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

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Ferroelectrics as a kind of crucial functional materials have attracted much interest since ferroelectricity was discovered in 1920. Herein, an unusual high-frequency ferroelectric $(CH_3)_2NH{\cdot}HCl$@Cd-MOF was successfully obtained through dual-step synthetic methodology. A chiral porous Cd-MOF with the channel size of 6.8×6.8 Å was synthesized via self-assembling of chiral Schiff-base ligands and Cd^{2+} ions. Subsequently, polarizable $(CH_3)_2NH{\cdot}HCl$ was modified into the channel of Cd-MOF and hence a host-guest system of $(CH_3)_2NH{\cdot}HCl$@Cd-MOF was formed. The as-synthesized $(CH_3)_2NH{\cdot}HCl$@Cd-MOF displays obvious ferroelectricity at high frequency of 1 kHz. Such a high-frequency ferroelectric is extremely rare ferroelectrics in MOF-based ferroelectric materials, and the feature of high-frequency affords $(CH_3)_2NH{\cdot}HCl$@Cd-MOF possibility for ferroelectric memories. The results again demonstrate that post-synthetic modification is a promising approach for achieving rational and precise design of ferroelectric materials.

Introduction

Up to now, ferroelectricity has been proposed for one hundred years and researchers have devoted to ferroelectric's fundamental properties and potential applications since ferroelectricity was discovered.[1] Ferroelectric materials have been applied to piezoelectric sensors, dielectric capacitors, ferroelectric memories, optical devices and so forth.[2,3] Recently, ferroelectric are generally obtained utilizing materials crystallizing in polar point group, which is an indispensable condition to construct ferroelectricity.[4-6]Among strategies, "quasi-spherical theory" and "momentum matching theory" play an important role in designing molecular ferroelectric, proposed by Xiong et al.[7] Meanwhile, some achievements were made under the guidance of that theory, such as a ceramic-like molecular ferroelectric[8] and a kind of two-dimensional organic-inorganic hybrid rare-earth double perovskite ferroelectrics.[2] However, there are great challenges in rationally designing and precisely synthesizing ferroelectrics. Metal-organic frameworks (MOFs), as a class of porous crystalline material, have exhibit unique advantages in many fields owing to diverse structures and tuneable properties.[9-12] In recent years, researchers have always worked on improving or modulating the properties of MOFs by post-synthetic modification (PSM), which has been widely used in chemical sensing and asymmetric catalysis.[13-16] In the same way, post-synthetic modification is also a very important means to obtain new ferroelectric materials, and some progress has been made. For example, Xiong et al successfully obtained high temperature ferroelectric by using small molecule to modify $[H_2dabco]RbCl_3$.[17] Emilio Pardo et al reported a dual-step synthetic methodology for rationally designing chiral MOFs-based ferroelectrics.[18] Nevertheless, it should be noted that there are two factors need to take into account in synthesizing ferroelectrics by post- synthetic modification. (ⅰ): Select MOFs belonging to polar point group to create a non-central symmetric environment. (ⅱ): Choose small molecules with strong dipole moment to affect symmetry of structure in the post-modification process.[7,17-19]

Herein, a high-frequency ferroelectric $(CH_3)_2NH{\cdot}HCl$@Cd-MOF was constructed through two steps. Firstly, a chiral porous Cd-MOF with channel structure, formula as $[Cd_4(R\text{-}H_2L)_4(ina)_4]$, was successfully synthesized by a chiral Schiff-base ligand (R-H_3L = (*S,E*)-3-((2-hydroxy-3-methoxy-benzylidene)amino)-propane-1,2-diol, as shown in Fig. S1), auxiliary ligand (Hina = Isonicotinic acid) and $Cd(NO_3)_2{\cdot}4H_2O$ through solvothermal method and solvent evaporation. Subsequently, a host-guest system of $(CH_3)_2NH{\cdot}HCl$@Cd-MOF was obtained by post-synthetic modification that insert $(CH_3)_2NH{\cdot}HCl$ into the channel of Cd-MOF. $(CH_3)_2NH{\cdot}HCl$@Cd-MOF exhibits obvious ferroelectric performance under 1 kHz of high-frequency at ambient temperature, which not only is rare high-frequency ferroelectric in MOFs-based ferroelectrics but also is scarce ferroelectric built by post-synthetic approach. Meanwhile, such a high-frequency of 1 kHz indicates that it can show fast polarization switching, which is beneficial to ferroelectric memories. Combined with previous researches, it can be seen that post-synthetic modification is a potential approach to construct multifunctional ferroelectrics materials.

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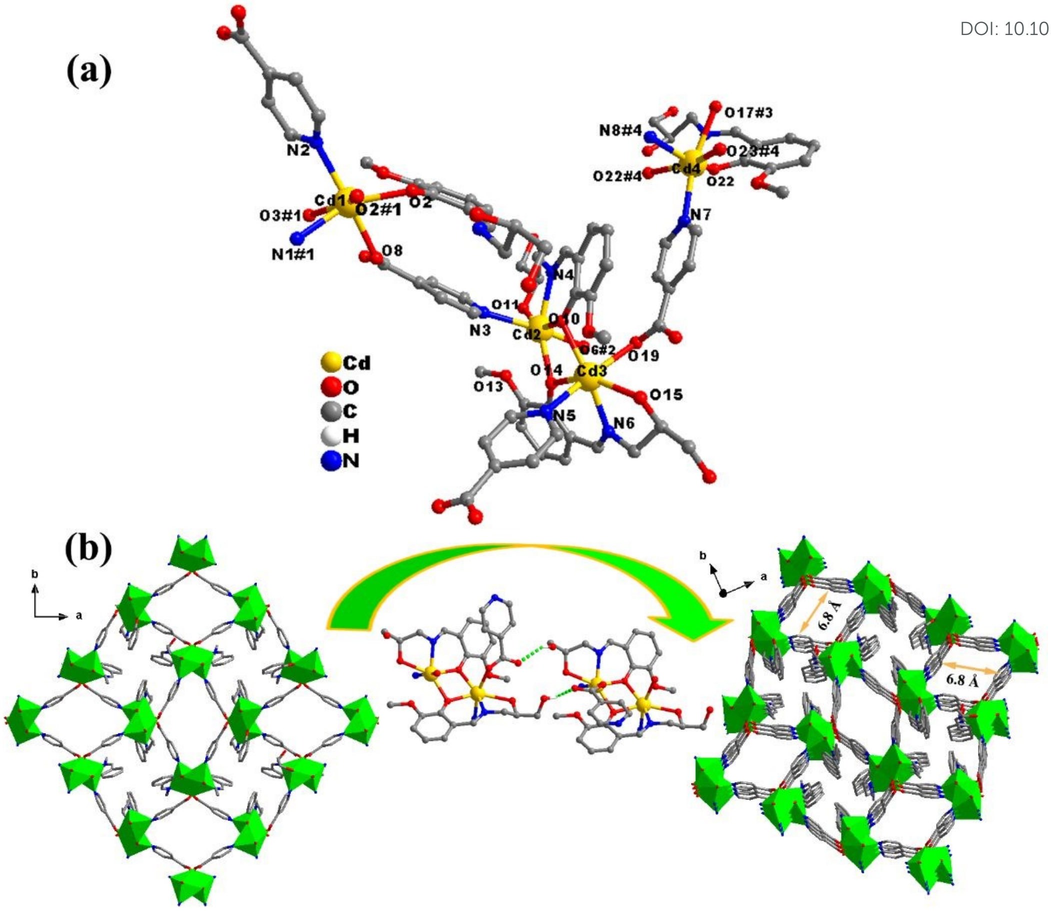

Fig. 1 (a) The minimum structural unit of Cd-MOF. (b) The 2D layered structure and 3D stacking diagram of Cd-MOF in the direction of *c*-axis. (Sectional hydrogen atoms are omitted for clarity, yellow, Cd; blue, N; red, O).

Results and discussion

General structure

Crystal structure analysis verifies that Cd-MOF crystallized in monoclinic system C2 space group. As shown in Fig. 1(a), there are four crystallography independent Cd^{2+} metal centers, four R-H_2L^- ligands and four deprotonated bridging ligands (ina$^-$). All of four Cd^{2+} ions adopt six-coordinated octahedral configurations and the coordination environment was the same. Herein, Cd1 was selected as an example to describe the structure. Cd1 is coordinated with six atoms respectively originating from one phenol hydroxyl oxygen atom (O2) in one ligand R-H_2L^-, one phenol hydroxyl oxygen atom (O2#1), one hydroxyl oxygen atom (O3#1) and one imino nitrogen atom (N1#1) of another ligand R-H_2L^-, one oxygen atom (O8) of one deprotonated bridging ligand (ina$^-$) and one nitrogen atom (N2) of another deprotonated bridging ligand (ina$^-$). Moreover, four coordinated atoms originating from two R-H_2L^- ligands compose equatorial plane of octahedron, and two atoms provided by two deprotonated bridging ligands (ina$^-$) are two vertices of octahedron. Two adjacent Cd^{2+} centers are connected by two phenolic hydroxyl oxygen atoms forming a dual-nuclear structural unit [$Cd_2N_4O_6$] (Fig. S2). Each dual-nuclear unit is linked by bridging ligand Hina constituting 2D layer structure, which is further connected by O-H···O hydrogen bond to compose 3D skeleton structure (Fig. 1(b)). And the channel size of Cd-MOF is 6.8×6.8 Å, which is roughly estimated in the *Diamond* software. The Cu–O/N bond length are in the range of 2.256(7)–2.507(9) Å, and the O–Cu–N/O bond angel is 71.2(3)–165.5(4)°, all of which are comparable to the analogous Cd(II) complexes in the literature.[20-22] What's more, powder X-ray diffraction patterns of Cd-MOF are almost consistent with its simulation of single crystals, indicating that the phase purity of synthesized Cd-MOF is better (Fig. S3). The crystallographic data and structure refinement, main bond length, bond angle and hydrogen bond data for Cd-MOF are respectively listed in Table S1, S2 and S3.

Characterization of $(CH_3)_2NH·HCl$@Cd-MOF

In order to demonstrate $(CH_3)_2NH·HCl$ was successfully modified into the channels of Cd-MOF, the Fourier-transform infrared (FT-IR) spectra of Cd-MOF, $(CH_3)_2NH·HCl$ and $(CH_3)_2NH·HCl$@Cd-MOF were measured. As shown in Fig. 2(a), vibration absorption peak of $(CH_3)_2NH·HCl$@Cd-MOF at 1585 cm^{-1} originates from the bending vibration of N-H of $(CH_3)_2NH·HCl$ (1587 cm^{-1}), and the slight shift might be attributed to the weak interaction between $(CH_3)_2NH·HCl$ and Cd-MOF, which reveals the successful synthesis of the $(CH_3)_2NH·HCl$@Cd-MOF. Meanwhile, the presence of Cl elements can be discovered in EDX mapping of $(CH_3)_2NH·HCl$@Cd-MOF (Fig. S4), while Cd–MOF without post-modification doesn't contain Cl elements, which further

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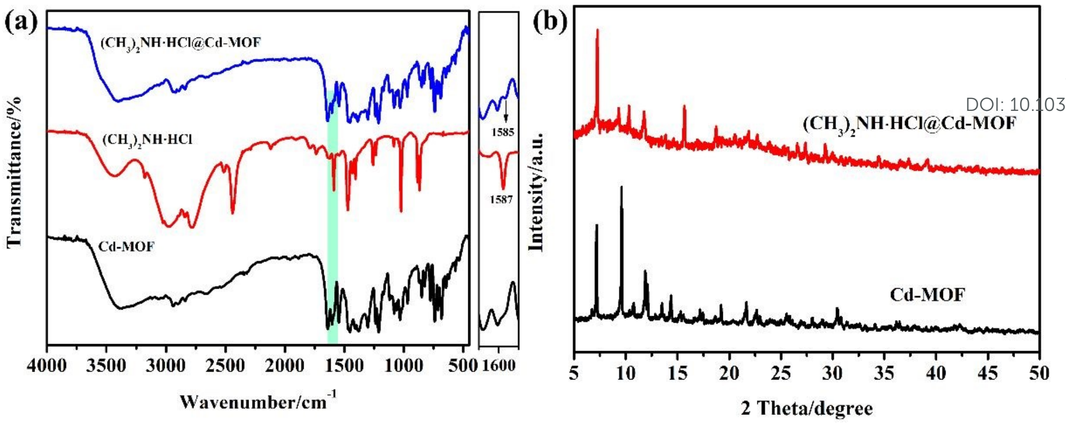

Fig. 2 (a) FT-IR spectra of Cd–MOF, $(CH_3)_2NH·HCl$ and $(CH_3)_2NH·HCl@Cd–MOF$. (b) Powder X-ray diffraction patterns of Cd–MOF and $(CH_3)_2NH·HCl@Cd–MOF$.

indicates that $(CH_3)_2NH·HCl@Cd$-MOF was successfully constructed.

The structural stability of $(CH_3)_2NH·HCl@Cd$-MOF was proved by powder X-ray diffraction patterns. In Fig. 2(b), the matched main patterns of $(CH_3)_2NH·HCl@Cd$-MOF and Cd-MOF testify its structural stability. However, partial diffraction peaks are slightly different, which might be caused by $(CH_3)_2NH·HCl$ introduced or impurity of the measured sample. What's more, thermogravimetric curves (Fig. S5) displays that larger weight loss of $(CH_3)_2NH·HCl@Cd$-MOF (3%) compared to Cd-MOF (1.5%) in the temperature range of 30-170°C, which is related to the escape of $(CH_3)_2NH·HCl$ from the channels of Cd-MOF.

Ferroelectric property of $(CH_3)_2NH·HCl@Cd$-MOF

Single crystal structure analysis verified that Cd-MOF crystallized in C2 space group belonging to polar point group, exhibiting potential ferroelectricity.[19] However, the as-synthesized Cd-MOF doesn't show ferroelectricity objectively. Fortunately, Cd-MOF possesses larger channels with the size of 6.8×6.8 Å, easily polarized ammonium salt $(CH_3)_2NH·HCl$ can be selected to insert into Cd-MOF in order to construct ferroelectric. Hysteresis loop indicates that $(CH_3)_2NH·HCl@Cd$-MOF presents obvious ferroelectric performance. As shown in Fig. 3(a), when test voltage is 100 V, both remnant polarity (P_r) and coercive field (E_c) are gradually decreasing with the frequency range from 0.5 to 10 kHz. When frequency is 0.5 kHz, saturated polarization starts slightly decreasing with applied electric filed increase, which indicate mild leakage current appears. Therefore, the frequency of 1 kHz is selected to research ferroelectric property in different voltage. The remnant polarity (P_r) and coercive field (E_c) are gradually increasing as the voltage varies from 30 to 100 V (Fig. 3(b)). When voltage is 100 V, the coercive field (E_c) is 1.88 kV/cm and remnant polarity (P_r) is 0.17 μC/cm^2, which are comparable to classic ferroelectric Rochelle salt (0.25 μC/cm^2)[23] and are on a par with partial MOF ferroelectrics.[24-28] The leakage current of $(CH_3)_2NH·HCl@Cd$-MOF is less than 10^{-7} A (Fig. S6), indicating that hysteresis loop dates from natural ferroelectricity.[29-31] According to reported work, it might be inferred that the ferroelectricity of $(CH_3)_2NH·HCl@Cd$-MOF could be relative to ammonium cations, which have been discovered to be beneficial to the generation of ferroelectricity.[18, 32-34] Furthermore, $(CH_3)_2NH·HCl@Cd$-MOF exhibits better ferroelectric performance at high frequency of 1 kHz, which is extremely rare in MOF-based ferroelectrics according to reported literature (Table S4). Meanwhile, such a high-frequency ferroelectric is also compared with some organic salts or perovskite ferroelectrics such as TMC−1 (1 kHz) [35], quinuclidinium periodate (40 Hz)[36] and HDA–BiI_5 (50 Hz)[37]. Moreover, high-frequency ferroelectrics indicates that they can show fast polarization switching, which is favour of practical application such as information storage.[38] That means high-frequency ferroelectric of $(CH_3)_2NH·HCl@Cd$-MOF possesses potential applied to ferroelectric memories.

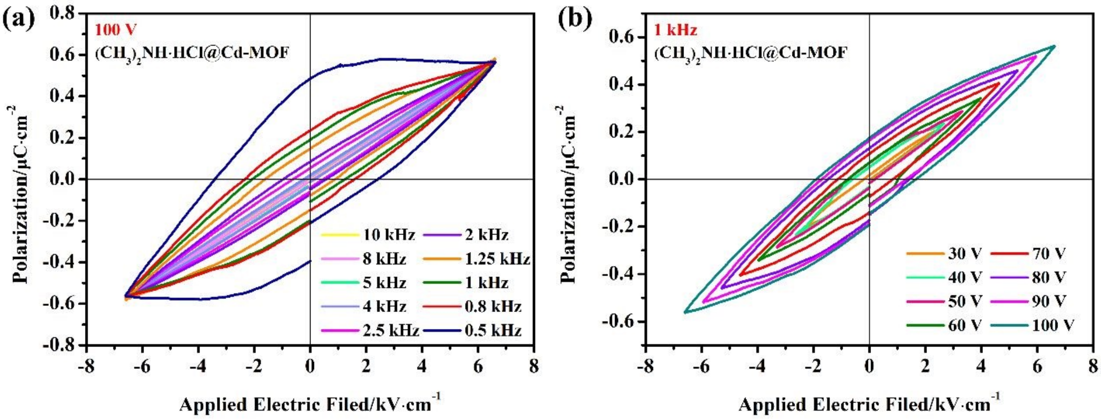

Fig. 3 Hysteresis loop of $(CH_3)_2NH·HCl@Cd$-MOF at room temperature: (a) hysteresis loop of $(CH_3)_2NH·HCl@Cd$-MOF in the range of 0.5-10 kHz when the test voltage is 100 V, (b) hysteresis loop of $(CH_3)_2NH·HCl@Cd$-MOF in the range of 30-100 V when the test frequency is 1 kHz.

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Dielectric property and DSC analysis of $(CH_3)_2NH{\cdot}HCl$@Cd-MOF

Dielectric properties of $(CH_3)_2NH{\cdot}HCl$@Cd-MOF were tested using a pellet by grinded crystal powder. As shown in Fig. S7, dielectric constant doesn't exhibit distinct anomaly when the temperature ranges from 30 to 270°C, which illustrates $(CH_3)_2NH{\cdot}HCl$@Cd-MOF doesn't appear to ferroelectric phase transition before its structure is destroyed. Moreover, the results can also be further demonstrated by DSC analysis. As shown in Fig. S8, no significant thermal change was observed before the decomposition temperature of Cd-MOF and $(CH_3)_2NH{\cdot}HCl$@Cd-MOF, which further indicates that the ferroelectric phase transition of $(CH_3)_2NH{\cdot}HCl$@Cd-MOF doesn't occur before the structural start collapsing. The thermal changes of Cd-MOF at 160.75°C and 198.14°C are caused by its structural change. The thermal change of $(CH_3)_2NH{\cdot}HCl$@Cd-MOF at 129.8°C is caused by escape of $(CH_3)_2NH{\cdot}HCl$, while the thermal changes at 161.72°C, 175.6°C and 211.07°C are attributed to structural collapse. Thermal changes of Cd-MOF and $(CH_3)_2NH{\cdot}HCl$@Cd-MOF are well-matched with TG analysis.

Conclusions

In summary, we have inserted polarizable ammonium salt $(CH_3)_2NH{\cdot}HCl$ into the channel of chiral porous Cd-MOF via a strategy of post-synthetic modification, achieving a host-guest system of $(CH_3)_2NH{\cdot}HCl$@Cd-MOF, which showed unusual high-frequency ferroelectricity with the remnant polarity (P_r) of 0.17 $\mu C/cm^2$ at the high frequency of 1 kHz. What' more, such a high-frequency ferroelectric is extremely rare in MOF-based ferroelectrics, and the characteristic of high-frequency affords $(CH_3)_2NH{\cdot}HCl$@Cd-MOF potential for memory devices. This work once again illustrates that post-synthetic modification plays an important role in rationally and precisely designing ferroelectrics, which will provide an impetus for further enlarging the scope of ferroelectric materials and constructing a number of multifunctional materials with ferroelectric, sensors and optoelectronic properties.

Experimental

Materials and Measurements

All chemicals were available and used without further purification. Elemental analyses of C, H and N were tested on a Perkin–Elmer 2400 elemental analyzer. Infrared spectra were collected by the FT-IR spectrometer using KBr pellets under the range of 4000-450 cm^{-1}. Powder X-ray diffraction (PXRD) patterns were measured on an EMPYREAN PANALYTICAL apparatus with single crystals powder in the range of 5-80° using Cu-Kα radiation. TG curves were attained with a NETZSCH STA409pc apparatus under a heating rate of 5 °C/min from 30 to 1200°C in the nitrogen protection. DSC curves were measured using DSC Q2000 with a heating rate of 5 °C/min under nitrogen atmosphere. EDX mapping was measured on the Hitachi S4800 and the accelerating voltage is 20 kV in test process. The P-E hysteresis loop and leakage current curves were performed at room temperature using a Premier II ferroelectric instrument. Temperature dependence of the dielectric constant was measured through E4980A Precision impedance analyzer. The electric polarization, dielectric constant and leakage current curves were measured using tablets, which were pressed using crystal powder, coated with silver paste on two opposite surfaces.

Synthesis of ligand R-H_3L

The Schiff-base ligand R-H_3L was obtained as following procedure. R-3-amino-1,2-propanediol (5 mmol, 0.456 g) was dissolved in methanol solution (5 mL), and then the methanol solution (5 mL) including o-vanillin (5 mmol, 0.761 g) was slowly added under stirring. Then, triethylamine (2.1 mL) was added in above mixed solution. Continue stirring two hours at room temperature, the light-yellow solution containing required product was obtained and used without further purification.[39]

Synthesis of Cd-MOF $[Cd_4(R\text{-}H_2L)_4(ina)_4]$

Ligand R-H_3L (0.5 mmol), auxiliary ligand Hina (0.5 mmol, 0.0612g) and $Cd(NO_3)_2{\cdot}4H_2O$ (0.5 mmol, 0.154g) were dissolved in methanol solution (15 mL), then ultrasound for 15 minutes. After that, the mixed solution was transferred to a Teflon-lined stainless-steel autoclave and reacted at 80°C for 3 days and slowly cooled to room temperature. Next to the mixture was filtered and the filtrate slowly evaporated at room temperature. Finally, yellow block crystals were obtained after about three weeks, which were collected through filtering and air-drying. Elemental analysis calcd for Cd-MOF (%): C, 44.58; H, 3.79; N, 6.12. Found (%): C, 44.39; H,3.98; N, 6.28.

Construction of $(CH_3)_2NH{\cdot}HCl$@Cd-MOF

The procedure of constructing $(CH_3)_2NH{\cdot}HCl$@Cd-MOF refers to previous research.[18,40] $(CH_3)_2NH{\cdot}HCl$ (2 mmol, 0.16 g) was dissolved in 15 mL of distilled water, next to grounded Cd-MOF (50 mg) were added to above solution and then ultrasound until the mixture was uniform. The suspension was maintained 24 hours at room temperature. Finally, the product was collected through centrifugation, repeatedly washing with distilled water and dried at room temperature.

Crystal data collection and refinement

Crystallographic data of Cd-MOF were collected on a Bruker Apex II diffractometer equipped with a CCD area detector and graphite–monochromatic Mo–Kα radiation (λ = 0.71073 Å). Absorption corrections were applied using the SADABS program. Structures were solved by direct methods and refined by the full–matrix least–squares method on F^2. All non–hydrogen atoms were refined with anisotropic thermal parameters, while all hydrogen atoms were added to appropriate positions in theory and refined with isotropic thermal parameters by a riding model. After the final refinement, a few high-electron-density Q peaks were discovered in Cd-MOF, which probably is caused by indefinable and disorder solvent molecules. Thus, *PLATON SQUEEZE* program was used to "squeeze" these free solvent molecules. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center with the deposition numbers CCDC 1949504.

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Conflicts of interest

"There are no conflicts to declare".

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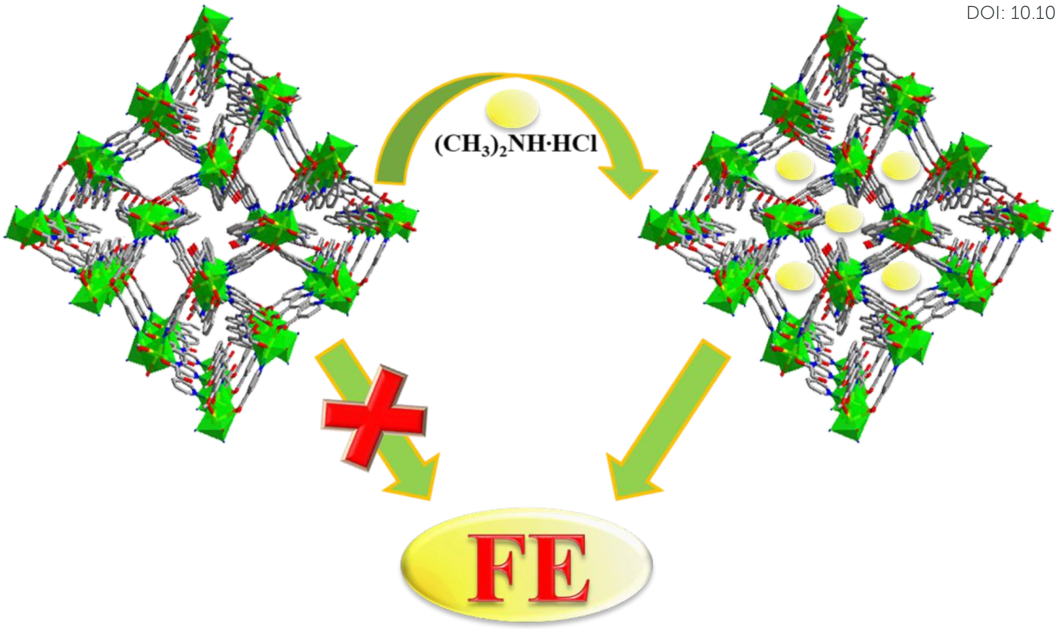

An unusual high-frequency ferroelectric was successfully synthesized via a strategy of post-synthetic modified metal-organic frameworks.