Cluster–oxalate frameworks with extra-large channels: solvent-free synthesis, chemical stability, and proton conduction

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Physical measurements:

Powder X-ray diffraction (XRD) data were obtained using a Rigaku D/MAX-rA diffractometer with Cu-Kα radiation (λ = 1.5418 Å). IR spectra (KBr pellets) were recorded on a Nicolet Impact 410 FTIR spectrometer. The thermogravimetric analyses were performed on a Netzsch STA 449c analyzer in a flow of N_2 with a heating rate of 10 ºC/min. Magnetic measurement was performed on the Quantum Design SQUID MPMS XL-7 magnetometer in a magnetic field of 1000 Oe in the temperature range of 2-300 K. Alternating current impedance measurements were carried out with a Solartron SI 1260 impedance/gain-phase analyzer over the frequency range from 0.1 Hz to 10 MHz with an applied voltage of 10 mV. The relative humidity was controlled by a STIK Corp. CIHI-150B incubator. The sample was pressed to form a cylindrical pellet of crystalline powder sample (~2 mm thickness ×5 mm ϕ) coated with C-pressed electrodes. Two silver electrodes were attached to both sides of pellet to form four end terminals (quasi-four-probe method). Single crystal X-ray diffraction data were collected on a New Gemini, Dual, Cu at zero, EosS2 diffractometer at room temperature. The crystal structures were solved by direct methods. The structures were refined on F^2 by full-matrix least-squares methods using the *SHELXTL* program package.[1]

Reference

1. G. M. Sheldrick, Acta Cryst., Sect. A, 2008, 64, 112.

Table S1. Hydrogen bond information for SCU-62

D-H···A[a]	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (deg)
N1-H1···O8#1	0.86	1.87	2.672(6)	154.8
N1-H2···O2#2	0.86	2.21	2.882(7)	135.4

[a] Symmetry transformations used to generate equivalent atoms: #1 1-x, 1-y, +z; #2 1/2+y, 1-x, -1/4+z.

Table S2. Hydrogen bond information for SCU-65

D-H···A[a]	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (deg)
N1-H1···O6#1	0.98	2.09	2.997(4)	152.8
N2-H2A···O10	0.89	2.45	3.233(4)	147.2
N2-H2B···O6#1	0.89	1.99	2.828(4)	157.5
N2-H2C···O1	0.89	2.34	2.882(4)	119.1
N2-H2C···O2	0.89	2.27	3.143(4)	165.3

[a] Symmetry transformations used to generate equivalent atoms: #1 2-x, 1-y, 1-z.

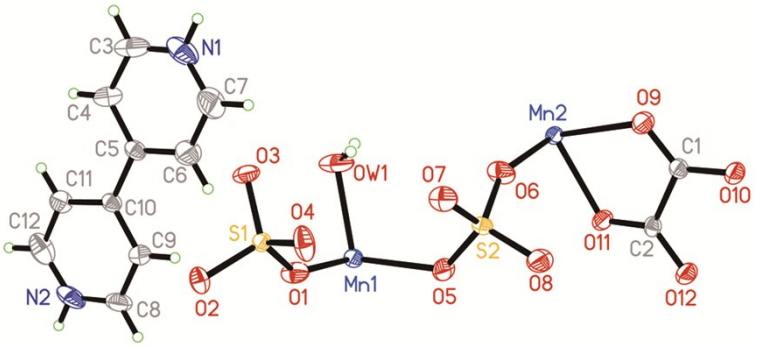

Fig. S1. ORTEP plot of the asymmetric unit of SCU-62, showing the labeling scheme and the 50% probability displacement ellipsoid.

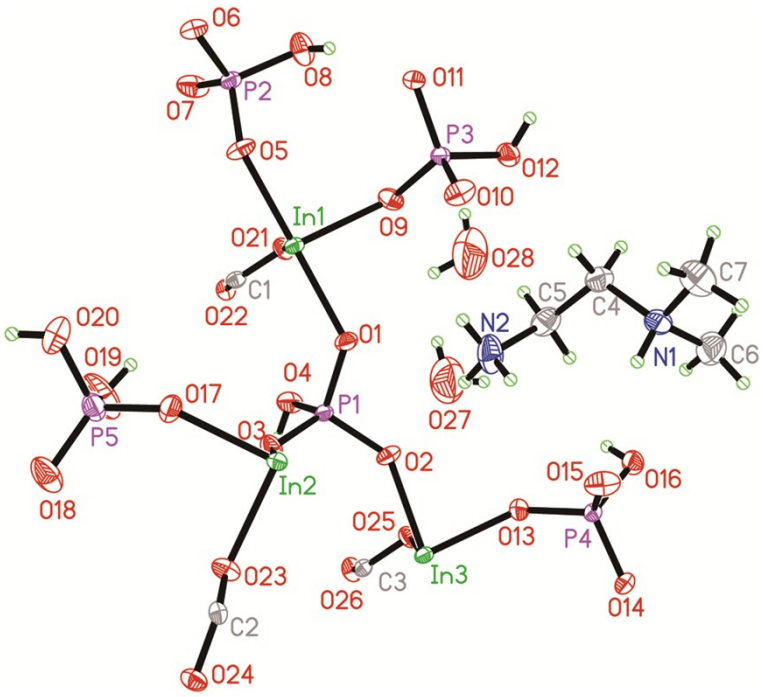

Fig. S2. ORTEP plot of the asymmetric unit of SCU-65, showing the labeling scheme and the 50% probability displacement ellipsoid.

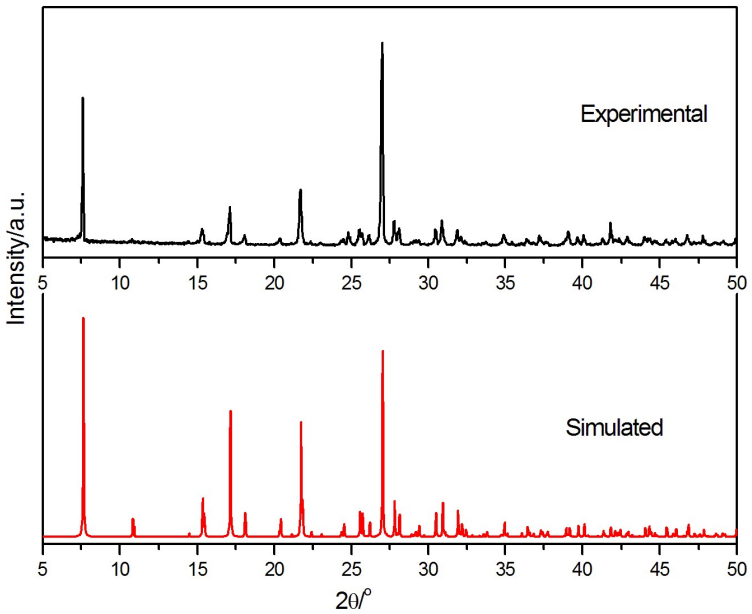

Fig. S3. Experimental and simulated powder XRD patterns of SCU-62.

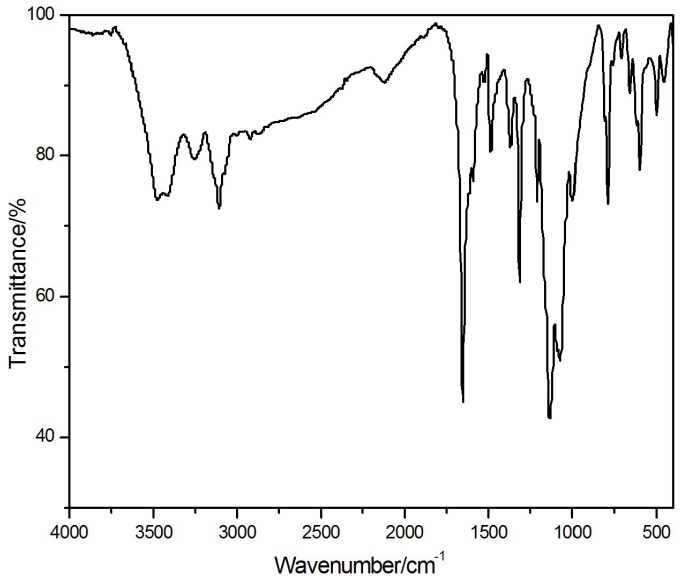

Fig. S4. IR spectrum of SCU-62. The strong bands at 1650 and 1320 cm^{-1} correspond to the C=O and C–O stretching vibrations in the oxalate groups, respectively. The strong bands in the region 995-1140 cm^{-1} are assigned to the asymmetric stretch of SO_4 tetrahedra. The weak bands for CH_2 bending vibration appear at 1485 cm^{-1}. The band at 1370 cm^{-1} is assigned to the C–N stretching vibration.

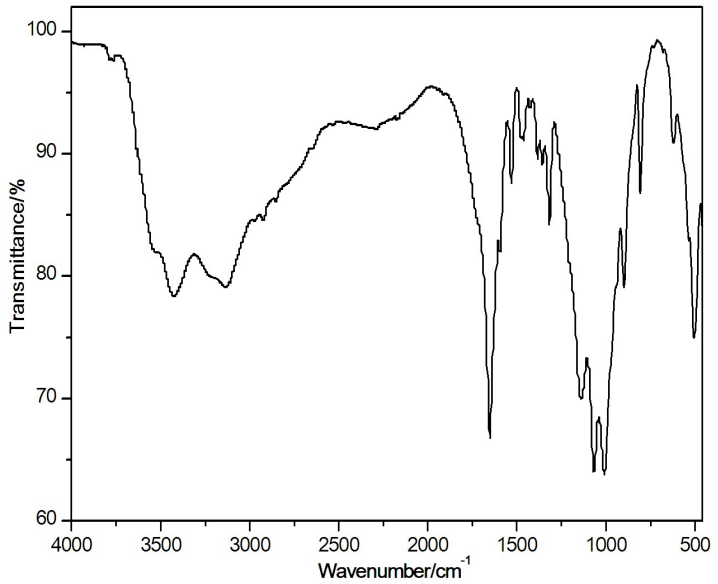

Fig. S5. IR spectrum of SCU-65. The bands at 1652 and 1316 cm^{-1} correspond to the C=O and C-O stretching vibrations in the oxalate groups, respectively. The strong bands in the region 1000-1150 cm^{-1} are assigned to the asymmetric stretch of PO_4 tetrahedra. Also present are the weak bands for CH_2 bending vibration at 1465 cm^{-1}, and a C−N stretching band at 1380 cm^{-1}.

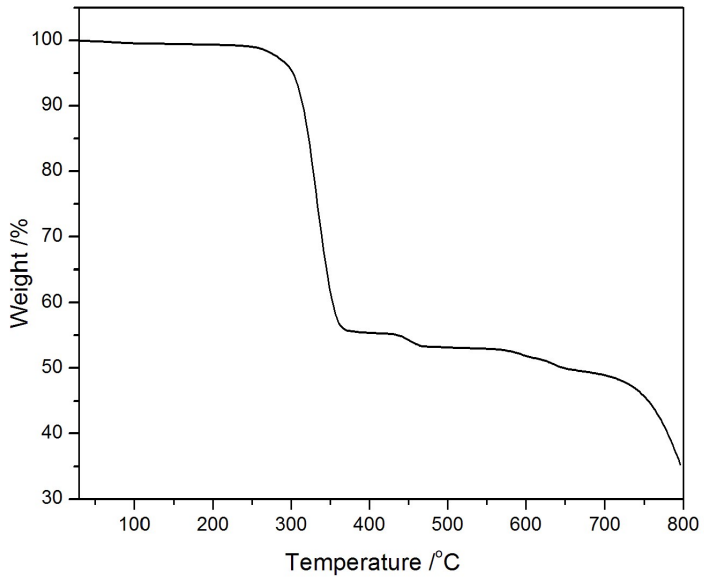

Fig. S6. TGA curve of SCU-62.

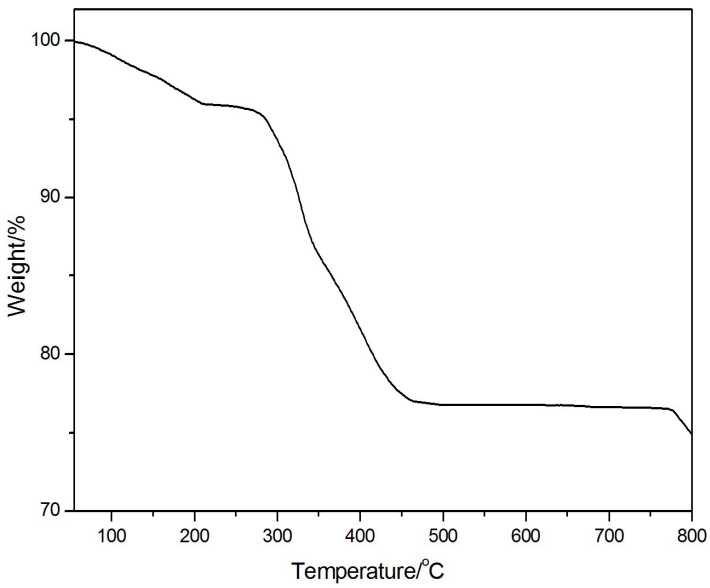

Fig. S7. TGA curve of SCU-65.

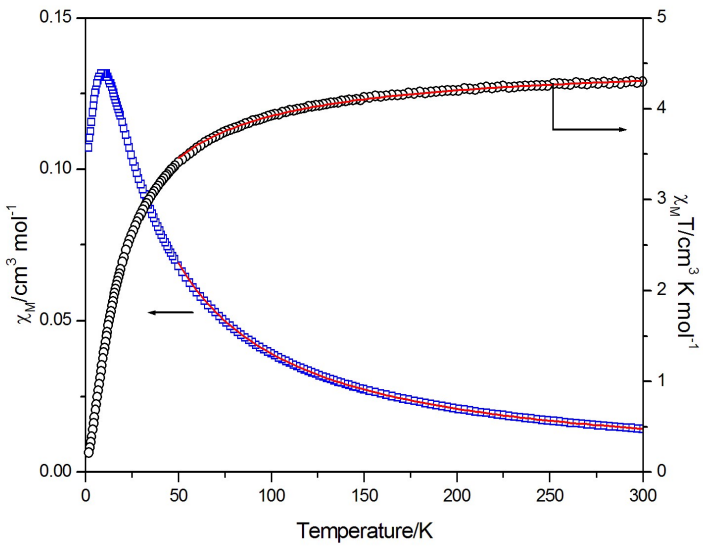

Fig. S8. Temperature dependence of χ_M and χ_MT for SCU-62. The solid lines are fit to the Curie-Weiss law in the high-temperature region.

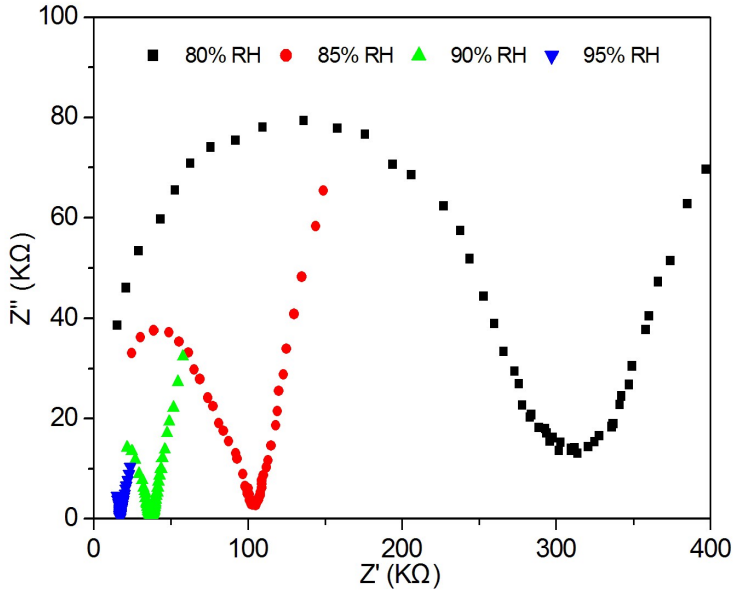

Fig. S9. Nyquist plots for SCU-65 at 85 °C under different RH conditions. The conductivity is 3.0×10^{-6} S·cm^{-1} (80% RH), 9.0×10^{-6} S·cm^{-1} (85% RH), 2.5×10^{-5} S·cm^{-1} (90% RH), and 5.5×10^{-5} S·cm^{-1} (95% RH).

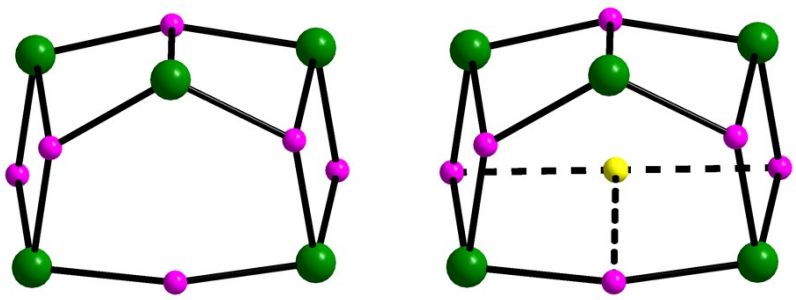

Fig. S10. (left) Topological representation of the lacunary D6R cluster. (right) The lacunary D6R cluster can be converted into a regular D6R unit by inserting a node at the crystallographic site position (1.0387, 1.6997, 2.3053).