Supporting Information

$Ba_4Ag_5(IO_3)_6(I_3O_8)_3(I_4O_{11})_2$: A Nonlinear Optical Crystal Containing Two Types of Polyiodate Anion

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Table S1. Crystallographic data for title compound

formula	$Ag_5Ba_4I_{23}O_{64}$
formula weight	5031.41
crystal system	Orthorhombic
space group	*Pnc*2
T (K)	293(2)
a (Å)	14.3909(3)
b (Å)	27.2447(5)
c (Å)	8.04490(10)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3154.21(10)
Z	2
D_c (g cm^3)	5.298
μ (mm^{-1})	15.362
goodness of fit on F^2	1.042
flack factor	-0.06(4)
R_1, wR_2 [I >2σ(I)][a]	0.0450, 0.1144
R_1, wR_2 (all data)[a]	0.0461, 0.1155

a: $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = \{\sum w[(F_o)^2 - (Fc)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$.

Table S2. Calculation of dipole moment for IO_3, IO_4, I_3O_8, I_4O_{11}, AgO_n (n = 4, 6) and net dipole moment for $Ba_4Ag_5(IO_3)_6(I_3O_8)_3(I_4O_{11})_2$.

Polar unit	Dipole moment (D = Debyes)			
	x-component	y-component	z-component	total magnitude
$I(1)O_3$	±12.459	±8.413	0.411	15.039
$I(2)O_3$	±6.560	±6.237	10.893	14.164
$I(3)O_3$	±8.502	±12.120	3.059	15.117
$I(4)O_4$	±0.767	±0.447	-12.886	12.916
$I(5)O_3$	±9.845	±12.713	3.145	16.384
$I_3(3\text{-}4\text{-}5)O_8$	±2.110	±1.040	-6.682	7.084
$I(6)O_4$	±0.000	±0.000	9.182	9.182
$I(7)O_3$	±12.235	±7.981	2.838	14.881
$I_3(7\text{-}6\text{-}7)O_8$	±24.470	±15.962	14.859	32.777
$I(8)O_3$	±0.591	±13.742	-4.604	14.504
$I(9)O_3$	±0.596	±6.611	-12.944	14.547
$I(10)O_4$	±2.422	±9.328	-2.953	10.079
$I(11)O_4$	±5.108	±3.425	-9.785	11.558
$I(12)O_3$	±5.926	±5.726	11.001	13.745
$I_4(9\text{-}10\text{-}11\text{-}12)O_{11}$	±2.200	±5.018	-14.681	15.670

Dipole moment from I-O groups (a unit cell)	0	0	19.200	19.200
$Ag(1)O_6$	±1.549	±0.286	0.508	1.655
$Ag(2)O_6$	0.000	0.000	0.320	0.320
$Ag(3)O_6$	0.000	0.000	1.013	1.013
$Ag(4)O_4$	0.000	0.000	-0.712	0.712
Dipole moment from Ag-O groups (a unit cell)	0	0	4.516	4.516
Net dipole moment (a unit cell)	0	0	23.716	23.716

Table S3. The values of independent second-harmonic generation tensors.

compound	second-harmonic generation tensors (pm/V)
$Ba_4Ag_5(IO_3)_6(I_3O_8)_3(I_4O_{11})_2$	$d_{15} = -0.842 \times 10^{-9}$
	$d_{24} = -0.633 \times 10^{-9}$
	$d_{33} = -0.879 \times 10^{-9}$

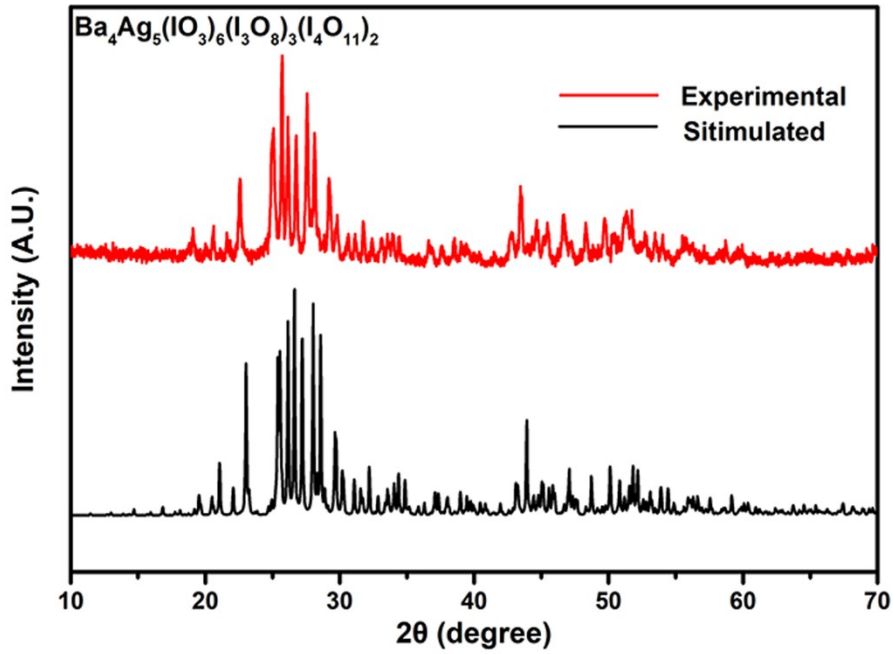

Figure S1. Simulated and measured powder X-ray diffraction patterns.

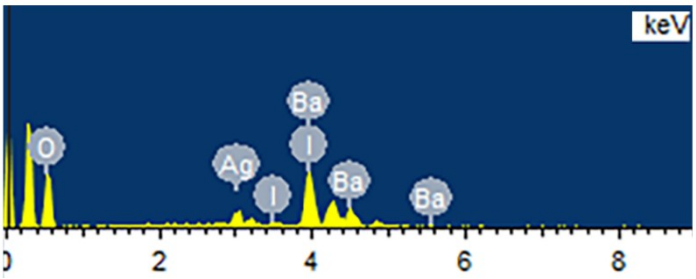

Figure S2. The EDS of $Ba_4Ag_5(IO_3)_6(I_3O_8)_3(I_4O_{11})_2$.

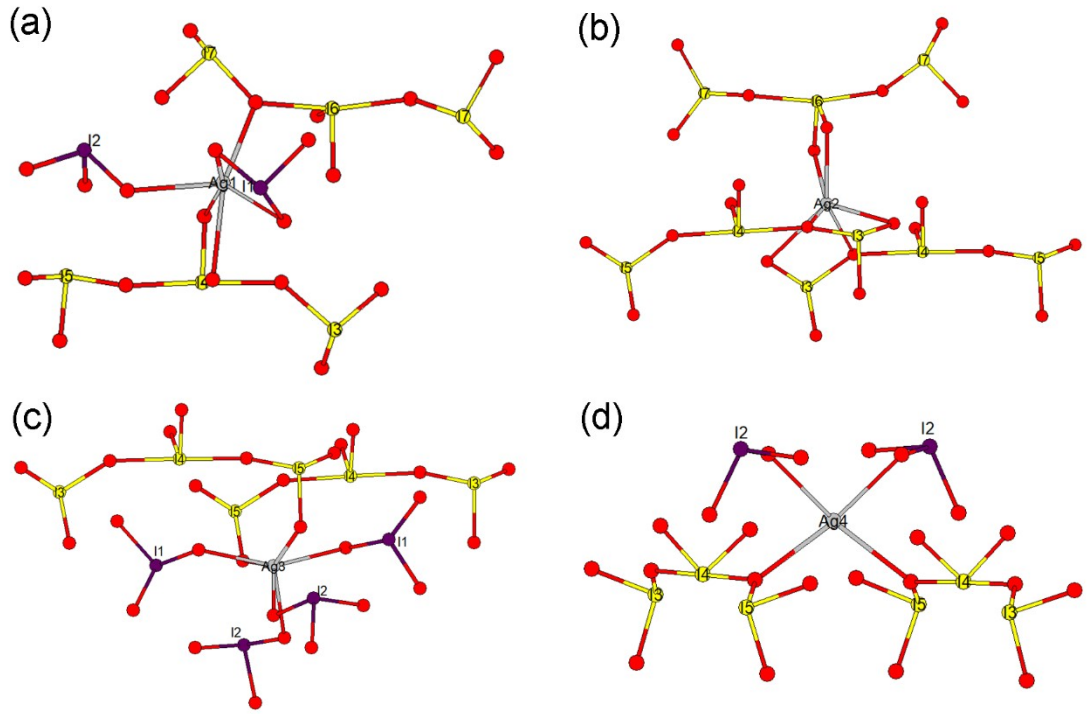

Figure S3. Views of the coordination mode of Ag(1) (a), Ag(2) (b), Ag(3) (c) and Ag(4) (d) atoms. Purple: IO_3, Yellow: I_3O_8, Blue: I_4O_{11}.

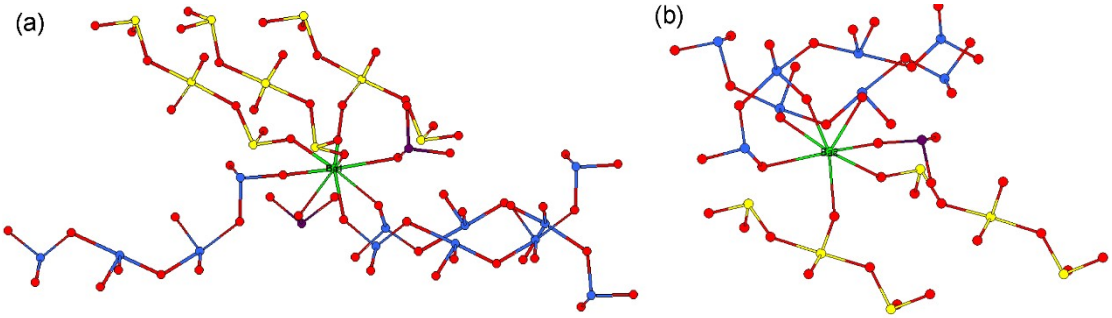

Figure S4. Views of the coordination mode of Ba(1) (a) and Ba(2) (b) atoms. Purple: IO_3, Yellow: I_3O_8, Blue: I_4O_{11}.

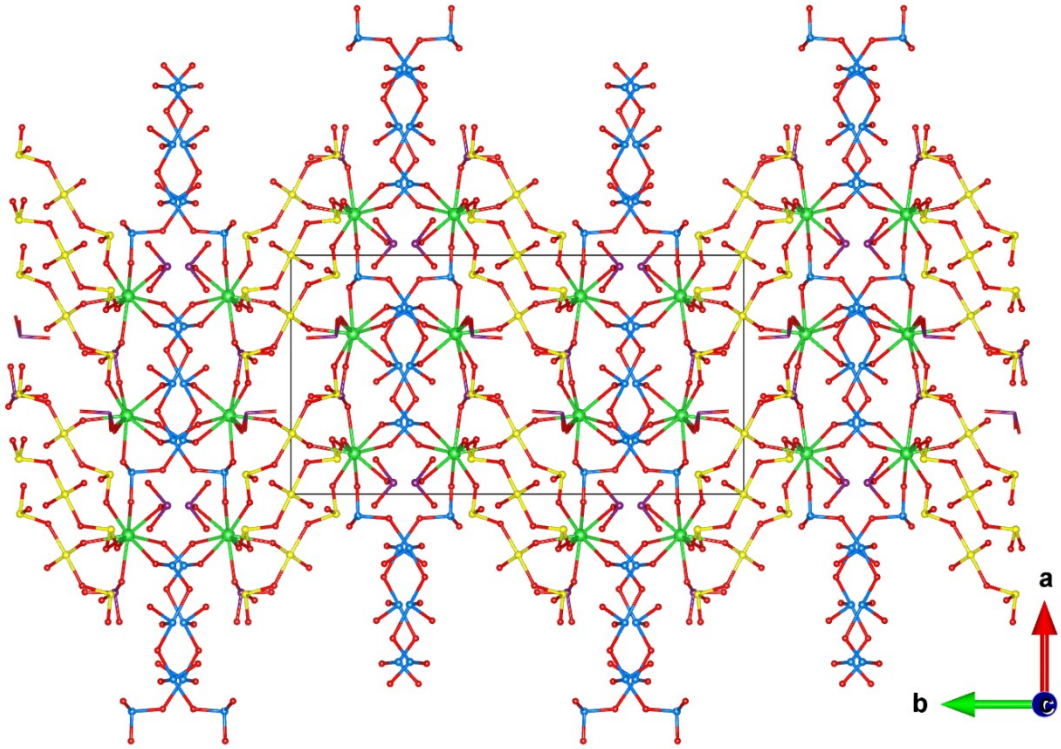

Figure S5. Views of 3D $[Ba_4(IO_3)_6(I_3O_8)_3(I_4O_{11})_2]^{5-}$ anionic framework along *c* direction. Purple: IO_3, Yellow: I_3O_8, Blue: I_4O_{11}.

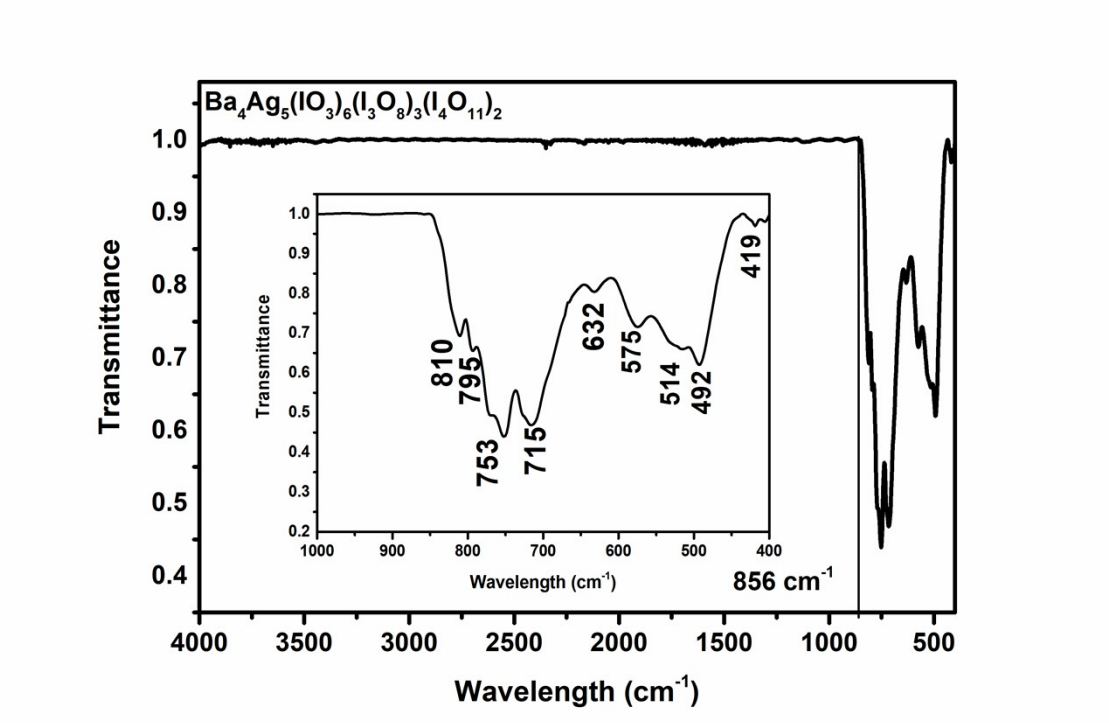

Figure S6. The infrared spectrum for $Ba_4Ag_5(IO_3)_6(I_3O_8)_3(I_4O_{11})_2$.

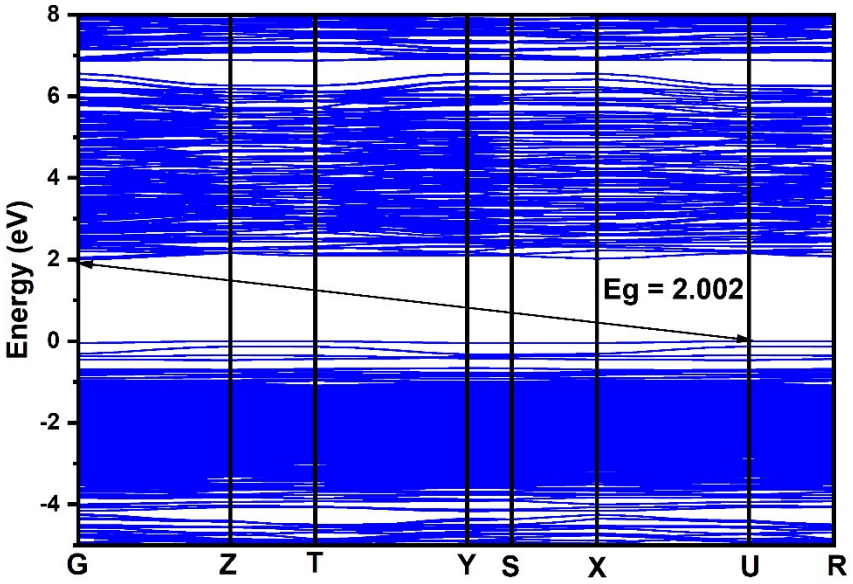

Figure S7. The calculated band structure for $Ba_4Ag_5(IO_3)_6(I_3O_8)_3(I_4O_{11})_2$.