Supporting information

Experimental Section

Materials and Synthesis

Imidazole (Macklin, AR), Niobium pentoxide (Macklin, AR), Hydrofluoric acid (48% aq., Aldrich) were used as received without further manipulation. A mixture of niobium pentoxide (1.49 mmol, 0.398g), imidazole (2.99 mmol, 0.204 g), hydrofluoric acid (1 mL) and 5 mL H_2O was sealed in a 25-mL teflon-lined bomb and was kept at 190 ℃ for 24 hours, which was then slowly cooled to room temperature to forming a clear solution. The solution was allowed to evaporate at around 293 K. After about one week, a colourless, transparent crystals of [HIm][NbOF$_4$] were formed. The purity of **1** was proved by power X-ray diffraction (Figure S2). Yield:0.580 g (76.1%, based on Nb). Elemental analysis calcd (%) for (**1**): C 14.14, N 10.93, H 1.94; found (%): C 14.24, N 11.07, H 1.59.

Physical Measurements

Elemental analysis for C, H and N was carried on a Vario MICRO analyser. Thermogravimetric analysis （TGA）was measured on a NETZSCH STA 449F3 instrument at a heating rate of 10 K·min^{-1} under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on the DSC 214 Polyma instrument in the temperature range of 240 K-320 K with a heating/cooling rate of 20 K·min^{-1} at atmospheric pressure. Powder X-ray diffraction patterns were recorded on a Rigaku DMax 2500 powder diffractometer.

X-ray diffraction experiments

Variable-temperature single-crystal X-ray diffraction studies were recorded on a Rigaku synergy diffractometer using the ω scan technique with Mo-Kα (λ = 0.71073 Å) radiation. All structures were solved by direct methods and refined by full-matrix least squares techniques in SHELX2016 program package. Bonds angles and selected bonds lengths are given in Table S2. The hydrogen bonds are shown in Table S1. CCDC 2130080 and 2130081 contain the supplementary crystallographic data for this paper. These data are freely available from The Cambridge Crystallographic Data Centre.

Dielectric measurements

The dielectric experiments for **1** was to grind the crystals into powder and then pressed them into dense pellets. The complex dielectric constant curves were performed at temperatures ranging from 230 K to 300 K on a Tonghui TH2828A impedance analyser with different frequencies and applied voltages of 1.0 V.
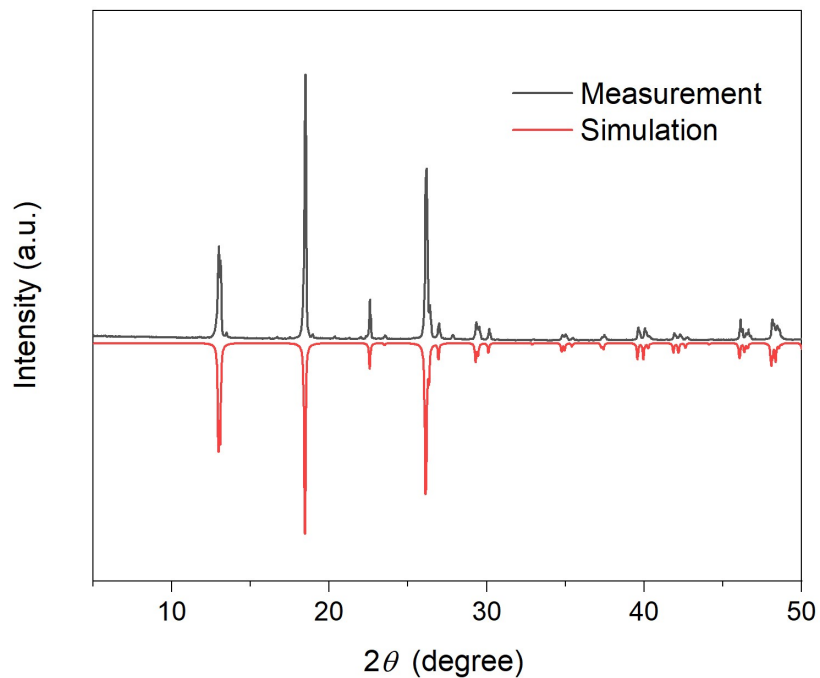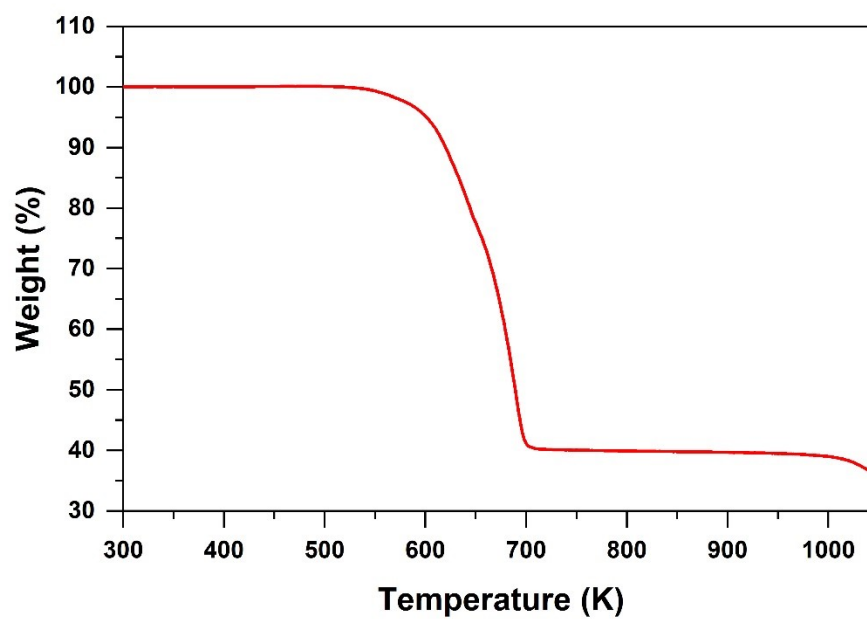
1. FigureS1-S4

Figure S2. The TG curves of **1** in flowing N_2 with a heating rate of 10 K/min.
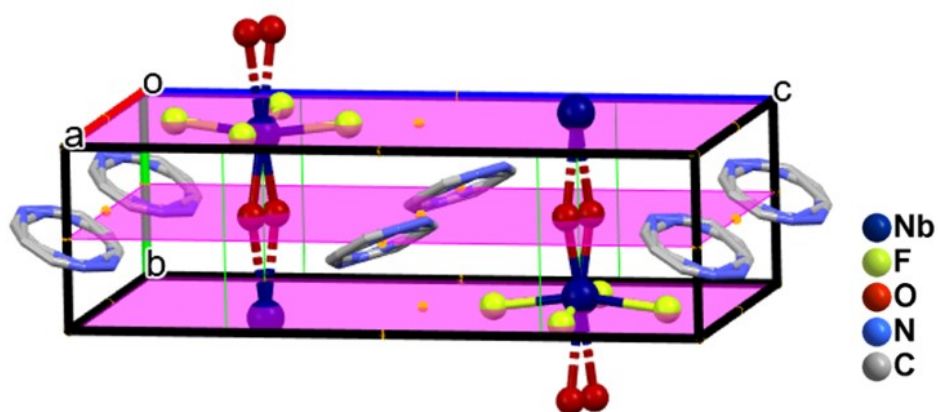
Figure S3. Packing diagram of **1** at 270 K. The green line represents the 2-fold of rotation and the pink plane represents the symmetry planes; hydrogen atoms of imidazole are omitted for clarity.
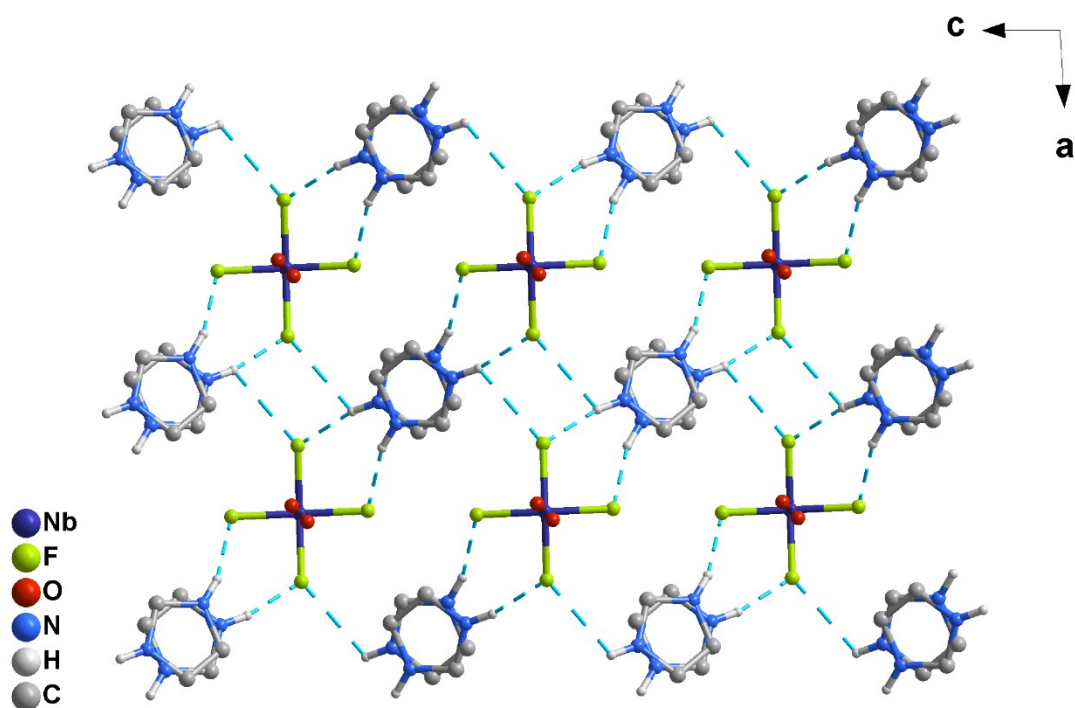

Figure S4. Hydrogen bonds of **1** at 270 K. The carbon-bonded hydrogen atoms are omitted for clarity.
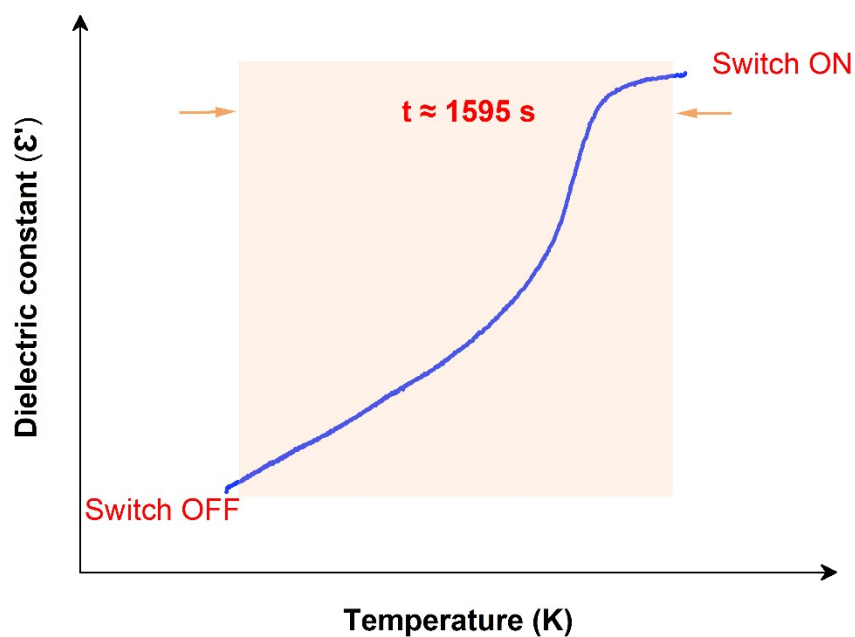
Figure S4. Schematic diagram of switchable response time for **1**.

2. TableS1-S3

Table S1. Selected hydrogen bonds for compounds **1** at 270 K.

1(270 K)				
D-H…A	d(D-H）[Å]	d (H…A）[Å]	d (D…A）[Å]	∠(DHA) [°]
N1-H1…F1	0.86	2.06	2.91	167
N2-H2…F2	0.86	2.13	2.97	162

Table S2. Selected bond lengths [Å] for **1** at 270 K and 305 K.

1 (270 K)		**1** (305 K)	
Nb1-F1	1.895(11)	Nb1-F1	1.904(5)
Nb1-F1[i]	1.895(10)	Nb1-F1[iv]	1.904(5)
Nb1-F2	1.894(10)	Nb1-F2	1.900(5)
Nb1-F2[i]	1.894(10)	Nb1-F2[iv]	1.900(5)
Nb1-O1	1.757(19)	Nb-O1	1.740(7)
Nb1-O1[i]	1.757(19)	Nb-O1[v]	2.198(7)
Nb1-O1[ii]	2.217(18)	N1-C1	1.329(13)
Nb1-O1[iii]	2.217(18)	N1-C3	1.331(13)
N1-C1	1.383(18)	N2-C2	1.328(13)

N1-C3	1.365(19)	N2-C3	1.326(13)
N2-C2	1.376(18)	C1-C2	1.380(2)
N2-C3	1.372(18)		
C1-C2	1.383(10)		

Symmetry codes: (i) 1-x, y, 1/2-z; (ii) x, -1+y, 1/2-z; (iii) x, -1+y, 1/2-z;

(iv) 3/2-x, 1-y, z; (v) x, y, z-1.

Table S3 Selected angles [°] for **1** at 270 K and 305 K.

1 (270 K)		**1** (305 K)	
F1-Nb1-F1^i	163.4(8)	F1-Nb1-F1^i	163.0(3)
F1-Nb1-O1^{ii}	87.6 (8)	F1-Nb1-O1	81.52(14)
F1^i-Nb1- O1^{ii}	75.9(8)	F1^i-Nb1- O1	81.52(14)
F1-Nb1-O1^{iii}	87.6(8)	F2-Nb1- F1^i	88.83(3)
F2-Nb1- F1^i	89.9(6)	F2-Nb1- F1	88.83(3)
F2-Nb1- F1	88.0(6)	F2^i-Nb1- F1	88.83(3)
F2^i-Nb1- F1	89.9(6)	F2^i-Nb1- F1^i	88.83(3)
F2^i-Nb1- F1^i	88.0(6)	C3-N1-C1	106(2)
C3-N1-C1	108.8(11)	C3-N2-C2	103(4)
C3-N2-C2	108.8(11)	N2-C2-C1	108(3)
N2-C2-C1	107.5(10)	N1-C1-C2	103.9(19)
N2-C3-N1	107.6(10)		
N1-C1-C2	107.3(10)		

Symmetry codes: (i) 1-x, y, 1/2-z; (ii) x, -1+y, 1/2-z; (iii) x, -1+y, 1/2-z.

3. Calculations of ΔS and N for the cooling and heating cycles

In the cooling cycle

$$\Delta S_1 = \int_{T1}^{T2} \frac{QdT}{T}$$

$$\approx \frac{\Delta H}{T_c}$$

$$= \frac{3.301\, J{\cdot}g^{-1} \times 254\, g{\cdot}mol^{-1}}{284.4\, K}$$

=2.948 J·mol^{-1}·K^{-1}

$\Delta S_1 = R\ln N_1$

$$N_1 = exp\left(\frac{\Delta S_1}{R}\right) = exp\left(\frac{2.948\ J\cdot mol^{-1}\cdot K^{-1}}{8.314\ J\cdot mol^{-1}\cdot K^{-1}}\right)$$

=1.425

In the heating cycle

$$\Delta S_2 = \int_{T1}^{T2}\frac{QdT}{T}$$

$$\approx \frac{\Delta H}{T_c}$$

$$= \frac{3.899\ J\cdot g^{-1} \times 254\ g\cdot mol^{-1}}{276.13\ K}$$

=3.586 J·mol⁻¹·K⁻¹

$\Delta S_2 = RlnN_2$

$$N_1 = exp\left(\frac{\Delta S_2}{R}\right) = exp\left(\frac{3.586\ J\cdot mol^{-1}\cdot K^{-1}}{8.314\ J\cdot mol^{-1}\cdot K^{-1}}\right)$$

=1.539