IX SIMPOSIO de Investigación EN CIENCIAS EXPERIMENTALES

Towards magnetic and luminescent MOFs based on Ln(III) Ions

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INTRODUCTION

During the last two decades, MOFs (metal-organic frameworks) investigation has become of great attention for both the academia and the industry.[1] The structural diversity present in MOFs has significantly expanded the application of these new materials, which broadens from gas storage and separation, catalysis, biomedicine delivery, to chemical sensing.[2]

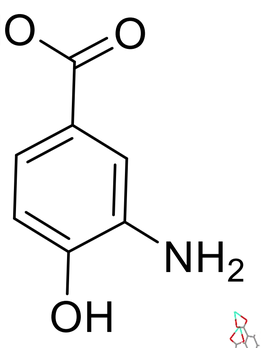
In this context, this work presents the synthesis and characterization of a family of three-dimensional MOFs based on Ln(III) ions and 3-amino-4-hydroxy benzoic acid (HL) multitopic ligand.

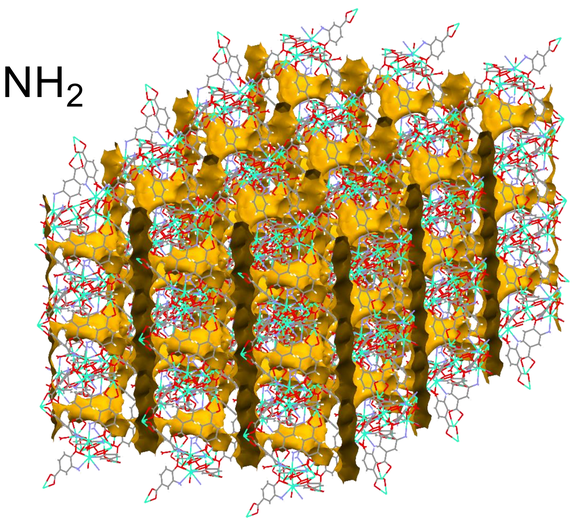
The reaction between HL with the corresponding lanthanide salt afforded ten new isostructural MOFs with the general formulae $[Ln_5L_6(OH)_3(DMF)_3]_n \cdot 4DMF \cdot 4H_2O$; Ln= Nd (**1**), Sm (**2**), Eu (**3**), Gd (**4**), Tb (**5**), Dy (**6**), Ho (**7**), Er (**8**), Tm (**9**) and Yb (**10**).

Magnetic *ac* measurements studies has been carried out with compounds (**6**) and (**8**) showing no maxima in out-of-phase molar magnetic susceptibility plots. Taking into account that in each node five metal ions are interconnected among them, Y- Dy and Y-Er diluted sample's magnetic properties have been studied with the aim of isolating each paramagnetic metallic centre.

Photoluminescence properties have been examined in compound (**5**) at room temperature. Additionally, emission response of (**5**) has been studied in the presence of several solvents.

Finally, motivated by the possible solvent accessible volume of the structures, gas adsorption isotherms have been collected for compound (**6**).

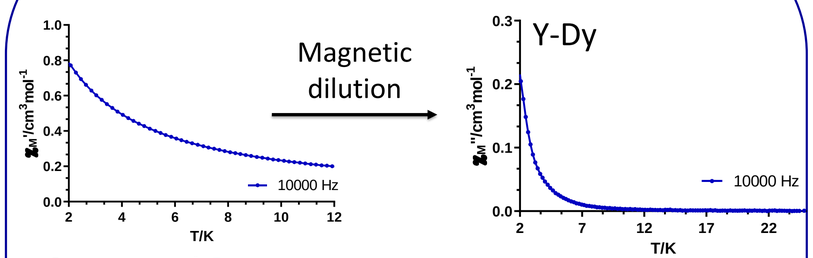




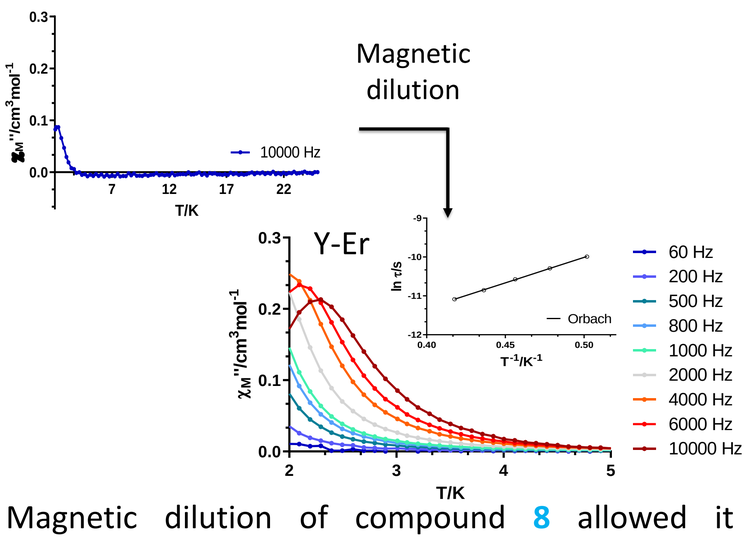
PROPERTIES

Magnetic ac measurements

Compound **6**



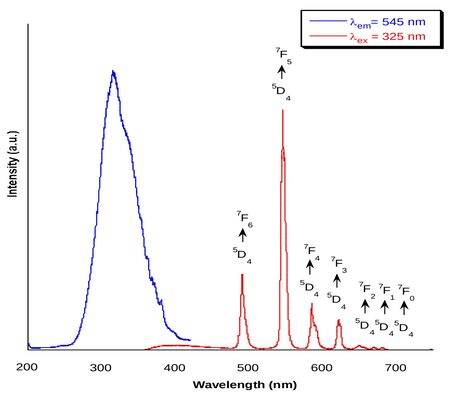
Compound **8**

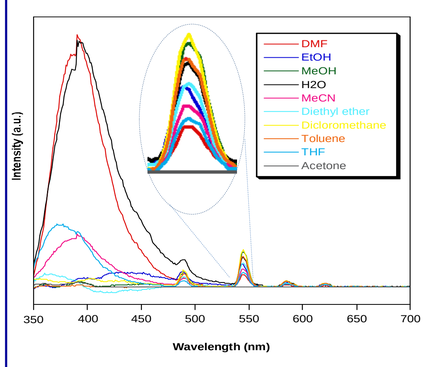


Magnetic dilution of compound **8** allowed it showing SMM behaviour, from which an effective energy barrier of U_{eff}=18.21 K for the reversal of the magnetization and $\tau_0 = 5.26 \cdot 10^{-10}$ s is estimated.

Photoluminescence

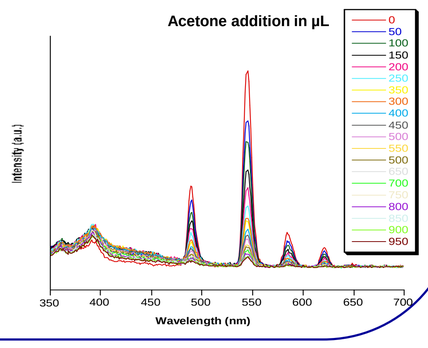
Compound **5** excitation (blue, 325 nm) and emission (red, 545 nm) spectra at room temperature.





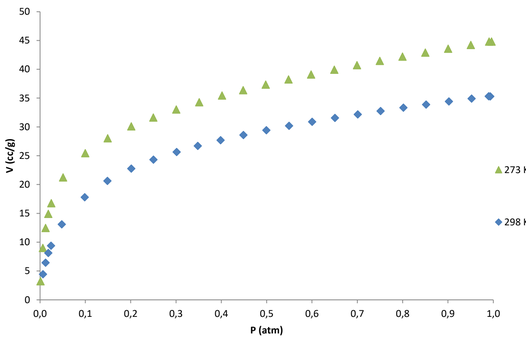
Emissive response of compound **5** when it is dispersed into different solvents.

Quenching capacity of acetone



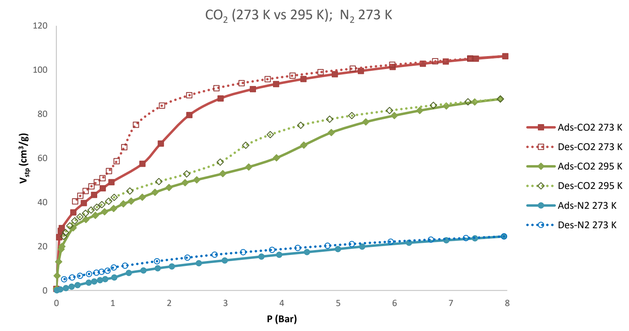
Adsorption properties

1



Compound **6** CO_2 adsorption isotherm at 273 K (green) and 298 K (blue) at 1 atm.

2



Comparison of high pressure CO_2 adsorption isotherm at 273 K (red) and 298 K (green) with respect to N_2 adsorption isotherm at 273 K (blue) of compound **6**.

CONCLUSIONS

- We have been able to synthesise and fully characterize a family of lanthanide based metal-organic frameworks that show magnetic, photoluminescence and adsorption properties
- Magnetic dilution performed on compound **6** did not allow it for presenting single-molecule magnet (SMM) behaviour, contrary to what happens in compound **8** where the isolation of the paramagnetic centres yielded SMM behaviour
- Compound **5** presents important emission properties derived principally from Tb^{3+} ion emission and presents different emission response with respect to solvent change stimuli
- CO_2 adsorption measurements of compound **6** suggest that the MOF did not collapse at high pressure and it is stable at different temperatures which suggests that can be a good candidate for gas adsorption.

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