Supporting Information (SI) concerning the manuscript:

High Proton Conduction in a Chiral Ferromagnetic Metal-Organic Quartz-like Framework

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Experimental Section

Materials. $(NH_4)_3[Cr(ox)_3] \cdot 3H_2O$ was synthesized according to literature methods.[1] All chemicals were of reagent grade quality, and they were purchased from commercial sources and used as received.

$(NH_4)_4[MnCr_2(ox)_6] \cdot 4H_2O$ (1): Well-formed large violet prisms of **1** suitable for single-crystal X-ray diffraction were obtained by slow diffusion of ethanol in an aqueous solution (2 mL) containing stoichiometric amounts of $MnCl_2 \cdot 4H_2O$ (0.1 g, 0.5 mmol) and the preformed $(NH_4)_3[Cr(ox)_3] \cdot 3H_2O$ (0.42 g, 1 mmol). They were isolated by filtration on paper and air-dried. Analysis calculated for $C_{12}H_{24}Cr_2MnN_4O_{28}$ (831.3): C, 17.34; H, 2.91; N, 6.74. Found: C, 17.21; H, 2.65; N, 6.89; IR (KBr) 1707, 1670 and 1639 (CO) cm^{-1}.

Physical Techniques. Elemental analyses (C, H, N) were performed at the Service Central d'Analyse du CNRS in Vernaisson (France). IR spectra were recorded in KBr pellets on a Bio-Rad FTS165 spectrophotometer.

Crystal Structure Data Collection and Refinement. Crystal data for **1**: $C_{12}H_{21}Cr_2MnN_4O_{26.5}$, hexagonal, space group $P6_522$, a = 19.411(2) Å, c = 16.0339(12) Å, V = 5232.0(15) $Å^3$, T = 200(1) K, λ = 0.71073 Å, Z = 6, ϱ_{calc} = 1.491 $g.cm^{-3}$, μ = 1.062 mm^{-1}, Flack parameter = 0.01(4), 5096 unique reflections and 3681 observed with $I > 2\sigma(I)$. All the measured independent reflections were used in the analysis. The structure was solved by direct methods and refined with full-matrix least-squares technique on F^2 using the SHELXS-97 and SHELXL-97 programs.[2] The hydrogen atoms of water and ammonium molecules weren't localized. Refinement of 224 variables with anisotropic thermal parameters for all atoms gave $R = 0.0578$ and $R_w = 0.1484$, with $S = 1.045$. The final Fourier-difference map showed maximum and minimum height peaks of 0.585 and -0.725 $e.Å^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-826007. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Proton Conductivity Measurements. The conductivity measurements were carried out using a an Agilent 4294A precision impedance analyzer by a quasi-four-probe method in the frequency range from 40 Hz to 110 MHz. For the measurement, the powdered sample was compressed into diameter of 7 mm

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[1] Bailar, J. C.; Jones, E. M. *Inorg. Synth.* **1939**, *1*, 37.
[2] Sheldrick, G. M. *SHELX97*, release 97-2; Institüt für Anorganische Chemie der Universität Göttingen: Göttingen, Germany, **1998**.

and thickness of 0.10 cm using a sample holder between two steel electrodes. The humidity of the sample holder for each measurement was tuned using dry N2 that had been passed through water or a saturated aqueous solution of NaBr.

Magnetic Measurements. Variable-temperature (2.0–300 K) magnetic susceptibility under an applied field of 1 T ($T \geq 30$ K) and 100 G ($T < 30$ K) and variable-field (0–5.0 T) magnetization measurements at $T = 2.0$ K were carried out on polycrystalline samples of **1** with a Quantum Design MPMS SQUID-based magnetometer. The magnetic susceptibility data were corrected for the diamagnetism of the constituent atoms and the sample holder.

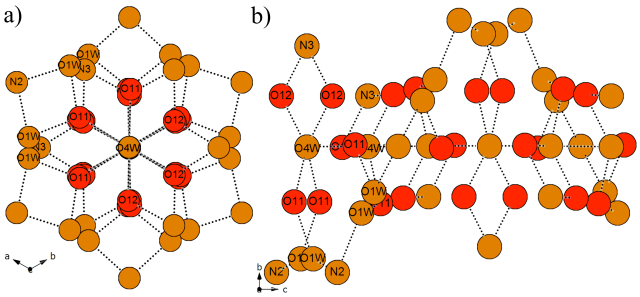

Figure S1. Detailed views of a fragment of **1** in the *ab* (a) and *bc* (b) planes, respectively, emphasizing the hydrogen bonds between proton bearers (ammonium, water) and oxygen atoms (O11, O12) of non-bridging oxalate ligands. Free water molecules and ammonium cations are in orange, whereas carbonyl-oxygen atoms are in red. Hydrogen bonds are represented by dotted lines.

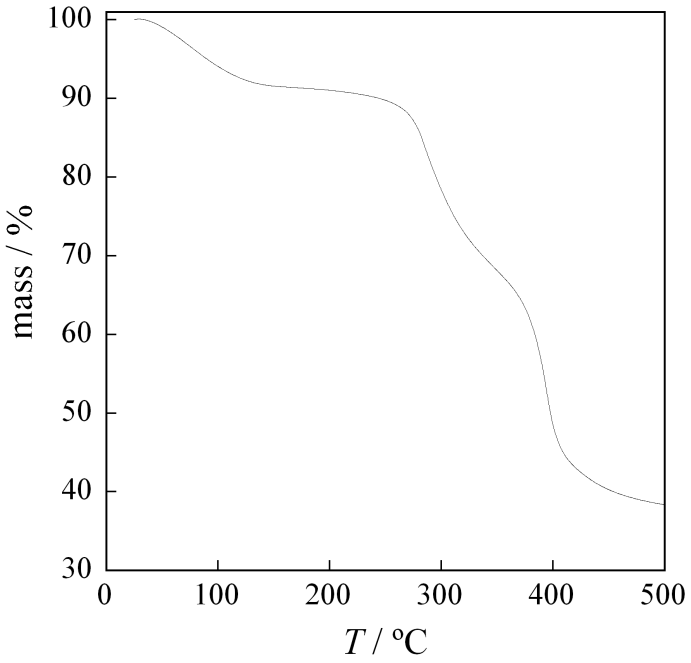

Figure S2. Thermogravimetric analysis (TGA) of **1** under dry N_2 atmosphere.

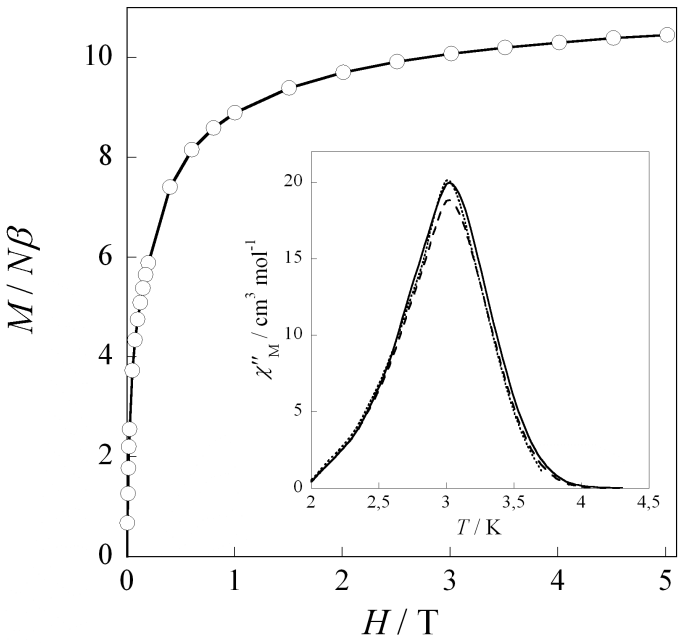

Figure S3. Field dependence of the magnetization (M) of **1** (○) at 2.0 K. The solid line is an eye-guide. The inset shows the temperature dependence of the out-of-phase *ac* magnetic susceptibility χ_M" for **1** with a 1.0 Oe field oscillating at frequencies of 100 (‒‒),- 900 (···) and 1400 (–) Hz.