Supporting Information

Anomalous Dielectric Behavior and Thermal Motion of Water Molecules Confined in Channels of Porous Coordination Polymer Crystals

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General Materials and Methods

The crystals of $[Ln_2Cu_3(IDA)_6]nH_2O$ (Ln = La, Nd, Sm, Gd, Ho, Er) belong to a trigonal system with space group $P\bar{3}c1$. The lattice constants and volumes of the porous spaces are listed in the Table S1.

Molecular dynamics (MD) simulations were performed using the Material Studio Modeling v5.0 software package (Accelrys Inc., San Diego, CA); the universal force field, as implemented in the Forcite Plus module, and the option for Ewald electrostatic and van der Waals interactions were used at the ultra-fine level of quality. The atomic coordinates of the host lattice as determined by X-ray crystal structure analyses were used and kept fixed during the simulation. The positions of water molecules were optimized at 100 K, and the simulation was performed in steps of 1 fs for 500 ps under the conditions of constant volume and constant temperature.

The typical size of the crystal used for dielectric measurements was $1.0 \times 1.0 \times 1.5$ mm^3, and the thickness of the crystal used for hysteresis measurements was 0.4–0.5 mm. The gold conduction paste painted on the crystal surfaces was used as electrodes.
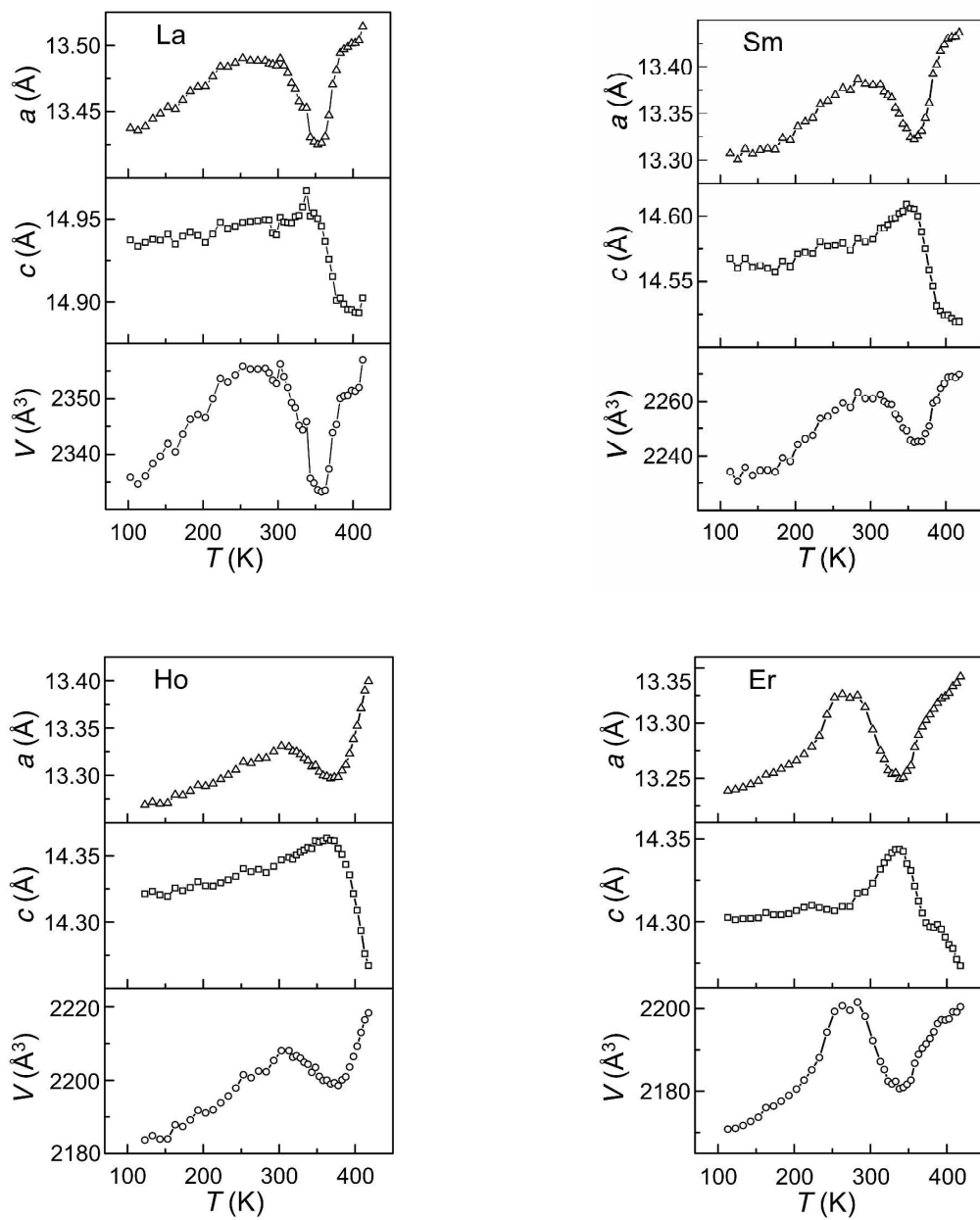
Figure S1. Temperature dependences of the lattice constants of $[Ln_2Cu_3(IDA)_6]nH_2O$ (Ln = La, Sm, Ho, Er).

Table S1. Lattice constants of $[Ln_2Cu_3(IDA)_6]nH_2O$ (Ln = La, Nd, Sm, Gd, Ho, Er) at 273 K.

	La	Nd	Sm	Gd	Ho	Er
a (Å)	13.495(2)	13.457(2)	13.410(1)	13.415(1)	13.388(2)	13.347(1)
c (Å)	14.912(2)	14.698(2)	14.581(2)	14.462(1)	14.306(2)	14.260(1)
V (Å^3)	2351.8(6)	2305.0(5)	2270.9(4)	2253.9(3)	2220.5(6)	2200.1(2)
Porous Space (Å^3)	745.9	715.0	698.0	686.1	668.7	642.1
Space Group	$P\bar{3}c1$ (#165)	$P\bar{3}c1$ (#165)	$P\bar{3}c1$ (#165)	$P\bar{3}c1$ (#165)	$P\bar{3}c1$ (#165)	$P\bar{3}c1$ (#165)
Z value	2	2	2	2	2	2
Residuals: R_1 (I>2σ) [a]	0.040	0.038	0.036	0.037	0.038	0.024
Residuals: wR_2 (I>2σ) [b]	0.133	0.112	0.115	0.083	0.096	0.072

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega F_o^2]^{1/2}$