Flexible Single Crystals of Coordination Polymers - Structures and Properties

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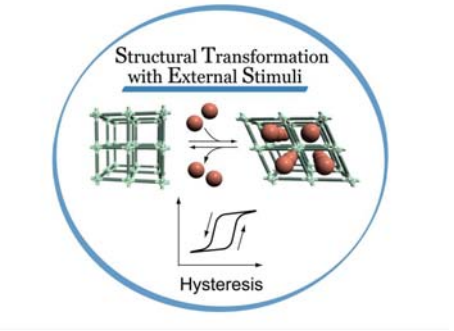
The recent advent of porous coordination polymers (PCPs) or metal-organic frameworks (MOFs), as new functional microporous materials, has attracted the attention of chemists due to scientific interest in the creation of unprecedented regular nano-sized spaces and in the finding of novel phenomena, as well as commercial interest in their application for storage, for separation and in heterogeneous catalysis.[1-4] One of the advantages of PCPs, as compared with other microporous inorganic materials such as zeolites, is flexibility accompanied with regularity, which provides unique sorption behaviors such as gated sorption for specific guests.



Recently, we have obtained interesting array structures of adsorbed benzene,[6] acetylene,[7] O_2 [5,8] molecules and so on. In addition to the confinement phenomena, we have found flexible porous frameworks, which respond to specific guests. $[Cu(dhbc)_2(4,4'\text{-bpy})]_n \cdot nH_2O$ is composed of 2D sheet with π-stack pillars of dhbc, exhibiting dynamic pore contraction without guest.[9] This is a surprising substance because the crystallinity is maintained over the two phases.

After the advent of this type of compounds, there has been growing interest in flexible and dynamic frameworks, in particular, those that reversibly change their structures and properties in response to external stimuli. This so-called “structural dynamism” would be a key principle for highly selective accommodation and separation of specific molecules, which often occurs in proteins. Hence the design and synthesis of a host framework that can interact with certain guest molecules in a switchable way has implications for a generation of advanced materials, with potential applications for molecular sensing and actuators. In addition to this flexibility, we have designed and synthesized a bimodal microporous two–fold interpenetrated network,[10] $\{[Ni(bpe)_2(N(CN)_2)](N(CN)_2)(5H_2O)\}_n$, having two types of channels for $N(CN)_2^-$ and neutral water molecules. The dehydrated framework provides a dual function of specific anion exchange of free $N(CN)_2^-$ for the smaller N_3^- anions, resulting in selective gas sorption.

References

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