# Supporting Information

# Y<sub>8</sub>O(OH)<sub>15</sub>(CO<sub>3</sub>)<sub>3</sub>Cl: An Excellent Short-Wave UV Nonlinear Optical Material Exhibiting Infrequent Three-Dimensional Inorganic Cationic Framework

Yiting Zhang,<sup>a</sup> Ying Long,<sup>a</sup> Xuehua Dong,<sup>a</sup> Lei Wang,<sup>b</sup> Ling Huang,<sup>b</sup> Hongmei Zeng,<sup>a</sup> Zhien Lin,<sup>a</sup> Xin Wang<sup>a</sup> and Guohong Zou<sup>a\*</sup>

<sup>a</sup>College of Chemistry, Sichuan University, Chengdu, 610064, P. R. China.
<sup>b</sup>College of Chemistry and Materials Science, Sichuan Normal University, Chengdu, 610068, P. R. China.

E-mail: zough@scu.edu.cn

## **CONTENTS**

1. Synthesis of Y<sub>8</sub>O(OH)<sub>15</sub>(CO<sub>3</sub>)<sub>3</sub>Cl.

# 2. Instrumentations for physical property measurements.

3. Computational Descriptions.

## 4. Tables and Figures.

Table S1. Crystal data and structural refinements for Y<sub>8</sub>O(OH)<sub>15</sub>(CO<sub>3</sub>)<sub>3</sub>Cl.

Table S2. Atomic coordinates, equivalent isotropic displacement parameters and bond-valence calculations for

### Y<sub>8</sub>O(OH)<sub>15</sub>(CO<sub>3</sub>)<sub>3</sub>Cl.

Table S3. Selected Bond lengths (Å) and Angles (°) for Y<sub>8</sub>O(OH)<sub>15</sub>(CO<sub>3</sub>)<sub>3</sub>Cl.

Fig. S1. Photograph of Y<sub>8</sub>O(OH)<sub>15</sub>(CO<sub>3</sub>)<sub>3</sub>Cl crystals.

Fig. S2. Calculated and experimental powder X-ray diffraction (PXRD) patterns for Y<sub>8</sub>O(OH)<sub>15</sub>(CO<sub>3</sub>)<sub>3</sub>Cl.

Fig. S3. Powder XRD patterns for the white precipitaten after ion-exchange.

Fig. S4. TGA curve for  $Y_8O(OH)_{15}(CO_3)_3Cl$ .

**Fig. S5.** IR spectrum for  $Y_8O(OH)_{15}(CO_3)_3Cl$ .

Fig. S6. UV transmittance spectroscopy for Y<sub>8</sub>O(OH)<sub>15</sub>(CO<sub>3</sub>)<sub>3</sub>Cl.

Fig. S7. Calculated band structure of Y<sub>8</sub>O(OH)<sub>15</sub>(CO<sub>3</sub>)<sub>3</sub>Cl

**Fig. S8**. The arrangement of CO<sub>3</sub> anionic groups in  $Y_8O(OH)_{15}(CO_3)_3Cl$  along *a* axis (a), *b* axis (b), *c* axis (c)

# References

#### 1. Synthesis of Y<sub>8</sub>O(OH)<sub>15</sub>(CO<sub>3</sub>)<sub>3</sub>Cl.

All starting materials  $Y(NO_3)_3 \cdot 6H_2O$  (99%),  $Na_2CO_3$  (99.9 %) and HCl (38%) were procured from Aladdin and used without further purity. Crystals of  $Y_8O(OH)_{15}(CO_3)_3Cl$  were synthesized via hydrothermal method.  $Y(NO_3)_3 \cdot 6H_2O$  (0.38g, 1mmol),  $Na_2CO_3$  (0.10g, 0.94mmol) and 10 mL H<sub>2</sub>O were mixed, the pH of the mixture was about 6.0 and then a few drops of 12mol/L HCl were added to adjust the pH between 3.0-4.0.Then the mixture was stirred for 20 minutes and introduced into the Teflon autoclaves (23ml) and heated at 210°C for 5 days, and then slowly cooled to ambient temperature at a rate of 3 °C/h. Colorless and transparent hexagonal crystals of  $Y_8O(OH)_{15}(CO_3)_3Cl$  shown in Figure S1were obtained, washed with ethanol and dried in air. The yields are about 36% (on the base of Y).



Fig. S1. Photograph of Y<sub>8</sub>O(OH)<sub>15</sub>(CO<sub>3</sub>)<sub>3</sub>Cl crystals.

#### 2. Instrumentations for physical property measurements.

Suitable single crystals were selected under an optical microscope. The intensity data were collected on a Bruker SMART BREEZE diffractometer with graphite-monochromated MoK<sub> $\alpha$ </sub> radiation( $\lambda$ =0.71073Å) at room temperature. All absorption corrections were per-formed by using the SADABS program. The structure was solved by direct methods and refined by full-matrix least squares on *F*<sup>2</sup> using the SHELX-97 program package<sup>[1,2]</sup>. All of the structures were verified using the ADDSYM algorithm from the program PLATON and no higher symmetries were found.<sup>[3]</sup> All hydrogen atoms were located geometrically or in a difference Fourier map, and refined with a riding model. IR spectra (KBr pellets) were recorded on a Vertex 70 Fourier transform infrared spectrometer. Thermal analyses were performed in a dynamic nitrogen atmosphere using a Netzsch STA 409 PC thermal analyzer, and with a heating rate of 10 °C/min and in the range of 100-800 °C. Powder XRD patterns were obtained using a Rigaku Smartlab powder X-ray diffractometer with CuK $\alpha$  radiation ( $\lambda$  =

1.54056 Å), in the angular range of  $2\theta = 5-70^\circ$ , and with a scan step width of 0.05° and a fixed time of 0.2 s. The UV transmittance spectroscopy was recorded at room temperature using a PerkinElmer Lamda-950 UV/vis/NIR spectrophotometer in the range of 200-2500nm, and the absorption (K/S) data were calculated from the Kubelka-Munk function<sup>[4]</sup>. The birefringence was measured on a Nikon ECLIPSE LV100 POL polarizing microscope. The wavelength of the light source was 589.6 nm. The formula of the calculated birefringence can be expressed as follows:  $\triangle R$  (retardation) =  $\triangle n \times T$ , where  $\triangle R$  denotes the optical path difference,  $\triangle$  n represents birefringence, and T denotes the thickness of the crystal. Powder second-harmonic generation (SHG) signals were measured using the method adapted from Kurtz and Perry<sup>[5]</sup>. Since SHG efficiencies were known to depend strongly on particle size, polycrystalline samples were ground and sieved into the following particle size ranges: 25-45, 45-62, 62-75, 75-109, 109-150 and 150-212 µm. The measurements were performed with a Q-switched Nd:YAG laser at 1064 nm and a frequency doubling at 532 nm, for visible and UV SHG, respectively. To make relevant comparisons with known NLO materials, crystalline KDP and BBO were also ground and sieved into the same particle size ranges and used as the references for visible and UV SHG, respectively. The samples were pressed between glass microscope cover slides and secured with tape in 1-mm thick aluminum holders containing an 8-mm diameter hole. They were then placed in a light-tight box and irradiated with a pulsed laser. A cutoff filter was used to limit background flash-lamp light on the sample, and an interference filter was used to select the second harmonic for detection with a photomultiplier tube attached to a RIGOL DS1052E 50-MHz oscilloscope. This procedure was then repeated using the standard nonlinear optical materials KDP and BBO, and the ratio of the second-harmonic intensity outputs was calculated. No index-matching fluid was used in any of the experiments. Ion-exchange reactions were performed by stirring about 200 mg of Y<sub>8</sub>O(OH)<sub>15</sub>(CO<sub>3</sub>)<sub>3</sub>Cl sample in 5 mL of 1 M aqueous solution of NaNO<sub>3</sub>. The reactions were performed at room temperature for 24 h. The reaction products were recovered by filtration, washed with excess H<sub>2</sub>O, and dried in air for 1 d. White precipitate was formed when a few drops of 1mol/L AgNO<sub>3</sub> were added to the filtrate. A contrast blank experiment was performed by stirring about 200 mg of  $Y_8O(OH)_{15}(CO_3)_3Cl$  sample in 5 mL distilled water for 24 h. No precipitate was formed when a few drops of 1mol/L AgNO<sub>3</sub> were added. The white precipitate was confirmed to be AgCl by powder XRD.

#### 3. Theoretical calculation.

Our ab initio calculations for compound  $Y_8O(OH)_{15}(CO_3)_3Cl$  were performed using the full-potential projector augmented wave (PAW) method<sup>[6]</sup>, as implemented in the Vienna ab initio Simulation Package (VASP) package<sup>[7-10]</sup>. The exchange-correlation (XC) interaction was treated by the Perdew-Burke-Ernaerhof (GGA-PBE)<sup>[11]</sup> functional. The valence electrons of the component elements were treated as H 1s<sup>1</sup>, O 2s<sup>2</sup>2p<sup>4</sup>, C 2s<sup>2</sup>2p<sup>2</sup>, Cl 3s<sup>2</sup>3p<sup>5</sup>, Y 4s<sup>2</sup>4p<sup>6</sup>4d<sup>1</sup>5s<sup>2</sup> Hydrogen atomic positions of the OH<sup>-</sup> groups were obtained by fixed-lattice constant optimization based on the X-ray crystal structure. A  $\Gamma$ -centered 3×3×2 Monkhorst-Pack grid for the Brillouin zone sampling<sup>[12]</sup> and a cutoff energy of 450 eV for the plane wave expansion were found to get convergent lattice parameters. In geometry optimizations, all the atomic positions and lattice constants were fully relaxed until the quantum mechanical forces became less than 0.05eV/Å, and the total energy was converged to 0.1 meV.

To obtain the linear optical properties, the complex dielectric function  $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$  has been determined in the random phase approximation from the PBE wavefunctions. The imaginary part of the dielectric function due to direct inter-band transitions is given by the expression,

$$\varepsilon_{2}(\mathbf{h}\omega) = \frac{2e^{2}\pi}{\Omega\varepsilon_{0}} \sum_{k,v,c} \left| \left\langle \psi_{k}^{c} \left| u \cdot r \right| \psi_{k}^{v} \right\rangle \right|^{2} \delta(E_{k}^{c} - E_{k}^{v} - E),$$

where  $\Omega$ ,  $\omega$ , u, v and c are the unit-cell volume, photon frequencies, the vector defining the polarization of the incident electric field, valence and conduction bands, respectively. The real part of the dielectric function is obtained from  $\varepsilon_2$  by a Kramers-Kronig transformation,

$$\varepsilon_{1}(\omega) = 1 + \left(\frac{2}{\pi}\right) \int_{0}^{+\infty} d\omega' \frac{{\omega'}^{2} \varepsilon_{2}(\omega)}{{\omega'}^{2} - {\omega}^{2}},$$

In calculation of the static  $\chi^{(2)}$  coefficients, the so-called length-gauge formalism derived by Aversa and Sipe<sup>[7]</sup> and modified by Rashkeev *et al*<sup>[13]</sup> is adopted, which has been proved to be successful in calculating the second order susceptibility for semiconductors and insulators.<sup>[14-17]</sup> In the static case, the imaginary part of the static second-order optical susceptibility can be expressed as:

$$\begin{aligned} \chi^{abc} \\ &= \frac{e^3}{h^2 \Omega} \sum_{nml,k} \frac{r_{nm}^a (r_{ml}^b r_{ln}^c + r_{ml}^c r_{ln}^b)}{2\omega_{nm} \omega_{ml} \omega_{ln}} [\omega_n f_{ml} + \omega_m f_{ln} + \omega_l f_{nm}] \\ &+ \frac{ie^3}{4h^2 \Omega} \sum_{nm,k} \frac{f_{nm}}{\omega_{mn}^2} [r_{nm}^a (r_{mn;c}^b + r_{mn;b}^c) + r_{nm}^b (r_{mn;c}^a + r_{mn;a}^c) + r_{nm}^c (r_{mn;b}^a + r_{mn;a}^b)] \end{aligned}$$

where *r* is the position operator,  $\hbar\omega_{nm} = \hbar\omega_n - \hbar\omega_m$  is the energy difference for the bands *m* and *n*,  $f_{mn} = f_m - f_n$  is the difference of the Fermi distribution functions, subscripts *a*, *b*, and *c* are Cartesian indices, and  $r^b_{mn;a}$  is the so-called generalized derivative of the coordinate operator in *k* space,

$$r_{nm;a}^{b} = \frac{r_{nm}^{a}\Delta_{mn}^{b} + r_{nm}^{b}\Delta_{mn}^{a}}{\omega_{nm}} + \frac{i}{\omega_{nm}} \times \sum_{l} (\omega_{lm}r_{nl}^{a}r_{lm}^{b} - \omega_{nl}r_{nl}^{b}r_{lm}^{a}),$$

where  $\Delta^{a}_{nm} = (p^{a}_{nn} - p^{a}_{mm}) / m$  is the difference between the electronic velocities at the bands *n* and *m*.

# 4. Tables and Figures

formula	Y <sub>8</sub> O(OH) <sub>15</sub> (CO <sub>3</sub> ) <sub>3</sub> Cl
fw	1197.88
crystal system	Hexagonal
space group	P63
a (Å)	9.5089(3)
b (Å)	9.5089(3)
c (Å)	14.6730(4)
α(°)	90
β(°)	90
γ(°)	120
V (Å <sup>3</sup> )	1148.97(6)
Z	2
$\rho$ (calcd) (g/cm <sup>3</sup> )	3.462
temperature (K)	296(2)
$\lambda$ (Å)	0.71073
F(000)	1124
Final R indices (I> $2\sigma$ (I))a R <sub>1</sub> /wR <sub>2</sub> <sup>a</sup>	0.0524/0.1056
GOF on F <sup>2</sup>	1.039
Absolute Structure Parameter	0.00 (2)

Table S1. Crystal data and structure refinement for Y<sub>8</sub>O(OH)<sub>15</sub>(CO<sub>3</sub>)<sub>3</sub>Cl.

 ${}^{a}R_{1}(F) = \Sigma ||F_{o}| - |F_{c}|| \Sigma |F_{o}|. wR_{2}(F_{o}^{2}) = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w(F_{o}^{2})^{2}]^{1/2}.$ 

atom	x		у		Ζ		U <sub>(eq)</sub>	
C1	0.2472 (11)		0.9673 (11)		0.5924 (9)		0.010 (2)	
Y1	1.0000		1.0000		0.75416 (19)		0.0077 (4)	
Y2	0.86978 (13)		0.58806 (12)		0.87548 (8)		0.0082 (3)	
Y3	0.56985 (12)		0.70689 (12)		0.78590 (7)		0.0081 (3)	
Y4	0.3333		0.6667		0.5790 (2)		0.0100 (4)	
Cl1	0.3333		0.6667		1.0819 (13)		0.085 (3)*	
01	1.1937 (8)		1.0099 (8)		0.8657 (6)		0.0098 (16)	
O2	1.0214 (8)		0.7447 (9)		0.7542 (6)		0.0113 (15)	
O3	0.6331 (9)		0.4806 (9)		0.9672 (5)		0.0120 (17)	
O4	0.6274 (8)		0.4939 (8)		0.7846 (7)		0.0079 (15)	
O5	0.4977 (9)		0.8656 (9)		0.8820 (6)		0.0107 (17)	
O6	0.3333		0.6667		0.7291 (9)		0.009 (3)	
07	0.3080 (10)		0.8815 (9)		0.6262 (6)		0.0153 (19)	
08	0.1978 (10)		1.0315 (9)		0.6515 (6)		0.0147 (18)	
09	0.2352 (9)		0.9801 (8)		0.5070 (7)		0.0120 (16)	
<b>Table S3.</b> Selected Bond Distances (Å) and Angles (°) for $Y_8O(OH)_{15}(CO_3)_3Cl$ .								
C(1)-O(9)		1.269(1	6)	Y(2)-	O(3)	2.3	71(8)	
C(1)-O(8)		1.278(1.	3)	Y(2)-	O(1)#5	2.3	76(7)	
C(1)-O(7) 1.312(1		1.312(12	2) Y(2)		2)-O(4) 2		-14(8)	
Y(1)-O(8)#2 2.30		2.309(8)	2.309(8)		Y(2)-O(2)		06(9)	
Y(1)-O(8)#3 2.3		2.309(8)	2.309(8)		Y(2)-O(4)#7		31(8)	
Y(2)-O(5)#4 2.337		2.337(7)	.337(7)		Y(2)-O(3)#7		-15(8)	
Y(2)-O(9)#6 2		2.342(9)	2.342(9)		Y(2)-O(4)#7		31(8)	
Y(2)-O(3) 2.		2.371(8)	2.371(8)		Y(2)-Y(4)#8		19(3)	
Y(2)-O(1)#5		2.376(7)		Y(2)-	Y(2)-Y(3)#4		739(16)	
Y(2)-O(5)#4		2.337(7)		Y(2)-O(3)#7		2.4	-15(8)	
Y(3)-O(6)		2.245(5)	2.245(5)		Y(3)-O(1)#5		53(7)	
Y(3)-O(2)#5		2.291(7)		Y(3)-	Y(3)-O(5)#1		93(8)	
Y(3)-O(4)		2.347(8)		Y(3)-	Y(3)-O(5)		02(8)	

**Table S2.** Atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for  $Y_8O(OH)_{15}(CO_3)_3Cl$ .  $U_{(eq)}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Y(3)-O(7)#1	2.348(9)	Y(4)-O(7)	2.281(7)
Y(4)-O(6)	2.204(12)	Y(4)-O(7)#9	2.281(7)
Y(4)-O(3)#10	2.279(8)	Y(4)-O(7)#1	2.281(7)
Y(4)-O(3)#11	2.279(8)	Y(4)-O(3)#12	2.279(8)
O(9)-C(1)-O(8)	123.5(9)	O(8)#1-Y(1)-O(8)#2	82.1(3)
O(9)-C(1)-O(7)	121.5(10)	O(8)#1-Y(1)-O(8)#3	82.1(3)
O(8)-C(1)-O(7)	115.0(11)	O(8)#2-Y(1)-O(8)#3	82.1(3)
O(1)#4-Y(1)-O(2)	137.6(3)	O(2)-Y(2)-O(5)#4	69.3(3)
O(1)#5-Y(1)-O(2)	69.3(3)	O(2)-Y(2)-O(9)#6	106.7(3)
O(1)-Y(1)-O(2)	67.3(3)	O(5)#4-Y(2)-O(9)#6	75.7(3)
O(6)-Y(3)-O(2)#5	97.8(2)	O(6)-Y(3)-O(5)	75.4(3)
O(6)-Y(3)-O(4)	119.7(2)	O(2)#5-Y(3)-O(5)	68.4(3)
O(2)#5-Y(3)-O(4)	132.8(3)	O(4)-Y(3)-O(5)	144.1(4)
O(6)-Y(4)-O(3)#10	136.0(2)	O(7)-Y(4)-O(7)#9	111.2(2)
O(6)-Y(4)-O(3)#11	136.0(2)	O(6)-Y(4)-O(7)#1	72.3(2)
O(6)-Y(4)-O(3)#12	136.0(2)	C(1)-O(7)-Y(4)	136.0(8)
C(1)-O(8)-Y(1)#14	148.3(7)	C(1)-O(9)-Y(2)#12	136.4(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x+y,-x+1,z #2 x+1,y,z #3 -y+2,x-y+2,z #4 -y+2,x-y+1,z #5 -x+y+1,-x+2,z #6 y,-x+y,z+1/2 #7 -x+y+1,-x+1,z #8 -x+1,-y+1,z+1/2 #9 -y+1,x-y+1,z #10 -y+1,x-y,z #11 x-y,x,z-1/2 #12 y,-x+y+1,z-1/2 #13 -x+1,-y+1, z-1/2 #14 x-1,y,z



**Fig. S2.** Experimental and calculated XRD patterns for compounds  $Y_8O(OH)_{15}(CO_3)_3Cl$ . The black curve is the calculated one obtained from single crystal X-ray structure analyse, the red is the experimental one for pure phase, the blue is the experimental one after ion-exchange.



Fig. S3. Powder XRD patterns for the white precipitaten after ion-exchange.



Fig. S4. TGA curve of compound Y<sub>8</sub>O(OH)<sub>15</sub>(CO<sub>3</sub>)<sub>3</sub>Cl.



**Fig. S5**. The IR spectrum for  $Y_8O(OH)_{15}(CO_3)_3Cl$ .



Fig. S6. UV transmittance spectroscopy for  $Y_8O(OH)_{15}(CO_3)_3Cl$ .



Fig. S7. Calculated band structure of  $Y_8O(OH)_{15}(CO_3)_3Cl$  (the Fermi level is set at 0 eV).



**Fig. S8**. The arrangement of CO<sub>3</sub> anionic groups in  $Y_8O(OH)_{15}(CO_3)_3Cl$  along *a* axis (a), *b* axis (b), *c* axis (c).

#### **References:**

- [1] G. M. Sheldrick, A short history of SHELX, Acta Crystallogr A, 2008, 64, 112-122.
- [2] G. M. Sheldrick, SHELXTL-97, Program for crystal structure solution. University of Göttingen, Germany, 1997.
- [3] A. Spek, Single-crystal structure validation with the program PLATON, J. Appl. Cryst., 2003, 36, 7-13.
- [4] (a) P. Kubelka, F. Munk, Z. Technol. Phys. 1931, 12, 593-601; (b) J. Tauc, Mater. Res. Bull., 1970, 5, 721-729.
- [5] S. Kurtz, T. Perry, J. Appl. Phys., 1968, 39, 3798-3813.
- [6] P. E. Blochl, Projector augmented-wave method. Phys. Rev. B: Condens. Matter, 1994, 50 (24), 17953-17979.
- [7] G. Kresse, VASP, 5.3.5; http://cms.mpi.univie.ac.at/vasp/vasp.html, 2014.

[8] G. Kresse, J. Furthmuller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys.

Rev. B: Condens. Matter, 1996, 54 (16), 11169-11186.

[9] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B: Condens. Matter*, **1999**, *59* (3), 1758-1775.

[10] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple. *Phys. Rev. Lett.*, **1996**, 77 (18), 3865-3868.

[11] H. J. Monkhorst, J. D. Pack, Special points for Brillouin-zone integrations. *Phys. Rev. B: Condens. Matter*, **1976**, *13* (12), 5188.

[12] C. Aversa, J. E. Sipe, Nonlinear optical susceptibilities of semiconductors: Results with a length-gauge analysis. *Phys Rev B*, 1995, *52* (Copyright (C) 2010 The American Physical Society), 14636-14645.

[13] S. N. Rashkeev, W. R. L. Lambrecht, B. Segall, Efficient ab initio method for the calculation of frequency-dependent second-order optical response in semiconductors. *Phys. Rev. B.*, **1998**, *57* (Copyright (C) 2010 The American Physical Society), 3905.

[14] B. Champagne, D. M. Bishop, Calculations of nonlinear optical properties for the solid state. *Adv. Chem. Phys.*, 2003, *126*, 41-92.

[15] A. H. Reshak, S. Auluck, I. V. Kityk, Specific features in the band structure and linear and nonlinear optical susceptibilities of La<sub>2</sub>CaB<sub>10</sub>O<sub>19</sub> crystals. *Phys. Rev. B.*, **2007**, *75* (Copyright (C) 2010 The American Physical Society), 245120.

[16] Y.-Z. Huang, L.-M. Wu, X.-T. Wu, L.-H. Li, L. Chen, Y.-F. Zhang, Pb<sub>2</sub>B<sub>5</sub>O<sub>9</sub>I: An Iodide Borate with Strong Second Harmonic Generation. J. Am. Chem. Soc., 2010, 132 (37), 12788-12789.

[17] Z. Ma, J. Hu, R. Sa, Q. Li, Y. Zhang, K. Wu, Screening novel candidates for mid-IR nonlinear optical materials from I<sub>3</sub>-V-VI<sub>4</sub> compounds. *J. Mater. Chem. C.*, **2017**, *5* (8), 1963-1972.