Ditopic Nitrogen ligands and Zinc(II) or copper(II) coordination polymers

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Coordination polymer or Metal-Organic Frameworks (CP/MOFs) often obtained by (self)-assembling of oligonuclear metal clusters (the so-called Secondary Building Units or SBUs) are the subjects of an increasing number of studies due to their interesting properties and promising applications in numerous important fields, such as gas storage, molecular recognition, catalysis, etc. [1] An interesting class of polynucleating ligands, appropriate to drive the self-assembly of MOFs, is represented by N-donor units containing two moieties interconnected by various spacers, which can afford different lengths, linear or non-linear geometries and conformationally rigid or flexible molecular skeletons having an infinite one-(1D), two-(2D) or three-(3D) dimensional framework or periodic nets.[2] Yaghi et al. have successfully developed porous materials (such as metal carboxylate) with controllable shape and size of the cavities.[3] Some of these metal carboxylates appeared to have unusual magnetic properties [4] while some other exhibited high efficiency for gas absorption such as dihydrogen, dinitrogen etc.

On this basis, we have designed, synthesize and characterized new CP/MOFs by treating a simple unit zinc formate and the trinuclear core [Cu3(µ-C3H3N2)3(µ3-OH)(H3CCOO)2(C3H4N2)] (Fig.1-a) with three different N-donor containing ligands (either rigid or flexible) showing in Fig.1-b. The resulting compound (the CP {[Zn(OCHO)22(µ-N2H12C12)]∞ of Fig.2) from the reaction of zinc formate dihydrate and 1,2-bis(4-pyridyl)ethane consists of a 1D zig-zag CP having the monomeric unit built by a homodinuclear Zn(II) bridged with a N2H12C12 ligand. Its structure is built-up π-π stacking intermolecular interactions and/or C-H…π and C-H…O weak interactions.

These compounds were characterized by elemental analyses, FT-IR, X-ray analyses and DFT calculations. Some of these compounds are CP/MOFs while other are supramolecular species were completely characterized and their X-ray structural analyses revealed fascinating architectures with waved channels. The synthesis, the structural characterization and the DFT calculations of these coordination polymers will be discussed.


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