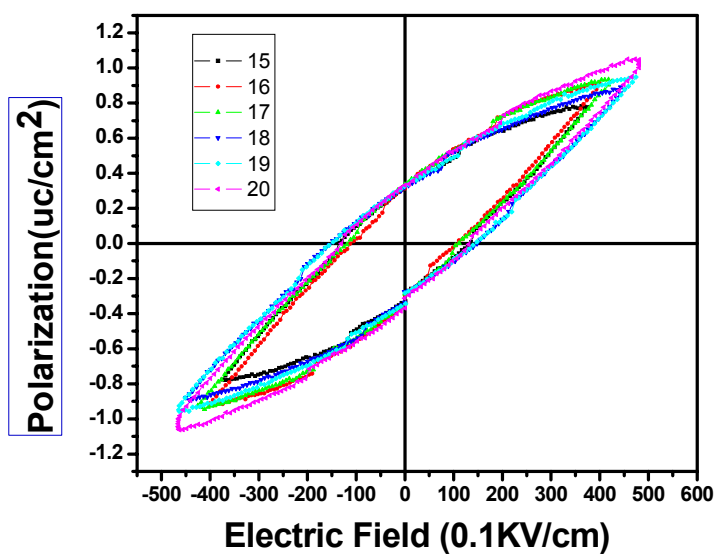


### Supporting information

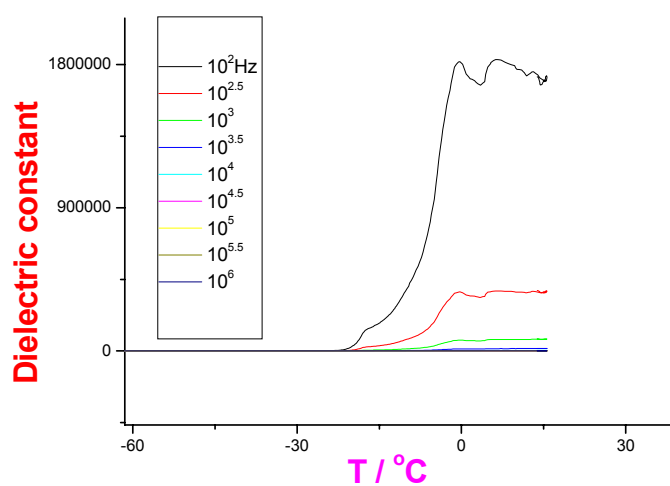
**The measurement of SHG responses:** Approximate estimations of the second order nonlinear optical intensity were obtained by comparison of the results from a powder sample (80-150  $\mu\text{m}$  diameter) in the form of a pellet (Kurtz powder test),<sup>9</sup> with that obtained for KDP. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate the SHG signal. The backward scattered SHG light was collected using a spherical concave mirror and passed through a filter that transmits only 532 nm radiation. Thus, the SHG responses of **1** are about 20 times larger than that of KDP, respectively.

**The measurement of electric hysteresis loop:** The ferroelectric property of solid state sample was measured by a powder sample in the form of a pellet using an RT66 ferroelectric tester at room temperature while sample was immersed in insulating oil. The electric hysteresis loop was observed by Virtual Ground Mode (The curve is smoothly fitted).

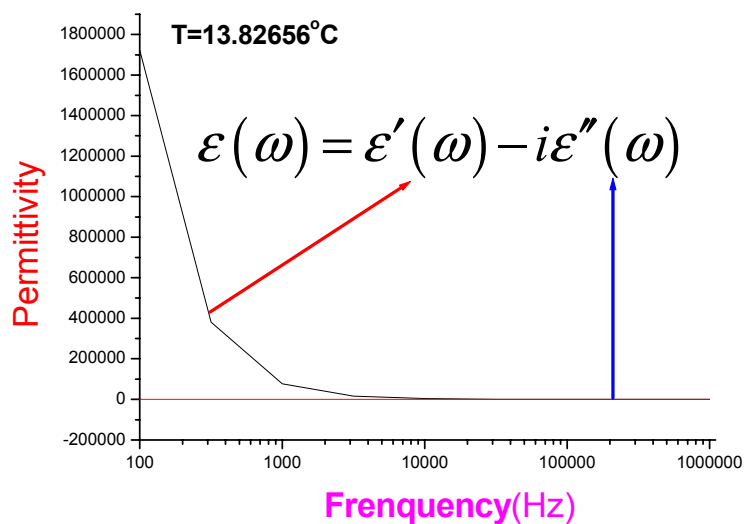
4. **The measurement of permittivity** is conducted using an automatic impedance HP4191A Analyzer with frequency of 100 to 1M Hz. (Reference: Zhu, J.-S. et al., *J. Appl. Phys.* **2004**, *95*, 3126, E-mail address: jszhu@nju.edu.cn).



**Figure 1S.** The electric hysteresis loop of MOF **2** was observed by Virtual Ground Mode in a powdered sample in the form of a pellet using an RT66 ferroelectric tester at room temperature.



**Figure 2S.** The temperature dependence of the real part of the dielectric response of MOF **1** at different frequencies.



**Figure 3S.** The frequency dependence of permittivity ( $\epsilon=\epsilon'(\omega)-i\epsilon''(\omega)$ ) of MOF **1** at the temperature of 13.8 °C.