Electronic Supplementary Material (ESI) for Chemical Communications.

An organic-inorganic hybrid material $[Me_3NCH_2CH_2F]FeBr_4$ exhibits three-step SHG on/off

Haina Zhang, Lingyu Wang, Wenjing Guo, Hu Cai,* Zhenhong Wei*

School of Chemistry and Chemical Engineering, Nanchang University, Nanchang, 330031, P. R. China.

Experimental section

Variable-temperature powder X-ray diffraction (PXRD) measurements and Fourier transform-infrared spectroscopy (FT-IR, ALPHA) were performed to measure the purity of the compound. DSC measurement was performed on a NETZSCH DSC 214 instrument with a rate of 20 K min^{-1}. For complex dielectric measurements, the polycrystalline samples were ground into powder and then pressed into a thin plate. After that, the plate is cut into a rectangular shape with dimensions slightly and coated with silver glue on both sides of the rectangle to connect with the electrode for dielectric measurements. The dielectric constant measurement was carried out on TH2828 analyzer over the frequency range 500 Hz - 1 MHz to record the behavior of phase transition. The SHG response of the compound was obtained on an Edinburgh FLS 920 instrument revealed that the compound was a multi-step nonlinear switching material. Single crystal data were obtained using a Rigaku Saturn 007 diffractometer at room temperature with Mo ± Kα radiation ($\lambda = 0.710703$ A). The structure was solved by the direct method and refined using the full matrix least squares technique. Non-H atoms were anisotropic refined using all reflections of $I > 2\sigma(I)$. Hydrogen atoms are added geometrically and refined using the $U_{iso} = 1.2\ U_{eq}$ model, and the associated bond lengths and angles are listed in **Table S1**.

Material synthesis and crystal growth

All reagents and solvents in this experiment were of reagent grade and used without further purification. (2-Fluoroethyl)trimethylammonium bromide [$Me_3NCH_2CH_2F$]Br and tetramethylamine iodide [Me_4N]I were synthesized by the reaction of equimolar amounts of trimethylamine (30 wt% in water) with 1-bromo-2-fluoroethane and iodoform in methanol at 90 °C for 6 h. The solvent is removed under pressure to give a mixture, which was recrystallized in n-hexane/ethanol = 1: 2 mixed solvents to give colorless solid.

[Me_4N]$FeBr_4$ was obtained by adding excess Ag_2CO_3 to the [Me_4N]I aqueous solution with stirring, resulting in the formation of AgI precipitate. After filtering, the clear solution was acidized by excess HBr solution. Subsequently, the $FeBr_3$ solution was slowly dripped into the above solution, followed by thorough stirring to achieve homogeneity, and then the mixture was left to stand for the solvent to evaporate. Yield: 1.50 g, 74.63 %.

The crystals of [$Me_3NCH_2CH_2F$]$FeBr_4$ (**1**) were grown by slow evaporation of the HBr aqueous / methanol solution containing equimolar amounts of [$Me_3NCH_2CH_2F$]Br and iron (III) bromide. Yield: 2.04 g, 85%.**^{1}H NMR** (400 MHz, D_2O) δ 5.08 - 5.12 (m, 1H), 4.97 - 5.00 (m, 1H), 3.80 - 3.91 (t, J = 4.0, 1H), 3.82 - 3.84 (t, J = 4.0, 1H), 3.30 (s, 9H) (**Figure S6**). **^{19}F NMR** (176 MHz, D_2O) δ -218.0 - -218.5 (m, 1F) (**Figure S7**). Anal. Calcd for $C_5H_{13}NFFeBr_4$: C, 12.47; H, 2.72; N, 2.90%; Found: C 12.54, H 2.691, N 2.99%. IR (KBr, cm^{-1}): 1465(vs), 1268(w), 1209(w), 1134(s), 1127(w), 1088(w), 1044(s), 946(vs), 871(m).

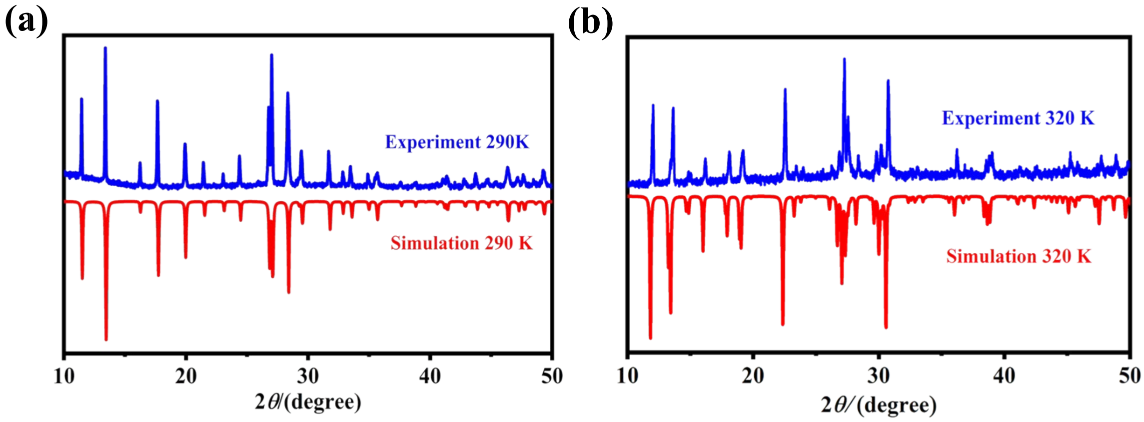

Fig. S1. The powder XRD of **1** at 290 K (a) and $[Me_4N]FeBr_4$ at 320 K (b), with the simulated one in red and the measured one in blue. The measured data is matched well with the simulated data from the single crystal diffraction which means that both compounds are pure.

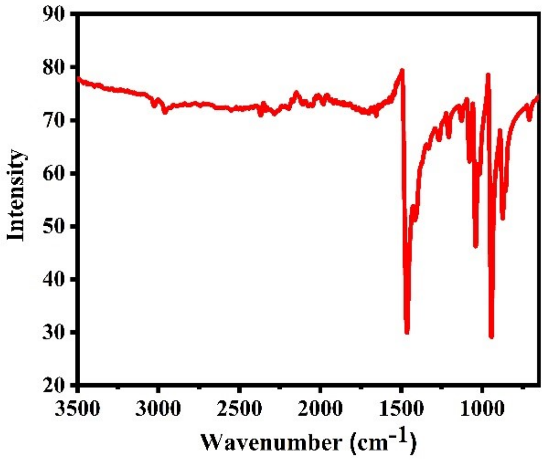

Fig. S2. The infrared spectrum of **1**.

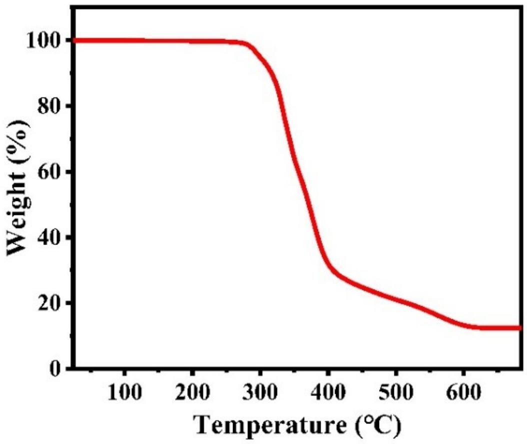

Fig. S3. TGA curve of compound **1**.

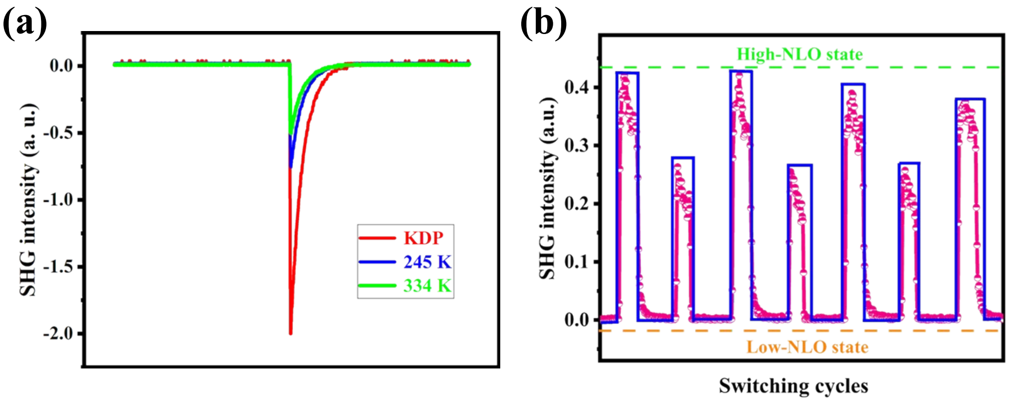

Fig. S4. (a) Oscilloscope traces of SHG signals for KDP and **1** at 245 K and 334 K. (b) The reversible and recoverable switching of SHG effect of $[Me_4N]FeBr_4$.

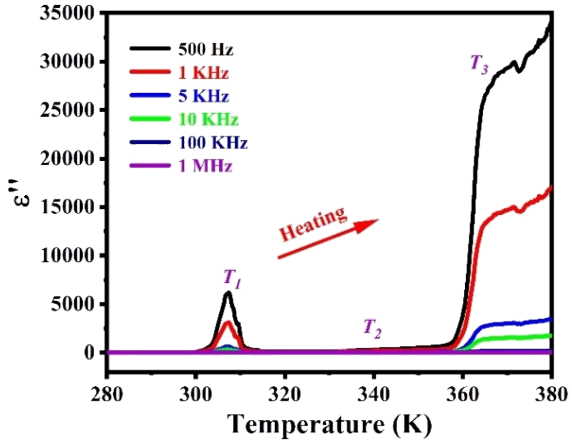

Fig. S5. Imaginary part of the dielectric permittivity of **1** measured at different frequencies in a heating cycle.

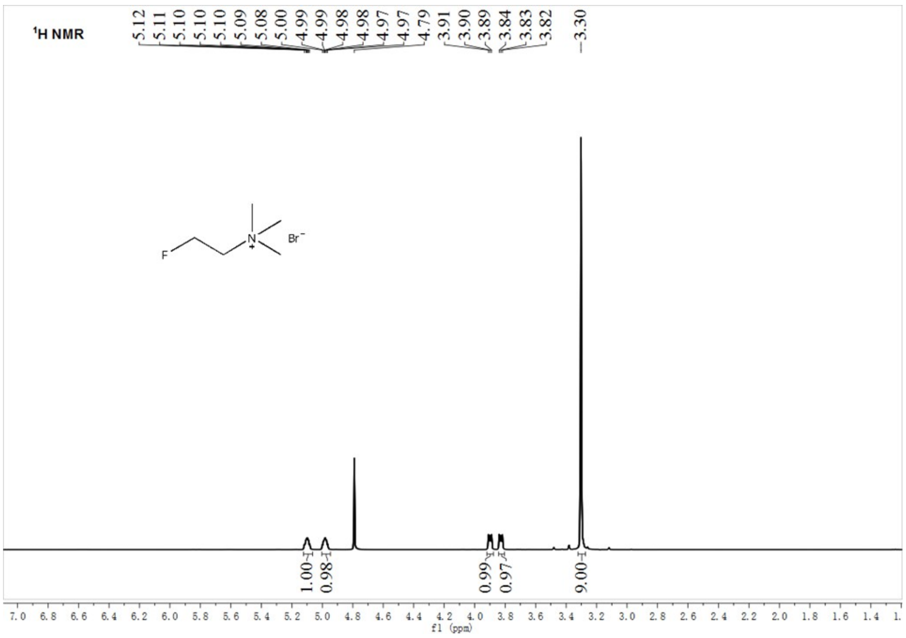

Fig. S6. ^{1}H NMR spectrum of [$Me_3NCH_2CH_2F$]Br.

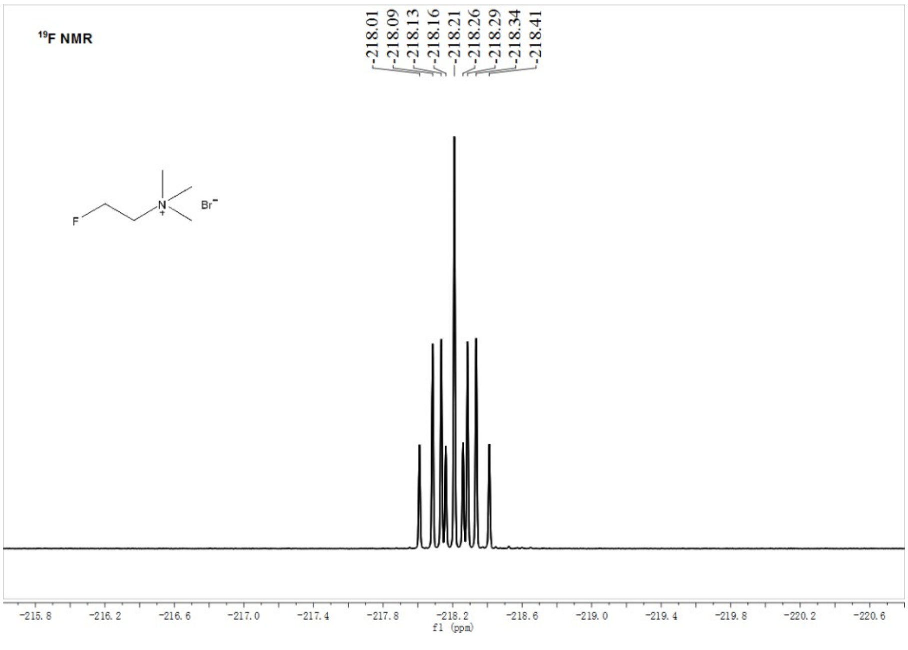

Fig. S7. ^{19}F NMR spectrum of [$Me_3NCH_2CH_2F$]Br.

Tab. S1 Crystal data and structure refinements for **1** at 290 K and 320 K.

Formula	$C_5H_{13}NFFeBr_4$	$C_5H_{13}NFFeBr_4$

Temperature	290 K	320 K
Formula weight	481.61	481.61
Crystal system	orthorhombic	orthorhombic
Space group	$Cmc2_1$	*Pbcm*
a (Å)	15.0498(16)	6.8804(11)
b (Å)	16.3256(16)	13.614(2)
c (Å)	10.7180(11)	15.219(2)
V(Å)^3	2633.4(5)	1425.6(4)
Z	8	4
D_{calc} (g.cm^{-3})	2.430	2.244
F(000)	1800	900
θ_{max}	24.990	24.999
μ(Mo Ka,mm^{-1})	13.253	12.241
Reflections collected	5579	6829
Unique reflections	2173 [R($_{\text{int}}$) = 0.0564]	1312 [R($_{\text{int}}$) = 0.0911]
No. of variables	122	125
Final R indices ($I \geq 2\sigma$)	R_1 = 0.0567, wR_2 = 0.1534	R_1 = 0.0741, wR_2 = 0.2209
R indices (all data)	R_1 = 0.0708, wR_2 = 0.1612	R_1 = 0.1711, wR_2 = 0.2916
Goodness-of-fit	1.057	0.958
Max./min. peak (e. Å^{-3})	2.74, -2.15	1.10, -0.85

Table S2. Selected bond lengths (Å) and angles (°) of **1** at 290 K.

1 at 290 K			
Br1-Fe1	2.329(3)	Fe1-Br2	2.353(4)
Fe1-Br3	2.347(4)	Fe2-Br4^1	2.341(3)

Fe2-Br4	2.341(3)	Fe2-Br5	2.333(4)
Fe2-Br6	2.336(4)		
Br1^{1}-Fe1-Br1	110.57(18)	Br1^{1}-Fe1-Br2	109.77(12)
Br1-Fe1-Br2	109.77(12)	Br1^{1}-Fe1-Br3	108.68(11)
Br1-Fe1-Br3	108.68(11)	Br3-Fe1-Br2	109.34(17)
Br4-Fe2-Br4^{2}	109.86(19)	Br5-Fe2-Br4	109.24(11)
Br5-Fe2-Br4^{2}	109.24(11)	Br5-Fe2-Br6	109.63(18)
Br6-Fe2-Br4	109.43(11)	Br6-Fe2-Br4^{2}	109.43(11)

Symmetry code：^{1}1-*x*, 2-*x*, +*y*, +*z*; ^{2}1-*x*, +*y*, +*z*

Table S3. Selected bond lengths (Å) and angles (°) for **1** at 320 K.

1 at 320 K			
Br4-Fe1	2.24(4)	Br1-Fe1	2.29(5)
Fe1-Br3	2.51(4)	Fe1-Br3^{1}	2.51(4)
Fe1A-Br4A^{1}	2.40(3)	Fe1A-Br4A	2.40(3)
Fe1A-Br1A^{1}	2.40(4)	Fe1A-Br1A	2.40(4)
Fe1A-Br3A^{1}	2.16(3)	Fe1A-Br3A	2.16(3)
Br4-Fe1-Br1	119(2)	Br4-Fe1-Br3^{1}	111.6(14)
Br4-Fe1-Br3	111.6(14)	Br1-Fe1-Br3^{1}	108.7(14)
Br1-Fe1-Br3	108.7(14)	Br4A-Fe1A-Br1A	100.3(18)
Br4A^{1}-Fe1A-Br1A	101.9(18)	Br3A-Fe1A-Br4A	111(2)
Br3A-Fe1A-Br1A	112(2)		

Symmetry code: ^{1}+*x*, +*y*, 1/2-*z*