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Rare-earth Squarate Frameworks with *scu* topology

Zhe Wang,[a] Zhanning Liu,*[a,b,c] Changsong Xie, Rongming Wang and Daofeng Sun*[a]

a. School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao, Shandong, 266580, China.
b. School of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao, 266590, China.
c. State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China.

Content

Materials and Characterization

Synthesis

The **RE-sq** (RE = Y, Nd, Eu, Tb *etc*), was synthesized by solvothermal reaction. Take **Y-sq** for example, 40 mg $Y(NO_3)_3$, 20 mg squaric acid (H_2sq) and 417 mg 2-fluorobenzoic acid (2-FBA) was dissolved in 3 mL DMF and 1.5 mL deionized water. The mixture was stirred at room temperature for 20 min to fully dissolve the solid reactant. After that, the solution was transferred into a 25 mL Teflon-lined autoclave and heated at 120ºC for 48h. After cooling to room temperature, colorless plate shaped crystals were obtained. The crystals were washed several times with DMF and deionized water and finally dried at 80ºC overnight.

Elemental analysis (%) calcd for **Tb-sq**: C 27.9, H 1.9, N 3.2, O 29.8; found: 26.3, H 1.9, N 2.7 and O 28.6. For **Nd-sq**, calcd: C 28.9, H 1.9, N 3.3, O 30.9; found: C 27.6, H 1.9, N 3.0, O 27.9. For **Y-sq**, calcd: C 33.4, H 2.2, N 3.9, O 35.6; found: C 32.9, H 2.2, N 3.6, O 34.8; For **Eu-sq**, calcd: C 28.4, H 1.9, N 3.2, O 30.3; found: C 27.9, H 1.8, N 2.9, O 29.2.

Characterization

Single crystal X-ray diffraction data was collected with a Supernova diffractometer equipped with Cu-K_α (λ = 1.54184 Å) and a CCD detector. The structure was solved by direct method using the software Olex2. The powder X-ray diffraction data was collected on a PANalytical diffractometer with Cu-K_α radiation. Thermogravity analysis and different scanning calorimetry (TG-DSC) were performed under air using the Mettler-Toledo instrument from 30 to 900˚C with a heating rate 10˚C/min. The scanning electron microscopy (SEM) was tested by JEOL-7900. Fourier transformed infrared spectroscopy (FTIR) was performed on a Thermo Nicolet 6700 spectrometer in the range 550~4000 cm^{-1}.

Proton conductivity

The **Tb-sq** powder was fully grinded with phosphoric acid. After that the powder sample was washed with deionized water and dried. Then the sample was pressed into a cylindrical pellet with a diameter of 3 mm (thickness of ~1.74 mm). Two sides of the pellet were connected to gold wires using silver glue. Impedance spectroscopy data were collected using a 1260 A Impedance/Gain-Phase analyzer from 10^7 to 0.1 Hz. To estimate the activation energy (E_a) of the solid electrolyte and to understand the ion conductivity mechanism, the conductivity was measured at various temperature from 80 to 140˚C. The conductivity was calculated using the equation $\sigma=l/SR$, where σ is the conductivity (S cm^{-1}), l is the thickness of the pellet (cm), S is the electrode area (cm^2) and R is the bulk resistance (Ω). The E_a was estimated by the equation $\sigma_T = \sigma_0 \exp(-E_a/k_BT)$, where σ_0 is the pre-exponential factor, k_B is the Boltzmann constant and T is the temperature.

Luminescence sensing

A 30 mg portion of **Tb-sq** powder was fully grounded and dispersed in 20 mL deionized water. The obtained dispersion was ultrasound treated for 1h. 2 mL of the dispersion was transferred to the quartz cuvette. The fluorescence emission spectra were recorded upon an excitation of 325 nm. A freshly prepared aqueous solution (1M) containing MnO_4^- or $Cr_2O_7^{2-}$ was incrementally added to the dispersion containing **Tb-sq** and the mixture was

fully stirred. The emission spectra was *in situ* recorded.

Table S1 Crystallographic data of compound **Nd_sq**

Identification code	Nd_sq
Empirical formula	C_8NdO_8
Formula weight	368.32
Temperature/K	300
Crystal system	tetragonal
Space group	*P*4/*nbm*
a/Å	10.0014(2)
b/Å	10.0014(2)
c/Å	5.4087(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	541.02(3)
Z	2
ρ_{calc}g/cm^3	2.261
μ/mm^{-1}	36.949
F(000)	344.0
Crystal size/mm^3	0.1 × 0.1 × 0.03
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	12.516 to 133.122
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 10, -5 ≤ l ≤ 6
Reflections collected	2337
Independent reflections	269 [R_{int} = 0.0344, R_{sigma} = 0.0170]
Data/restraints/parameters	269/6/21
Goodness-of-fit on F^2	1.264
Final R indexes [I>=2σ (I)]	R_1 = 0.0364, wR_2 = 0.0968
Final R indexes [all data]	R_1 = 0.0371, wR_2 = 0.0975
CCDC number	2215184

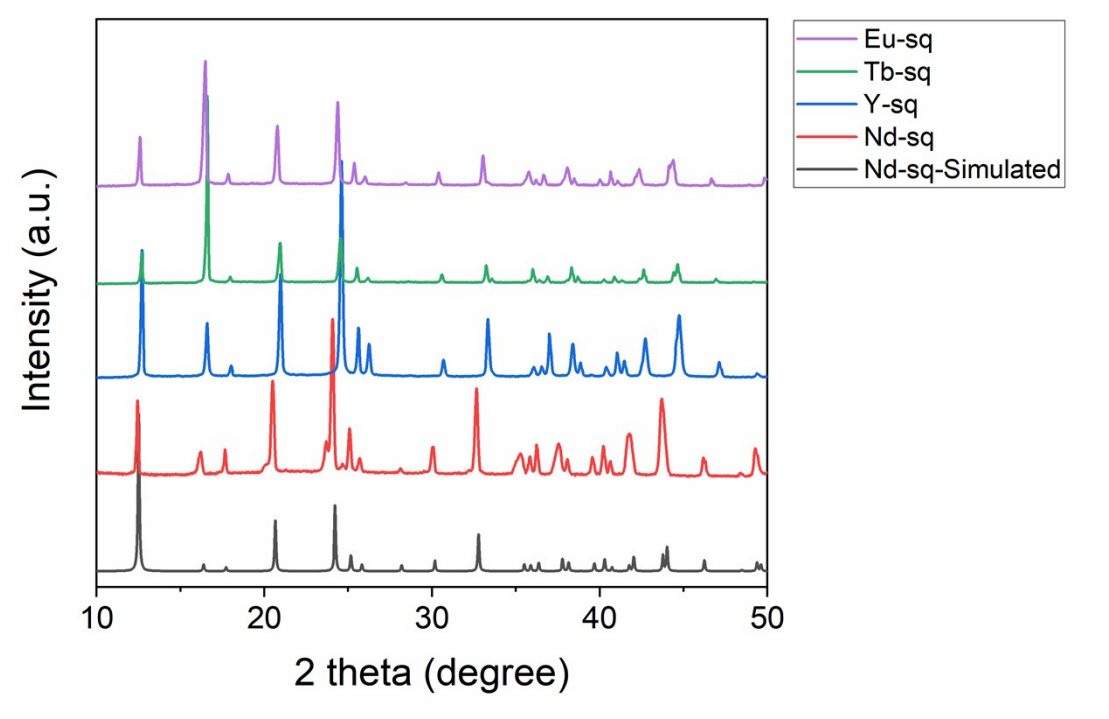

Figure S1 XRD patterns of the synthesized RE-sq. Color code: **Eu-sq** (purple), **Tb-sq** (green), **Y-sq** (blue), **Nd-sq** (red) and the simulated pattern based on the **Nd-sq** (black, obtained from single crystal X-ray diffraction).

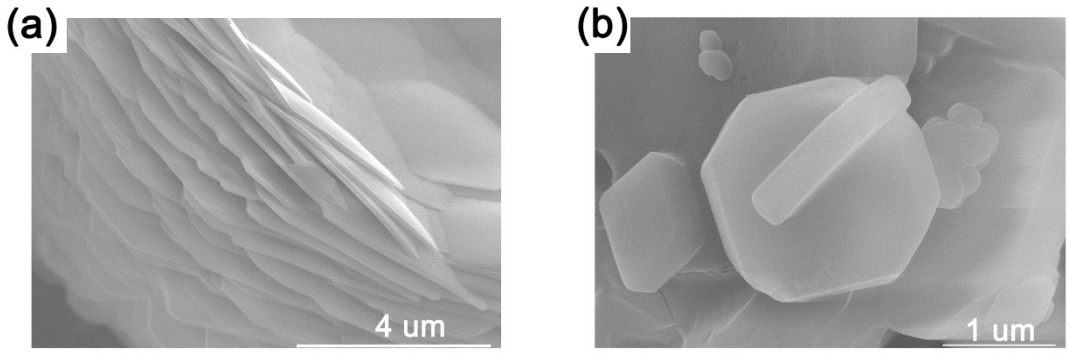

Figure S2 SEM images (a) of **Tb-sq** and the zoomed one (b).

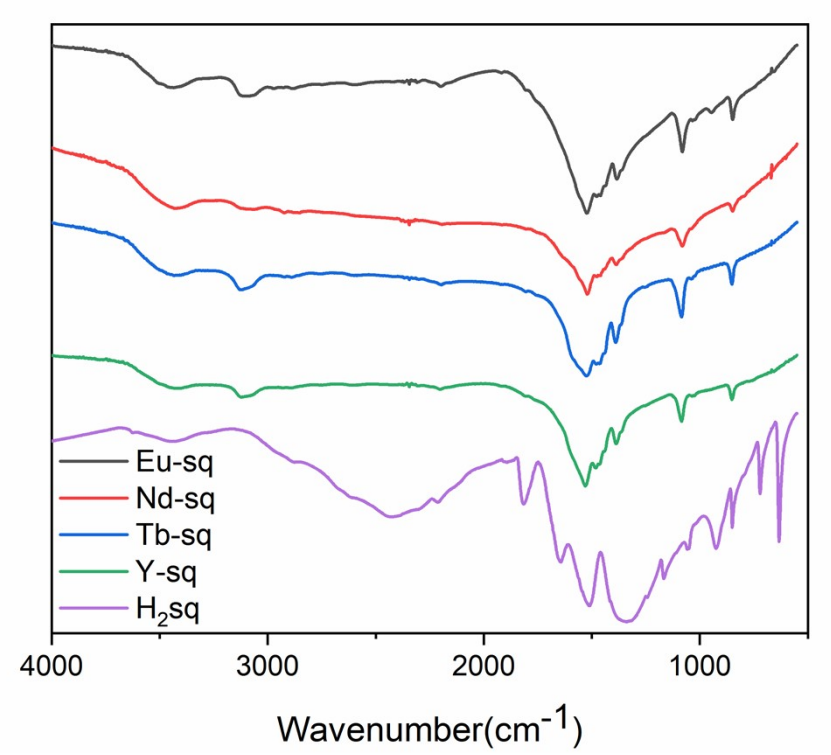

Figure S3 FTIR spectra of the RE-sq (where RE = Eu, Nd, Tb, Y *etc*) in KBr.

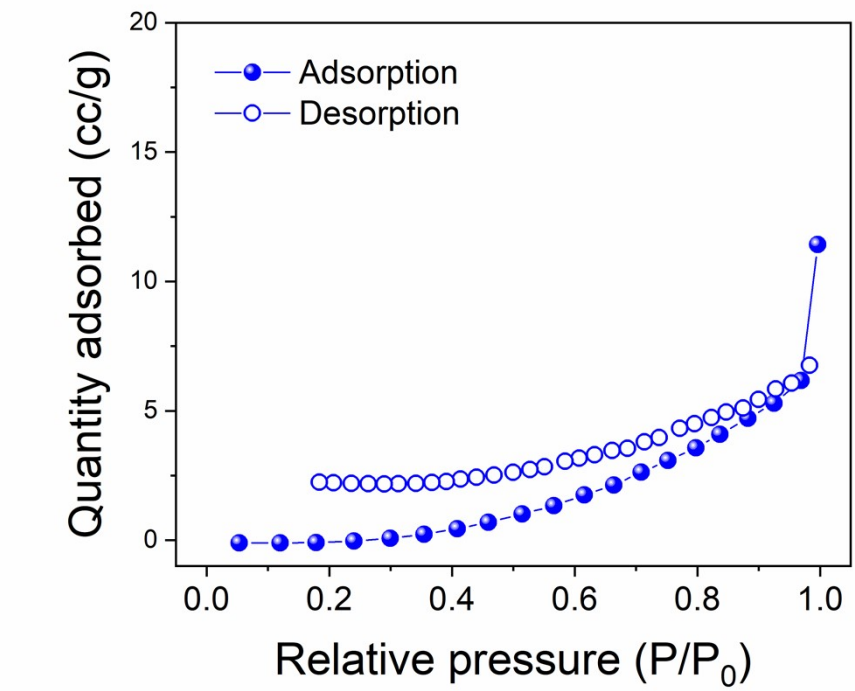

Figure S4 N_2 isotherm of **Tb-sq** at 77K. Filled circles, adsorption; Open circles, desorption.

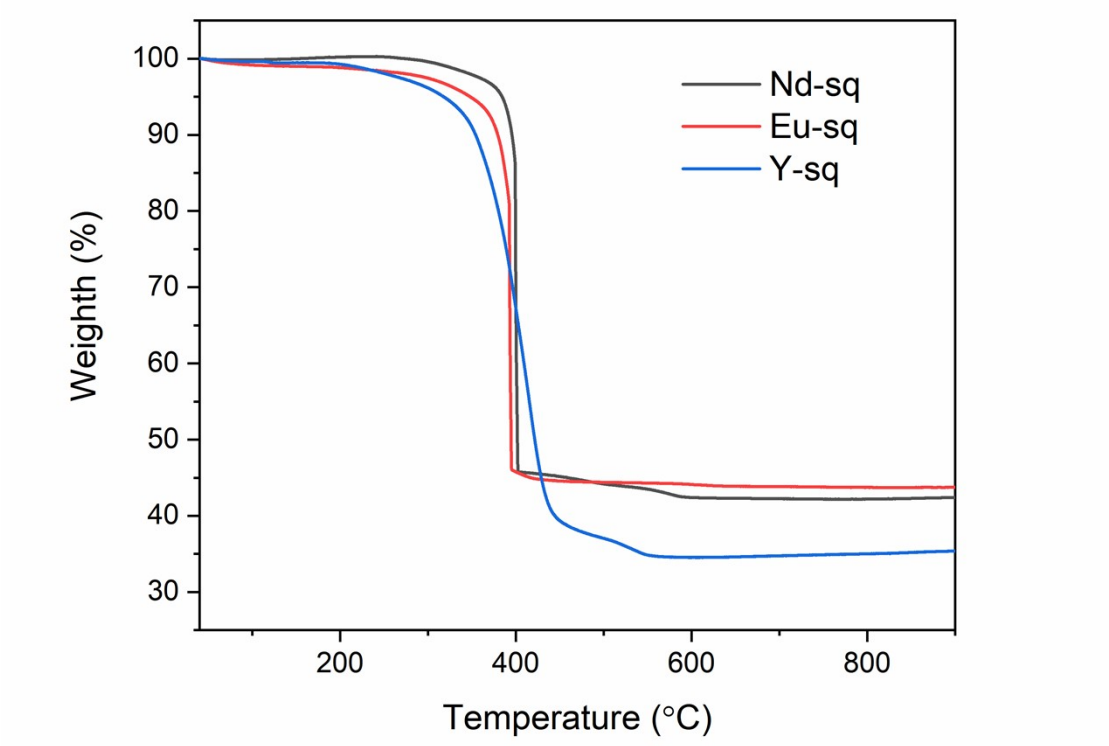

Figure S5 TG curves of **Nd-sq** (black), **Eu-sq** (red) and **Y-sq** (blue) under air with the heating rate 10˚C/min.

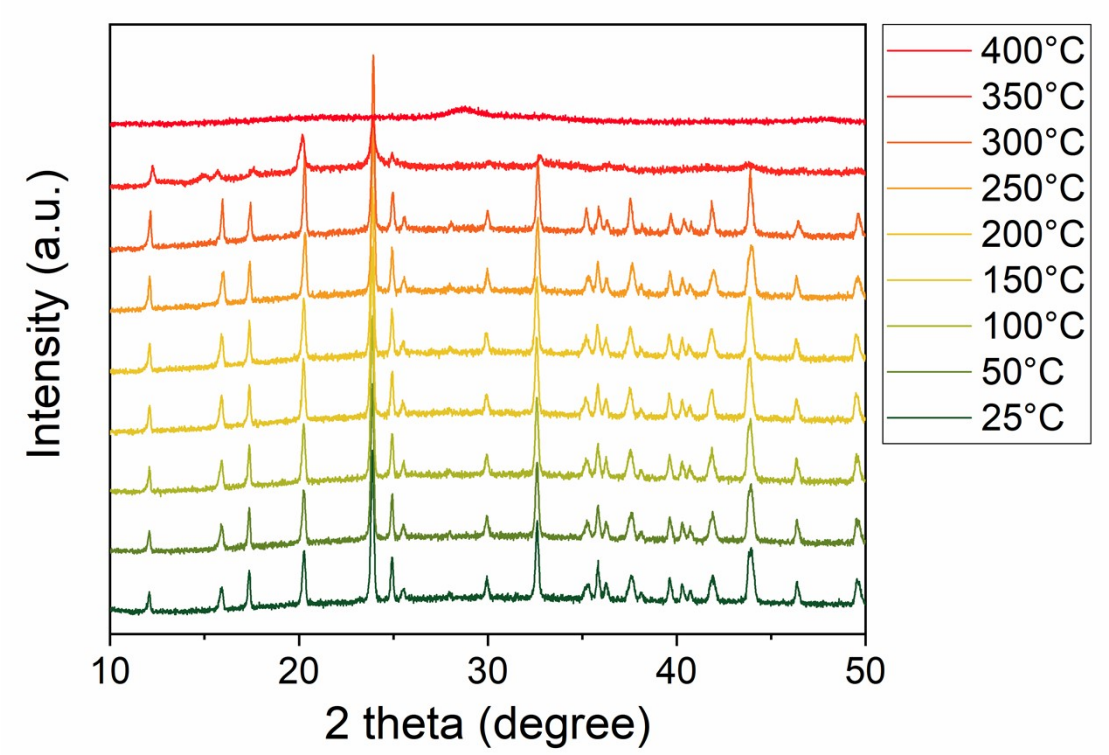

Figure S6 *In situ* variable temperature powder X-ray diffraction patterns of **Tb-sq** in air.

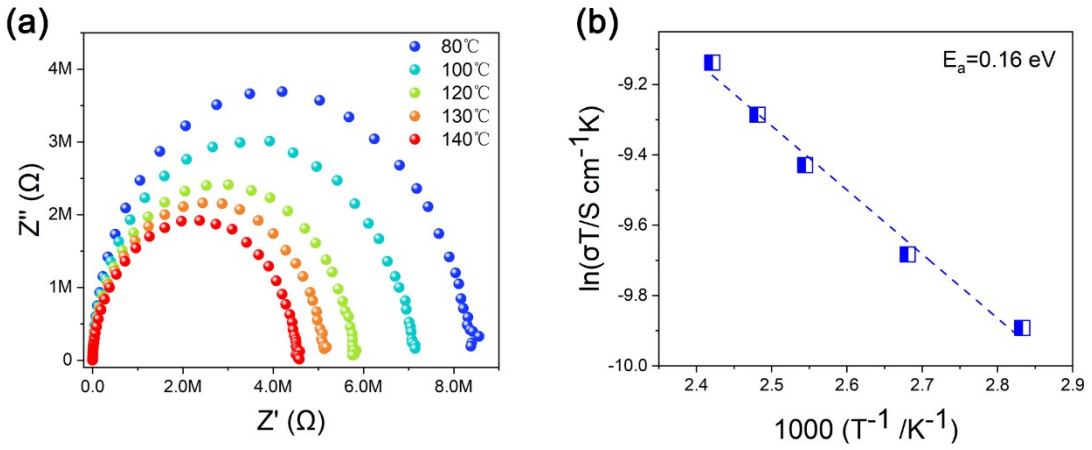

Figure S7 (a) Nyquist plots of the pristine **Tb-sq** at various temperatures (anhydrous), (b) Arrhenius plots of the **Tb-sq**.

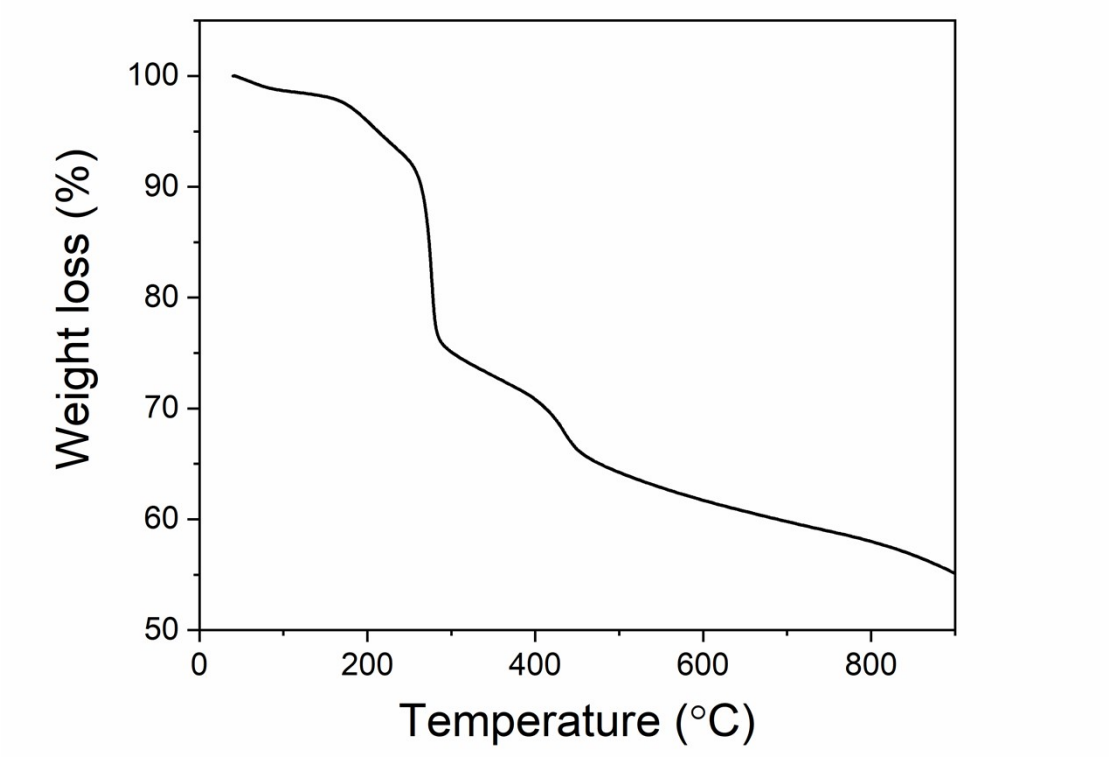

Figure S8 TG curve of phosphoric acid loaded **Tb-sq**.

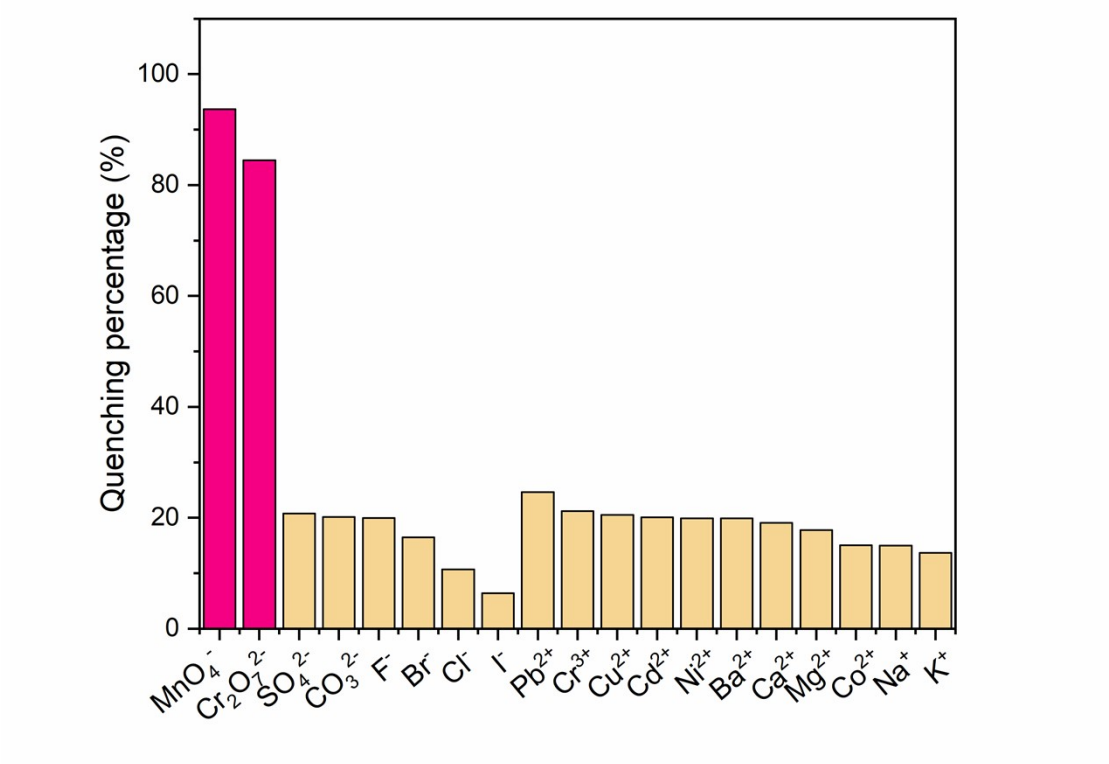

Figure S9 Luminescence selectivity of **Tb-sq** toward sensing of various ions at equal concentration.

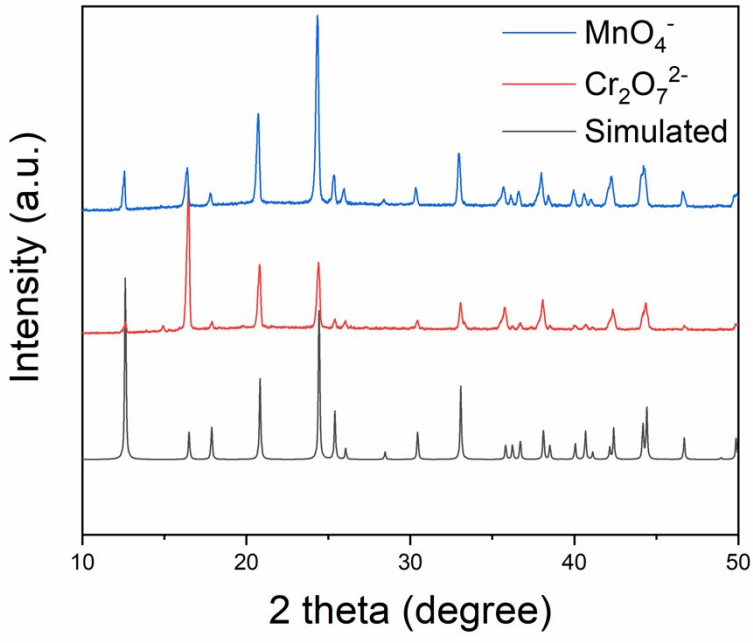

Figure S10 XRD patterns of **Tb-sq** after immersing in the aqueous solution of MnO_4^- (blue) and $Cr_2O_7^{2-}$ (red).

Table S2 K_{sv} values of other reported luminescence probes for $Cr_2O_7^{2-}$ and MnO_4^-.

Luminescence probe	K_{sv} (M^{-1}) for $Cr_2O_7^{2-}$	K_{sv} (M^{-1}) for MnO_4^-	Ref
$\{[Eu_2Na(Hpddb)(pddb)_2(CH_3COO)_2]\cdot 2.5(DMA)\}_n$	6.45×10^3	2.84×10^3	1
$\{[Eu_2(L)_2(H_2O)_2]\cdot 5H_2O\cdot 6DMAC\}_n$	1.05×10^3		2
$\{[Tb_2(L)_2(H_2O)_2]_{\cdot 5}H2O\cdot 6DMAC\}_n$		1.2×10^3	2
$\{[Zn(L_2)(NDC)]\cdot 2H_2O\}_n$		5.48×10^3	3
$[Eu_2(H_2O)(DCPA)_3]_n$	8.7×10^3		4
Tb-sq	7.28×10^3	8.27×10^3	This work

Reference:

1. S. Xu, J. Shi, B. Ding, Z. Liu, X. Wang, X. Zhao, and E. Yang, *Dalton Trans.*, 2019, **48**, 1823-1834.
2. J. Ma, and W. Liu, *Dalton Trans.*, 2019, **48**, 12287-12295.
3. Y. Su, R. Wang, O. A. Blatova, Y. Shi, and G. Cui, *CrystEngComm*, 2022, **24**, 182-191.
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