Development of co-crystalline organic materials with arbitrary composition ratio

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Abstract

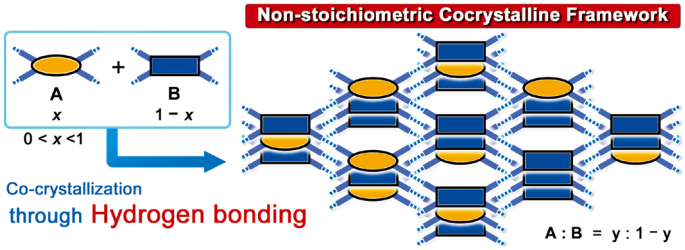
Porous crystalline materials constructed by mixing multiple components in indefinite ratios are attracting attention. Stepwise adjustment of functions by sweeping the mixing ratio is possible, and furthermore, the emergence of new functions is expected. However, it is not easy to obtain the precise crystal structure information necessary to establish design guidance. In this study, crystalline porous crystals with non-stoichiometric compositions were constructed by co-crystallization of two types of constituent molecules in arbitrary proportions. The molecular arrangement in the crystals was elucidated by single crystal X-ray structure analysis, and the composition ratio of both components was also determined. Furthermore, the distribution of each component in a single crystal was clarified by micro-Raman spectroscopy using a single crystal.

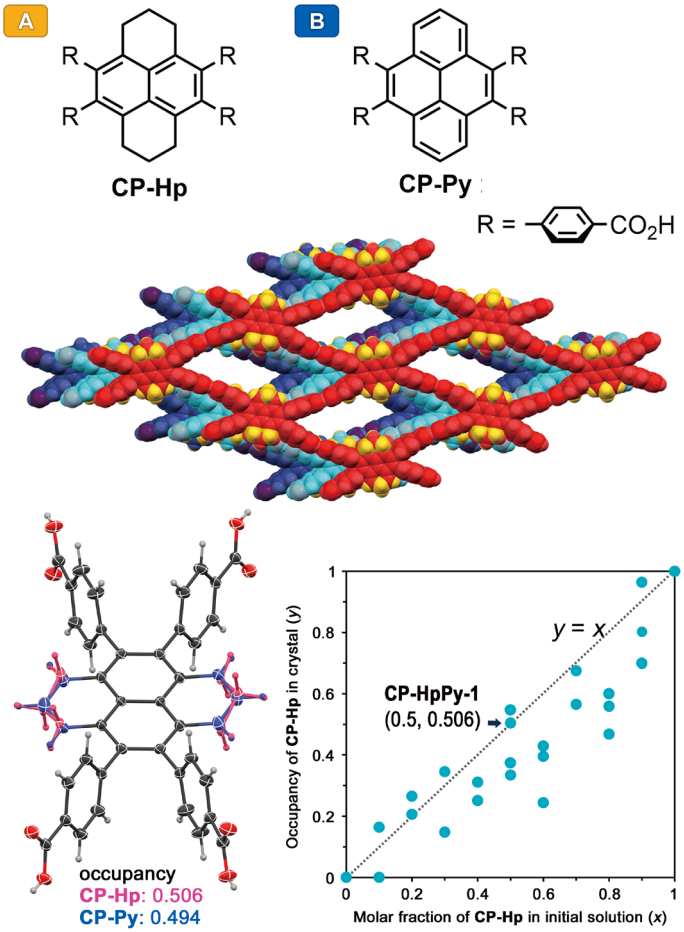
Background & Results

The advent of non-stoichiometric co-crystals, in which multiple components are mixed in various proportions, has been recognized as an attractive system in materials science because of the possibility of tuning functions by component ratios and, in some cases, the possibility of developing completely new functions. Many non-stoichiometric co-crystals have been constructed by co-crystallization of compounds using charge-transfer interactions, halogen bonding, hydrogen bonding, and so on. However, it is difficult to construct non-stoichiometric co-crystals of arbitrary composition using only organic molecules, as evidenced by the fact that the recrystallization operation eliminates a small amount of impurities and increases the purity of the compounds. We are particularly interested in porous framework crystals. In the present study, we have demonstrated proof-of-concept of an non-stoichiometric co-crystalline HOF with a well-defined crystalline structure despite the mixture of components in various composition ratios, using tetracarboxylic acid derivatives with hexahydropyrene and pyrene skeletons, respectively. The molecular arrangement in the crystals was elucidated by single crystal X-ray structural analysis, and the composition ratio was determined. Furthermore, micro-Raman spectroscopy using single crystals has revealed the distribution of each component in a single crystal grain.

Significance of the research and Future perspective

Crystalline structures created by mixing multiple components are an important target for development in materials science because they allow for fine tuning of functions depending on the mixing ratio and have the potential to create functions that are not possible with structures formed from single components. However, in general, even when organic molecules are mixed, each component often gives separate crystals. In this regard, we have obtained a guideline for constructing arbitrarily mixed single-crystalline organic materials by making good use of intermolecular interactions such as hydrogen bonding.





Patent

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