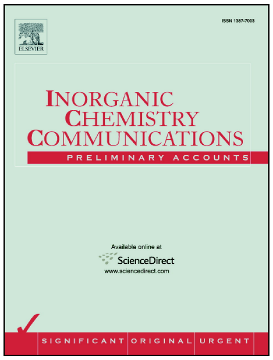

Structural diversity, luminescent and magnetic properties of Tb(III)/Gd(III) metal–organic frameworks constructed by Tris(p-carboxyphenyl)phosphane oxide

Chenxu Jiao, Jinfang Liang, Lingling Gao, Jie Zhang, Xiaoqing Wang, Liming Fan, Tuoping Hu

PII:	S1387-7003(18)30628-2
DOI:	doi:10.1016/j.inoche.2018.08.016
Reference:	INOCHE 7082
To appear in:	*Inorganic Chemistry Communications*
Received date:	6 July 2018
Revised date:	13 August 2018
Accepted date:	13 August 2018

Please cite this article as: Chenxu Jiao, Jinfang Liang, Lingling Gao, Jie Zhang, Xiaoqing Wang, Liming Fan, Tuoping Hu , Structural diversity, luminescent and magnetic properties of Tb(III)/Gd(III) metal–organic frameworks constructed by Tris(p-carboxyphenyl)phosphane oxide. Inoche (2018), doi:10.1016/j.inoche.2018.08.016

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communicaitons

journal homepage: www.elsevier.com/locate/icc

Structural Diversity, Luminescent and Magnetic Properties of Tb(III)/Gd(III) Metal–Organic Frameworks Constructed by Tris(*p*-carboxyphenyl)phosphane Oxide

Chenxu Jiao[a], Jinfang Liang[a], Lingling Gao[a], Jie Zhang[a], Xiaoqing Wang[a], Liming Fan[a], Tuoping Hu*[a]

[a] *Department of Chemistry, College of Science, North University of China, Taiyuan 030051, China.*

ARTICLEINFO

Aritcle history:
Received xxxxxx
Accepted xxxxxx
Available online xxxxxx

Keywords:
Tris(p-carboxylphenyl)phosphine oxide
Metal-organic frameworks
Structural diversity
Luminescent sensing
Magnetic properties

ABSTRACT: Two lanthanide metal-organic frameworks (LOFs), namely, $\{[Tb(L^{3-})(H_2O)]\cdot 3CH_3CN\}_n$ (**1**) and $\{(Me_2NH_2^+)_{0.5}\cdot[Gd(L^{3-})(HCOO^-)_{0.5}H_2O]\cdot DMF\cdot 4EtOH\cdot H_2O\}_n$ (**2**) have been constructed by tris(4-carboxyphenyl)phosphane oxide (H_3L) under solvothermal conditions. Structural analyses indicate that complex **1** appears a 3D 6-connected $\{4^{12}.6^3\}$ net based on the binuclear $\{Tb_2(COO)_2\}$ clusters. Complex **2** is also a 3D framework. Furthermore, the photoluminescence of **1** in the solid state and different solvent emulsions were studied, the results indicate that **1** shows characteristic green emission of Tb^{3+} ion and has better fluorescent recognition for sorts of organic solvent molecules and Fe^{3+} ion. Finally, the result of the variable-temperature magnetic susceptibilities suggests that complex **2** have antiferromagnetic behavior between Gd(III) ions.

With the development of the society, a lot of industrial pollutants have casually been thrown away without some suitable handling, causing many ecological problems and severe harm to human health and safety [1]. Among them, noxious nitrobenzene derivatives (NDVs) can lead to mental disorder and cell canceration, while the overload of Fe^{3+} ion can perturb cellular homeostasis and metaboly [2]. Therefore, it is necessary to look for a kind of material that can quickly and efficiently detect NDVs and Fe^{3+} ion. Lanthanide metal-organic frameworks (LOFs) as luminescent probes have been paid much attention owing to the unique optical properties deriving from f-f transitions, including high color purity, visible colors with the naked eyes and relatively long luminescence life span [3].

The adjacent metal ions in LOFs can form multinuclear secondary building units (SBUs) by joining the carboxyl groups, which can significantly enhance the magnetic properties of the LOFs. Due to the diverse arrangement of spin electrons in metal ions, the magnetic interaction between metal ions in SBUs is more complicated [4]. Furthermore, compared with transition metal ions, the diverse 4f orbits of lanthanide metal ions make the structure of LOFs more complicated and varied [5].

We selected the aromatic multicarboxylate ligand of tris(*p*-carboxyphenyl) phosphane oxide (H_3L) for the following reason: 1) it has characteristics of the multiple sites and three chains turning freely to help to construct multidimensional structures. 2) H_3L possesses π-Electron-rich aromatic backbones, which facilitate the construction of complexes with excellent fluorescent properties and magnetic properties. Under above background, two luminescent coordination polymers based on H_3L and lanthanide ions were constructed, namely, $\{[Tb(L^{3-})(H_2O)]\cdot 3CH_3CN\}_n$ (**1**) and $\{(Me_2NH_2^+)_{0.5}\cdot[Gd(L^{3-})(HCOO^-)_{0.5}H_2O]\cdot DMF\cdot 4EtOH\cdot H_2O\}_n$ (**2**). In addition, fluorescent properties of complex **1** and the magnetic properties of **2** have also been studied in details.

Single crystal X-ray diffraction analyses reveal that complex **1** crystallizes in triclinic system with *P*-1 space group. The unit cell contains one Tb^{III} ion, one L^{3-} ligand, one coordinated H_2O and three lattice CH_3CN molecules. As shown in Fig. 1, Tb^{III} ion is eight-coordinated by one O atom from one coordinated H_2O molecule [$Tb1^{iv}{-}O1W = 2.364$ Å], one O atom from P=O moiety of L^{3-} ligand [$Tb1^{iv}{-}O5 = 2.262$ Å] and six O atoms from four different L^{3-} ligands [$Tb1^{iv}{-}O3^{iv} = 2.275$ Å, $Tb1^{iv}{-}O4^{iv} = 2.278$ Å, $Tb1^{iv}{-}O6^{vi} = 2.481$ Å, $Tb1^{iv}{-}O7^{vi} = 2.452$ Å, $Tb1^{iv}{-}O8^{iii} = 2.463$ Å, $Tb1^{iv}{-}O9^{iii} = 2.446$ Å], exhibiting a distorted $\{TbO_8\}$ geometry.

The H_3L ligand is completely deprotonated and adopts $(\kappa^1\text{-}\kappa^1)\text{-}(\kappa^1\text{-}\kappa^1)\text{-}(\kappa^1\text{-}\kappa^1)\text{-}\kappa^1\text{-}\mu_5$ coordination mode. The two $(\kappa^1\text{-}\kappa^1)\text{-}\mu_2$ carboxyl groups of L^{3-} ligand joint with two Tb^{III} ions to form a binuclear $\{Tb_2(COO)_2\}$ cluster (Tb···Tb distances being 5.229 Å), which was further bridged by the L^{3-} ligands to obtain finally a fascinating 3D framework (Fig. 2a).

Topologically [6], when the $\{Tb_2(COO)_2\}$ SBU is regarded as a 6-connected node, the 3D structure of complex **1** can be simplified a 6-connected network with the point symbol of $\{4^{12}.6^3\}$.

*Corresponding author.
E-mail address: hutuopingsx@126.com.