## **Supporting Information**

## A Layered Hybrid Rare-Earth Double Perovskite-Type Molecule-Based Compound with Electrical and Optical Response Properties

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Figure S1. Crystal morphology of 1.



**Figure S2.** IR spectra of **1** in KBr pellets was measured on a Shimadzu IRPrestige-21 spectrometer at room temperature.



Figure S3. TGA curves of 1.



Figure S4. PXRD patterns of 1 recorded at room temperature.



**Figure S5.** Characterizations of the phase transition behavior of **1**. DSC curves measured at different scanning rates.



**Figure S6**. The crystal structures of **1** at 293 K viewed along the (a) *a*-, (b) *b*- and (c) *c*-axis, respectively. Purple: Rb; cyan: Eu; red: O; blue: N; gray: C; white: H.



**Figure S7**. The crystal structure of **1** at 478 K, showing the disordered state of the NO<sub>3</sub><sup>-</sup> ions and organic cations. Purple: Rb; cyan: Eu; red: O; blue: N; gray: C; white: H. Orange plane: mirror plane; green line: two-fold axis.



Figure S8. An asymmetric unit of 1 (a) at 293 K and (b) at 478 K.



Figure S9. The lifetime measurement of 1.



Figure S10. The quantum yield measurement of 1.

D-H···A	H····A	D····A	D–H···A	
1 (293 K)				
N5-H5C····N4 <sup>i</sup>	2.427	3.403	173.45	
N5-H5C…O11 <sup>i</sup>	2.090	2.999	153.39	
$N5-H5C\cdots O12^{i}$	2.120	2.965	143.46	
N6-H6C…N4 <sup>ii</sup>	2.421	3.389	169.24	
N6-H6C····O10 <sup>ii</sup>	2.023	2.962	159.86	
N6-H6C····O12 <sup>ii</sup>	2.203	3.011	138.97	
Symmetry codes: (i) -x+2, -y, -z+2; (ii) x, y+1, z-1.				

Table S1. Selected hydrogen bonds (Å, °) for 1.