$[Al(H_2O)_6](IO_3)_2(NO_3)$: A Material with Sizable Birefringence Induced by Synergism of Double Superior Functional Motifs

Zhiyong Bai,[a][c] Chun-Li Hu, [b] Dongmei Wang, [a] Lehui Liu, [a] Lizhen Zhang, [a][d] Feifei Yuan, [a] Yisheng Huang, [a] and Zhoubin Lin*[a][d]

[a] Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, P. R. China. E-mail: lzb@fjirsm.ac.cn

[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, P. R. China.

[c] University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

[d] Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, Fujian, 350108, China

Experiment

1. **Synthesis**. The chemical reagent $Al(NO_3)•9H_2O$ (3mmol, 1.1250g) and I_2O_5(3mmol, 1.0014g) were dissolved in the 5 mL distilled water and then stirred to ensure solution dissolves clearly. The solution was evaporated at room temperature and after about four days large transparent single crystal with dimensions of 12×8×5 mm^3 was obtained (Figure S4).
2. **Powder X-ray Diffraction.** Powder X-ray diffraction analyses of AINO were carried out at room temperature on a Miniflex 600 diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å). Data were collected in the angular range of 2θ = 10-70° with a scan step width of 0.008° and a scan time of 0.5 s. The experimental powder X-ray diffraction patterns are in agreement with those simulation results on the basis of the single-crystal crystallographic data.
3. **Single Crystal X-ray Diffraction.** The single crystal X-ray diffraction was performed on a Rigaku ROD, Synergy Custom system, HyPix diffractometer equipped with mirror-monochromatic Ga Kα radiation (λ=1.3405Å) at 298 K. A suitable sample of AINO was selected and used for data collection. The data were corrected for Lorentz factor, polarization and absorption. By means of Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. All of the atoms were refined with anisotropic displacement parameters and secondary extinction correction. The structure was verified by Platon and no higher symmetry was found. Crystallographic data for structural refinements, atoms coordination, thermal parameters, and selected bond lengths and bond angles are listed in Tables S1 to S8.
4. **Birefringence Measurement.** The birefringence of AINO was measured on a polarizing microscope (ZEISS Axio Scope. A1) equipped with Berek compensator. The wavelength of the light source is 546 nm. Attributable to the clear boundary lines of the first-, second- and third-order interference color, the relative error is small enough. During the measurement, the retardation was recorded and then the crystal's thickness was measured. According to the given retardation and thickness of crystal, the birefringence was calculated with following equation,

   $$\triangle n = R / d \qquad (1)$$

   where, Δn represents the birefringence, R the retardation, and d the thickness of the crystal selected as measurement sample.
5. **Transmittance Spectrum.** The UV-Vis-NIR transmittance spectrum of AINO were recorded at room temperature in a Perkin-Elmer Lambda 900 UV/Vis/NIR spectrophotometer in the 200-1000 nm wavelength range.
6. **Thermal Analysis.** Thermogravimetric (TG) analysis of AINO was performed on a NETZSCH STA 449F3 instrument in a temperature range of 30-1000 ℃ at a 10 ℃ /min heating rate.
7. **Computational Details.** Single-crystal structural data of compound AINO were used for the theoretical calculations. The electronic structures and optical properties were performed using a plane-wave basis set and pseudo-potentials within density functional theory (DFT) implemented

in the total-energy code CASTEP. For the exchange and correlation function, Perdew–Burke–Ernzerhof (PBE) in the generalized gradient approximation (GGA) was chosen. The interactions between the ionic cores and the electrons were described by the norm-conserving pseudopotential. The following valence-electron configurations were considered in the computation: Al-$3s^2 3p^1$, I-$5s^2 5p^3$, N-$2s^2 2p^3$, O-$2s^2 2p^4$ and H-$1s^1$. The number of plane waves included in the basis sets was determined by a cutoff energy of 900 eV. The numerical integration of the Brillouin zone was per-formed using a Monkhorst-Pack k-point sampling of 4 × 3× 5. It's worth noting that 120 empty bands were included during the optical properties calculations to ensure the accuracy of refractive indices. The other parameters and convergent criteria were the default values of CASTEP code.

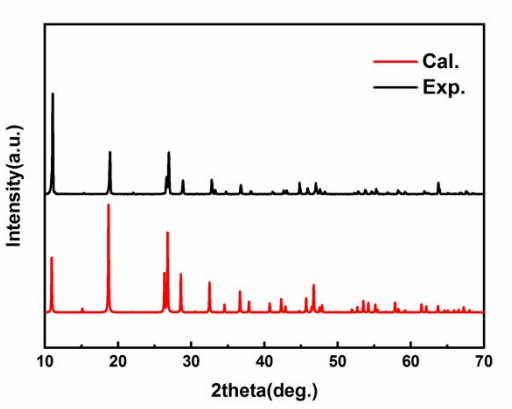

Figure S1. Powder X-ray diffraction patterns for AINO

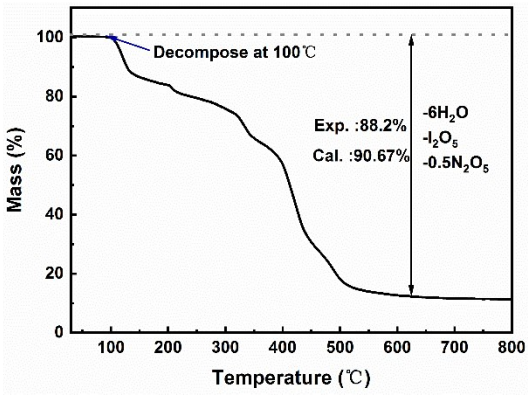

Figure S2. Thermogravimetric analysis (TGA) for AINO

As shown in figure S2, AINO started a decomposition and mass loss at about 100℃, and completed the decomposition at about and 500 ℃ with releasing of $6H_2O$, I_2O_5, and $0.5N_2O_5$. The experimental mass loss is 88.2%, in accordance with the theoretical value 90.67%.

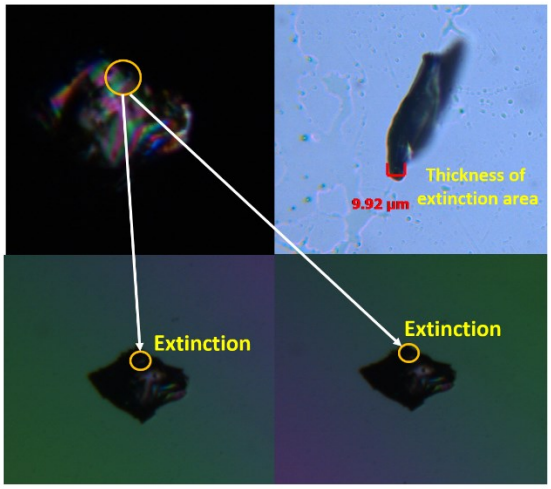

Figure S3. The photographs of extinction and thickness of crystal.

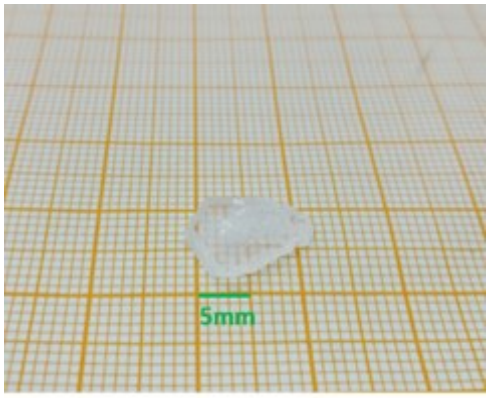

Figure S4. The as-grown single crystal of AINO with dimensions of 12×8×5 mm^3.

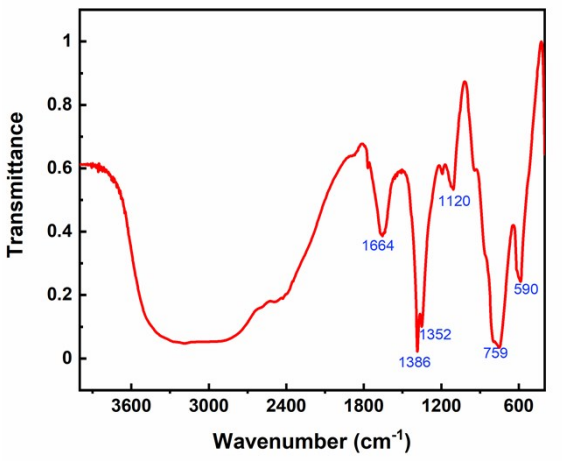

Figure S5. IR spectrums.

Table S1. Crystal data and structure refinement for AINO.

Empirical formula	$AlH_{12}I_2NO_{15}$
Formula weight	546.91
Temperature/K	293(2)
Crystal system	trigonal
Space group	*P-3m1*
a/Å	6.7200(7)
b/Å	6.7200(7)
c/Å	8.0975(10)
α/°	90
β/°	90
γ/°	120
Volume/Å3	316.68(8)
Z	1
ρcalcg/cm3	2.868
μ/mm-1	5.117
F(000)	258.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.002 to 54.904
Index ranges	-8 ≤ h ≤ 8, -8 ≤ k ≤ 8, -9 ≤ l ≤ 10
Reflections collected	2383
Independent reflections	307 [Rint = 0.0337, Rsigma = 0.0204]
Data/restraints/parameters	307/0/27
Goodness-of-fit on F2	1.305
Final R indexes [I>=2σ (I)]	R1 = 0.0160, wR2 = 0.0437
Final R indexes [all data]	R1 = 0.0162, wR2 = 0.0438
Largest diff. peak/hole / e Å-3	0.44/-0.69

Table S2. Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for AlNO. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
I001	3333.33	6666.67	1101.5(4)	16.5(2)
O003	4692(2)	5308(2)	2151(3)	28.4(6)
Al02	0	0	5000	15.0(5)
O004	2704(4)	1352(2)	3726(3)	23.5(6)
N009	0	0	0	23.5(17)
O00A	1867(8)	0	0	33.3(13)
	Bond valence sum (BVS)	I: 5.2	Al: 3.2	N: 4.84

Table S3. Anisotropic Displacement Parameters (Å2×103) for AlNO. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U11	U22	U33	U23	U13	U12
I001	15.6(2)	15.6(2)	18.2(3)	0	0	7.79(11)
O003	26.7(10)	26.7(10)	37.5(16)	3.9(6)	-3.9(6)	17.6(12)
Al02	15.4(7)	15.4(7)	14.1(12)	0	0	7.7(4)
O004	27.3(14)	23.1(9)	21.3(13)	4.3(5)	8.5(11)	13.7(7)
N009	29(3)	29(3)	12(4)	0	0	14.7(13)
O00A	29(2)	40(3)	35(3)	3(3)	1.4(13)	20.0(15)

Table S4. Bond Lengths for AlNO.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I001	O0031	1.796(3)	N009	O00A8	1.255(5)
I001	O0032	1.796(3)	N009	O00A7	1.255(5)
I001	O003	1.796(3)	N009	O00A9	1.255(5)
Al02	O0043	1.882(2)	N009	O00A	1.255(5)
Al02	O0044	1.882(2)	N009	O00A10	1.255(5)
Al02	O0045	1.882(2)	N009	O00A4	1.255(5)
Al02	O0046	1.882(2)	O00A	O00A10	1.255(5)
Al02	O0047	1.882(2)	O00A	O00A8	1.255(5)
Al02	O004	1.882(2)			

11-Y,1+X-Y,+Z; 2+Y-X,1-X,+Z; 3-X,-Y,1-Z; 4+Y-X,-X,+Z; 5+Y,-X+Y,1-Z; 6-Y+X,

+X,1-Z; 7-Y,+X-Y,+Z; 8-Y+X,+X,-Z; 9-X,-Y,-Z; 10+Y,-X+Y,-Z

Table S5. Bond Angles for AINO.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O0031	I001	O0032	99.43(12)	O00A8	N009	O00A7	180.0(8)
O0031	I001	O003	99.43(12)	O00A7	N009	O00A6	120.0
O0032	I001	O003	99.43(12)	O00A8	N009	O00A9	120.0
O0043	Al02	O004	87.19(11)	O00A6	N009	O00A9	180.0
O0044	Al02	O0045	92.81(11)	O00A10	N009	O00A6	60.0
O0044	Al02	O0046	180.00(12)	O00A6	N009	O00A	120.0
O0044	Al02	O004	87.19(11)	O00A8	N009	O00A6	60.0
O0046	Al02	O0045	87.19(11)	O00A8	N009	O00A10	120.0
O0043	Al02	O0044	92.81(11)	O00A10	N009	O00A	180.0
O0047	Al02	O0045	87.19(11)	O00A7	N009	O00A	120.0
O0047	Al02	O0044	87.19(11)	O00A9	N009	O00A	60.0
O0046	Al02	O004	92.81(11)	O00A7	N009	O00A10	60.0
O0043	Al02	O0046	87.19(11)	O00A10	N009	O00A9	120.0
O0047	Al02	O004	92.81(11)	O00A7	N009	O00A9	60.0
O0047	Al02	O0046	92.81(11)	O00A8	N009	O00A	60.0
O0043	Al02	O0047	180.00(13)	O00A8	O00A	N009	60.0
O0043	Al02	O0045	92.81(11)	O00A9	O00A	N009	60.0
O0045	Al02	O004	180.0	O00A9	O00A	O00A8	120.0

11-Y,1+X-Y,+Z; 2+Y-X,1-X,+Z; 3-Y+X,+X,1-Z; 4+Y,-X+Y,1-Z; 5-X,-Y,1-Z; 6-Y,+X-Y,+Z; 7+Y-X,-X,+Z; 8-Y+X,+X,-Z; 9+Y, -X+Y,-Z; 10-X,-Y,-Z

Table S6. Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for AINO.

Atom	x	y	z	U(eq)
H00A	2994.27	2673.18	3370	35
H00B	2488.8	561.08	2837.94	35

Table S7. Atomic Occupancy for AINO.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
H00A	0.5	H00B	0.5	O00A	0.5