

pH effect on hydrothermal synthesis of the copper organodiphosphonate polymers: Investigation of luminescence and magnetic properties

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Keywords: Hydrothermal synthesis; Copper organodiphosphonate; Magnetism

The synthesis of metal organic frameworks (MOFs) under hydrothermal condition is of great interest. This synthetic method not only affords the opportunity to prepare coordination compounds with novel structures and properties but also provides an environmentally friendly approach for the construction of MOFs through crystal engineering. Synthesis of MOFs depends on different parameters such as the metal or ligand type, pH value, stoichiometric ratio, mineralizing agent, reaction temperature and time.¹ In this study, pH effect of the solution on polymer formation under subcritical conditions was investigated. Multifunctional 1,2-phenylenebis(methylene))bis(phosphonic acid (HL₄) and 4,4'-bipyridine (bpy) were selected as ligands due to the potential coordination sites. Three MOFs, [Cu²⁺₃(HL³⁻)₂]_n (**1**),² [Cu²⁺₄(L⁴⁻)₂(OH₂)₄]_n·H₂O (**2**) and [Cu²⁺₄(bpy)(HL³⁻)₂(OH⁻)₂]_n·2H₂O (**3**) were synthesized as a result of changing the pH values (Initial pH: 2.20, 3.50 and 6.00 to 3.50, respectively). Single crystal X-ray analysis (Fig. 1, top) showed that while the copper atoms in **1** have four and six coordination numbers (CNs), **2** and **3** showed five CNs. From the analysis of magnetic susceptibility measurements (Fig. 1, bottom), all the Cu valences were confirmed to be +2, and antiferromagnetic interactions were characterized.

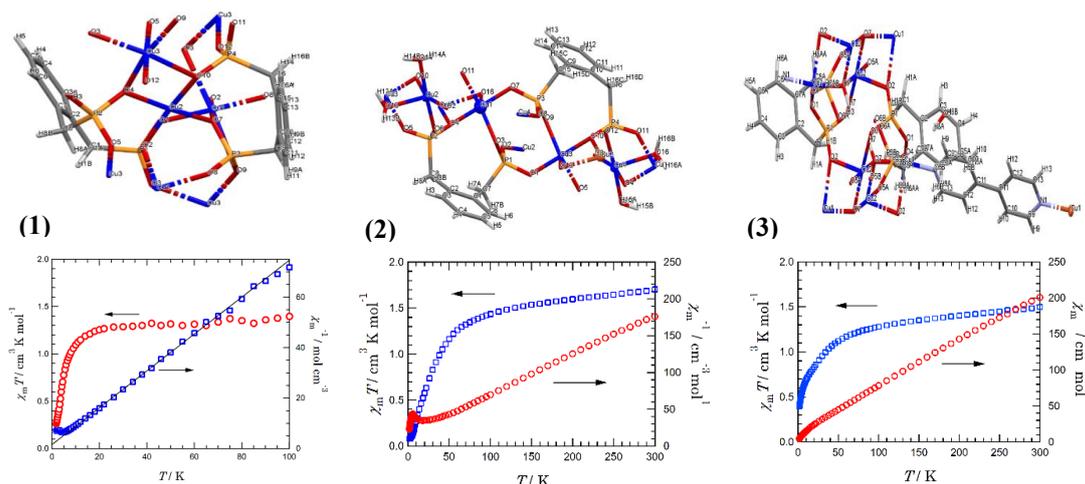


Figure 1. Crystal structures (Colour codes: Cu, blue; P, orange; O, red; N, light blue; C, gray; H, white) and temperature dependence of $\chi_m T$ and χ_m^{-1} for **1** - **3** on the formula basis.

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