

**Electronic Supporting Information (ESI)** for the manuscript:

**A novel oxalate-based three-dimensional coordination polymer showing  
magnetic ordering and high proton conductivity**

Marta Mon, Julia Vallejo, Jorge Pasán, Oscar Fabelo, Cyrille Train,\* Michel Verdaguer,  
Shin-ichi Ohkoshi, Hiroko Tokoro, Kosuke Nakagawa and Emilio Pardo\*

## Experimental Section

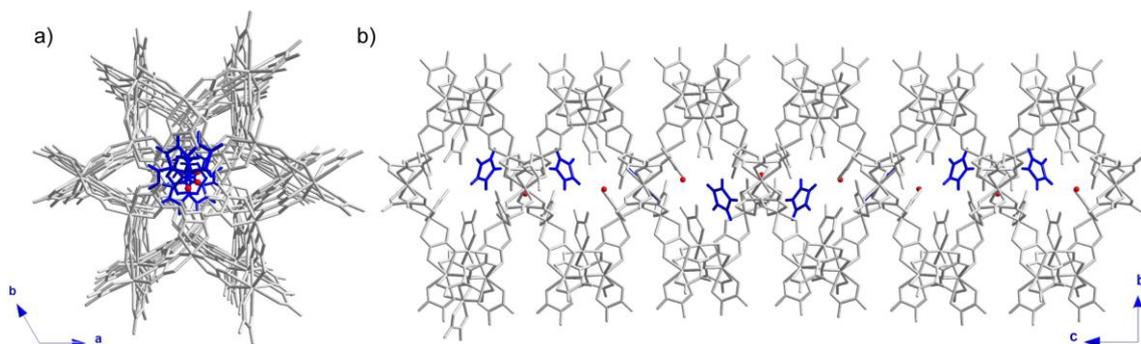
**Physical Techniques.** Elemental (C, H, N) analyses were performed at the Microanalytical Service of the Universitat de València. IR spectra were recorded in KBr pellets on a Bio-Rad FTS165 spectrophotometer.

**Table S1. Summary of Crystallographic Data for 2**

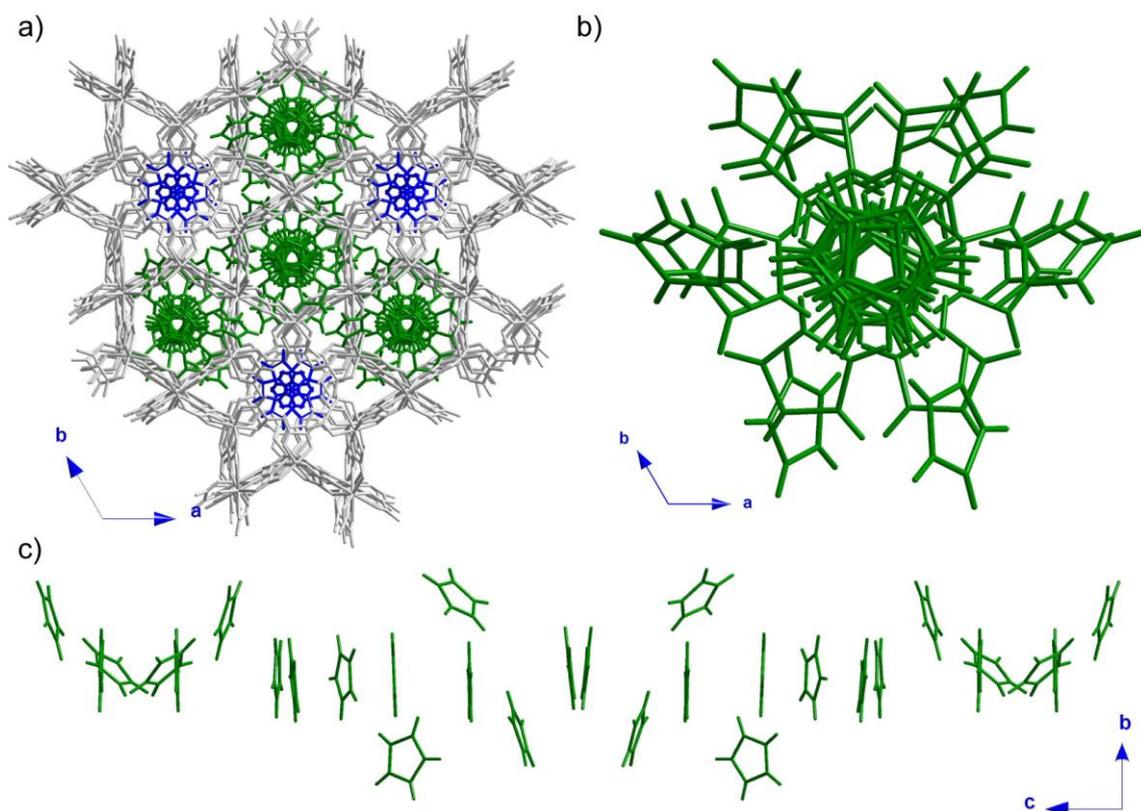
Compound	2	2*
Formula	C <sub>48</sub> H <sub>42</sub> Cr <sub>4</sub> Mn <sub>2</sub> N <sub>16</sub> O <sub>49</sub>	C <sub>48</sub> H <sub>42</sub> Cr <sub>4</sub> Mn <sub>2</sub> N <sub>16</sub> O <sub>49</sub>
<i>M</i> (g mol <sup>-1</sup> )	1944.85	1944.85
Crystal system	Hexagonal	Hexagonal
Space group	<i>P</i> 6 <sub>5</sub> 22	<i>P</i> 6 <sub>5</sub> 22
<i>a</i> (Å)	18.80530(10)	18.80530(10)
<i>b</i> (Å)	18.80530(10)	18.80530(10)
<i>c</i> (Å)	43.3432(4)	43.3432(4)
<i>V</i> (Å <sup>3</sup> )	13274.30(19)	13274.30(19)
<i>Z</i>	6	6
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	0.847	0.949
$\mu$ (mm <sup>-1</sup> )	0.713	1.008
<i>T</i> (K)	45.0	45.0
Measured reflections	137416	137416
Unique reflections (Rint)	8076 (0.0443)	8076 (0.0443)
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	7646	7646
Goof	1.744	1.048
<i>R</i> <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] (all data)	0.1279 (0.1301)	0.0540 (0.0563)
<i>wR</i> <sup>b</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] (all data)	0.3485 (0.3537)	0.1728 (0.1765)
Flack parameter	0.07(6)	0.08(3)

<sup>a</sup>  $R = \sum(|F_o| - |F_c|) / \sum|F_o|$ . <sup>b</sup>  $wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ .

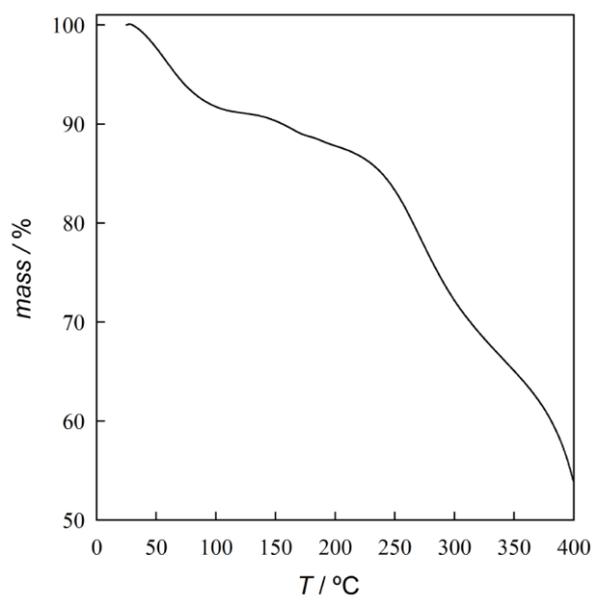
\* Final model, after applying a Squeeze subroutine (see main text).



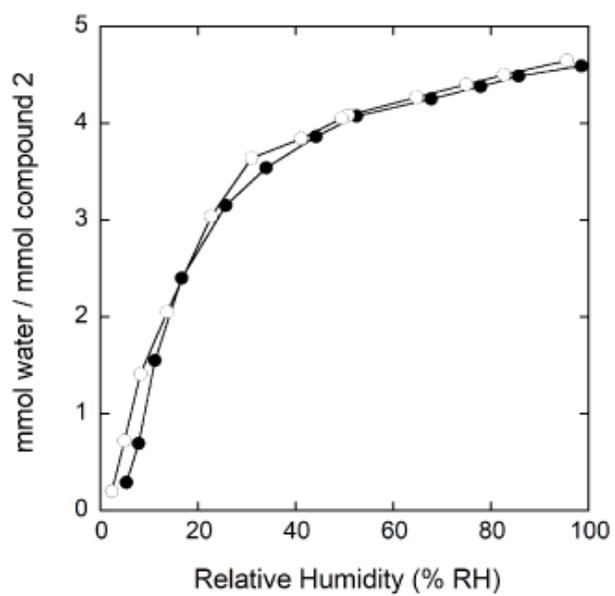
**Figure S1.** Views of the helical arrangement of the imidazolium cations in the smaller pores A of the anionic 3D network in the  $ab$  (a) and  $bc$  (b) planes, respectively. Oxalate ligands and imidazolium cations are depicted as grey and blue sticks, respectively, whereas the water molecule is represented with a red sphere.



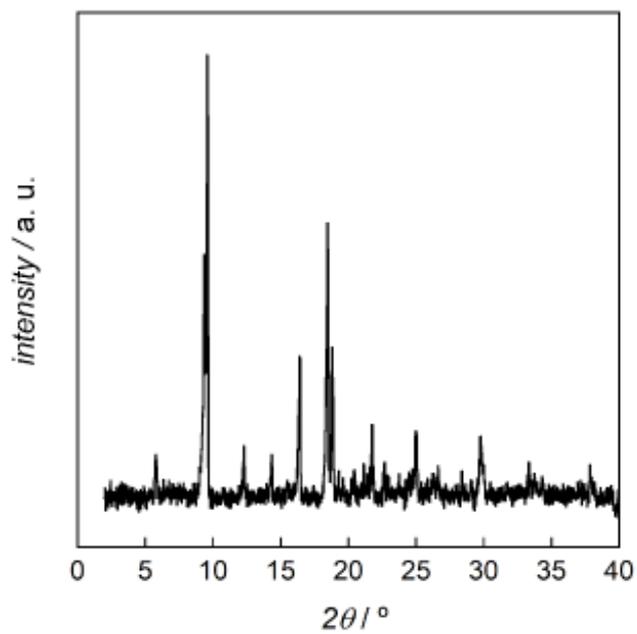
**Figure S2.** (a) View of the 3D structure of **2** along the *c* axis. Oxalate ligands are depicted as grey sticks. Refined and non-refined imidazolium cations are shown as blue and green sticks, respectively. Perspective view of the packing of the imidazolium cations located in the larger B pores in the *ab* (b) and *bc* (c) planes, respectively.



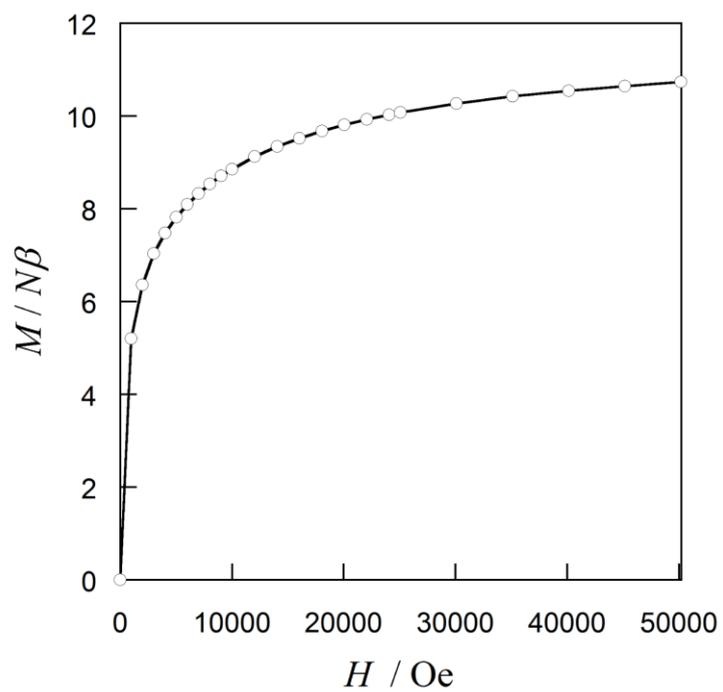
**Figure S3.** Thermogravimetric Analysis of **2** under dry N<sub>2</sub> atmosphere in the 25-400 °C range.



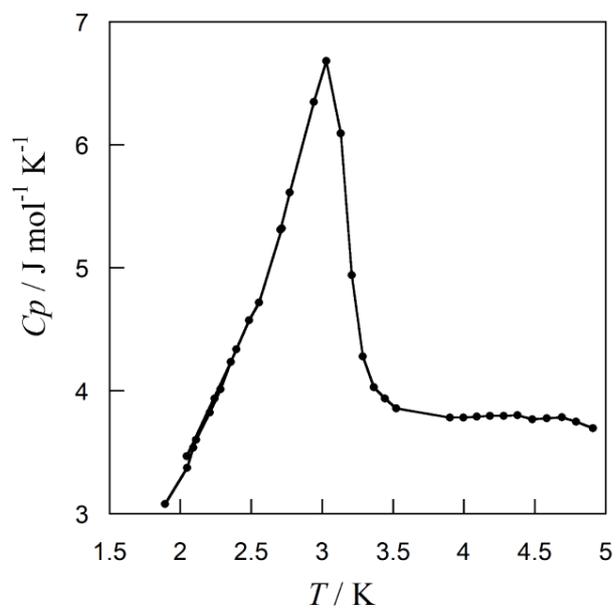
**Figure S4.** Water vapour adsorption isotherm acquired at 298 K for the activated compound 2. Closed symbols represent adsorption and open symbols desorption branch.



**Figure S5.** PXRD pattern profile of **2** after water adsorption isotherm measurement.



**Figure S6.** Field dependence of the magnetization ( $M$ ) of **2** in Bohr magnetons  $N\beta$ , at  $T = 2.0$  K ( $\circ$ ). The solid line is a guide-line for the eyes.



**Figure S7.** Temperature dependence the heat capacity of **2**, demonstrating the long range magnetic ordering phase transition at 3.0 K.