Superprotonic conductivity in a metalloporphyrin-based MOF

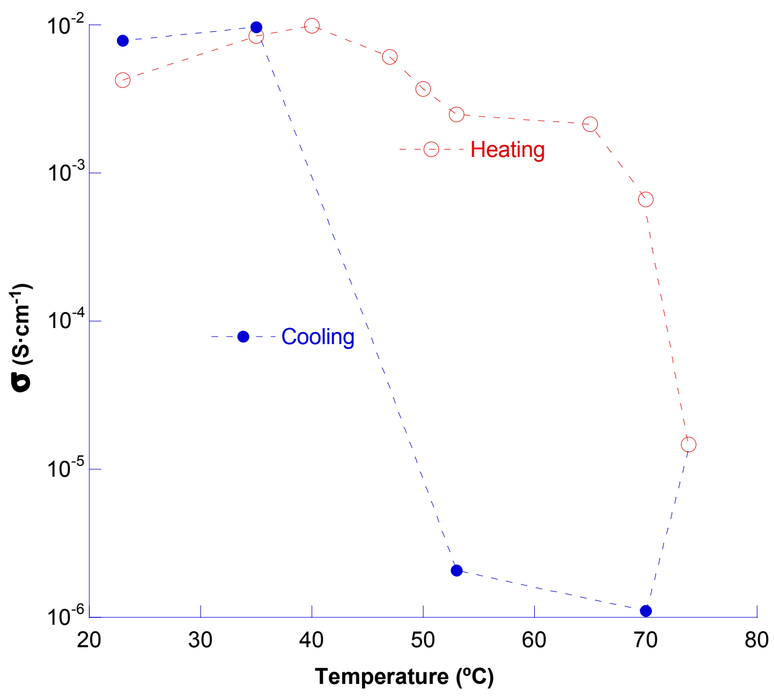
A. Fidalgo-Marijuan*[1,3], G. Barandika[2,3], B. Bazán[1,3], M. K. Urtiaga[1], I. R. de Larramendi[2] and M. I. Arriortua[1,3]

[1]Department of Mineralogy and Petrology and [2]Department of Inorganic Chemistry, University of the Basque Country (UPV/EHU), Barrio Sarriena s/n, 48940 Leioa, Spain.
[3]BCMaterials, Basque Center for Materials, Applications and Nanostructures, Parque Tecnológico de Zamudio, Ibaizabal Bidea, Edificio 500-Planta 1, 48160 Derio, Spain.

Introduction

MOF materials exhibit great potential for a broad range of applications taking advantage of their high surface area and pore sizes and tuneable chemistry[1]. In particular, metalloporphyrin-based MOFs are becoming of great importance in many fields due to the bioessential functions of these macrocycles that are being mimicked. On the other hand, during the last years, proton-conducting materials have aroused much interest, and those presenting high conductivity values are potential candidates to play a key role in some solid-state electrochemical devices such as batteries and fuel cells[2]. In this way, using metalloporphyrins as building units we have obtained a new crystalline material with formula $[H(bipy)]_2[(MnTPPS)(H_2O)_2]\cdot 2bipy\cdot 14H_2O$, where bipy is 4,4´-bipyidine and TPPS is the *meso*-tetra(4-sulfonatephenyl) porphyrin. The crystal structure was determined by single crystal X-ray diffraction and thermal characterization was carried out by thermogravimetric (TG/DSC) and X-ray thermodiffraction (XRTD) measurements.

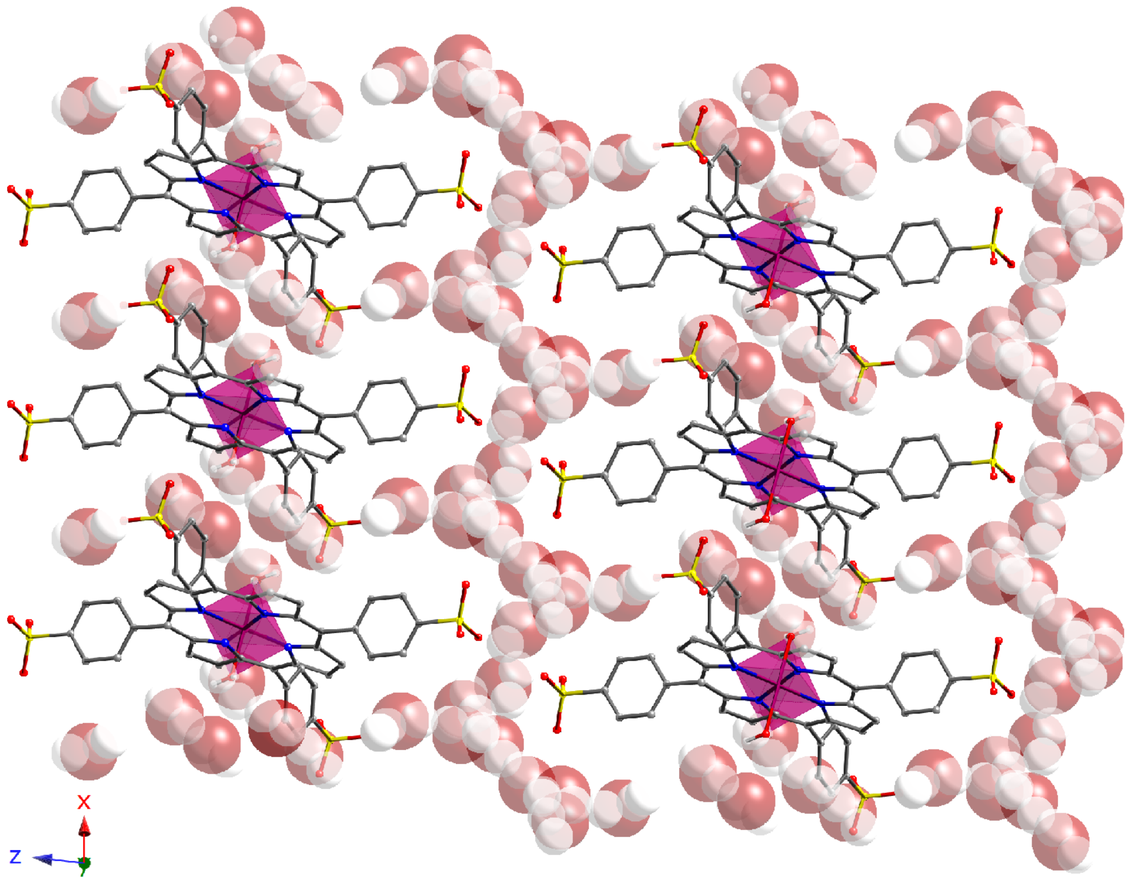
Proton conductivity measurements



The compound was tested for proton conduction (σ) showing values of $1x10^{-2}$ S·cm^{-1} at 40 ºC and 98% relative humidity (RH). Unexpectedly, when the temperature rises above 40 ºC the proton conductivity decreases, but recovers when cooling the system.

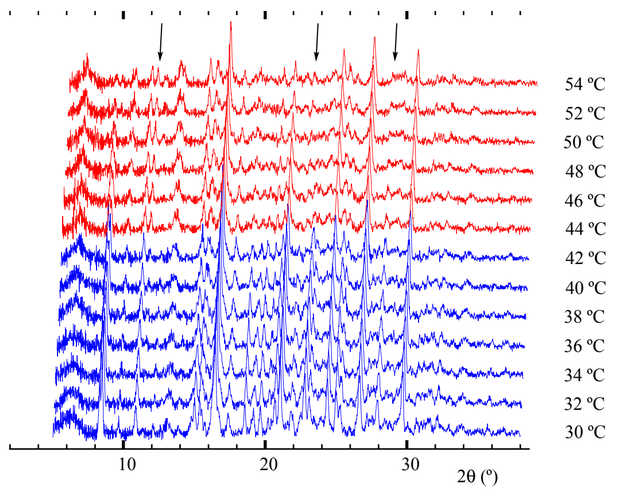
The least-squares fit of the Arrhenius plots in the temperature range from 23 ºC to 40 ºC produced the activation energy (Ea) with the value of 0.407 eV, indicating the Grotthuss mechanism[3] along the zig-zag water chains.

Crystal Structure



The compound $[H(bipy)]_2[(MnTPPS)(H_2O)_2]\cdot 2bipy\cdot 14H_2O$ shows a zig-zag water chain along the [100] direction located between the sulfonate groups of the metalloporhyrin.

X-ray thermodiffraction at 98% RH



A temperature dependent X-ray analisys under humid conditions (98% RH) shows a lost of intensity in the diffraction peaks around 22.5º and 28º in 2θ. This can be attributed to a change or rupture of the water chains acusing a continuous decrease in the proton conductivity.

Conclusions

We have obtained a metalloporphyring-based MOF that shows very high proton conductivity values ($1x10^{-2}$ S·cm^{-1}) at 40ºC and 98% RH, due to the interconected zig-zag water chains of the crystalline structure.

References

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