Electronic Supplementary Information

Ferroelectricity in perovskite realized by switchable skewed conformation

Zhuoer Cai,‡[a] Yinan Zhang,‡[a], Xiu-Ni Hua*[b], Hai-Bao Duan*[b] and Baiwang Sun*[a]

[a.] *School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, P. R. China.*

[b.] *School of Environmental Science, Nanjing Xiaozhuang University, Nanjing 211171, P. R. China.*

Content

The calculation of the dipole moment

Based on the point charge model, the positive charge center is determined by the coordinates of nitrogen atoms, while the negative charge center is determined by the coordinates of the cadmium atoms (Table S1). We calculated the average coordinates of all cadmium and nitrogen atoms within a unit cell and estimated the polarization value as following equations (Table S2).

$$P_c = lim\frac{1}{V}\sum q_i \times c_i = \frac{(4 \times 0.709 - 4 \times 0.462) \times 1.6 \times 10^{-19} \times 6.7}{1151.72 \times 10^{-30}}$$

$$m^2 = 9_{\mu C/cm^2}$$

The stability of the sample

The polycrystalline powder sample and the single-crystal sample were both exposed to air for 11 days. The powder sample was subjected to Powder X-ray Diffraction (PXRD) testing (Fig. S2), while the single-crystal sample was observed under a polarizing microscope to examine its morphology (Fig. S18).

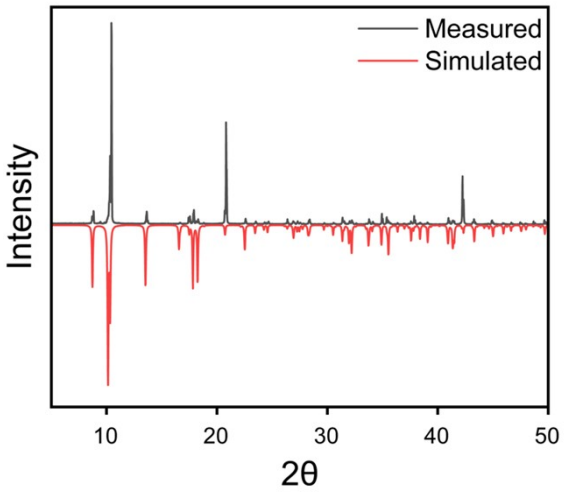

Fig. S1 Measured and simulated PXRD patterns of **1**.

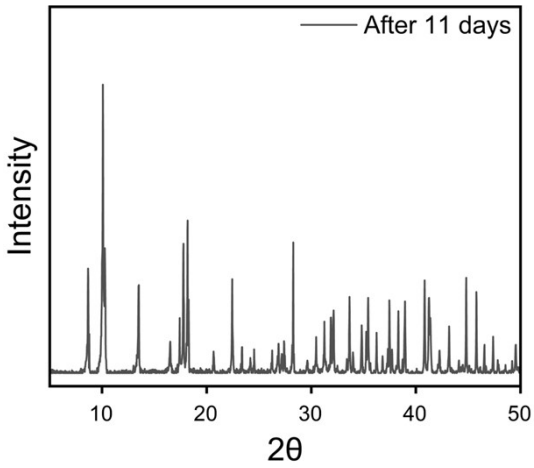

Fig. S2 Measured PXRD patterns of **1** after exposed to air for 11 days.

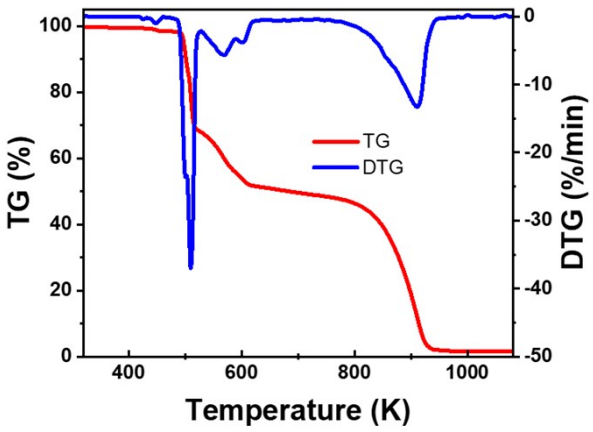

Fig. S3 Thermogravimetric analysis patterns of **1**.

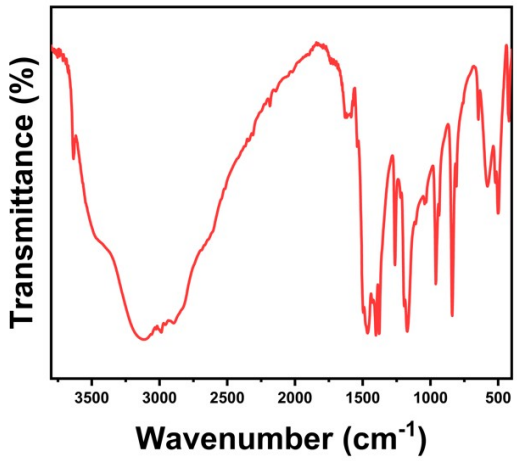

Fig. S4 Infrared pattern of **1** (solid sample, with a mass ratio of 1:100 to potassium bromide) at room temperature.

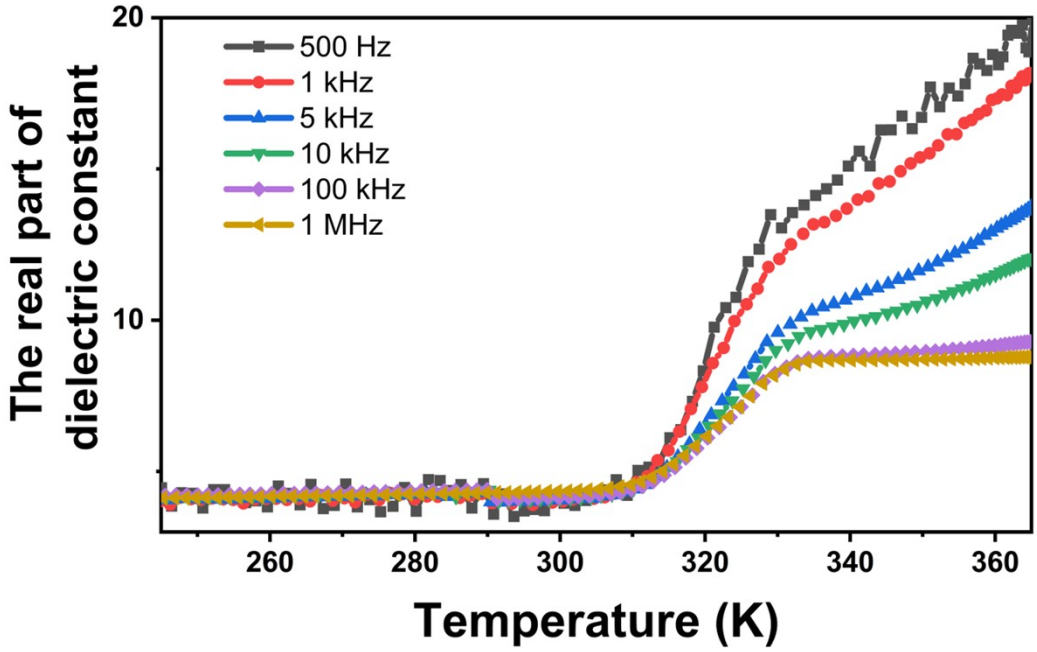

Fig. S5 The real part of dielectric constant of **1** at different frequencies.

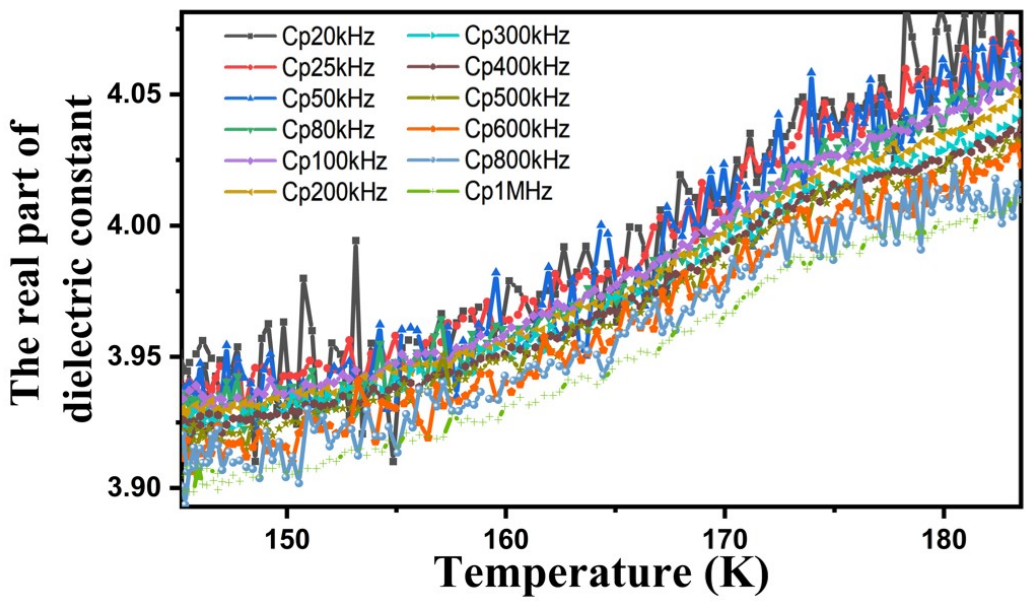

Fig. S6 The real part of dielectric constant of **1** near 170 K with different frequencies.

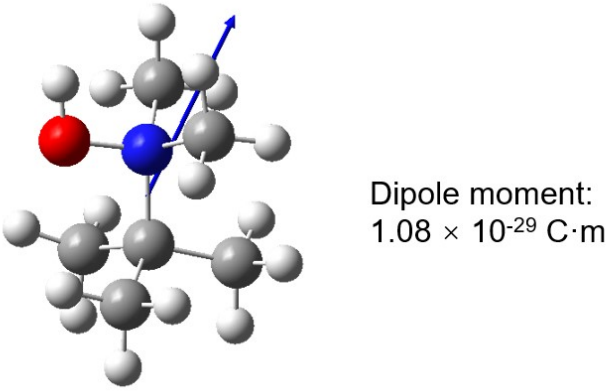

Fig. S7 Dipole moment magnitude and direction of *N*-(*t*ert-butyl)-*N*,*N*-dimethylhydroxylammonium.

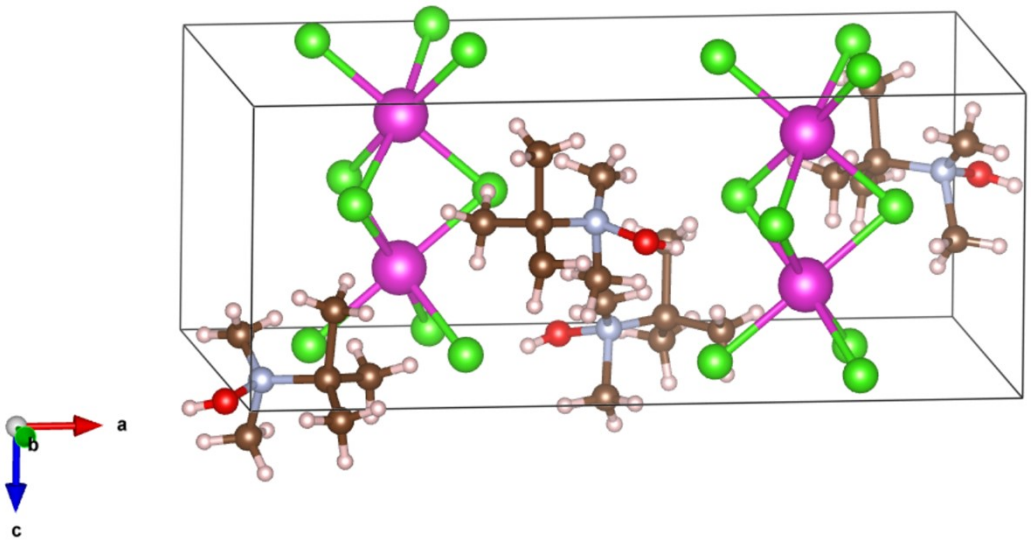

Fig. S8 Optimized crystal structure of **1**.

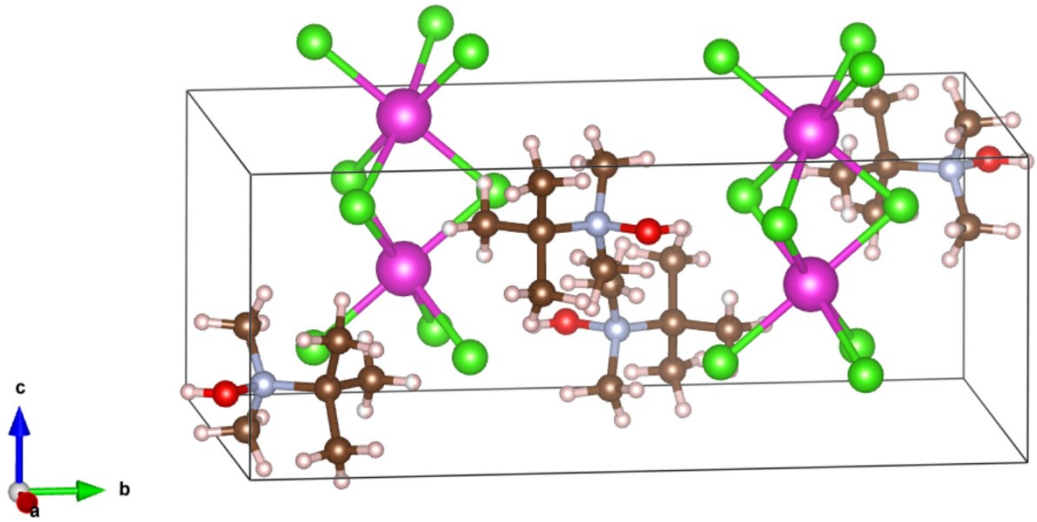

Fig. S9 Transition structure of ferroelectric flipping process.

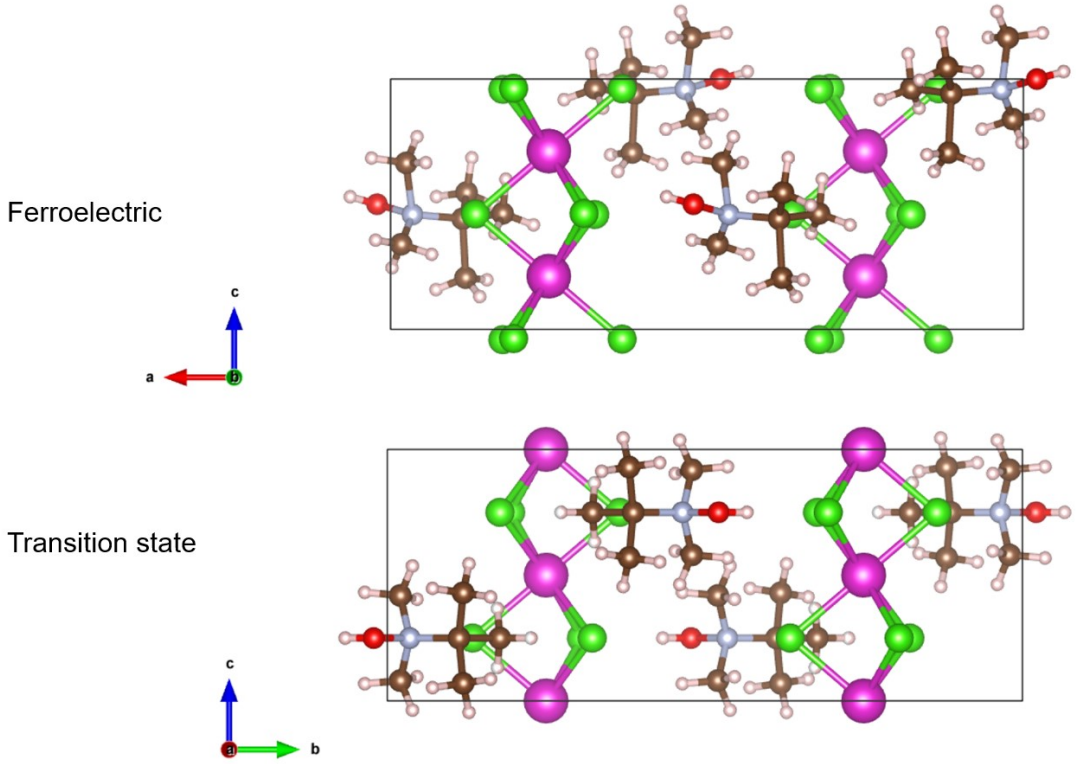

Fig. S10 Comparison of ferroelectric structure and transition state.

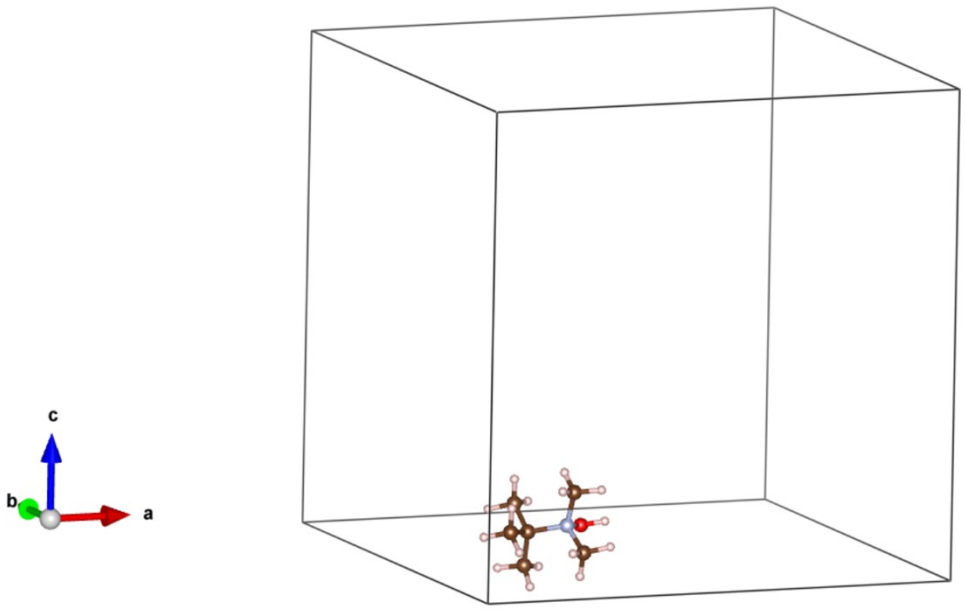

Fig. S11 Optimized molecular structure of *N*-(*t*ert-butyl)-*N*,*N*-dimethylhydroxylammonium.

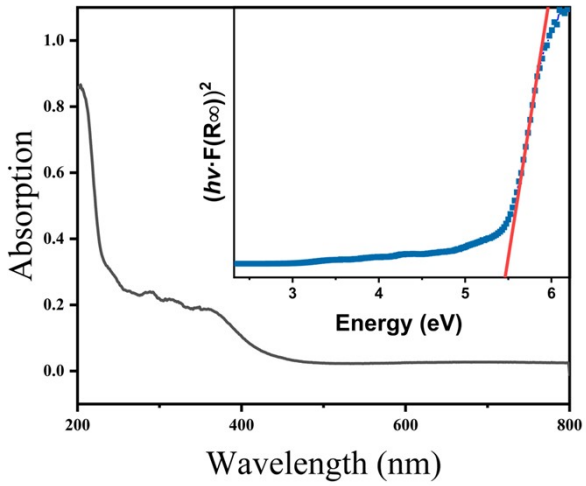

Fig. S12 UV-vis spectrum of **1** (solid sample and barium sulfate as an optical substrate at room temperature.

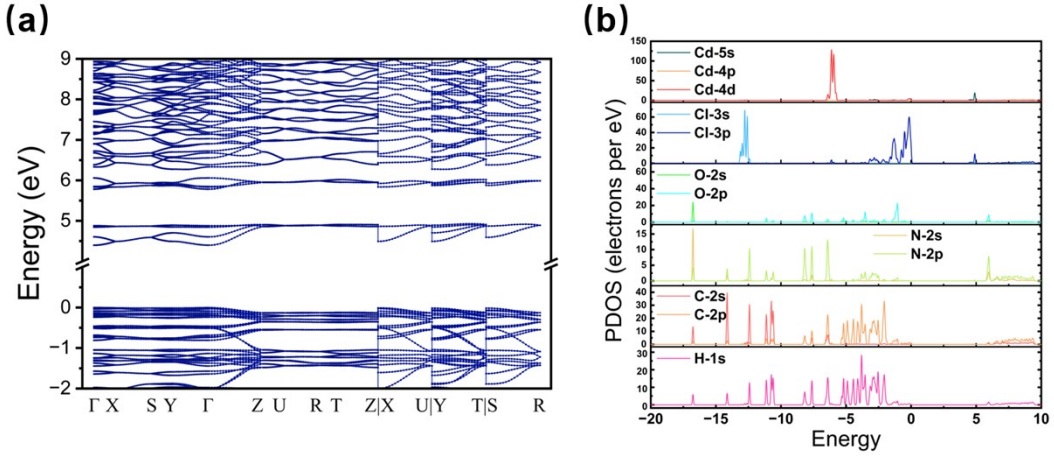

Fig. S13 Bandgap (a) and projected density of state (b) of **1**.

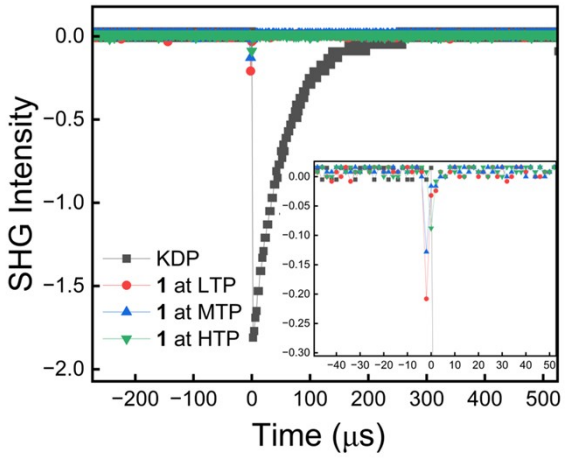

Fig. S14 Second harmonic generation (SHG) signal of **1** at different phase compared with KDP.

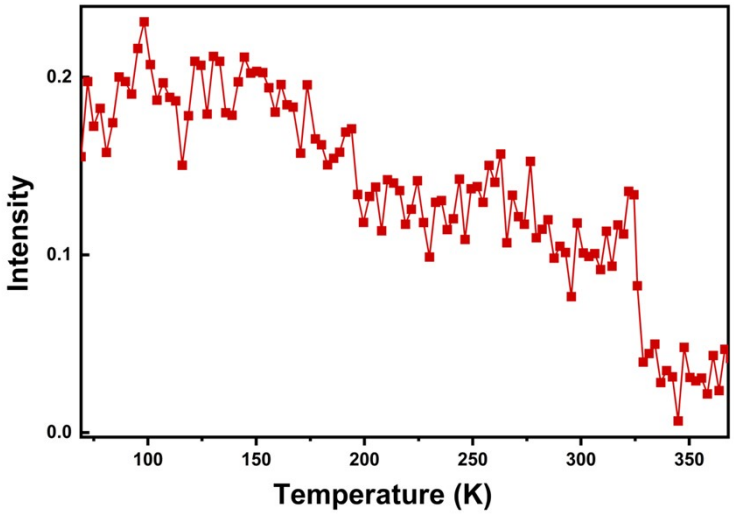

Fig. S15 Temperature-dependent SHG intensity of **1**.

Fig. S16 Morphology of **1**.

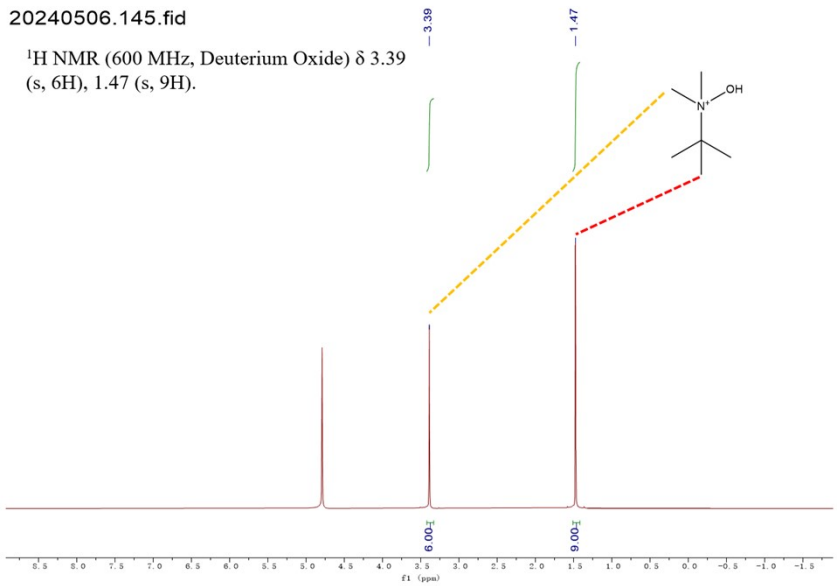

Fig. S17 ^{1}H NMR (600 MHz, D_2O solvent, 300 K temperature) spectrum of **1**.

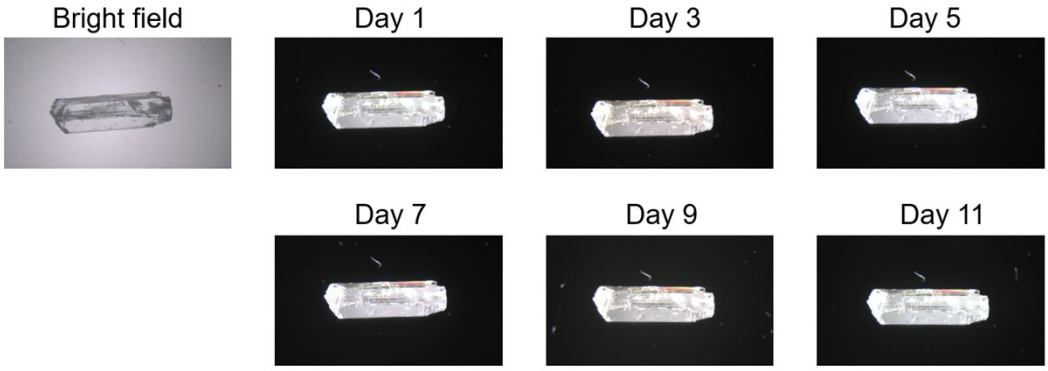

Fig. S18 The surface morphology of **1** after air exposure under the optical microscopy for 11 days.

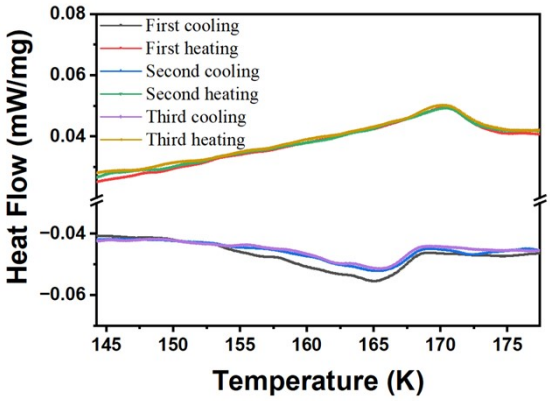

Fig. S19 Multiple DSC cycles around 170 K of **1**.

Table S1 The coordinates of N atoms and Cd atoms within the lattice.

Label	X	Y	Z
N1	0.4655	0.7751	0.459
N1	0.5345	0.2249	0.959
N1	0.9655	0.2249	0.459
N1	0.0345	0.7751	0.959
Cd1	0.74996	0.64532	0.7124
Cd1	0.75004	0.64532	0.2124
Cd1	0.25004	0.35468	0.2124
Cd1	0.24996	0.35468	0.7124

Table S2 The average coordinates of N atoms and Cd atoms within the lattice.

Element	X	Y	Z
N	0.5	0.5	0.709
Cd	0.5	0.5	0.462

Table S3 Crystal data and structure refinement.

CCDC number	2402677	2402678	2402679
Empirical formula	$C_6H_{16}CdCl_3NO$	$C_6H_{16}CdCl_3NO$	$C_6H_{16}CdCl_3NO$
Formula weight	336.95	336.95	336.95
Temperature [K]	100.15	230.00	360.00
Crystal system	orthorhombic	orthorhombic	hexagonal
Space group	$Pca2_1$ (29)	$Pca2_1$ (29)	$P\bar{6}2c$ (190)
a [Å]	19.9919(6)	17.1239(6)	10.064(2)
b [Å]	13.4707(3)	10.1317(3)	10.064(2)
c [Å]	17.1535(4)	6.7718(2)	6.7844(16)
α [°]	90	90	90
β [°]	90	90	90
γ [°]	90	90	120
Volume [Å^3]	4619.5(2)	1174.87(6)	595.1(3)
Z	16	4	2
ρ_{calc} [gcm^{-3}]	1.938	1.905	1.881
μ [mm^{-1}]	2.544	2.501	2.469
F(000)	2656	664	332
Crystal size [mm^3]		0.15×0.14×0.13	
Crystal colour		clear light colourless	
Crystal shape	block	block	block
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)
2θ range [°]	4.35 to 52.76 (0.80 Å)	7.62 to 50.04 (0.84 Å)	7.61 to 54.85 (0.77 Å)
Reflections collected	26993	11508	4685
Independent	9299	2050	495
reflections	R_{int} = 0.0524	R_{int} = 0.0623	R_{int} = 0.0701
	R_{sigma} = 0.0551	R_{sigma} = 0.0420	R_{sigma} = 0.0356
Completeness to θ = 25.242°	99.4 %	99.1 %	99.2 %
Goodness-of-fit on F^2	1.034	1.064	1.098
Final *R* indexes	R_1 = 0.0372	R_1 = 0.0539	R_1 = 0.0282
[$I \geq 2\sigma(I)$]	wR_2 = 0.0834	wR_2 = 0.1387	wR_2 = 0.0734
Final *R* indexes	R_1 = 0.0537	R_1 = 0.0583	R_1 = 0.0416
[all data]	wR_2 = 0.0958	wR_2 = 0.1449	wR_2 = 0.0822