Electronic Supporting Information for

Dual-cubic-cage based lanthanide sulfate-carboxylpyrazolate frameworks with highly hydrolytic stability and remarkable proton conduction

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**Section S1: General Methods**

**Chemicals:** All chemical reagents were obtained from commercial supplies without further purification.

**Instrumentation:** Elemental analysis (EA) was carried out on a Vario EL-Cube. Powder X-ray diffraction (PXRD) patterns of the samples were recorded by a Rigaku Dmax 2500 X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å). Metal contents were measured by an Ultima2 (Horbiba Jobin Yvon) inductively coupled plasma optical emission spectrometer (ICP-OES). Thermal analysis was carried out on a Netzsch STA449C thermal analyzer at a temperature range of 25 to 800 °C under air atmosphere with a heating rate of 10 °C min⁻¹. Gas sorption measurements were performed on a Micromeritics ASAP 2020 surface area and pore size analyzer. Fourier-transform infrared (FT-IR) spectra were recorded using a Nicolet iS10 spectrophotometer in 3750–450 cm⁻¹ region.
Section S2: Synthetic Procedures of Ln-SCP

(1) Synthesis of Eu-SCP

Eu$_2$O$_3$ (0.25 mmol, 0.088 g), H$_3$PDC (0.5 mmol, 0.086 g), ZnSO$_4$·7H$_2$O (0.25 mmol, 0.072 g and water (15 mL) were mixed in a 23 mL teflon-lined stainless steel container and stirred for 30 min, then heated to 150 °C for 60 h. After cooling to room temperature at 5 °C min$^{-1}$, single crystals were obtained after washing with water (ca. 35% yield based on H$_3$PDC). EA data: C 11.76%; H 2.43%; N 5.36%; S 4.50. ICP data: Eu 39.40%; Zn 0.94%.

(2) Synthesis of Gd-SCP

Gd$_2$O$_3$ (0.25 mmol, 0.091 g), H$_3$PDC (0.5 mmol, 0.086 g), ZnSO$_4$·7H$_2$O (0.25 mmol, 0.072 g and water (15 mL) were mixed in a 23 mL teflon-lined stainless steel container and stirred for 30 min, then heated to 150 °C for 60 h. After cooling to room temperature at 5 °C min$^{-1}$, single crystals were obtained after washing with water (ca. 35% yield based on H$_3$PDC). EA data: C 12.71%; H 2.37%; N 5.89%; S 4.67. ICP data: Gd 37.46%; Zn 1.44%.

(3) Synthesis of Dy-SCP

Dy$_2$O$_3$ (0.25 mmol, 0.093 g), H$_3$PDC (0.5 mmol, 0.086 g), ZnSO$_4$·7H$_2$O (0.25 mmol, 0.072 g and water (15 mL) were mixed in a 23 mL teflon-lined stainless steel container and stirred for 30 min, then heated to 150 °C for 60 h. After cooling to room temperature at 5 °C min$^{-1}$, single crystals were obtained after washing with water (ca. 35% yield based on H$_3$PDC). EA data: C 10.26%; H 2.35%; N 4.98%; S 5.13. ICP data: Dy 40.56%; Zn 1.53%.

(4) Synthesis of Ho-SCP

Ho$_2$O$_3$ (0.25 mmol, 0.094 g), H$_3$PDC (0.5 mmol, 0.086 g), ZnSO$_4$·7H$_2$O (0.25mmol, 0.072g and water (15 mL) were mixed in a 23 mL teflon-lined stainless steel container and stirred for 30 min, then heated to 150 °C for 60 h. After cooling to room temperature at 5 °C min$^{-1}$, single crystals were obtained after washing with water (ca. 30% yield based on H$_3$PDC). EA data: C 9.13%; H 2.24%; N 4.23%; S 5.54. ICP data: Ho 38.21%; Zn 1.00%.
### Section S3: Crystallographic Data

**Table S1** Crystallographic data of Ln-SCP

<table>
<thead>
<tr>
<th>Compound Reference</th>
<th>Eu-SCP</th>
<th>Gd-SCP</th>
<th>Dy-SCP</th>
<th>Ho-SCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>(C(<em>{60})H(</em>{96})Eu(<em>{20})N(</em>{24})O(<em>{138})S(</em>{12}))\cdot[+\text{guests}]</td>
<td>(C(<em>{60})H(</em>{96})Gd(<em>{20})N(</em>{24})O(<em>{138})S(</em>{12}))\cdot[+\text{guests}]</td>
<td>(C(<em>{60})H(</em>{96})Dy(<em>{20})N(</em>{24})O(<em>{138})S(</em>{12}))\cdot[+\text{guests}]</td>
<td>(C(<em>{60})H(</em>{96})Ho(<em>{20})N(</em>{24})O(<em>{138})S(</em>{12}))\cdot[+\text{guests}]</td>
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<tr>
<td>Formula Mass</td>
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<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
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<td>a/Å</td>
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<td>17.7222(4)</td>
<td>17.5393(3)</td>
<td>17.5393(3)</td>
</tr>
<tr>
<td>b/Å</td>
<td>17.7222(4)</td>
<td>17.7222(4)</td>
<td>17.5393(3)</td>
<td>17.5393(3)</td>
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<tr>
<td>c/Å</td>
<td>17.7222(4)</td>
<td>17.7222(4)</td>
<td>17.5393(3)</td>
<td>17.5393(3)</td>
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<tr>
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<td>90</td>
<td>90</td>
<td>90</td>
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<td>γ/°</td>
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<td>90</td>
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<td>90</td>
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<tr>
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<td>293(2)</td>
<td>293(2)</td>
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<tr>
<td>No. of Independent Reflections</td>
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<td>2270</td>
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<td>Final R(_1) Values ((I &gt; 2\sigma(I)))</td>
<td>0.0349</td>
<td>0.0416</td>
<td>0.0217</td>
<td>0.0219</td>
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<tr>
<td>Final wR(F(^2)) Values ((I &gt; 2\sigma(I)))</td>
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<td>0.0934</td>
<td>0.0559</td>
<td>0.0639</td>
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<tr>
<td>Final R(_1) Values (all data)</td>
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<td>0.0416</td>
<td>0.0225</td>
<td>0.0220</td>
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<tr>
<td>Final wR(F(^2)) Values (all data)</td>
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<td>0.0934</td>
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<td>0.0643</td>
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<td>Goodness of Fit on (F^2)</td>
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<td>1880637</td>
<td>1880638</td>
<td>1880639</td>
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</table>
Section S4: Structural Pictures

**Fig. S1** PDC$_3^-$ ligand and its coordination mode in Eu-SCP.

**Fig. S2** Coordination environments of Eu$^{3+}$ ions in Eu-SCP (symmetry codes: (i) $y, z, x$; (ii) $-y, z, x$; (iii) $z, x, y$; (iv) $x, 1-y, z$; (v) $1-y, z, x$; (vi) $z, x, 1-y$; (vii) $z, -x, y$; (viii) $x, -y, z$).
**Fig. S3** Rectangular tile-based structure of Eu-SCP containing two kinds of cubic cages denoted by pink and blue cubes.

**Fig. S4** Electron density map in the cavity region of Eu-SCP produced by X-ray crystallography.
**Fig. S5** Proton-transfer pathways of Eu-SCP constructed by host sulfate, guest complex, coordinated and lattice water arrayed orderly.
Section S5: Photography

Fig. S6 Microscopic image of Eu-SCP sample.
Section S6: Fourier-Transform Infrared (FT-IR) Spectroscopy

Fig. S7 FT-IR spectra of Eu-SCP, Gd-SCP, Dy-SCP and Ho-SCP.
Section S7: Powder X-ray Diffraction (PXRD)

Fig. S8 PXRD patterns of Eu-SCP, Gd-SCP, Dy-SCP and Ho-SCP.
Section S8: Stability Analysis

(a) Thermal Gravimetric Analysis (TGA)

Fig. S9 TGA curves of Eu-SCP, Gd-SCP, Dy-SCP and Ho-SCP in the air.

(b) Thermal PXRD

Fig. S10 Thermal PXRD patterns of Eu-SCP, indicating that the sample could be stable up to 250 °C.
(c) Chemical Stability Analysis

**Fig. S11** PXRD patterns of Eu-SCP in different organic solvents for 20 h.

**Fig. S12** PXRD patterns of Eu-SCP in different pH water for 12 h.
**Section S9: Gas-Sorption Measurements**

The samples were activated by soaking in CH$_3$OH three days and CH$_3$OH was renewed two times every day before testing.

**Fig. S13** CO$_2$ adsorption-desorption isotherms of Eu-SCP at 298 K.
**Section S10:** Ultraviolet-Visible (UV-Vis) Spectroscopy

![UV-Vis diffuse-reflectance spectra](image)

**Fig. S14** UV-Vis diffuse-reflectance spectra of Eu-SCP, Gd-SCP, Dy-SCP, Ho-SCP and H$_3$PDC.
Section S11: Photoluminescence

Fig. S15 Excitation spectra of (a) H₃PDC, (b) Gd-SCP and (c) Dy-SCP monitored at 460nm, 525nm and 573nm, respectively, at 298 K.

Fig. S16 Emission spectra of (a) H₃PDC, (b) Gd-SCP and (c) Dy-SCP monitored at 263nm, 323nm and 365nm, respectively, at 298 K.
**Fig. S17** Excitation spectrum of Ho-SCP monitored at 560 nm (in red) and Emission spectrum of Ho-SCP monitored at 323 nm (in blue) at 298 K, consistent with the adsorption spectrum of Ho-SCP (in black).

**Fig. S18** Excitation spectrum of Eu-SCP at 298 K.
**Fig. S19** Fluorescence emission spectra ($\lambda_{ex} = 395$ nm) of Eu-SCP between 77 and 523 K.

**Fig. S20** Linear Fitting of fluorescence intensity to temperature of Eu-SCP. It can be seen that there is a gradual decrease in the fluorescent intensity with rising the temperature from 77 to 448 K, following a linear correlation, then a more rapid drop because of the fluorescence significantly quenched when the temperature $> 448$ K. This deviation from the linear fitting at temperature $> 448$ K is probably owing to the departure of the bonded water molecules.
**Figure. S21** Temperature-dependent fluorescence lifetime diagram of Eu-SCP (77 ~ 498 K). It can be seen that the fluorescence lifetime of Eu-SCP decreases with increasing temperature, also obeying the linear relationship in the temperature range < 448 K.

**Figure. S22** Fluorescence emission decays of fresh Eu-SCP and dehydrated Eu-SCP heated at 250 °C (λ_ex = 395 nm, λ_em = 395 nm, lifetime = 348 μs for fresh Eu-SCP, 462 μs for dehydrated Eu-SCP) at 298 K.
Figure. S23 Fluorescence emission spectra of A: Eu-SCP (with CIE of $x = 0.6481$, $y = 0.345$) and B: Eu-SCP-250 (activated at 250 °C, with CIE $x = 0.6632$, $y = 0.3348$) at 298 K. By comparison, the dehydrated Eu-SCP displayed slightly wider fluorescence emission peak and longer fluorescence lifetime than the freshly-synthesized sample.

Figure. S24 Energy level diagram of Eu$^{3+}$, Gd$^{3+}$, Dy$^{3+}$ and Ho$^{3+}$ ions and H$_3$PDC ligand,
referring to the related literature on LMCT energy transfer. The dashed arrows represent possible non-radiative energy transfer pathways.

All the compounds were monitored at the positions of the maximum excitation/emission peaks. There is an intense adsorption band centered at 250 nm in the UV-Vis adsorption spectrum of H₃PDC (Fig. S15), which could be attributed to π-π* electron transition. The emission spectrum (Fig. S16b) of Gd-SCP has a broad band originated from the PDC³⁻ ligand, because the excited energy level of Gd³⁺ ion is much higher than the energy level of ligand triplet state, namely where ligand to metal energy transfer (LMCT) process has been inhibited. Dy-SCP not only has the characteristic peaks related to Dy³⁺ ion but also has the typical band of PDC³⁻ ligand (Fig. S15c and Fig. S16c). As shown in the Fig. S17, the downward peaks of the emission spectrum of Ho-SCP could be due to the cancellation of PDC³⁻ characteristic band by the Ho³⁺ ion. Among Ln-SCP, only Eu-SCP displays the fluorescence that can be seen by naked eyes. As shown in Fig. S14, the characteristic band of PDC³⁻ ligand is shaded by the strong emission peaks in relation to 5D⁵⁻-5Fⁿ (n = 0,1,2,3,4) transitions of Eu³⁺ ion, which indicates the effective ligand to metal energy transfer of Eu-SCP.
Section S12: Magnetism

(a) Plots of $\chi_m T$ and $\chi_m^{-1}$ versus $T$

**Fig. S25** Temperature dependence of $\chi_m T$ and $\chi_m^{-1}$ for Gd-SCP.

**Fig. S26** Temperature dependence of $\chi_m T$ and $\chi_m^{-1}$ for Dy-SCP.
Fig. S27 Temperature dependence of $\chi_m T$ and $\chi_m^{-1}$ for Ho-SCP.

(b) Plots of $\chi'_m$ and $\chi''_m$ versus $T$

Fig. S28 Temperature dependence of ac susceptibilities, $\chi'_m$ and $\chi''_m$, at different frequencies for Eu-SCP.
**Fig. S29** Temperature dependence of ac susceptibilities, $\chi_m^\prime$ and $\chi_m^\prime\prime$, at different frequencies for Gd-SCP.

**Fig. S30** Temperature dependence of ac susceptibilities, $\chi_m^\prime$ and $\chi_m^\prime\prime$, at different frequencies for Dy-SCP.
Fig. S31 Temperature dependence of ac susceptibilities, $\chi_m'$ and $\chi_m''$, at different frequencies for Ho-SCP.

(c) Plots of $M$ versus $H$

Fig. S32 Plot of $M$ versus $H$ for Eu-SCP.
Fig. S33 Plot of $M$ versus $H$ for Gd-SCP.

Fig. S34 Plot of $M$ versus $H$ for Dy-SCP.

Fig. S35 Plot of $M$ versus $H$ for Ho-SCP.
Section S13: Proton conduction

Impedance analysis: The samples were put into a home-made mold with a radius of 0.2 cm to get circular pellets, whose thickness was measured by a Vernier caliper. Then the pellets were smeared on both sides by silver colloid, which were for fixing copper wires. The proton conductive capacities were estimated by using a Zahner (IM6) electrochemical impedance spectrometer, over a frequency range from 100 mHz to 10 MHz, under varying temperatures (25 to 65 °C) and different relative humidity (RH, 33% to 97%). The proton conductivity was calculated by using the following equation

\[ \sigma = \frac{l}{SR} \]

where \( \sigma \) is the conductivity (S cm\(^{-1}\)). \( l \) is the thickness (cm) of the pellet, \( S \) is the cross-sectional area (cm\(^2\)) of the pellet, \( R \) is the bulk resistance (\( \Omega \)). The activation energy \( (E_a) \) was calculated from the following equation

\[
\ln \sigma_T = \ln \sigma_0 - \frac{E_a}{kT}
\]

where \( \sigma \) is the conductivity (S cm\(^{-1}\)), \( K \) is the Boltzmann constant (eV/K) and \( T \) is the temperature (K).

Fig. S36 Water vapor adsorption-desorption isotherms of Eu-SCP.
Fig. **S37** Nyquist plots (at different RH) of Eu-SCP pre-heated to 190 °C.

Fig. **S38** Relative humidity dependences of proton conductivity of the freshly-synthesized Eu-SCP and its dehydrated form (pre-heated at 190 °C) at room temperature. Under < 75% RH, its $\sigma$ values are significantly lower than that of the sample untreated thermally; while at >75% RH, two sets of $\sigma$ data are close to each other. By comparing $\sigma$ values of as-synthesized and thermally-treated samples, it could be concluded that the coordinated and free water molecules significantly contribute to proton conduction.
**Fig. S39** Arrhenius plot of proton conductivity of Eu-SCP under 55% R.H. condition.

\[ E_a = 0.19 \text{eV} \]
**Table S2** List of the selected studies with high proton conductivity at 298-313 K

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\sigma / \text{S cm}^{-1})</th>
<th>(E_a / \text{eV})</th>
<th>Condition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>EuL</td>
<td>(1.0 \times 10^{-7})</td>
<td>0.91</td>
<td>25 °C, 97% R.H.</td>
<td>2</td>
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<tr>
<td>DyL</td>
<td>(1.52 \times 10^{-7})</td>
<td>0.87</td>
<td>25 °C, 97% R.H.</td>
<td>2</td>
</tr>
<tr>
<td>LaCr(ox)(_2)10H(_2)O</td>
<td>(1.0 \times 10^{-5})</td>
<td>0.32</td>
<td>25 °C, 95% R.H.</td>
<td>3</td>
</tr>
<tr>
<td>[Eu(_2)(CO(_3))(ox)(_2)H(_2)O(_2)] \cdot 4H(_2)O</td>
<td>(1.01 \times 10^{-5})</td>
<td>0.47</td>
<td>25 °C, 0% R.H.</td>
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<tr>
<td>YbO(OH)P-CEFs</td>
<td>(7.61 \times 10^{-5})</td>
<td>0.57</td>
<td>25 °C, 95% R.H.</td>
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<tr>
<td>NdTBP-CEFs</td>
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<td>0.32</td>
<td>25 °C, 95% R.H.</td>
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<tr>
<td>CoLa-II-SC</td>
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<tr>
<td>GdHPA-II</td>
<td>(3.2 \times 10^{-4})</td>
<td>0.23</td>
<td>25 °C, 95% R.H.</td>
<td>7</td>
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<tr>
<td>Eu-SCP</td>
<td>(1.19 \times 10^{-3})</td>
<td>0.19</td>
<td>21 °C, 98% R.H.</td>
<td>This Work</td>
</tr>
<tr>
<td>PCMOF-5</td>
<td>(1.3 \times 10^{-3})</td>
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<td>25 °C, 97% R.H.</td>
<td>8</td>
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<tr>
<td>(\text{N}_2\text{H}_5[\text{CeEu(C}_2\text{O}_4)_3(\text{N}_2\text{H}_5)] \cdot 4\text{H}_2\text{O})</td>
<td>(3.42 \times 10^{-3})</td>
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<td>25 °C, 100% R.H.</td>
<td>9</td>
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<tr>
<td>(\text{N}_2\text{H}_5[\text{Nd}_2(\text{C}_2\text{O}_4)_4(\text{N}_2\text{H}_5)] \cdot 4\text{H}_2\text{O})</td>
<td>(2.7 \times 10^{-3})</td>
<td>0.11</td>
<td>25 °C, 100% R.H.</td>
<td>9</td>
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</table>


Section S14: References


