

The Effect of Lead(II) Lone Electron Pair and Non-Covalent Interactions on the Supramolecular Assembly and Fluorescence Properties of Pb(II)-Pyrrole-2-Carboxylato Polymer

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Abstract : Recently, the growing interest of chemists in metal-organic coordination polymers (MOCs) is primarily derived from their intriguing structures and potential applications in catalysis, gas storage, molecular sensing, ion exchanges, nonlinear optics, luminescence, etc. Currently, we are devoting considerable effort to finding the proper method of synthesizing new coordination polymers containing S- or N-heteroaromatic carboxylates as linkers and characterizing the obtained Pb(II) compounds according to their structural diversity, luminescence, and thermal properties. The choice of Pb(II) as the central ion of MOCs was motivated by several reasons mentioned in the literature: i) a large ionic radius allowing for a wide range of coordination numbers, ii) the stereoactivity of the 6s² lone electron pair leading to a hemidirected or holodirected geometry, iii) a flexible coordination environment, and iv) the possibility to form secondary bonds and unusual non-covalent interactions, such as classic hydrogen bonds and $\pi \cdots \pi$ stacking interactions, as well as nonconventional hydrogen bonds and rarely reported tetrel bonds, Pb(lone pair) $\cdots \pi$ interactions, C-H \cdots Pb agostic-type interactions or hydrogen bonds, and chelate ring stacking interactions. Moreover, the construction of coordination polymers requires the selection of proper ligands acting as linkers, because we are looking for materials exhibiting different network topologies and fluorescence properties, which point to potential applications. The reaction of Pb(NO₃)₂ with 1H-pyrrole-2-carboxylic acid (2prCOOH) leads to the formation of a new four-nuclear Pb(II) polymer, [Pb₄(2prCOO)₈(H₂O)]_n, which has been characterized by CHN, FT-IR, TG, PL and single-crystal X-ray diffraction methods. In view of the primary Pb-O bonds, Pb1 and Pb2 show hemidirected pentagonal pyramidal geometries, while Pb3 and Pb4 display hemidirected octahedral geometries. The topology of the strongest Pb-O bonds was determined as the (4·8²) fcs topology. Taking the secondary Pb-O bonds into account, the coordination number of Pb centres increased, Pb1 exhibited a hemidirected monocapped pentagonal pyramidal geometry, Pb2 and Pb4 exhibited a holodirected tricapped trigonal prismatic geometry, and Pb3 exhibited a holodirected bicapped trigonal prismatic geometry. Moreover, the Pb(II) lone pair stereoactivity was confirmed by DFT calculations. The 2D structure was expanded into 3D by the existence of non-covalent O/C-H $\cdots \pi$ and Pb $\cdots \pi$ interactions, which was confirmed by the Hirshfeld surface analysis. The above mentioned interactions improve the rigidity of the structure and facilitate the charge and energy transfer between metal centres, making the polymer a promising luminescent compound.

Keywords : coordination polymers, fluorescence properties, lead(II), lone electron pair stereoactivity, non-covalent interactions

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