

**A dual-function europium sulfite-oxalate complex for proton
conduction and selection of Fe³⁺ ions**

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Materials and instrumentation

The IR spectrum was equipped with KBr pellets and taken on a Perkin Elmer Spectrum GX spectrometer in the range of 4000 - 400 cm^{-1} . Powder X-ray diffraction (PXRD) was obtained from Bruker D8 VENTURE diffractometer with Cu radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV, 40 mA) radiation over a 2θ range of 3° - 50° . Thermogravimetric analysis (TGA) was performed using a TA Q600 TGA thermogravimetric analyzer at a scanning rate of $10^\circ \text{C}/\text{min}$ in air atmosphere. CHN analysis was carried out using atomic absorption spectroscopy (Euro Vector EA 3000 CHNS analyzer). The electrochemical impedance spectra (EIS) were measured in a CHI660E electrochemical workstation by applying an alternating current amplitude voltage of 200 mV over the frequency range from 1 to 10^6 Hz. Luminescent spectra were measured on an F-4500FL spectrophotometer.

Fluorescence sensing experiments

Initially, 5 mg of **1** was taken and incorporated into 3 mL of H_2O , and the suspension was made by sonication for 20 minutes at room temperature to wait for subsequent fluorescence tests.

Furthermore, the stability of luminescence in water and various pH solutions was investigated. Aqueous solutions spanning a pH range of 2 - 13 were prepared, and 5 mg of sample **1** was added to each solution, followed by ultrasonication to form stable suspensions. Due to the solubility of inorganic cations in water, water is chosen as the solvent. To detect the luminescence selectivity and anti-interference ability of different inorganic cations, 5 mg samples were dispersed in aqueous solutions (3mL, 1×10^{-2} mol/L) of Co^{2+} , Cr^{3+} , Fe^{3+} , K^+ , Li^+ , Mn^{2+} , Na^+ , Zn^{2+} , respectively, and sonicated for 20 min to obtain a well-proportioned suspension, followed by fluorescence testing.

To exploit the quenching effect of Fe^{3+} on **1**, the sensitivity of Fe^{3+} selection was studied in detail. Different concentrations of solutions containing Fe^{3+} were made up, and 5 mg of compound **1** was added to the solutions, which were then sonicated to make suspensions.

Measurements of proton conductivity

To investigate the proton conductivity behavior at different temperatures and 98% RH, a series of tests was conducted utilizing a CHI 660E electrochemical workstation. Firstly, 70

mg of the powder sample was weighed with precision, ground, and compressed into a tablet measuring 7 mm in diameter and approximately 0.75 mm in thickness using a tablet press. The samples were treated with a uniform coating of conductive silver adhesive and then fixed with copper wires serving as electrodes. The prepared round pieces were then stabilized in a vial containing 98% humidity for 48 hours, following which they were subjected to subsequent testing.

General Characterization

PXRD

The experimental PXRD patterns of sample **1** was compared with the powder diffractogram obtained from single crystal diffraction data. The result demonstrates the structural integrity and high purity of **1**, which is suitable for the subsequent analysis of thermal stability, fluorescence, and proton conductivity (Fig. S2).

IR

In europium sulfite-oxalate complex, In the europium sulfite-oxalate complex, the absorption band at 3397 cm^{-1} corresponds to the stretching vibrations of the bond O-H, which presumably originate from the coordinated water molecules. The absorption bands at 1646 and 1616 cm^{-1} correspond to the asymmetric C=O stretching vibrations from the oxalate group. The bands at ca. $930\text{-}990\text{ cm}^{-1}$ are associated with the stretching vibrations of S=O bonds. The weak bands at ca. $526\text{-}790\text{ cm}^{-1}$ are associated with the stretching vibrations of Eu-O bonds (Fig. S3).

TGA

Good thermal stability was important for the proton-conducting materials. It is imperative to consider the significance of thermal stability in the context of proton-conducting materials. The TGA curve of **1** (Fig. S4) was obtained through testing at room temperature. The thermogravimetric plot of **1** shows two successive weight loss steps: the first step occurs at $270\text{ - }387\text{ }^{\circ}\text{C}$ with a weight loss of 9.85% (calculated value 9.50%) due to the loss of water molecules. The second step occurs at $390\text{ - }485\text{ }^{\circ}\text{C}$ with a weight loss of 14.22%, which coincides with the dissolution of oxalate group that decomposes when heated. (calculated value 14.80%). The thermogravimetric curve of compound **1** plateaued above $485\text{ }^{\circ}\text{C}$, showing 75.93% residue at $800\text{ }^{\circ}\text{C}$. Compound **1** was analysed for thermogravimetric residue by single-crystal X-ray diffractometry, and it was observed

that the main components of compound 1 residues were $\text{Eu}_2\text{O}_2\text{SO}_4$ (Fig. S5).

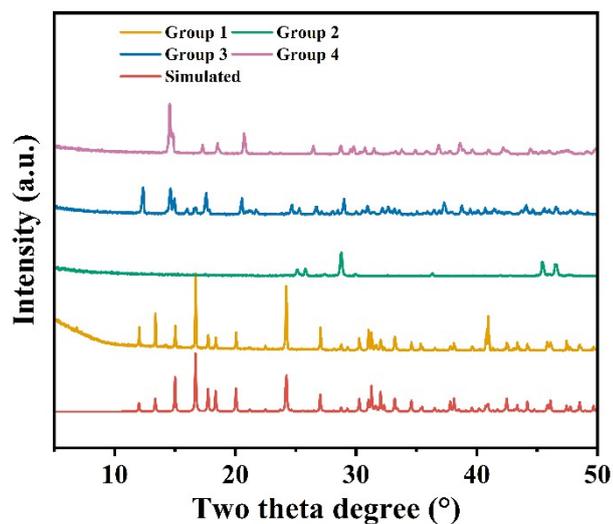


Fig. S1 PXR D patterns of simulated, group 1 - 4.

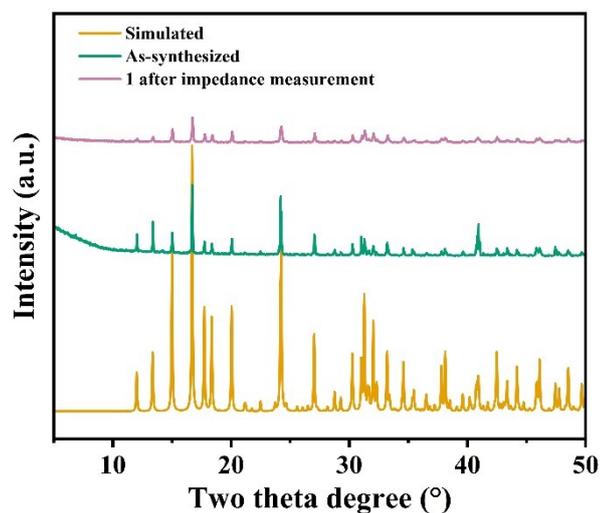


Fig. S2 PXR D patterns of simulated, as-synthesized, and after impedance test under 98% RH for compound 1.

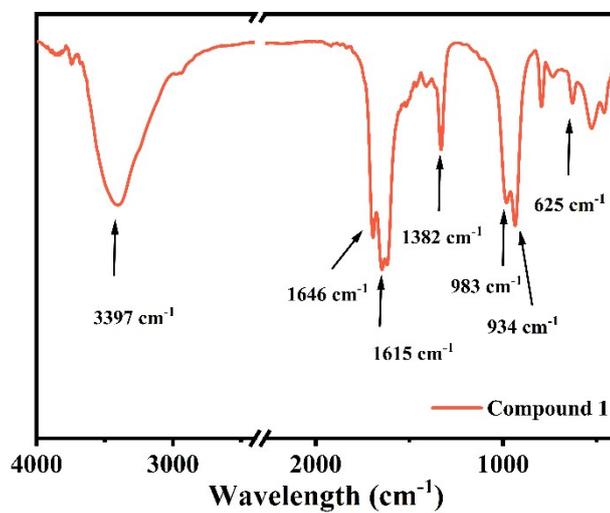


Fig. S3 FT-IR spectrum of compound 1

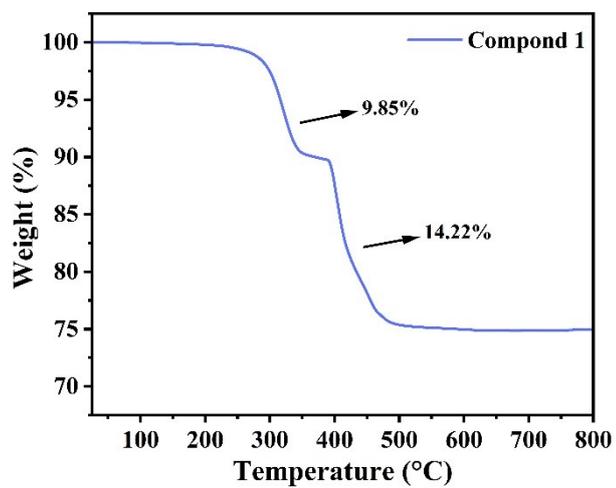


Fig. S4 (a) TGA curve of compound 1.

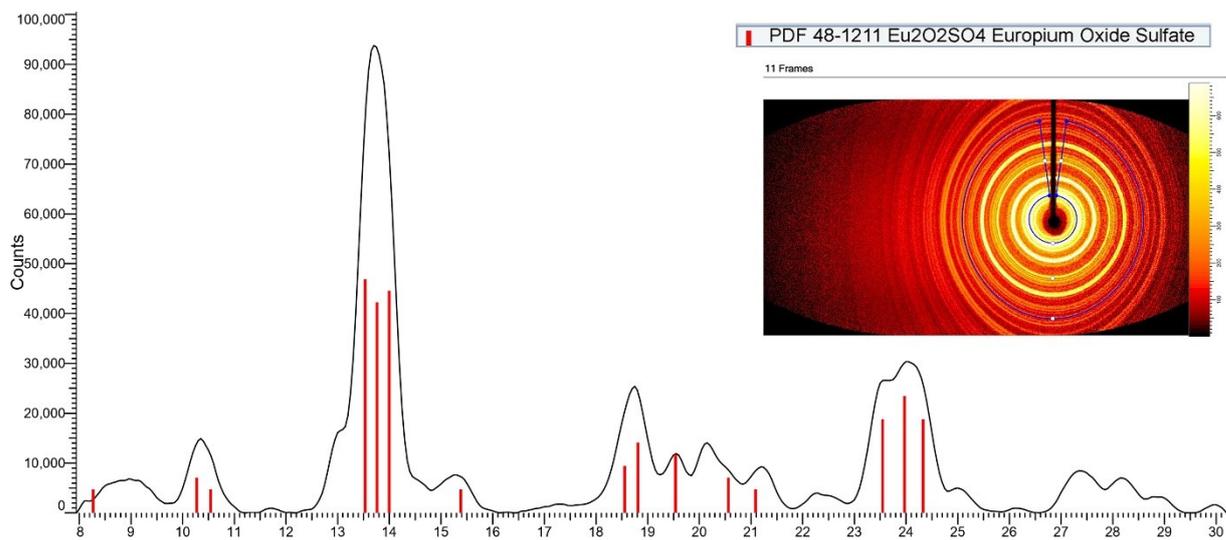


Fig. S5 PXRD patterns of the thermogravimetric residue and Eu₂O₂SO₄ (PDF 48-1211).

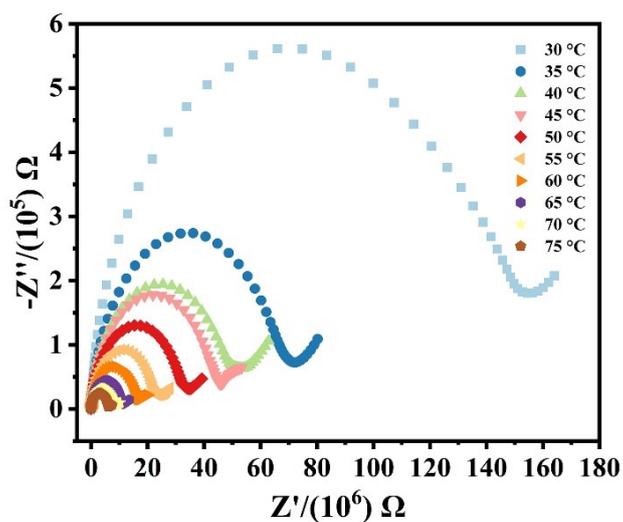


Fig. S6 Nyquist plots of **1** at 44% RH under different temperatures.

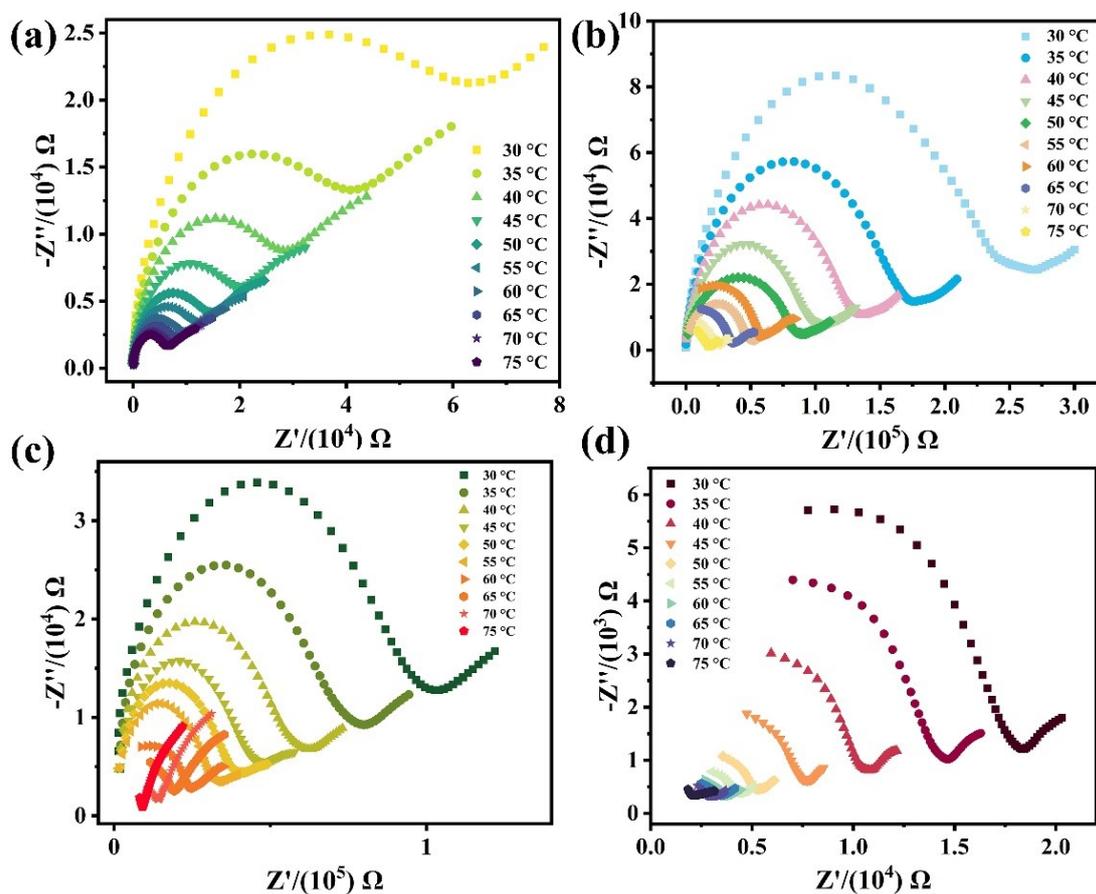


Fig. S7 (a) Nyquist plots of **1** at 58% RH under different temperatures. (b) Nyquist plots of **1** at 67% RH under different temperatures. (c) Nyquist plots of **1** at 76% RH under different temperatures. (d) Nyquist plots of **1** at 86% RH under different temperatures.

Table S1 Crystal data and structure refinement for compound **1**

CCDC number	2433824
Empirical formula	C ₂ H ₄ EuNaO ₉ S
Formula weight	379.06
Temperature/K	296(2)
Crystal system	Monoclinic
Space group	P2 ₁ /c
<i>a</i> /Å	6.5974(9)
<i>b</i> /Å	13.245(2)
<i>c</i> /Å	8.8593(13)
α /°	90°
β /°	92.415(4)°
γ /°	91.839(4)
<i>V</i> /Å ³	90°
<i>Z</i>	4
Calculated density/g·cm ⁻³	3.255
Absorption coefficient/mm ⁻¹	8.463
F(000)	712
Theta range for data collection/°	3.076 to 25.366°
Index ranges	-7<= <i>h</i> <=7, -15<= <i>k</i> <=15, -10<= <i>l</i> <=10
Reflections collected	9382
Independent reflections	1406 [R(int) = 0.0347]
Completeness to theta = 25.052°	99.2 %
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/ restraints/ parameters	1406 / 0 / 127
Goodness-of-fit on <i>F</i> ²	1.069
Final <i>R</i> indices [I>2sigma(I)]	<i>R</i> ₁ = 0.0172, <i>wR</i> ₂ = 0.0393
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0178, <i>wR</i> ₂ = 0.0398
Largest diff. peak and hole/(e/Å ⁻³)	0.593 and -0.692

Table S2 Selected bond lengths [Å] and angles [deg.] for compound **1**.

Eu(1)-O(1)	2.394(5)	S(1)-O(6)	1.534(4)
Eu(1)-O(6)#1	2.462(4)	S(1)-O(1)	3.2944(16)
Eu(1)-O(7)#2	2.508(4)	S(1)-O(7)	1.519(2)
Eu(1)-O(3)	2.574(5)	C(2)-O(9)	1.252(4)
Eu(1)-O(5)	2.578(6)	C(2)-O(5)	1.254(4)
Eu(1)-O(8)#3	2.597(4)	C(1)-O(4)	1.242(4)
Eu(1)-O(9)#3	2.620(4)	C(1)-O(8)	1.253(4)
Eu(1)-O(4)	2.674(4)	C(1)-C(2)	1.536(5)
Eu(1)-O(2)	2.747(4)		
O(1)-Eu(1)-O(6)#1	143.86(10)	O(5)-Eu(1)-O(8)#3	98.25(8)
O(1)-Eu(1)-O(7)#2	86.21(8)	O(1)-Eu(1)-O(9)#3	137.95(8)
O(6)#1-Eu(1)-O(7)#2	86.02(9)	O(6)#1-Eu(1)-O(9)#3	67.05(8)
O(1)-Eu(1)-O(3)	82.43(9)	O(7)#2-Eu(1)-O(9)#3	132.61(8)
O(6)#1-Eu(1)-O(3)	80.91(9)	O(3)-Eu(1)-O(9)#3	75.84(8)
O(7)#2-Eu(1)-O(3)	139.53(8)	O(5)-Eu(1)-O(9)#3	68.14(7)
O(1)-Eu(1)-O(5)	131.01(8)	O(8)#3-Eu(1)-O(9)#3	64.08(7)
O(6)#1-Eu(1)-O(5)	77.50(9)	O(1)-Eu(1)-O(4)	68.64(8)
O(7)#2-Eu(1)-O(5)	68.38(7)	O(6)#1-Eu(1)-O(4)	140.96(9)
O(3)-Eu(1)-O(5)	142.96(8)	O(7)#2-Eu(1)-O(4)	73.29(8)
O(1)-Eu(1)-O(8)#3	75.28(8)	O(3)-Eu(1)-O(4)	135.39(8)
O(6)#1-Eu(1)-O(8)#3	128.51(8)	O(5)-Eu(1)-O(4)	64.27(7)
O(5)-Eu(1)-O(2)	129.76(8)	O(6)-S(1)-O(1)	102.35(16)
O(8)#3-Eu(1)-O(2)	131.96(8)	O(6)-S(1)-O(7)	104.89(14)
O(9)#3-Eu(1)-O(2)	129.46(8)	O(1)-S(1)-O(7)	105.08(14)
O(4)-Eu(1)-O(2)	127.12(8)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+2, -z+1; #2 -x+1, -y+1, -z+1; #3 x+1, y, z

Table S3 Synthesis conditions of groups 1-4.

Experimental material							
Groups	Eu(NO ₃) ₃ ·6H ₂ O	NaHSO ₃	C ₂ H ₁₀ N ₆ ·H ₂ CO ₃	H ₂ C ₂ O ₄ ·2(H ₂ O)	H ₂ O	NH ₃ ·H ₂ O	NaOH
1	0.1 g	0.2 g	0.2 g	0.1 g	2 mL	×	×
2	0.1 g	0.2 g	×	0.1 g	2 mL	×	×
3	0.1 g	0.2 g	×	0.1 g	2 mL	√	×
4	0.1 g	0.2 g	×	0.1 g	2 mL	×	√

Group 1 measured a pH of 6. In order to make the pH of Groups 3 and 4 the same as that of Group 1, they were adjusted by adding ammonia with a pH of 12 and aqueous sodium hydroxide with a pH of 14, respectively. Before adjustment, the pH of Groups 3 and 4 was 2.

Table S4 Proton conductivity for compound **1**.

Temperature	Proton conductivity (σ)/ S·cm ⁻¹					
	44% RH	58% RH	67% RH	76% RH	86% RH	98% RH
30	1.08×10^{-9}	2.57×10^{-8}	5.66×10^{-8}	1.62×10^{-6}	9.082×10^{-6}	3.68×10^{-5}
35	2.33×10^{-9}	3.93×10^{-8}	8.45×10^{-7}	2.08×10^{-6}	1.13×10^{-5}	4.07×10^{-5}
40	3.41×10^{-9}	15.73×10^{-8}	1.10×10^{-6}	2.66×10^{-6}	1.53×10^{-5}	4.38×10^{-5}
45	3.67×10^{-9}	7.99×10^{-8}	1.42×10^{-6}	3.49×10^{-6}	2.18×10^{-5}	5.70×10^{-5}
50	4.84×10^{-9}	1.08×10^{-7}	1.67×10^{-6}	4.10×10^{-6}	3.11×10^{-5}	6.11×10^{-5}
55	7.00×10^{-9}	1.30×10^{-7}	2.53×10^{-6}	4.98×10^{-6}	3.86×10^{-5}	7.13×10^{-5}
60	1.00×10^{-8}	1.63×10^{-7}	2.94×10^{-6}	6.74×10^{-6}	4.41×10^{-5}	7.75×10^{-5}
65	1.49×10^{-8}	1.92×10^{-7}	4.09×10^{-6}	8.62×10^{-6}	4.82×10^{-5}	8.53×10^{-5}
70	1.95×10^{-8}	2.26×10^{-7}	6.00×10^{-6}	1.16×10^{-6}	5.50×10^{-5}	8.95×10^{-5}
75	2.74×10^{-8}	2.47×10^{-7}	8.16×10^{-6}	1.81×10^{-6}	7.26×10^{-5}	9.48×10^{-5}