Research paper

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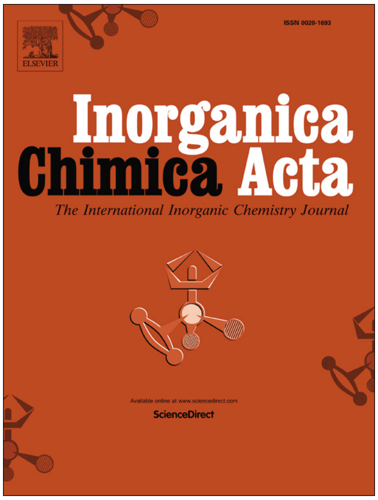

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An investigation on the structural diversification of metal phosphonates in varying combinations of phosphonate ligand, metal ions and auxiliary ligands

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ABSTRACT

Five new metal diphosphoantes, namely, $[Cu(H_2L^1)(2,2'\text{-bipy})]$ (**1**), $[Cu(H_2L^1)_{0.5}(H_3L^1)(2,2'\text{-bipy})][(H_2O)_3]$ (**2**), $[Cu_3(H_2L^1)_{1.5}(H_3L^1)_3(2,2'\text{-bipy})_3][H_2O]$ (**3**), $[Ni(4,4'\text{-bipy})(H_2O)_4][H_2L^1]$ (**4**), $[Cd(H_2L^1)(1,10\text{-phen})(H_2O)_2][(H_2O)_2]$ (**5**), (H_4L^1= (2,3,5,6-tetramethyl-1,4-phenylene)bis(methylene))bis(phosphonic acid, 2,2'-bipy= 2,2'-bipyridine, 4,4'-bipy= 4,4'-bipyridine, 1,10-phen= 1,10-phenanthroline) have been synthesized from a methylated phosphonate ligand and characterized systematically. The single-crystal X-ray diffraction analyses reveal weak interactions play important roles in the speciation of metal phosphonates. The photophysical property of compound **5** was also investigated.

Keywords:
Metal phosphonates; Crystal structures; Weak interactions; Hydrogen bonds

1. Introduction

Metal phosphonates as one kind of inorganic-organic hybrids have attracted tremendous attention because of their interesting crystal structures and potential applications in the fields of optical[1], magnetism[2], catalysis[3], gas storage[4]/separation[5], proton conductivity[6], and so on. The pursuit of novel crystal structure and high performance continually pushes forward the development of metal phosphonates. To modify the crystal structures, a few strategies have been developed which include: 1) Varying the synthesis conditions (such as metal/ligand ratio, pH value, temperature); 2) Decoration of the phosphonate ligand with other coordinating functionalities (carboxylic[7], hydroxyl[8], sulfonyl[9], pyridine[10]…); 3) Introduction of auxiliary ligands (2,2'-bipy, 4,4'-bipy, oxylic acid, and so on)[11-16]. With these strategies employed, the crystal structures of metal phosphonates can be tuned according to a target application.

The above mentioned strategies are mainly based on the tuning of covalent bonds, but non-covalent interactions (such as hydrogen bonds and other weak interactions) also play important roles in the assembly of coordination compounds. Incorporating hydrogen donor/acceptor functional groups into organic ligands appears as an attracting method to tune or enhance desired properties[17]. Tiny modification to the organic ligand could vary the strength and directionality of the intra/intermolecular interactions and result in dramatic structural differences[18]. The influence of conventional hydrogen bonds (O-H···O) in the construction of metal phosphonates