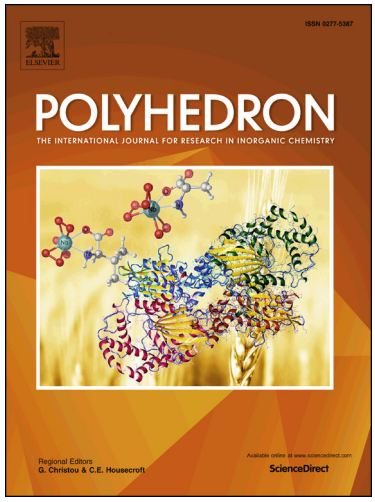

Linker dependent dimensionality in Zn(II)-coordination polymers containing a flexible bis-pyridyl-bis-amide ligand

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Revised

Linker dependent dimensionality in Zn(II)-coordination polymers containing a flexible bis-pyridyl-bis-amide ligand

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Abstract

A bis-pyridyl-bis-amide ligand containing a biphenylene scaffold was combined with four different dicarboxylic acids in the presence of $Zn(NO_3)_2 \cdot 6H_2O$ under solvothermal conditions, using DMF as solvent. The corresponding coordination frameworks were structurally characterized by single crystal diffraction analysis, the topological and thermal analysis were also conducted. The removing of the included DMF was investigated through solvent assisted activation protocol, the final outcomes being determined by ^{1}HNMR analysis. The dimensionality of the solid networks depends on the type of dicarboxylic acid employed. The use of isophthalic acid and 5-amino-isophthalic acid led to the isolation of 2D-frameworks (**PUM20** and **PUM32**, topological type **3,5L2**) , while a 1-D polymer was obtained using 2-methoxy-isophthalic acid (**PUM30**, of topological type SP 1-periodic, ladder-like). Finally, the use of terephthalic acid led to a pillared 2-fold interpenetrated 3D-structure (**PUM198**, of topological type **fet**).

Keywords

Coordination Polymers - Pillared MOFs – Amide linker – Zinc(II) – Topology

1. Introduction

The synthesis of Mixed-Ligand Coordination Polymers (MLCPs), also called heteroleptic CPs, relates to the construction of crystalline frameworks containing two different ligands combined with metal nodes. Hence, the self-assembly process occurring under solvothermal conditions is certainly more complicated than the one involving the construction of homoleptic CPs. However, MLCPs allow to reach more sophisticated structures with higher degree of functionalization, which in turn leads to tailoring of the material function.[1][2][3] The design usually followed for the construction of MLCPs is based on the so-called pillaring-strategy.[4][5] One of the most common methods to get pillaring passes through the construction of the paddlewheel-like SBU $M_2(O_2CR)_4L_2$.[6] Use of dicarboxylate linkers leads to formation of 2D planes containing the dinuclear SBUs connected by the dicarboxylate dianions. The planes can then be linked by divergent ligands L occupying the axial positions of the paddlewheel units, creating a 3D pillared framework. In this case, the term mixed-ligand Metal-Organic-Frameworks (MLMOFs) should be used, to emphasize the 3D dimensionality of the polymer. As pillaring struts, bis-pyridines are very common, the length of which dictates the dimension of the resulting channels, and then the porosity of the final material.[7] Following this approach, we chose to combine four different dicarboxylic acids, namely isophthalic acid H_2ipa, 2-methoxy-isophthalic acid H_2(MeO)-ipa, 5-