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$Zn(NH_3)CO_3$: A "Three-in-One" UV Nonlinear Optical Crystal Built by Polar Molecule Bonding Strategy

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Supplementary DFT calculations

In the static case, the imaginary part of the static second-order optical susceptibility can be expressed as:

$$\chi^{abc} = \frac{e^3}{\hbar^2\Omega}\sum_{nml,k}\frac{r^a_{nm}(r^b_{ml}r^c_{ln}+r^c_{ml}r^b_{ln})}{2\omega_{nm}\omega_{ml}\omega_{ln}}[\omega_n f_{ml}+\omega_m f_{ln}+\omega_l f_{nm}] + \frac{ie^3}{4\hbar^2\Omega}\sum_{nm,k}\frac{f_{nm}}{\omega^2_{mn}}[r^a_{nm}(r^b_{mn;c}+r^c_{mn;b})+r^b_{nm}(r^a_{mn;c}+r^c_{mn;a})+r^c_{nm}(r^a_{mn;b}+r^b_{mn;a})] \quad (1)$$

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,

$$r^b_{nm;a} = \frac{r^a_{nm}\Delta^b_{mn}+r^b_{nm}\Delta^a_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}}\times\sum_l(\omega_{lm}r^a_{nl}r^b_{lm}-\omega_{nl}r^b_{nl}r^a_{lm}) \quad (2)$$

where $\Delta^a_{nm} = (p^a_{nn} - p^a_{mm}) / m$ is the difference between the electronic velocities at the bands n and m. The $\chi^{(2)}$ coefficients here were calculated from PBE wave functions with a 5×7×9 k-point grid and about 168 bands.

Tables

Table S1. Crystallographic data for $Zn(NH_3)CO_3$.

Empirical formula	$Zn(NH_3)CO_3$
Formula weight	142.41
T (K)	293(2)
Crystal system	orthorhombic
Space group	$Pna2_1$
a (Å)	9.161(7)
b (Å)	7.592(6)
c (Å)	5.498(4)
V (Å^3)	382.4(5)
Z	4
ρ_{calcd} (g·cm^{-3})	2.474
μ (mm^{-1})	6.266
F (000)	280.0
R_{int}	0.0445
GOF on F^2	1.153
Flack factor	0.04(5)
R_1, wR_2 (I > 2σ(I)) [a]	0.0332, 0.0803
R_1, wR_2 (all data)	0.0343, 0.0812

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

Table S2. Atomic coordinates, equivalent isotropic displacement parameters (Å^2) and bond valence sums (BVS) of $Zn(NH_3)CO_3$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff	x	y	z	U_{eq}	BVS
Zn1	4a	0.14437(6)	-0.16822(8)	0.4629(3)	0.0213(2)	2.03
O1	4a	0.2213(5)	0.0466(6)	0.3001(10)	0.0278(10)	1.85
O2	4a	0.1587(5)	0.2783(7)	0.0786(10)	0.0276(11)	1.84
O3	4a	-0.0128(4)	0.1011(6)	0.2235(9)	0.0217(9)	1.84
N1	4a	0.0671(7)	-0.3304(7)	0.2051(12)	0.0301(13)	2.96
C1	4a	0.1234(7)	0.1420(8)	0.2035(13)	0.0186(11)	4.03
H1	4a	0.08704	-0.28608	0.05896	0.0360	0.99
H2	4a	-0.02908	-0.34146	0.22203	0.0360	0.99
H3	4a	0.10907	-0.43557	0.21995	0.0360	0.99

Table S3. Selected bond lengths (Å) of $Zn(NH_3)CO_3$.

Bond	Bond lengths	Bond	Bond lengths
Zn(1)–O(1)	1.989(5)	C(1)–O(1)	1.270(8)
Zn(1)–O(2)#1	1.956(5)	C(1)–O(2)	1.283(8)
Zn(1)–O(3)#2	1.940(5)	C(1)–O(3)	1.291(8)
Zn(1)–N(1)	2.007(6)		
Symmetry codes: #1 1/2-x, -1/2+y, 1/2+z; #2 -x, -y, 1/2+z.			

Table S4. Selected bond angles (deg.) of $Zn(NH_3)CO_3$.

Bond	Bond angles	Bond	Bond angles
O(1)–Zn(1)–N(1)	108.1(2)	N(1)–Zn(1)–O(3)#2	117.6(2)
O(1)–Zn(1)–O(2)#1	89.4(2)	O(1)–C(1)–O(2)	120.4(6)
O(1)–Zn(1)–O(3)#2	109.7(2)	O(1)–C(1)–O(3)	120.7(6)
O(2)#1–Zn(1)–O(3)#2	112.8(2)	O(2)–C(1)–O(3)	118.9(6)
N(1)–Zn(1)–O(2)#1	115.3(3)		
Symmetry codes: #1 1/2-x, -1/2+y, 1/2+z; #2 -x, -y, 1/2+z.			

Table S5. The local dipole moment (μ) of $Zn(NH_3)CO_3$ in Debye.

	μ_x	μ_y	μ_z	$\lvert\mu\rvert$
$ZnO_3(NH_3)$	-3.0699	-5.1258	-5.0941	7.85
$ZnO_3(NH_3)$	-3.0699	5.1258	-5.0941	7.85
$ZnO_3(NH_3)$	3.0699	5.1258	-5.0941	7.85
$ZnO_3(NH_3)$	3.0699	-5.1258	-5.0941	7.85
Total	0	0	-20.3764	

Figures

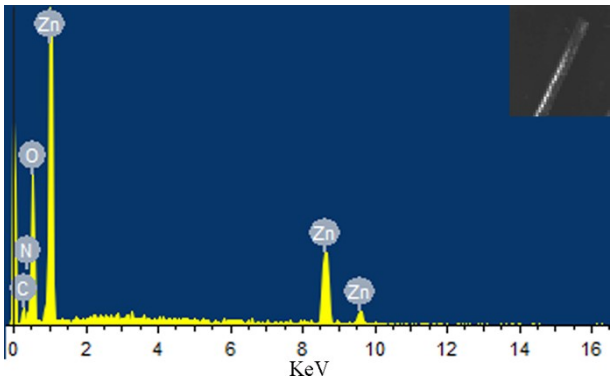

Figure S1. EDS spectrum of $Zn(NH_3)CO_3$.

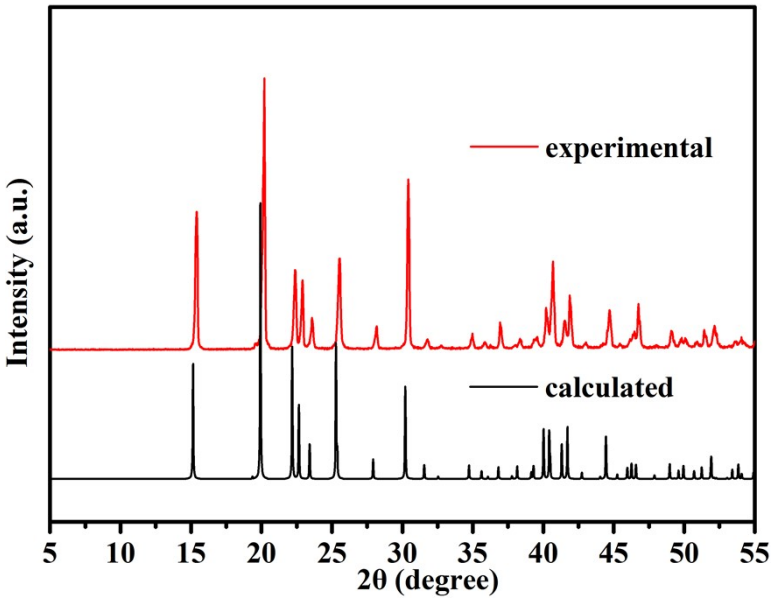

Figure S2. PXRD pattern of $Zn(NH_3)CO_3$.

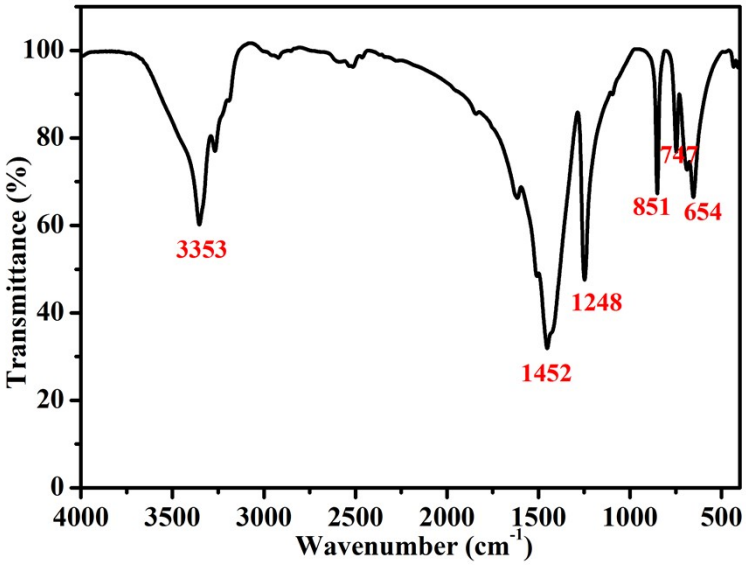

Figure S3. IR spectrum of $Zn(NH_3)CO_3$.

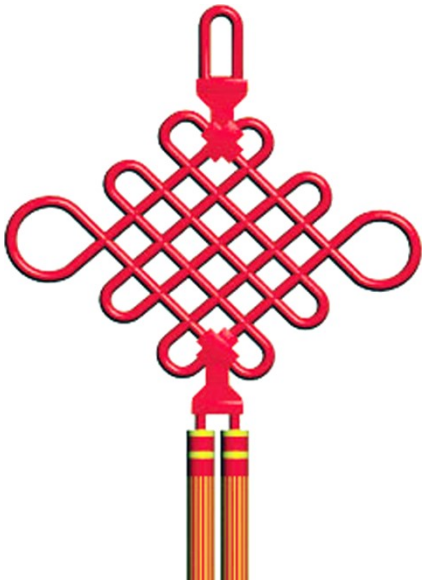

Figure S4. A Chinese knot.

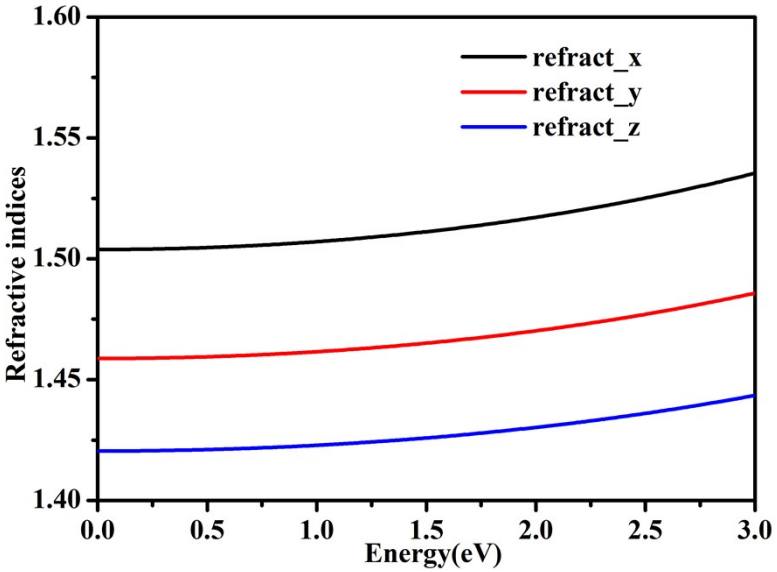

Figure S5. The calculated frequency-dependent refractive indices of $Zn(NH_3)CO_3$.

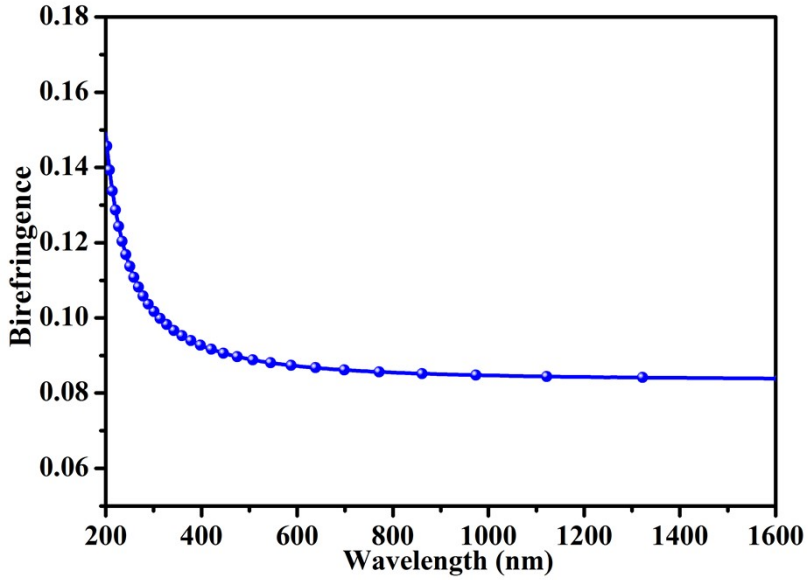

Figure S6. The birefringence of $Zn(NH_3)CO_3$.

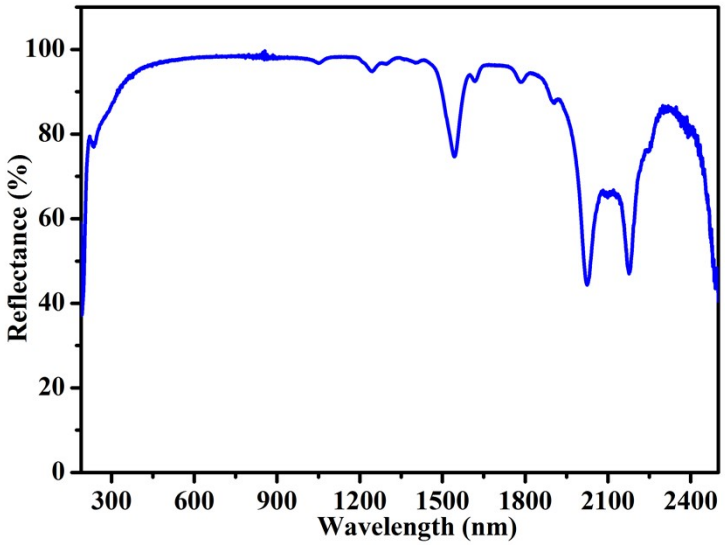

Figure S7. The UV-vis-NIR diffuse reflectance spectrum of $Zn(NH_3)CO_3$. The absorption peak at 1543, 1900–2300 nm may be caused by the overtone vibration of N–H bond.

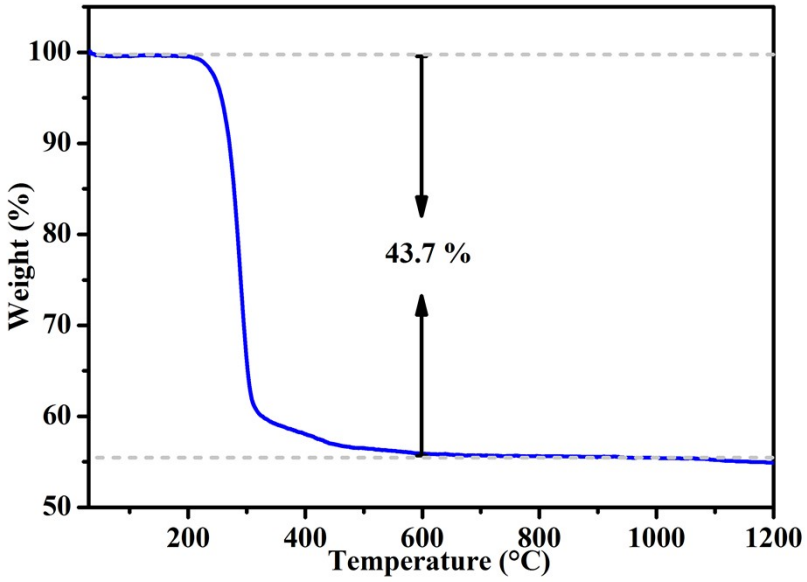

Figure S8. TG curve of $Zn(NH_3)CO_3$.

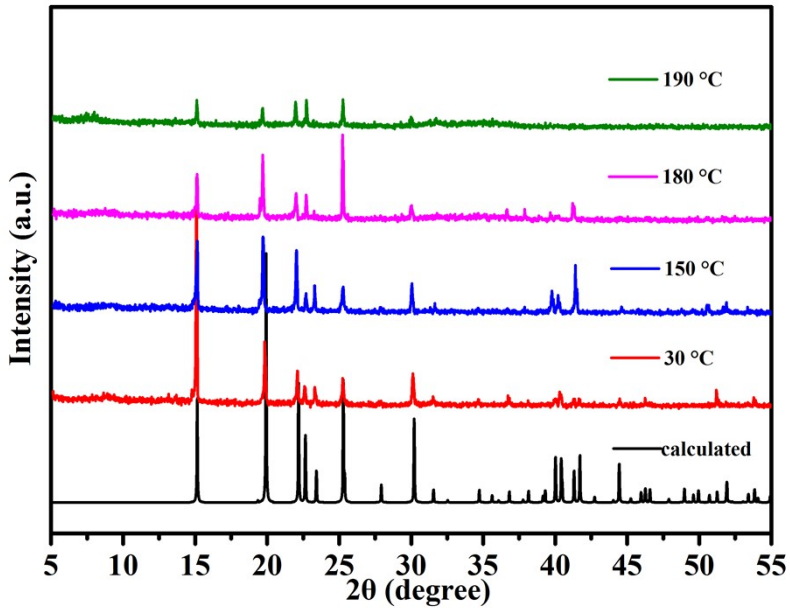

Figure S9. Variable temperature PXRD pattern of $Zn(NH_3)CO_3$.

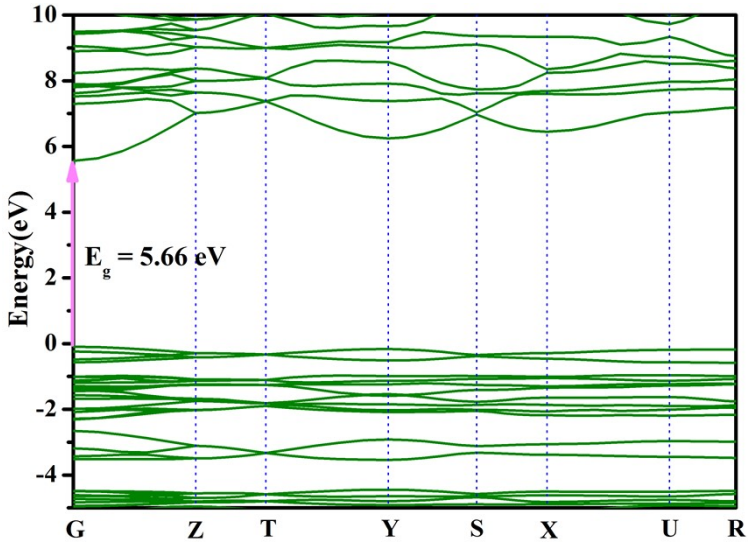

Figure S10. The calculated band structure of $Zn(NH_3)CO_3$.

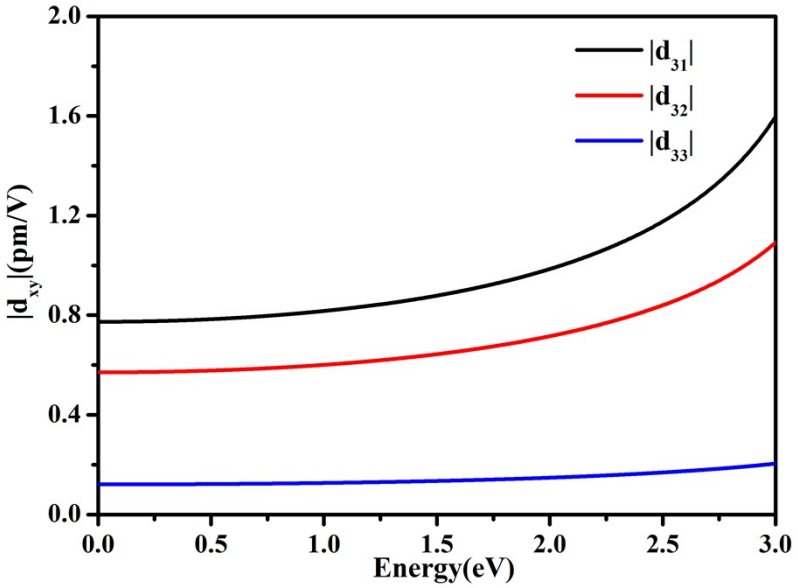

Figure S11. The frequency-dependent SHG coefficients of $Zn(NH_3)CO_3$.