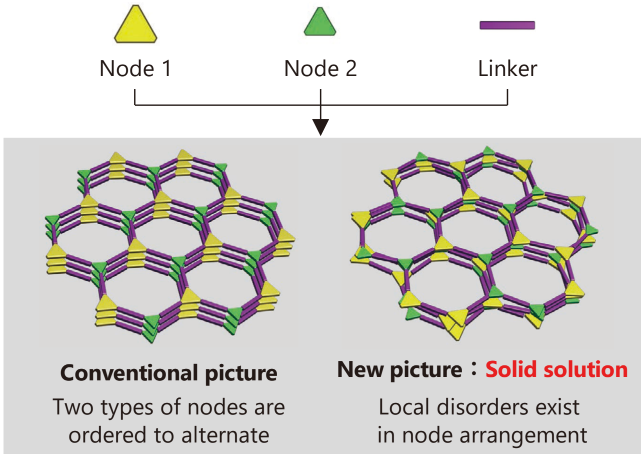
Background & Results

While most of the reported COFs have simple compositions involving only one or two types of monomers, there have been an increasing number of reports regarding multicomponent systems in recent years. A few examples have already been found where increase in the number of components brings about unique properties. However, it is not clear whether multicomponent COFs possess regularly ordered monomer sequences as expected; accordingly, the detailed investigation of structure–property correlations has scarcely progressed. Furthermore, many aspects remain unresolved regarding the requirements for forming multicomponent COFs.

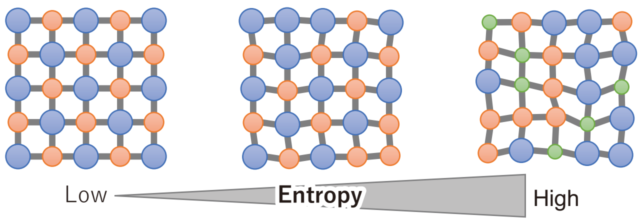
In view of this background, we are investigating the influence of the physical and chemical properties of monomers on the formation of multicomponent COFs, as well as elucidating the structure of resulting COFs. As a part of the project, this work thoroughly examined twelve ternary systems composed of monomers with different physical dimensions and chemical reactivities. The results revealed the following aspects regarding the examined hexagonal 2D COFs: (1) ternary COFs adopt a solid-solution-like structure that encompasses local disorders in monomer sequences and the resulting distortions; (2) ternary COFs are obtained only when such distortions are tolerated; otherwise, a mixture of two types of binary COFs is produced; and (3) the difference in reactivity between the combined monomers has a limited influence on the feasibility of 3-component COF formation. Accumulation of this kind of knowledge must lead clear guidelines that enable effective structural design of multicomponent COFs. Furthermore, the solid-solution-type structures have hardly been examined in organic crystals; thus, the achievements of this study present a new frontier in organic materials.

Significance of the research and Future perspective

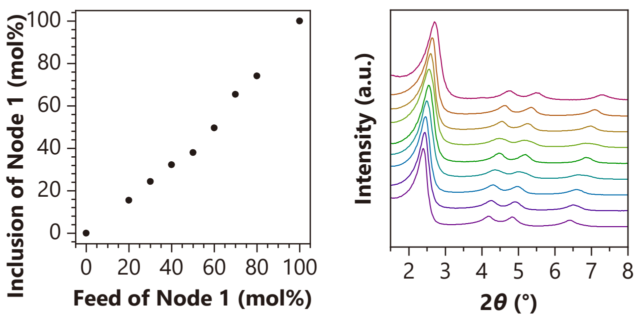
Viewing multicomponent COFs as "solid solutions" greatly enhances their structural design possibilities. This study aims to develop intricate functional materials that efficiently realize complex processes, such as energy conversion and multistep catalysis, by continuously tuning composition and lattice constants while maintaining crystallinity.



Conventional and new pictures of multicomponent COFs. Exemplified with the 2-node–1-linker hexagonal system.



Creating new functional organic materials by bringing in the concept of "entropy engineering" into the design of multicomponent COFs.



In some three-component COFs, it is feasible to continuously adjust the composition (left) and lattice constants (right) as in solid solutions.

Patent

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