Supplementary information for

Nonlinear organic-inorganic halide hybrids containing unprecedented linear [M^IX₂]⁻ coordination and

quasi-two-dimensional lone pairs

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Abstract: The organometallic halides perovskites are gaining rapidly increased attention owing to their remarkable optoelectronic performance. Amongst, divalent and trivalent metal cations (Pb^{2+} , Sn^{2+} , Bi^{3+} , Sb^{3+}) usually link to six halogen X atoms and form the asymmetric [MX₆] octahedron with weak optical anisotropy. Herein, we show a family of monovalent-metal-based hybrid halides [N(CH₃)₄]MCl₂ (M=Ga⁺, In⁺) with zero-dimensional configuration containing unprecedented linear [MX₂] units. Owing to reduced coordination number, the lone pairs on Ga⁺ and In⁺ exhibits quasi-two-dimensional distribution, thereby leading to narrowed bandgap, enhanced optical anisotropy as well as strong nonlinear second harmonic response of 1.3 and 1.4 times that of benchmark KH₂PO₄, respectively. These findings offer an avenue for inventing fresh hybrid materials and further open up their practical applications in laser frequency conversion, light absorbers and smart devices.

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Experimental Procedures

1. Reagents.

All of the starting chemicals were analytical grade from commercial source and used without further treatment.

2. Synthesis of Compound.

For [N(CH₃)₄]GaCl₂, 1.5 mmol (CH₃)₄NI (0.3000 g), 0.5 mmol Ga(NO₃)₃•XH₂O (0.1270 g) were placed in a mixture composed of 1 ml hydrochloride and 1 mL distilled water to form a transparent solution, and the solution were added to a 23 mL Teflon-lined vessel, and then nested in a stainless steel housing and sealed. The entire reactor was heated to 150 ° C for 2 h, and left to react at 150 ° C for 3 days. Afterwards, it was slowly cooled to 30 ° C at a cooling rate of 1.67 ° C • h⁻¹. Yellow crystals were directly obtained by suction filtration, and then dried and weighed with a yields of 91% (based on Ga). Yellow Single crystals of [N(CH₃)₄]InCl₂ were synthesized by using 1.5 mmol (CH₃)₄NI (0.3000 g), 0.5 mmol In(NO₃)₃•XH₂O (0.3443 g), 1 ml hydrochloric acid and 1 mL distilled water with the same above synthesis method (the yields is 94% based on In).

3. Powder X-ray diffraction.

Powder X-ray diffraction (XRD) of the crystals were performed on Bruker D8 Advanced diffractometer with Cu-K α radiation (λ = 1.54186 Å) in the angular range of 2 θ =10°-70° at a scanning rate of 10° /min at room temperature.

4. Single crystal structure determination.

Single crystal X-ray diffraction data of the compound was collected at 298 (K) using a Bruker APEX-II CCD diffractometer equipped with a CCD detector (graphite-monochromated Mo K α radiation, λ =0.71073 Å). Using Olex2^[1a], the structure was solved with the ShelXS^[1b] structure solution program using Direct Methods and refined with the ShelXL^[1c] refinement package using Least Squares minimisation. Relevant crystallographic data and structure refinement information for the compound are summarized in Table S1, selected bond distances are listed in Table S2. The CCDC numbers for [N(CH₃)₄]MCl₂ (M=Ga⁺, In⁺) are 1982812 and 1982813, respectively.

5. Second Harmonic Generation (SHG) Measurement.

The SHG measurement were performed on the sieved polycrystalline samples using a modified Kurtz-Perry method^[2]. Polycrystalline samples of the compound were ground and sieved into several particle size ranges (20-40, 40-60, 60-80, 80-100, 100-125, 125-150, 150-200 and 200-300 μ m) for the measurement. Microcrystalline KH₂PO₄ (KDP) was served as the standard and sieved into the same particle size ranges. The final SHG efficiency was evaluation comparing oscilloscope traces of the SHG signals of KDP and [N(CH₃)₄]MCl₂ (M=Ga⁺, In⁺) at the powder size of 200-300 μ m.

6. UV-Vis-NIR Diffuse Reflectance Spectrum.

The UV-Vis diffuse reflectance spectra were measured on a UV 2600 UV-Vis spectrophotometer. The BaSO₄ of spectral purity was used as a reference material (100 % reflectance). The absorption spectra were calculated from the reflectance spectra using the Kubelka–Munk function: $\alpha/S = (1-R)^2 / 2R$, where α is the absorption coefficient, S is the scattering coefficient, and R is the reflectance, respectively.^[3]

7. Infrared Spectrum.

IR spectra of the two compounds were performed on a Nicolet iS5 Fourier-transformed infrared (FTIR) spectrometer in the range of 4000–400 cm⁻¹. The dried KBr was mixed thoroughly with the samples and pressed into a slice to test.

8. Thermal Analysis.

The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was performed with a Netzsch STA 449 F5 analyzer. Crystal samples were added into an Al_2O_3 crucible and heated from 30 °C to 800 °C at a heating rate of 10 K/min under flowing nitrogen atmosphere.

9. First-principles calculation.

The atomic-level theoretical calculations for [N(CH₃)₄]MCl₂ (M=In, Ga) crystal were performed by density functional theory^[4] via Material Studio package, which has been applied on many metal halides successfully.^[5,6] The lattice cell and atomic position was fixed as same as single crystal XRD refinement. The kinetic energy cutoff of 900 eV and Monkhorst-Pack *k*-point meshes^[7] (3×3×4) were selected to ensure sufficient accuracy of the simulated results. The exchange–correlation functionals were described by generalized gradient density approximation (GGA) PBEsol functional^[8] and the ion-electron interactions for all elements were modeled by the norm-conversing pseudopotentials.^[9] The linear refractive index was calculated on basis of scissor-corrected methods.^[10] In addition, in order to elaborate the lone pair activity of Ga⁺ (In⁺) cations, the partial density of states of diamond-like LiGaS₂ and LiInS₂ were also calculated.^[11] Clearly, the different valance state of Ga lead to divergent band structure and optical response.

Empirical formula	[N(CH ₃) ₄]InCl ₂	[N(CH ₃) ₄]GaCl ₂
Formula weight	214.77	259.87
Temperature/K	173.0	173.0
Crystal system	tetragonal	tetragonal
Space group	P-42₁m	P-42₁m
a/Å	9.2755(6)	9.28070(10)
b/Å	9.2755(6)	9.28070(10)
c/Å	5.8368(4)	5.8414(2)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å3	502.17(7)	503.13(2)
Z	2	2
pcalcg/cm3	1.420	1.715
µ/mm- 1	3.198	2.806
F(000)	216.0	252.0
Crystal size/mm ³	0.18 × 0.16 × 0.12	0.18 × 0.14 × 0.12
Radiation	ΜοΚα (λ = 0.71073)	ΜοΚα (λ = 0.71073)
2O range for data collection/°	6.982 to 52.894	9.824 to 52.984
Index ranges	-11≤h≤11, -11≤k≤11, 0 ≤l≤7	-11≤h≤11, -11≤k≤11, -7≤l≤7
Reflections collected	2057	5724
Independent reflections	566 [R _{int} = 0.0589, R _{sigma} = 0.0419]	557 [R _{int} = 0.0353, R _{sigma} = 0.0172]
Data/restraints/parameters	566/0/24	557/6/23
Goodness-of-fit on F ²	1.106	1.145
Final R indexes [I>=2σ (I)]	R1 = 0.0744, wR2 = 0.2099	R1 = 0.0152, wR2 = 0.0416
Final R indexes [all data]	R1 = 0.0781, wR2 = 0.2133	R1 = 0.0152, wR2 = 0.0416
Largest diff. peak/hole / e Å ⁻³	1.21/-1.18	0.18/-0.38
Flack parameter	-0.03(3)	-0.16(3)

 Table S1. Crystal data and structure refinement for [N(CH₃)₄]MCl₂ (M=In, Ga)

bond	lengths (Å)	bond	lengths (Å)
Ga1-Cl	2.543(7)	N1-C1 ³	1.475(17)
Ga1-Cl ¹	2.543(7)	N1-C1 ⁴	1.475(17)
N1-C1 ¹	1.475(17)		
N1-C1 ²	1.475(17)		

Table S2. Selected bond lengths (Å) for (CH₃)₄NGaCl₂

1-X,1-Y,+Z; ²-X,-Y,+Z; ³+Y,-X,1-Z; ⁴-Y,+X,1-Z

		8 () (3)	2
bond	lengths (Å)	bond	lengths (Å)
In1-Cl	2.5491(12)	N1-C1 ³	1.496(3)
In1-Cl ¹	2.5491(12)	N1-C1 ⁴	1.496(3)
N1-C1	1.496(3)		
N1-C1 ²	1.496(3)		

Table S3. Selected bond lengths (Å) for (CH₃)₄NInCl₂

¹3-X,-Y,+Z; ²2-X,-Y,+Z; ³1-Y,-1+X,-Z; ⁴1+Y,1-X,-Z

Table S4. Selected bond angles (°) for (CH₃)₄NGaCl₂

			-
bond	angles (°)	bond	angles (°)
Cl1-In1-Cl1	179.77(5)	C1 ⁴ -N1-C1 ³	109.3(3)
C1 ² -N1-C1	109.3(3)	C1 ³ -N1-C1 ¹	109.55(14)
C1 ² -N1-C1 ³	109.55(14)	C1 ⁴ -N1-C1 ²	109.55(14)
C1 ⁴ -N1-C1	109.55(14)		

bond	angles (°)	bond	angles (°)
Cl1-Ga1-Cl1	179.8(3)	C1 ² -N1-C1 ⁴	109.0(14)
C1-N1-C1 ²	109.7(7)	C1 ³ -N1-C1 ²	109.7(7)
C1-N1-C1 ³	109.0(14)	C1 ¹ -N1-C1 ⁴	109.7(7)
C1 ³ -N1-C1 ⁴	109.7(7)		



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Figure S9. The HOMO of (a) Cs₃Sb₂I₉ and (b) [N(CH₃)₄]GaCl₂

Figure S10. The calculated refractive index of Cs₃Sb₂I₉

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