



Synthesis, crystal structure and dielectric properties of a new acetate bridged coordination polymer: $\{[La(\mu-CH_3COO)(PDC)(H_2O)_2] \cdot 2H_2O\}_n$

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ABSTRACT

An acetate bridged coordination polymer of lanthanum, formulated as $\{[La(\mu-CH_3COO)(PDC)(H_2O)_2] \cdot 2H_2O\}_n$ ($H_2PDC =$ pyridine-3,4-dicarboxylic acid) has been successfully grown by single gel diffusion technique at room temperature using hydrosilica gel and further characterized by elemental analysis, powder X-ray diffraction, FT-IR and UV–visible spectral studies. The compound crystallizes in triclinic space group, $P\bar{1}$. The metal centre is nine coordinated by oxygen atoms to form distorted tri-capped trigonal prism geometry. Single crystal X-ray diffraction studies reveal that the compound exists as one dimensional polymeric chain which is further assembled into 2D supramolecular framework via extensive hydrogen bonding. The dielectric and thermal decomposition behaviour of the sample was also studied.

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1. Introduction

Coordination polymers (CPs) are an important class of inorganic-organic hybrid materials with well regulated network structures displaying a wide variety of potential applications in the field of catalysis, gas adsorption/separation, nonlinear optics, magnetic materials and so on [1–5]. CPs can be self-assembled by the coordination of metal ions/clusters with rigid organic entities to form stable architecture with attractive structural topologies. In this regard, considerable efforts have been devoted to design and control the self-assembly of the coordination networks by judicious choosing of unsymmetrical ligands having two or more coordination sites with differing donor ability, thereby resulting in unprecedented structures with aesthetic architecture [6,7]. Nanoporous CPs with optimal pore system and physical properties can be obtained by optimizing the position of alkyl groups in the channels which will enhance the performance of adsorption and separation ability of these materials for gas purification [8,9]. However, increasing the molecular size and complexity of ligands

will induce interpenetration of coordination networks and reduces the pore volume. Thus, designing the porous CPs employing small low-symmetry ligands in combination with metal clusters represents a promising strategy to preserve high surface area and porosity with dense open metal sites [10]. In addition to the structural diversity of organic linker, the coordination geometry of metal ions, pH of the reaction medium, temperature and the presence of counter ions also influences the self assembly process. Recently, mixed ligand strategy has been employed for fabricating CPs with exceptional properties and structural flexibility [11]. However, designing and controlling the assembly of porous CPs to fulfil the application in feasible condition still remain as a challenge.

In the present work, we focus on the synthesis of a lanthanide coordination polymer using a heterocyclic organic linker, pyridine-3,4-dicarboxylic acid or cinchomeric acid (H_2PDC , Scheme 1), which is an asymmetric building block possessing both N- and O-coordinating centres. The crystallographic data of H_2PDC and its hydrochloride form have been reported earlier [12]. As a result of steric hindrance, the two proximal carboxylate groups of the ligand remain out of the plane, which will cause the carboxyl groups to connect the metal atoms in different directions to form unique structural features [13]. Having studied the literature, we have noticed that several transition and rare earth compounds of H_2PDC

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