The angle between the polar axis and the long molecular axis joining the phenolic oxygen to imino carbon is, respectively, 60°, 41°, 60° and 28° for the compounds in the Scheme below, together with their space groups.

The use of molecular hosts as tectons for the self-assembly of coordination polymers promises crystalline materials with embedded molecular recognition sites, as well as the more common lattice-type guest sites [1], [2], [3], [4], [5]. We have developed a range of host molecules based on the cyclootriveratrylene (CTV) framework with additional metal-binding groups at their upper rims.

Tripodal CTV-analogues have a distinctive open pyramidal shape which creates the specific guest-binding site. The rigid "corner-piece" shape also means that coordination polymers resulting from these ligands may have unusual structural and topological aspects to them. For example, 2D networks of linked metallo-cages; [1] rare (3,4)-connected network topologies such as (4:6)(4:6); and highly complex and unprecedented 3D topologies [2]. As these tectons are molecular hosts, host-guest interactions may play an important role in both the assembly of the coordination polymers and in their potential applications. Host-guest associations may be structure-directing, and generally, binding large guests in the molecular cavity of the ligand promotes formation of a coordination polymer instead of a discrete species [3], [4]. For example, binding of a large o-carborane guests dictates whether a discrete [Cd(OAc)₄] complex or 2D 4.8 coordination polymer is formed when L = tris(4-pyridyl)aminocyclooctatetraene [3] Self-inclusion motifs also play an important role. Crystalline clathrates of CTV-analogues are known to form a hand-shake dimer where an upper-rim R group of one host is the guest for another host and vice versa, and the same motif is found within coordination chains [5]. Host-guest interactions may also result in associations between networks, including within polycatenation motifs.

Here, different coordination polymers from ligands with N-donor, carboxylate, N-oxide or allyl metal-binding groups will be presented, and the importance of host-guest interactions of these ligands in terms of coordination polymer construction and functionality highlighted.

Keywords: supramolecular, crystal engineering, coordination polymers

MS24.P10

Kinetic assembly of porous coordination networks and ab initio powder structure determination

Masaki Kawano Division of Advanced Materials Science, Pohang University of Science and Technology (POSTECH), Pohang (South Korea). E-mail: mkawano@postech.ac.kr

The chemistry of porous coordination networks has undergone explosive growth in the last decade because of fascinating features. Porous coordination networks can be used for gas sorption/separation/storage, molecular recognition, drug delivery, catalysis, and so on. Especially porous materials have been paid much attention as potential hydrogen storage materials for fuel cells. Thanks to the high flexibility in design, a number of porous coordination networks were prepared and were analyzed by single crystal X-ray crystallography. Here we would like to report new aspects in porous coordination network chemistry. A pore of porous materials can be used as crystalline molecular flask in order not only make a reaction but also directly observe the reaction by X-rays [1-5]. In this talk, especially we will focus on selective kinetic assembly of porous coordination networks, the usage, and the ab initio powder structure determination [6-10]. The kinetic study of porous coordination networks compared with zeolite is a totally unexplored field, because of difficulties in powder structure determination. We succeeded in solving powder crystal structures having unit cells larger than 15000 Å³.


Keywords: supramolecular, crystal engineering, coordination polymers
Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs), which are constructed from metal ions and organic ligands, have been extensively investigated to provide the nanometer-sized space that is potentially applicable in separation, heterogeneous catalysis, and gas separation/storage. Recently, we reported porous crystalline materials that can be activated by photostimulation [1] and demonstrated that photochemical modification is a powerful method for the control of physical properties of PCPs or MOFs.

In this report, synthesis and properties of new PCPs containing trans-1,2-bis(4-pyridyl)ethylene (bpe) as a photoactive module will be presented. The photoactive PCPs adsorb gaseous molecules such as carbon dioxide. The bpe molecules quantitatively take place topochemical [2+2] cyclodaddition reactions and the PCPs show single-crystal to single-crystal (SCSC) transformations upon UV irradiation (> 300 nm). We will discuss not only the SCSC transformations but also the impact on the photochemical transformations on the sorption properties.

References


Keywords: microporous, photoreaction, adsorption

MS24.P13

Pressure-induced magnetic switching in molecular framework materials
Gregory J. Halder, Karena W. Chapman, John A. Schlueter, Jamie L. Manson, Peter J. Chupas, X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Illinois, USA.
Materials Science Division, Argonne National Laboratory, Illinois, USA.
Department of Chemistry & Biochemistry, Eastern Washington University, Cheney, Washington, USA. E-mail: halder@aps.anl.gov

The design and characterization of molecular materials with targeted functionalities, such as magnetism and/or nanoporosity, is part of a major international push aimed at developing systems with technologically important applications (e.g., molecular sensing and storage). As such, the accurate elucidation of their often complex structure-function relationships presents a crucial step in their advancement. For molecular magnetism, these approaches are commonly focused on variations of temperature and/or magnetic field, while comparatively little attention has been given to how these materials behave as a function of pressure. Here, we report magneto-structural investigations of magnetic molecular materials using synchrotron-based structural studies (powder diffraction and pair distribution function) and magnetic susceptibility measurements at high pressures. These studies have revealed a range of interesting phenomena such as orbital reorientations, spin crossover, phase transitions, and extreme compressibility [1].


Keywords: high pressure, magnetism, phase transition

MS24.P14

The crystal structure of Ziegler-Natta catalyst supports
Giuseppe Cruciani, Federica Malizia, Anna Fait, Department of Earth Sciences, University of Ferrara, Ferrara (Italy). Basell