Electronic supplementary information

An unusual high-frequency ferroelectric via a strategy of post-synthetic modified metal-organic frameworks

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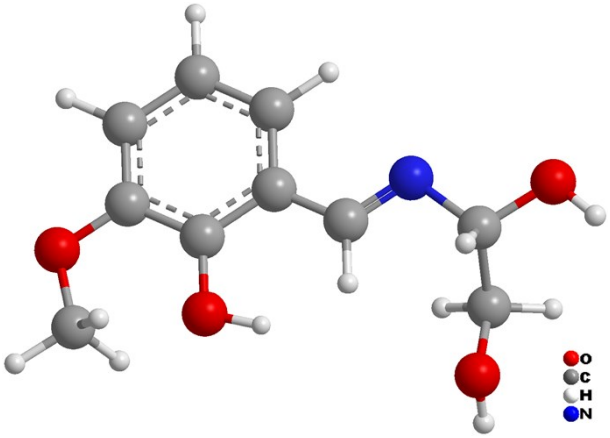

Fig. S1 Drawing of the ligand H_3L.

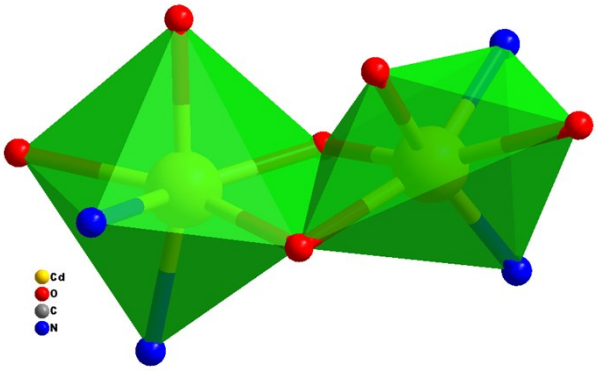

Fig. S2 Coordinated environment of Cd^{2+} and connection type between metal ions.

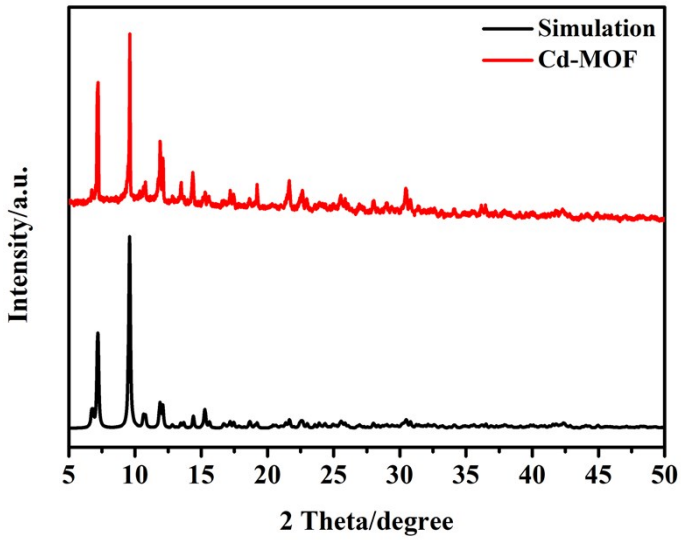

Fig. S3 The simulation and PXRD patterns for Cd-MOF.

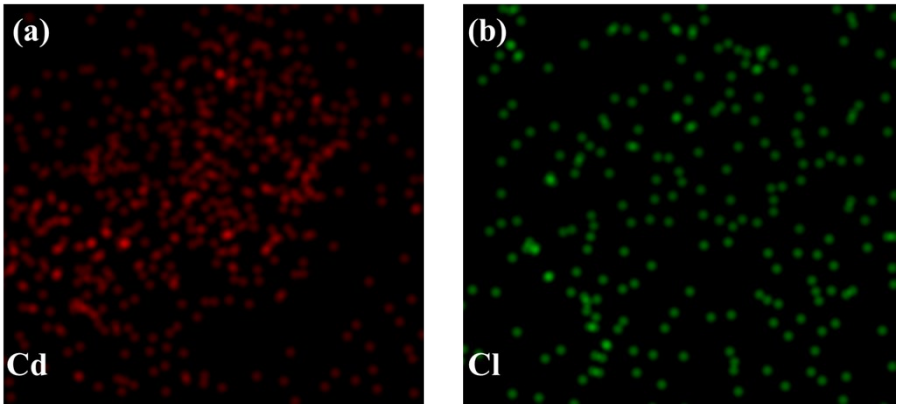

Fig. S4 EDX mapping of $(CH_3)_2NH{\cdot}HCl$@Cd-MOF.

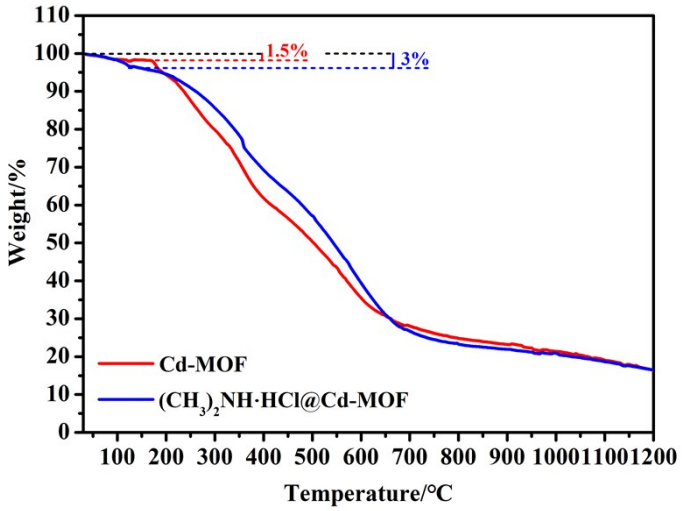

Fig. S5 TGA curves of Cd-MOF and $(CH_3)_2NH{\cdot}HCl$@Cd-MOF.

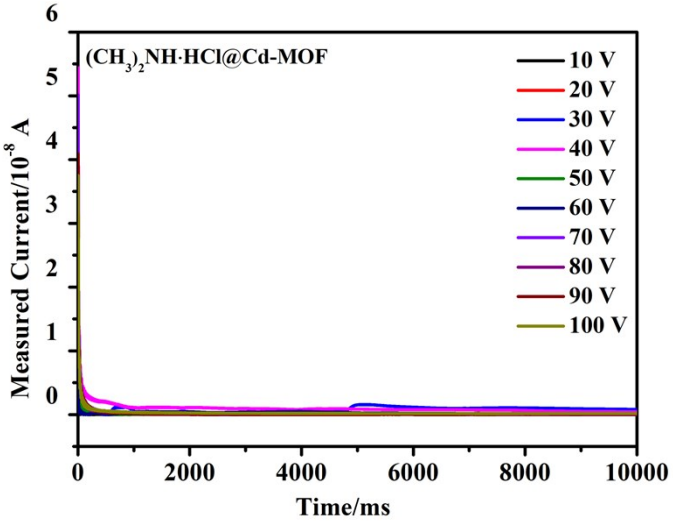

Fig. S6 Leakage curves of $(CH_3)_2NH{\cdot}HCl$@Cd-MOF.

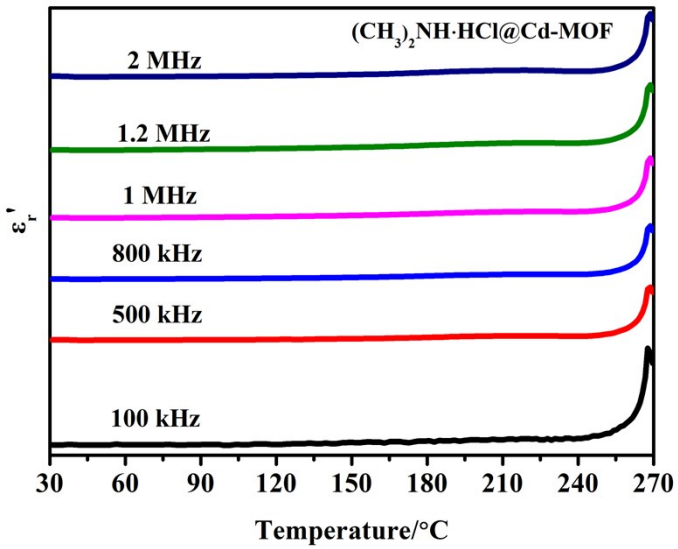

Fig. S7 Dielectric constant of $(CH_3)_2NH·HCl$@Cd-MOF under different frequency in the temperature of 30−270℃.

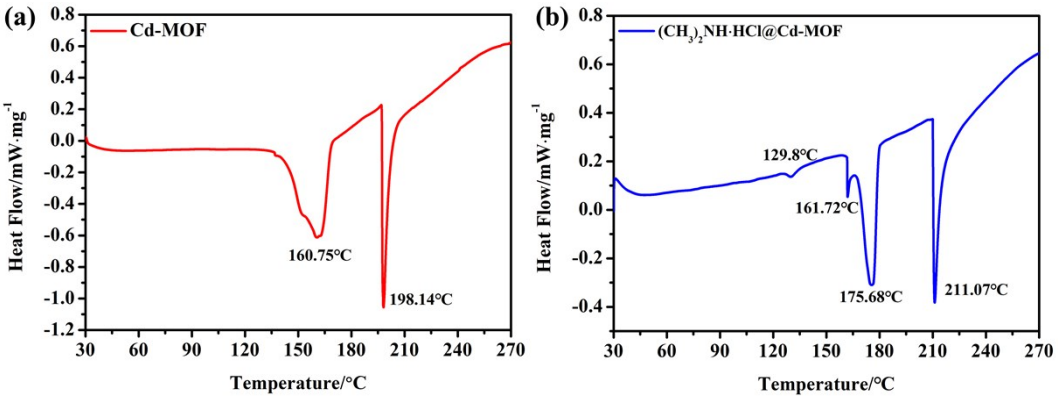

Fig. S8 DSC curves of Cd-MOF and $(CH_3)_2NH·HCl$@Cd-MOF.

Table S1 Crystal data and structure refinement of Cd-MOF.

Name	Cd-MOF
Empirical formula	$C_{68}H_{69}Cd_4N_8O_{24}$
Formula weight	1831.91
Temperature/K	293.15
Wavelength/Å	0.71073
Crystal system	Monoclinic
space group	C2
a/Å	25.895(2)
b/Å	26.301(2)
c/Å	12.2932(11)
α/°	90

β/°	91.478(4)
γ/°	90
Volume/Å^3	8369.7(13)
Z	4
ρ_{calc}mg/cm^3	1.4504
Absorption coefficient/mm^{-1}	1.074
F(000)	3668
Crystal size/ mm^3	0.03 x 0.02 x 0.01
Theta range for data collection/°	2.95 to 25.02
Index ranges	−30<=h<=30 −31<=k<=31 −14<=l<=14
Reflections collected	148974
Independent reflections	14755 [R(int) = 0.0543]
Absorption correction	Semi−empirical from equivalents
Max. and min. transmission	0.7457 and 0.6435
Refinement method	Full−matrix least−squares on F^2
Data/restraints / parameters	14755 / 21 / 960
Goodness−of−fit on F^2	1.051
Final R indices [I>2sigma(I)]	R_1 = 0.0563, wR_2 = 0.1536
R indices (all data)	R_1 = 0.0578, wR_2 = 0.1552
Absolute structure parameter	0.05(4)
Largest diff. peak/hole / e Å^{-3}	2.93 and -1.59

Table S2 Selected bond lengths [Å] and angles [°] for Cd-MOF.

Bond lengths (Å)		Bond angles (°)	
Cd(1)−O(3)#1	2.507(9)	Cd(3)−N(5)	2.387(11)
Cd(1)−N(1)#1	2.282(10)	Cd(3)−N(6)	2.307(11)
Cd(1)−O(2)	2.260(8)	Cd(3)−O(15)	2.446(10)
Cd(1)−O(2)#1	2.279(8)	Cd(3)−O(14)	2.264(8)
Cd(1)−O(8)	2.334(9)	Cd(3)−O(10)	2.299(7)
Cd(1)−N(2)	2.390(10)	Cd(3)−O(19)	2.354(9)
Cd(2)−N(3)	2.420(7)	Cd(4)−O(17)#3	2.398(9)
Cd(2)−O(6)#2	2.410(9)	Cd(4)−O(23)#4	2.465(9)

Cd(2)−O(11)	2.442(9)	Cd(4)−O(22)	2.256(7)
Cd(2)−O(14)	2.275(8)	Cd(4)−O(22)#4	2.271(8)
Cd(2)−O(10)	2.275(8)	Cd(4)−N(7)	2.381(10)
Cd(2)−N(4)	2.300(11)	Cd(4)−N(8)#4	2.282(11)

Bond angles (°)

N(1)#1−Cd(1)−O(3)#1	71.7(3)	N(5)−Cd(3)−O(15)	89.4(3)
N(1)#1−Cd(1)−O(8)	86.4(4)	N(6)−Cd(3)−N(5)	86.0(4)
N(1)#1−Cd(1)−N(2)	96.3(4)	N(6)−Cd(3)−O(15)	71.7(3)
O(2)−Cd(1)−O(3)#1	136.5(3)	N(6)−Cd(3)−O(19)	96.9(4)
O(2)#1−Cd(1)−O(3)#1	149.7(3)	O(14)−Cd(3)−N(5)	97.9(4)
O(2)#1−Cd(1)−N(1)#1	80.3(3)	O(14)−Cd(3)−N(6)	80.8(3)
O(2)−Cd(1)−N(1)#1	143.7(3)	O(14)−Cd(3)−O(15)	152.5(3)
O(2)−Cd(1)−O(2)#1	73.7(3)	O(14)−Cd(3)−O(10)	74.3 (3)
O(2)#1−Cd(1)−O(8)	109.7(3)	O(14)−Cd(3)−O(19)	106.6(3)
O(2)−Cd(1)−O(8)	79.2(3)	O(10)−Cd(3)−N(5)	105.4(3)
O(2)#1−Cd(1)−N(2)	86.8(3)	O(10)−Cd(3)−N(6)	152.0(3)
O(2)−Cd(1)−N(2)	106.9(3)	O(10)−Cd(3)−O(15)	132.5 (3)
O(8)−Cd(1)−O(3)#1	80.2(3)	O(10)−Cd(3)−O(19)	78.5(3)
O(8)−Cd(1)−N(2)	163.5(4)	O(19)−Cd(3)−N(5)	165.5(4)
N(2)−Cd(1)−O(3)#1	85.2(3)	O(19)−Cd(3)−O(15)	78.1(3)
N(3)−Cd(2)−O(11)	87.1(2)	O(17)#3−Cd(4)−O(23)#4	80.7(3)
O(6)#2−Cd(2)−N(3)	162.0(4)	O(22)−Cd(4)−O(17)#3	77.8(3)
O(6)#2−Cd(2)−O(11)	77.3(3)	O(22)#4−Cd(4)−O(17)#3	108.9(3)
O(14)−Cd(2)−N(3)	107.3(3)	O(22)#4−Cd(4)−O(23)#4	150.9 (3)
O(14)−Cd(2)−O(6)#2	77.9(3)	O(22)−Cd(4)−O(23)#4	134.3(3)
O(14)−Cd(2)−O(11)	132.8(3)	O(22)−Cd(4)−O(22)#4	74.7(3)
O(14)−Cd(2)−O(10)	74.6(3)	O(22)−Cd(4)−N(7)	106.1(3)
O(14)−Cd(2)−N(4)	151.4(4)	O(22)#4−Cd(4)−N(7)	87.1(3)
O(10)−Cd(2)−N(3)	88.9(3)	O(22)#4−Cd(4)−N(8)#4	80.9(3)
O(10)−Cd(2)−O(6)#2	109.1(3)	O(22)−Cd(4)−N(8)#4	145.2(3)
O(10)−Cd(2)−O(11)	152.0(3)	N(7)−Cd(4)−O(17)#3	164.0(4)
O(10)−Cd(2)−N(4)	80.9(3)	N(7)−Cd(4)−O(23)#4	85.9(3)
N(4)−Cd(2)−N(3)	86.6(4)	N(8)#4−Cd(4)−O(17)#3	87.2(4)
N(4)−Cd(2)−O(6)#2	96.7(4)	N(8)#4−Cd(4)−O(23)#4	72.0(3)
N(4)−Cd(2)−O(11)	71.2(3)	N(8)#4−Cd(4)−N(7)	96.9(4)

Table S3 Selected hydrogen bond lengths [Å] for Cd-MOF.

D	A	d(D−H)	d(H...A)	<DHA	d(D...A)
O3	O7 #2	0.83(3)	2.28(12)	116(11)	2.748(12)
O23	O18#1	0.83(3)	1.95(10)	142(15)	2.653(12)

D: Donor; A: Acceptor

Symmetry transformations used to generate equivalent atoms: #1: 2−x,y,1−z #2: −1/2+x, 1/2+y, z #3: x −1/2, y−1/2, z #4: 1−x,y,1−z

Table S4 The list of frequency, remnant polarity (Pr) and coercive field (Ec) in molecule ferroelectrics.

Compounds	*f*/Hz	P_r/μC·cm^{-2}	E_c/ kV·cm^{-1}	Ref.
$(CH_3)_2NH{\cdot}HCl$@Cd−MOF	1000	0.17	1.88	This work
[a]$(CH_3NH_3)_{12}\{Cu^{II}_{24}[(S,S)\text{-hismox}]_{12}(OH_2)_3\}\cdot 178H_2O$	10-200	1.06	−	1
$[Nd(C_4H_5O_6)(C_4H_4O_6)][3H_2O]$	50	0.2	−	2
[b]R- $[Zn_4(HL)_2(L)_2(CH_3OH)_2](NO_3)_2$	100	6.3	1.49	3
[c]$[Cd(Imazethapyr)_2]$	200	0.006	1.1	4
$[Cu_3(4,4-bpy)_5]_2[H_2SiW_{11}O_{39}]\cdot 5H_2O$	200	0.015	2.2	5
[d]$[Cu_2L_4(H_2O)_2]\cdot(ClO_4)_4\cdot(H_2O)_5\cdot(CH_3OH)$	0.1	−	16	6
[d]$[Cu_3L_6(H_2O)_3]\cdot(ClO_4)_5\cdot(NO_3)\cdot(H_2O)_{11}$	0.1	−	30	6
[e]$\{[Zn(TBPR)\subset 0.25(HClO_4)](0.25HClO_4)\}n$	500	1.8	2.5	7
[f] PD−DMACoF	50	−	−	8
[g]$[R,R-ZnLDy(\mu-OAc)(NO_3)_2]$	1	−	17	9
[h]$(DAMP)_3(Cu_4Br_4)_2(H_2O)_3$	12	2.5	1.0	10

[a]H_2Me_2-(S,S)-hismox = bis[(S)-histidine]oxalyl diamide, [b]H_2L = 2-[(1-benzyl-2-hydroxy-ethylimino)-me-thyl]-6-methoxy-phenol), [c]H−Imazethapyr = 2−(4,5−dihydro−4−methyl−4−(1−methylethyl)−5−oxo−1H−imidazol−2−yl)−5−ethyl−3−pyridine-carboxylic acid, [d]L=PhPO(NH-3-pyridyl)$_2$, [e]TBPR = (S)−N−2−tetrazoylbenzylproline, [f]PD−DMA = perdeuterodimethylammonium, [g]H_2L=phenol,2,2−[2,2−diphenyl−1,2−ethanediyl]bis[(E)−nitrilomethyl−idyne]−bis(6−methoxy), [h]DAMP = (S)−1,4−diallyl−2−methylpiperazine

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