Supporting Information

An organic-inorganic hybrid perovskite material $[Me_3NCMe_3]GaCl_4$ exhibits a two-step off-on-off SHG response with large temperature interval

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Measurement Methods

Single-crystal and powder X-ray crystallography.

X-ray single-crystal diffraction experiments were performed utilizing a Rigaku Saturn 924 diffractometer, outfitted with Mo-Kα radiation (λ = 0.71073 Å). X-ray diffraction (XRD) analyses were executed employing a PANalytical X'Pert3 diffractometer, equipped with a Cu Kα X-ray source (λ = 1.5418 Å, 40 kV, 150 mA), with a scan rate set at 10° min^{-1} for the measurements.

Thermal analyses.

Differential scanning calorimetry (DSC) measurements were performed with a NETZSCH DSC 200F3 instrument. Crystalline samples underwent both heating and cooling processes at a consistent rate of 20 K min^{-1} under aluminum crucibles and nitrogen atmosphere.

SHG and dielectric measurements.

The second harmonic generation (SHG) was examined using INSTEC instruments. Complex dielectric permittivities were assessed utilizing the DMS-1000 dielectric temperature spectrum measuring system. Silver conductive paste was utilized to coat the surfaces of the samples, serving dual roles as the top and bottom electrodes.

NMR measurements.

The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Advance III 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C). The samples were dissolved either in D_2O, with tetramethylsilane (TMS) serving as the internal reference standard. Chemical shifts (δ) were recorded in parts per million (ppm) and referenced to TMS (δ = 0) for ^{1}H.

Experimental

In a 100 mL two-neck reaction flask, [$Me_2NC(Me_3)$] (5.00 g, 49.41 mmol) was dissolved in 20 mL of anhydrous methanol. Heat the solution to 90°C and slowly add methyl iodide (7.01 g, 49.41 mmol) dropwise. After the reaction is complete after 12 h, the organic solvent was removed by rotary evaporation. Wash the crude product with ethanol, filter, and dry to obtain a white solid product. The product is [$Me_3NC(Me_3)$]I with a yield of 80%. **^{1}H NMR (400 MHz, D_2O):** δ 3.07 (s, 9H), 1.50 (s, 9H). Dissolve [$Me_3NC(Me_3)$]I (0.49 g, 2.02 mmol) in deionized water. Add Ag_2CO_3 (0.28 g, 1.01 mmol) to the solution and stir for 3 h. Filter the clear solution and add concentrated hydrochloric acid (37%) until no bubbles are produced. Slowly add an aqueous solution of $GaCl_3$ (0.33 g, 2.0 mmol) dropwise to the above solution, and stir for 1 hour. Allow the solution to evaporate naturally to obtain white crystals. The experimental yield is 0.35 g, with a yield of 81%.

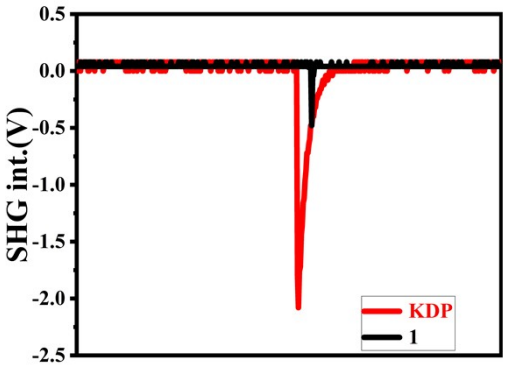

Fig. S1 Comparison chart of **1** and KDP signals.

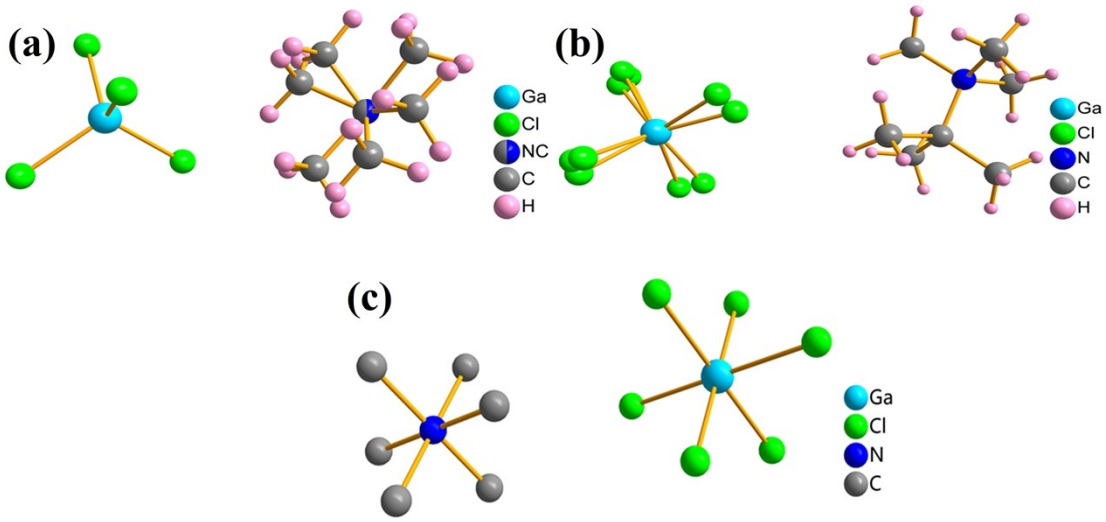

Fig. S2 The single crystal structures of compound **1** at different temperatures of 230 K (a), 293 K (b), and 350 K (c).

Table S1. Some materials with two-step frequency doubling.

Compounds	Switching method	Temperature difference
$[C_6H_{11}NH_3]_2[CdCl_4]$	low-high-low	160 K
$[C_4H_{10}N]_2[CdCl_4]$	off-on-off	20 K
$[Me_4N][GaCl_4]$	off-on-off	100 K
$[Me_3NCMe_3][GaCl_4]$	off-on-off	70 K

Table S2. Crystal data and structure refinements for **1** at LTP, ITP and HTP.

Formula	$[Me_3NCMe_3]GaCl_4$		
Temperature	230 K	293 K	350 K
Formula weight	327.76	327.74	327.74
Crystal system	orthorhombic	orthorhombic	cubic
Space group	*Pbcm*	$Pmc2_1$	$Pm\bar{3}m$
a (Å)	6.8857(3)	7.3448(5)	7.2333(5)
b (Å)	13.7480(6)	7.0749(6)	7.2333(5)
c (Å)	14.6331(6)	14.0244(12)	7.2333(5)
V (Å)	1385.24(10)	728.76(10)	378.45(8)
Z	4	2	1
D_{calc} (g.cm^{-3})	1.572	1.494	1.306
F(000)	664.0	332.0	142
$2\theta_{max}$	61.7	61.368	61.088
μ(Mo Ka,mm^{-1})	2.721	2.586	2.484
Reflections collected	15084	7999	952
Unique reflections	1960 [R_{int} = 0.0410, R_{sigma} = 0.0253]	1973 [R_{int} = 0.0456, R_{sigma} = 0.0344]	142 [Rint = 0.0364, Rsigma = 0.0217]
No. of variables	98	135	9
Final R indices (I ≥ 2σ)	R_1 = 0.0545, wR_2 = 0.1167	R_1 = 0.0792, wR_2 = 0.2302	R_1 = 0.1939, wR_2 = 0.5625
R indices (all data)	R_1 = 0.0761, wR2 = 0.1246	R_1 = 0.1088, wR_2 = 0.2550	R_1 = 0.2662, wR_2 = 0.5991

Goodness-of-fit	1.065	1.074	2.005
Flack parameter	-	0.05(8)	-

Table S3. Selected bond lengths (Å) and angles (°) of **1** at 230 K.

1 at 230 K			
Ga1-Cl1	2.178(2)	Ga1-Cl3	2.1637(13)
Ga1-Cl2	2.1729(17)	Ga1-Cl3[1]	2.1637(13)
Cl2-Ga1-Cl1	108.15(8)	Cl3-Ga1-Cl1	108.84(5)
Cl2-Ga1-Cl1	108.15(8)	Cl3[1]-Ga1-Cl2	109.26(5)
Cl3[1]-Ga1-Cl1	108.84(5)	Cl3-Ga1-Cl2	109.26(5)

Symmetry codes: [1] +x, +y, 3/2-z.

Table S4. Selected bond lengths (Å) and angles (°) of **1** at 293 K.

1 at 293 K			
Ga1 -Cl1[1]	2.134 (9)	Ga1 -Cl1A	2.10 (2)
Ga1 -Cl2	2.179 (17)	Ga1 -Cl3A[1]	2.148 (19)
Ga1- Cl3	2.155 (14)	Ga1-Cl2-A[1]	2.162 (16)
Cl1[1]-Ga1-Cl1	126(2)	Cl1A[1]-Ga1-Cl3A	119(3)
Cl1-Ga1-Cl2	104.6(11)	Cl1A-Ga1-Cl2A[1]	111(2)
Cl1-Ga1-Cl3	106.2(7)	Cl1A[1]-Ga1-Cl2A[1]	121.8(19)
Cl1[1]-Ga1-Cl3A[1]	97(2)	Cl1A[1]-Ga1-Cl2A	111(2)
Cl1-Ga1-Cl3A[1]	111(2)	Cl1[1]-Ga1-Cl2A[1]	113.3(17)
Cl1-Ga1-Cl2A[1]	100.4(17)	Cl3A-Ga1-Cl2A[1]	107(2)
Cl3-Ga1-Cl2	108.9(19)	Cl3A-Ga1-Cl2A	109(2)
Cl3-Ga1-Cl2A[1]	103(2)	Cl3A[1]-Cl3A-Ga1	82(2)
Cl1A[1]-Ga1-Cl1A	89(4)	Cl2A[1]-Cl2A-Ga1	83.1(14)
Cl1A-Ga1-Cl3A	107(2)		

Symmetry codes: [1] 1-x, +y, +z.

Table S5. Selected bond lengths (Å) and angles (°) of **1** at 350 K.

1 at 350 K			
Ga01-Cl02[1]	2.36(2)	Ga01-Cl02[3]	2.36(2)
Ga01-Cl02[2]	2.36(2)	Ga01-Cl02[4]	2.36(2)
Ga01-Cl02	2.36(2)	Ga01-Cl02[5]	2.36(2)
Cl02-Ga01-Cl02[2]	90	Cl02[5]-Ga01-Cl02[3]	90.0
Cl02-Ga01-Cl02[3]	90	Cl02[2]-Ga01-Cl02[3]	180.0
Cl02-Ga01-C021[1]	90	Cl02[1]Ga01-Cl02[3]	90
Cl02[5]-Ga01-C021[1]	90	Cl02[2]-Ga01-Cl02[5]	90
Cl02[5]-Ga01-C021[4]	90	Cl02[4]-Ga01-Cl02[1]	180.0
Cl02[4]-Ga01-Cl02[3]	90	Cl02[2]-Ga01-Cl02[1]	90
Cl02-Ga01-Cl02[4]	90	Cl02[2]-Ga01-Cl02[4]	90
Cl02-Ga01-Cl02[5]	180.0		

Symmetry codes: [1] 2-z, 2-x, 2-y; [2] 2-y, 2-z, 2-x; [3] +y, +z, +x; [4] +z, +x, +y; [5] 2-x, 2-y, 2-z.