# Supporting information

## A rare-earth double perovskite ferroelastic for low-bias X-ray detection

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## Physical measurements

### IR measurements

The infrared spectrum of **1** was recorded at room temperature on a Shimadzu IR-60 spectrometer using a KBr pellet.

### PXRD measurements

PXRD data were collected on a PANalytical X'Pert PRO X-ray diffractometer using Cu−K$\alpha$ radiation ($\lambda$ = 1.54184 Å), scanning the 2$\theta$ range from 5° to 50° with a step size of 0.02°.

### TGA measurements

**1** was measured using a NETZSCH TG 209F$^3$ instrument under ambient pressure with nitrogen protection. The sample was placed in an $Al_2O_3$ crucible and heated from room temperature to 900 K at a rate of 10 K·min$^{-1}$.

### DSC measurements

DSC measurements were conducted using a NETZSCH instrument under standard atmospheric pressure at heating/cooling rates of 20, 15, 10, 5, and 2 K·min$^{-1}$, yielding five corresponding measure curves.

### Ferroelastic measurements

Ferroelastic domain characterization was conducted on a Nikon ECLIPSE Ci-POL polarizing microscope, equipped with a temperature control stage. Real-time orthogonal polarized light observation was performed to monitor the domain structure evolution of **1** across the phase transition temperature.

### DFT computational

All calculations were performed using the Vienna Ab initio Simulation Package (VASP) with the projector-augmented wave (PAW) pseudopotentials. The exchange-correlation interaction was described by the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) functional. A plane-wave cutoff energy of 520 eV was used. The Brillouin zone was sampled with a Monkhorst-Pack k-point mesh of 3×4×6. The energy convergence criterion was set to 1.0×10$^{-6}$ eV/atom, and the force convergence criterion was

$1.0\times10^{-2}$ eV/Å. A DFT+U correction was applied to the Ce 4*f* orbitals with a Hubbard U parameter of $U^f = 5.0$ eV.

**Dielectric measurements**

The dielectric constant $\varepsilon$ ($\varepsilon = \varepsilon' - i\varepsilon''$) of **1** was measured over a frequency range of 500 Hz−1 MHz and a temperature range of 300 K−390 K using a Tonghui TH2828A analyzer at a fixed measurement voltage of 1 V. For the measurement, a pressed-pellet sample of **1** was sandwiched between two parallel copper electrodes using carbon conductive adhesive, which served as the sample holder.

**Single−crystal X−ray crystallography**.

Variable-temperature single-crystal X-ray diffraction data for **1** were collected on a *Rigaku Varimax*$^{TM}$ *DW* diffractometer equipped with Mo–$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) using the four-circle measurement method. Diffraction data acquisition was performed with a *Hypix−6000HE* detector, and data processing including empirical absorption correction was carried out with the Crystal-clear software package (Rigaku OD, 2018). The crystal structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ using the SHELXLTL software package. All non-hydrogen atoms were refined anisotropically, and only reflections with $I > 2\sigma(I)$ were used in the refinement. Hydrogen atom positions were generated geometrically and refined using a riding model, with thermal parameters set as $U_{iso} = 1.2U_{eq}$. Molecular structure plots and crystal packing diagrams were prepared with DIAMOND software (Brandenburg & Putz, 2005). Bond distances and angles were calculated with DIAMOND, and other relevant crystallographic calculations were performed using SHELXLTL.

The $\Delta S$ and N for **1** were determined from the DSC curve acquired at a heating rate of 10 K min$^{-1}$.

$$\Delta S = \int_{T_1}^{T_2} \frac{Q}{T} dT \approx \frac{\Delta H}{T} = \frac{6.19\, J \cdot g^{-1} \times 775.18\, g \cdot mol^{-1}}{400\, K} \approx 11.996\, J \cdot mol^{-1} \cdot K^{-1}$$

$$N = \exp\left(\frac{\Delta S}{R}\right) = \exp\left(\frac{11.996\, J \cdot mol^{-1} \cdot K^{-1}}{8.314\, J \cdot mol^{-1} \cdot K^{-1}}\right) \approx 4.233$$

At 253 K, a quantitative analysis was performed on the coordination environment of the $Rb^{+}$. The bond-length distortion index ($\Delta D$) and bond-angle variance ($\sigma^2$) were calculated to evaluate the geometry distortion, using the following formulas:

$$D = \frac{1}{6}\sum_{i=1}^{6} \times \left[\frac{(d_i - \langle d \rangle)}{\langle d \rangle}\right]^2$$

where $d_i$ is the length of the Rb−O bond, and $d$ is the average length of the six Rb−O bonds.

$$\sigma^2 = \frac{1}{12}\sum_{j=1}^{12} \times (\theta_j - 90)^2$$

where $\theta_j$ represents the adjacent O−Rb−O bond angles within the octahedron, for which the ideal value is 90°.

## Figures:

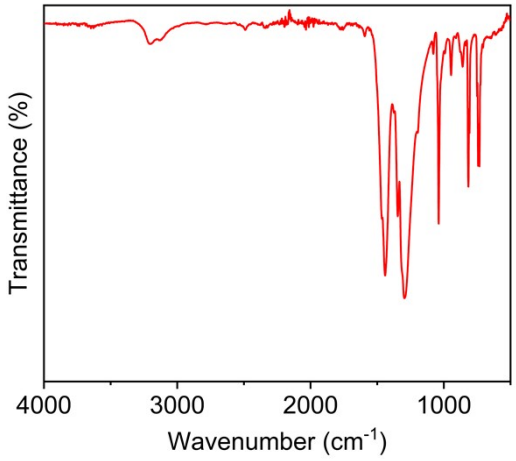


**Fig. S1** Infrared spectrum of **1** measured at 293 K.

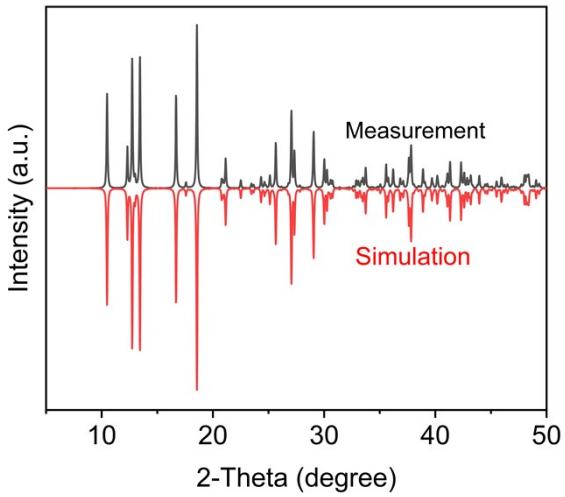


**Fig. S2** Comparison of the experimental and simulated single-crystal X-ray diffraction patterns for **1** measured at room temperature.

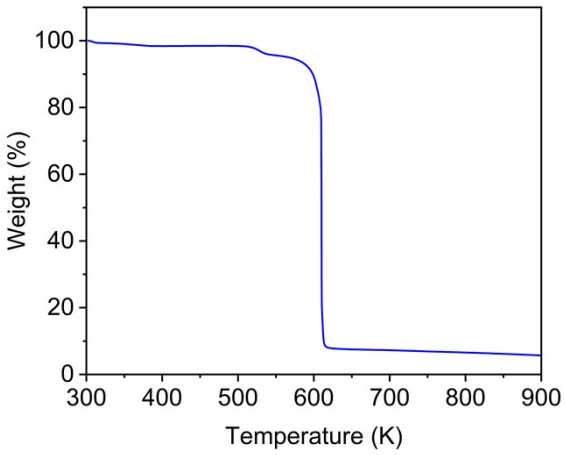


**Fig. S3** TGA measurement of **1**.

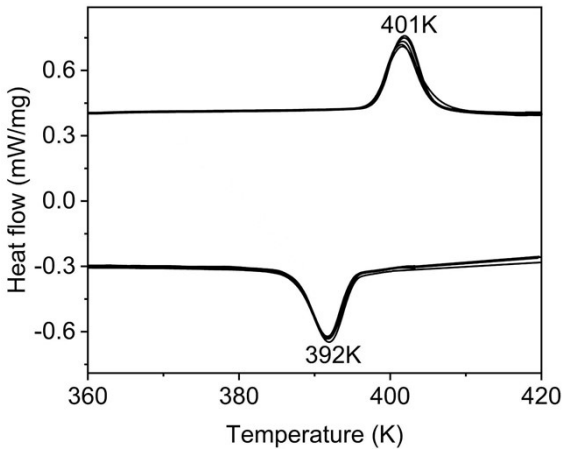


**Fig. S4** Five-cycle DSC measurement of **1**.

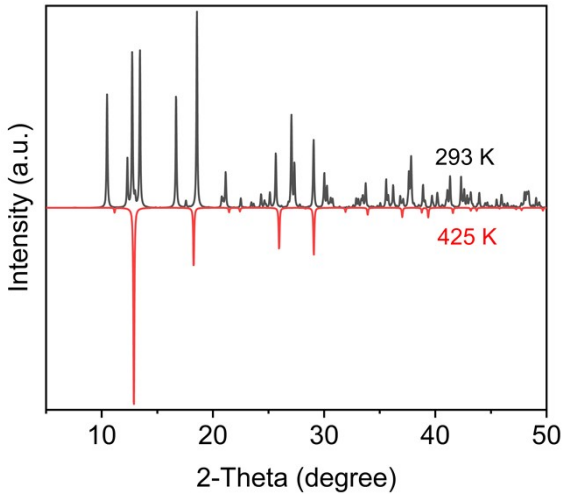


**Fig. S5** Comparison of in-situ variable-temperature X-ray diffraction patterns for **1** collected at 293 K and 425 K.

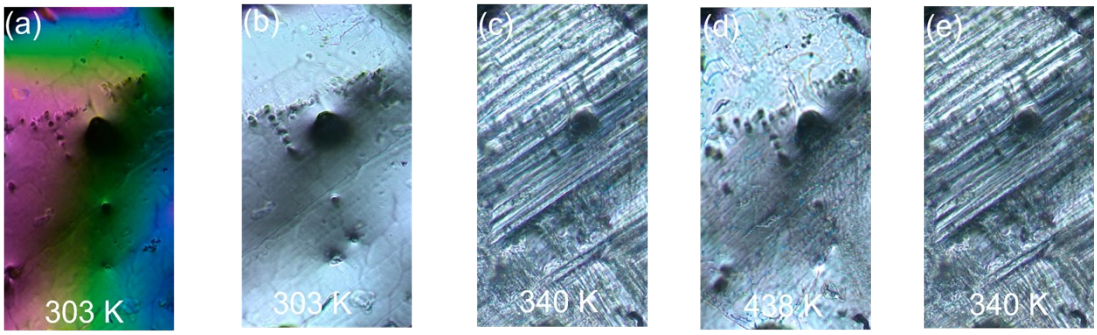


**Fig. S6** Optical micrographs of crystal **1** under natural light during heating and cooling processes. Figure S6a shows the photograph taken under a polarizing microscope at 303 K.

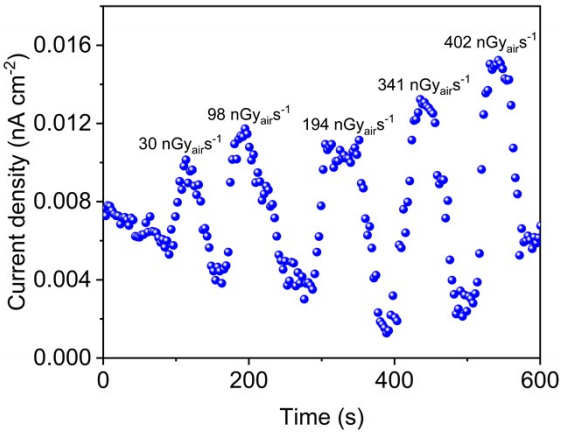


**Fig.S7** The X-ray detection response behavior of **1** at 0 V bias.

## Tables:

Table S1. Crystal structure and refinement detail of **1** at 253 K and 425 K.

| *T* / K | 253 | 425 |
|---|---|---|
| Formula weight | 775.88 | 1154.87 |
| Crystal system | orthorhombic | Cubic |
| Space group | $P2_12_12_1$ | *F*432 |
| *a* / Å | 21.2321(5) | 13.7238(8) |
| *b* / Å | 13.8822(3) | 13.7238(8) |
| *c* / Å | 8.3964(2) | 13.7238(8) |
| *α* / ° | 90 | 90 |
| *β* / ° | 90 | 90 |
| *γ* / ° | 90 | 90 |
| *V* / Å$^3$ | 2474.82(10) | 2584.8(5) |
| *Z* | 4 | 4 |
| $D_{calc}$ / g·cm$^3$ | 2.082 | 2.968 |
| *μ* / mm$^{-1}$ | 3.903 | 5.252 |
| *F*(000) | 1508.0 | 2205.0 |
| *2θ range* / ° | 2.415 to 30.963 | 4.200 to 30.973 |
| Reflns collected | 27909 | 2383 |
| $R_{int}$ | 0.0277 | 0.1331 |
| No. of parameters | 344 | 22 |
| $R_1$[a], $wR_2$[b] [$I>2\sigma(I)$] | 0.0393, 0.0962 | 0.2513, 0.5590 |
| $R_1$, $wR_2$ [all data] | 0.0500, 0.1004 | 0.3349, 0.5865 |
| GOF | 1.034 | 1.939 |
| $\Delta\rho$[c] / e·Å$^{-3}$ | 1.200 / −0.827 | 3.523 / −1.798 |
| CCDC | 2526909 | 2526920 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b] $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2) / \Sigma|F_o|^2]^{1/2}$

Table S2. Selected bond lengths for **1** at 253 K.

| Bond | Length/ Å | Bond | Length/ Å |
|---|---|---|---|
| Ce(1)−O(4) | 2.599(6) | C(4)−C(3) | 1.492(11) |
| Ce(1)−O(6) | 2.605(7) | C(4)−H(4A) | 0.9700 |
| Ce(1)−O(17) | 2.613(7) | C(4)−H(4B) | 0.9700 |
| Ce(1)−O(7) | 2.612(7) | N(4)−O(12) | 1.213(8) |
| Ce(1)−O(9) | 2.614(7) | N(1)−O(3) | 1.266(9) |

| | | | |
|---|---|---|---|
| Ce(1)−O(1) | 2.616(5) | O(13)−N(5) | 1.206(12) |
| Ce(1)−O(10) | 2.621(4) | N(8)−C(7) | 1.460(10) |
| Ce(1)−O(15) | 2.623(7) | N(8)−C(6) | 1.469(10) |
| Ce(1)−O(14) | 2.622(7) | N(8)−H(8) | 0.8600 |
| Ce(1)−O(16) | 2.641(7) | N(7)−C(1) | 1.465(10) |
| Ce(1)−O(11) | 2.661(5) | N(7)−H(7) | 0.8600 |
| Ce(1)−O(2) | 2.677(5) | C(6)−C(5) | 1.517(11) |
| Rb(1)−O(18) | 2.826(5) | C(6)−H(6A) | 0.9700 |
| Rb(1)−F(2) | 2.903(8) | C(6)−H(6B) | 0.9700 |
| Rb(1)−F(1) | 2.983(7) | F(1)−C(2) | 1.395(16) |
| O(9)−N(3) | 1.188(14) | C(8)−F(2) | 1.462(17) |
| O(14)−N(5) | 1.277(15) | C(8)−C(7) | 1.473(11) |
| O(16)−N(6) | 1.265(14) | C(8)−C(5) | 1.502(12) |
| O(10)−N(4) | 1.275(7) | C(8)−H(8A) | 0.9800 |
| O(1)−N(1) | 1.255(7) | C(1)−C(2) | 1.462(11) |
| O(4)−N(2) | 1.282(13) | C(1)−H(1A) | 0.9700 |
| O(11)−N(4) | 1.247(8) | C(1)−H(1B) | 0.9700 |
| O(15)−N(5) | 1.276(14) | C(7)−H(7A) | 0.9700 |
| O(2)−N(1) | 1.231(8) | C(7)−H(7B) | 0.9700 |
| N(2)−O(5) | 1.224(11) | C(2)−C(3) | 1.475(12) |
| N(2)−O(6) | 1.237(12) | C(2)−H(2) | 0.9800 |
| O(7)−N(3) | 1.334(14) | C(3)−H(3A) | 0.9700 |
| O(17)−N(6) | 1.253(14) | C(3)−H(3B) | 0.9700 |
| N(3)−O(8) | 1.229(7) | C(5)−H(5A) | 0.9700 |
| N(6)−O(18) | 1.228(7) | C(5)−H(5B) | 0.9700 |
| C(4)−N(7) | 1.458(11) | | |

Table S3. Selected bond angles for **1** at 253 K.

| Bond | Angles [°] | Bond | Angles [°] |
|---|---|---|---|
| O(4)−Ce(1)−O(6) | 48.4(3) | O(10)−Ce(1)−O(2) | 133.62(14) |
| O(4)−Ce(1)−O(17) | 68.1(2) | O(15)−Ce(1)−O(2) | 66.8(3) |
| O(6)−Ce(1)−O(17) | 68.0(2) | O(14)−Ce(1)−O(2) | 110.7(3) |
| O(4)−Ce(1)−O(7) | 69.1(2) | O(16)−Ce(1)−O(2) | 109.3(2) |
| O(6)−Ce(1)−O(7) | 66.5(2) | O(11)−Ce(1)−O(2) | 178.0(2) |
| O(17)−Ce(1)−O(7) | 131.3(2) | O(18)−Rb(1)−F(2) | 129.7(3) |

| | | | |
|---|---|---|---|
| O(4)−Ce(1)−O(9) | 112.7(2) | O(18)−Rb(1)−F(1) | 115.4(3) |
| O(6)−Ce(1)−O(9) | 111.1(2) | F(2)−Rb(1)−F(1) | 88.7(3) |
| O(17)−Ce(1)−O(9) | 178.1(3) | N(3)−O(9)−Ce(1) | 99.0(6) |
| O(7)−Ce(1)−O(9) | 48.59(16) | N(5)−O(14)−Ce(1) | 96.7(6) |
| O(4)−Ce(1)−O(1) | 65.7(3) | N(6)−O(16)−Ce(1) | 95.7(5) |
| O(6)−Ce(1)−O(1) | 110.1(2) | N(4)−O(10)−Ce(1) | 97.3(4) |
| O(17)−Ce(1)−O(1) | 68.4(2) | N(1)−O(1)−Ce(1) | 97.0(4) |
| O(7)−Ce(1)−O(1) | 112.7(2) | N(2)−O(4)−Ce(1) | 97.1(6) |
| O(9)−Ce(1)−O(1) | 113.5(2) | N(4)−O(11)−Ce(1) | 96.1(4) |
| O(4)−Ce(1)−O(10) | 115.2(3) | N(5)−O(15)−Ce(1) | 96.6(6) |
| O(6)−Ce(1)−O(10) | 70.3(2) | N(1)−O(2)−Ce(1) | 94.7(3) |
| O(17)−Ce(1)−O(10) | 110.3(2) | O(5)−N(2)−O(6) | 121.2(11) |
| O(7)−Ce(1)−O(10) | 69.1(2) | O(5)−N(2)−O(4) | 122.5(11) |
| O(9)−Ce(1)−O(10) | 67.7(2) | O(6)−N(2)−O(4) | 115.8(7) |
| O(1)−Ce(1)−O(10) | 178.17(15) | N(3)−O(7)−Ce(1) | 95.1(5) |
| O(4)−Ce(1)−O(15) | 129.27(19) | N(6)−O(17)−Ce(1) | 97.4(5) |
| O(6)−Ce(1)−O(15) | 177.2(3) | O(9)−N(3)−O(8) | 125.8(13) |
| O(17)−Ce(1)−O(15) | 109.9(3) | O(9)−N(3)−O(7) | 116.8(5) |
| O(7)−Ce(1)−O(15) | 114.8(2) | O(8)−N(3)−O(7) | 117.2(12) |
| O(9)−Ce(1)−O(15) | 71.0(3) | O(18)−N(6)−O(17) | 122.7(12) |
| O(1)−Ce(1)−O(15) | 67.1(3) | O(18)−N(6)−O(16) | 119.8(12) |
| O(10)−Ce(1)−O(15) | 112.5(3) | O(17)−N(6)−O(16) | 117.4(5) |
| O(4)−Ce(1)−O(14) | 178.2(3) | N(2)−O(6)−Ce(1) | 98.1(6) |
| O(6)−Ce(1)−O(14) | 133.11(19) | N(7)−C(4)−C(3) | 99.4(10) |
| O(17)−Ce(1)−O(14) | 111.2(3) | N(7)−C(4)−H(4A) | 111.9 |
| O(7)−Ce(1)−O(14) | 112.1(3) | C(3)−C(4)−H(4A) | 111.9 |
| O(9)−Ce(1)−O(14) | 68.0(3) | N(7)−C(4)−H(4B) | 111.9 |
| O(1)−Ce(1)−O(14) | 112.5(3) | C(3)−C(4)−H(4B) | 111.9 |
| O(10)−Ce(1)−O(14) | 66.6(3) | H(4A)−C(4)−H(4B) | 109.6 |
| O(15)−Ce(1)−O(14) | 49.2(3) | N(6)−O(18)−Rb(1) | 149.2(5) |
| O(4)−Ce(1)−O(16) | 110.3(3) | O(12)−N(4)−O(11) | 122.5(7) |
| O(6)−Ce(1)−O(16) | 113.3(2) | O(12)−N(4)−O(10) | 119.7(7) |
| O(17)−Ce(1)−O(16) | 48.36(17) | O(11)−N(4)−O(10) | 117.8(6) |
| O(7)−Ce(1)−O(16) | 179.4(3) | O(2)−N(1)−O(1) | 120.2(5) |

| | | | |
|---|---|---|---|
| O(9)−Ce(1)−O(16) | 131.8(2) | O(2)−N(1)−O(3) | 121.2(7) |
| O(1)−Ce(1)−O(16) | 66.7(2) | O(1)−N(1)−O(3) | 116.6(7) |
| O(10)−Ce(1)−O(16) | 111.4(2) | C(7)−N(8)−C(6) | 108.1(8) |
| O(15)−Ce(1)−O(16) | 65.3(2) | C(7)−N(8)−H(8) | 113.1 |
| O(14)−Ce(1)−O(16) | 68.4(3) | C(6)−N(8)−H(8) | 113.2 |
| O(4)−Ce(1)−O(11) | 112.0(3) | C(4)−N(7)−C(1) | 109.0(9) |
| O(6)−Ce(1)−O(11) | 69.1(3) | C(4)−N(7)−H(7) | 116.0 |
| O(17)−Ce(1)−O(11) | 65.7(2) | C(1)−N(7)−H(7) | 112.3 |
| O(7)−Ce(1)−O(11) | 111.7(2) | O(13)−N(5)−O(15) | 115.3(13) |
| O(9)−Ce(1)−O(11) | 112.4(2) | O(13)−N(5)−O(14) | 126.8(12) |
| O(1)−Ce(1)−O(11) | 130.07(14) | O(15)−N(5)−O(14) | 117.5(7) |
| O(10)−Ce(1)−O(11) | 48.24(14) | N(8)−C(6)−C(5) | 105.2(8) |
| O(15)−Ce(1)−O(11) | 112.0(3) | N(8)−C(6)−H(6A) | 110.7 |
| O(14)−Ce(1)−O(11) | 68.9(3) | C(5)−C(6)−H(6A) | 110.7 |
| O(16)−Ce(1)−O(11) | 68.6(2) | N(8)−C(6)−H(6B) | 110.7 |
| O(4)−Ce(1)−O(2) | 68.4(3) | C(5)−C(6)−H(6B) | 110.7 |
| O(6)−Ce(1)−O(2) | 112.0(3) | H(6A)−C(6)−H(6B) | 108.8 |
| O(17)−Ce(1)−O(2) | 112.9(2) | C(2)−F(1)−Rb(1) | 139.7(8) |
| O(7)−Ce(1)−O(2) | 70.3(2) | F(2)−C(8)−C(7) | 102.9(12) |
| O(9)−Ce(1)−O(2) | 68.9(2) | F(2)−C(8)−C(5) | 109.9(13) |
| O(1)−Ce(1)−O(2) | 48.06(14) | C(7)−C(8)−C(5) | 103.2(9) |
| F(2)−C(8)−H(8A) | 113.3 | C(8)−C(7)−H(7A) | 110.9 |
| C(7)−C(8)−H(8A) | 113.3 | N(8)−C(7)−H(7B) | 110.9 |
| C(5)−C(8)−H(8A) | 113.3 | C(8)−C(7)−H(7B) | 110.9 |
| C(8)−F(2)−Rb(1) | 146.1(9) | H(7A)−C(7)−H(7B) | 109.0 |
| C(2)−C(1)−N(7) | 105.2(10) | F(1)−C(2)−C(1) | 105.8(12) |
| C(2)−C(1)−H(1A) | 110.7 | F(1)−C(2)−C(3) | 111.5(13) |
| N(7)−C(1)−H(1A) | 110.7 | C(1)−C(2)−C(3) | 104.3(10) |
| C(2)−C(1)−H(1B) | 110.7 | F(1)−C(2)−H(2) | 111.6 |
| N(7)−C(1)−H(1B) | 110.7 | C(1)−C(2)−H(2) | 111.6 |
| H(1A)−C(1)−H(1B) | 108.8 | C(3)−C(2)−H(2) | 111.6 |
| N(8)−C(7)−C(8) | 104.1(9) | C(2)−C(3)−C(4) | 103.9(10) |
| N(8)−C(7)−H(7A) | 110.9 | C(2)−C(3)−H(3A) | 111.0 |
| C(4)−C(3)−H(3A) | 111.0 | C(8)−C(5)−H(5A) | 110.8 |

| | | | |
|---|---|---|---|
| C(2)−C(3)−H(3B) | 111.0 | C(6)−C(5)−H(5A) | 110.8 |
| C(4)−C(3)−H(3B) | 111.0 | C(8)−C(5)−H(5B) | 110.8 |
| H(3A)−C(3)−H(3B) | 109.0 | C(6)−C(5)−H(5B) | 110.8 |
| C(8)−C(5)−C(6) | 104.8(9) | H(5A)−C(5)−H(5B) | 108.9 |

Table S3. Selected bond lengths and bond angles for **1** at 425 K.

| Bond | Length/ Å | Bond | Angles [°] |
|---|---|---|---|
| O(2)−N(1) | 1.85(13) | O(1)−Rb(1)−N(1) | 0.000(6) |
| Rb(1)−O(1) | 1.34(8) | N(1)−O(1)−Rb(1) | 180.0 |
| Rb(1)−N(1) | 2.29(14) | O(1)−N(1)−O(2) | 157.8(17) |
| F(1)−N(2) | 1.61(14) | O(1)−N(1)−Rb(1) | 0.000(6) |
| O(1)−N(1) | 0.95(14) | O(2)−N(1)−Rb(1) | 157.8(17) |

Table S4. Elemental analysis data for **1**.

| Compound | Element | Calcd (%) | Found (%) |
|---|---|---|---|
| **1** | C | 12.38 | 12.34 |
| | H | 2.08 | 2.06 |
| | N | 14.44 | 14.46 |
| | O | 37.12 | 37.13 |