

Syntheses of Two New Lanthanide Metal-Organic Frameworks Based on a Rigid Acetylenic Ligand.

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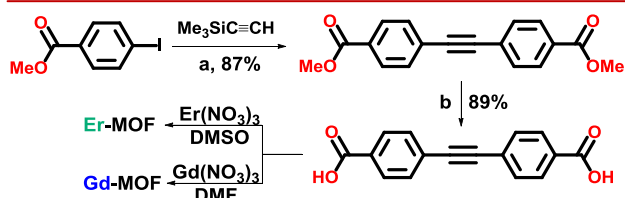
Keywords: metal-organic frameworks, acetylenic ligand, lanthanides.

Introduction

Lanthanides cations have been largely employed in the construction of metal-organic frameworks (MOFs) due to their high coordination number and photoluminescent properties.¹ These materials have several technological applications such as, LEDs and chemical sensors.² Judicious choice of the ligands can lead to structures with different topologies and characteristics (*i.e.* charged, neutral or porous networks).³ For example, a carboxylic ligand has many coordination modes and forms neutral networks.⁴ Thus, the aim of this work is to use a rigid dicarboxylic acetylenic ligand, 4,4'-ethynylatedibenzoic acid (H₂edb) (**Scheme 1**), for the construction of new lanthanide MOFs.

Results and Discussion

The ligand H₂edb was synthesized in three steps via Sonogashira cross-coupling reaction in a good yield. The lanthanide MOFs were obtained by solvothermal synthesis (**Scheme 1**).



Scheme 1. Synthetic route of the ligand. a) Pd(PPh₃)₂Cl₂, CuI, Et₃N, DBU, H₂O; b) 1) KOH/MeOH, 2) HCl; c) Py, MeOH/DMSO; d) Et₃N, MeOH/DMSO.

The X ray single crystal diffraction analysis reveals that the Er-MOF, [Er₂(edb)₃(DMSO)(OH₂)₂].xH₂O, crystallizes in the P-1 space group. Er-MOF contains binuclear subunits cross-linked together by the edb ligands. Each Er(III) ion is in a distorted square antiprism geometry, 8-coordinated by 4 oxygen atoms from the edb, 3 from water molecules and 1 from DMSO molecule (**Figure 1a**). The chelating and bridging coordination modes of the ligand created 2-D metal-organic framework layers that pile up forming a 3D supramolecular framework with voids, as shown by the topological analysis (**Figure 1b**).

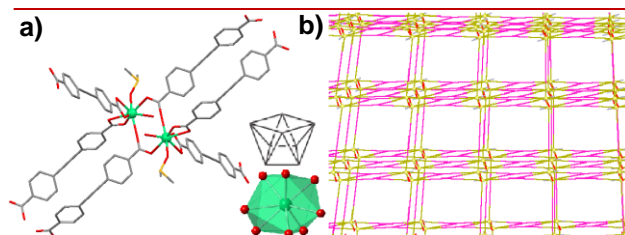


Figure 1. a) Subunit formed by the ligand and Er(III). b) Framework of the Er-MOF.

The Gd-MOF, [Gd₂(edb)₃(OH₂)₄].xH₂O, crystallizes in the C2/c space group. Similarly to Er-MOF, Gd(III) ions are in a distorted square antiprism geometry, but coordinated by 6 oxygen atoms from the edb and 2 from water molecules, generating a subunit in a paddle-wheel fashion (**Figure 2a**). A hexagonal interpenetrated 3D metal-organic framework is observed for Gd-MOF (**Figure 2b**).

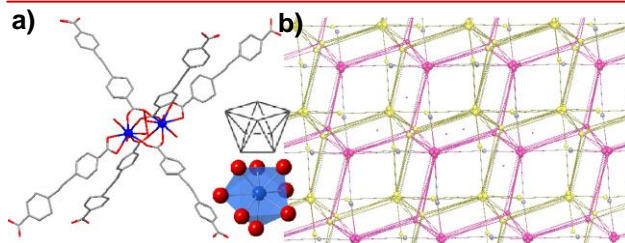


Figure 2. a) Paddle-wheel subunit. b) Hexagonal interpenetrated framework of the MOF.

Conclusions

2D-Er-MOF and 3D-Gd-MOF based on a rigid acetylenic dicarboxylic ligand were synthesized. The high coordination number of the lanthanides and the coordination modes of the ligand provided different topologies from a similar paddle-wheel subunit.

Acknowledgements

FAPERJ, CNPq, LDRX, LaReMN and LAMATE.

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