



A novel trinuclear zinc metal–organic network: Synthesis, X-ray diffraction structures, spectroscopic and biocompatibility studies



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abstract

Crystal structure and vibrational spectra of a new zinc metal–organic network, $\{[Zn_3(tp)_4]4H_2O\}_n \cdot 1$, have been studied. The compound was constructed from $Zn(NO_3)_2 \cdot 6H_2O$ and H_2tp ligand ($H_2tp = 1,4$ -benzenedicarboxylic acid) by solvothermal synthesis in DMF. Its framework is built from the trinuclear SBUs as eight-connected nodes and tp ligands as spacers. Each node consists of three Zn^{II} ions that are in a linear arrangement with $Zn–Zn$ distance of 3.271 Å. The distorted octahedral middle Zn atom is connected to six oxygen atoms ($Zn–O = 2.036–2.252$ Å) belonging to six different tp carboxylate group. Each of the two terminal Zn atoms is coordinated by four oxygen atoms ($Zn–O = 1.952–1.986$ Å) belonging to four carboxylate groups of tp ligands. Normal-coordinated analysis of the vibrational spectra together with force field calculations for $Zn(O_2CC)_n$ ($n = 4$ or 6) entities which is the most affected by coordination effect have been performed. The results show consistency of the lower values of force constants for ZnO_6 entity compare to ZnO_4 that could be related to the stronger inter-ligand repulsion in octahedron compare to tetrahedron. In-situ PXRD patterns show two gradual structural transformations from ambient to 400 °C and a new ZnO phase is formed between 400 and 500 °C that are in a good agreement with thermal gravimetric analysis. Photoluminescence measurement in the solid state shows an emission at 420 nm which is in accordance with other zinc carboxylate MOFs. The potential cytotoxicity of **1** was evaluated on human amniotic epithelial cells (hAECs) by XTT assay. The results clearly showed that this compound exerted little in vitro cytotoxic effect in a wide range of concentration and time intervals.

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1. Introduction

Metal–organic frameworks (MOFs) represent an incredibly growing class of nanoporous materials and are the latest class of ordered porous compounds. The drive behind this rapid development lies on the important specific structures, properties and potential applications [1–7]. On the basis of crystal engineering, structure–function relationships with the MOFs' promising application have thereby been developed in an organized approach [8]. One of the MOFs key benefits compared to porous organic (carbons) or inorganic analogues (zeolites, silica), is the possibility to achieve different compositions and structures through a change of the metal and/or the organic linkers. On the other hand, crystallization is a very complicated process, and minor changes in the chemical environment can have an unpredictable influence on the composition of the resulting compounds [9]. As most of metal–organic frameworks are crystalline, textural and structural

characterization can be calculated through crystallography and hence it has an important contribution to draw interest and inquiry in this new class of materials [10].

From the synthetic point of view, di and tri-carboxylates are one of the most successful classes of polytopic ligands in designing MOFs due to the relatively labile M–O bonds. Even though the reactions of many transition metals with dicarboxylates have been studied, those of Zn-based MOFs have been mainly significant. Yaghi and co-workers have reported a number of interesting structures based on zinc that show remarkable methane and hydrogen adsorption properties [11,12]. Although industrial applications of this type of MOFs have so far been well studied, toxicity results dealing with MOFs or coordination polymers are very scarce [13]. In general, the use of porous solids for biomedical applications requires a biologically friendly composition.

We have been so far reported some metal–organic polymeric structures by O- and also N-donors of bridging ligands with no toxicity studies [14–17]. Herein we report a new crystal structure derived from the zinc–terephthalic acid system, and investigate its toxicity. Generally, the Zn^{II} /terephthalic acid reaction system

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