Supporting Information for

$N_2H_4Zn(HC_3N_3O_3)$: Exceptionally Strong Second Harmonic Generation and Ultra-long Phosphorescence

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Experimental Procedures

Reagents

Aminoguanidine nitrate ($CH_6N_4 \cdot HNO_3$, ≥99%), Zinc Bromide ($ZnBr_2$, ≥99%), Ethylenediamine Sulfate ($C_2H_8N_2 \cdot H_2SO_4$, ≥99%), cyanuric acid ($C_3H_3N_3O_3$, ≥99%). All reagents were not further purified and were used directly.

Synthesis

$N_2H_4Zn(HC_3N_3O_3)$ was obtained by hydrothermal method. A mixture of Aminoguanidine nitrate (0.2742 g, 2.0 mmol), Zinc Bromide (0.2252 g, 1.0 mmol), Ethylenediamine Sulfate (0.3063 g, 2.0 mmol), cyanuric acid (0.2581 g, 2.0 mmol) and distilled water (3 mL) were placed into 23 mL Teflon-lined autoclave successively. Then, the temperature was raised from room temperature to 150 ℃ for two hours and held for 4 days, slowly cooling to room temperature over 5 days. Clean with anhydrous ethanol, colorless block crystals are obtained.

Instruments and Property Characterizations

Single crystal X-ray diffraction

The single crystal X-ray diffraction (XRD) data of the compound was collected at 298 (K) using a XtaLAB Synergy R diffractometer equipped with a HyPix detector (MoKα radiation, λ=0.71073 Å). Using the Olex2,[1] the structure was solved with the ShelXT and refined by adopting the intrinsic phasing method and least squares minimization.[2] Crystal information is summarized in Table 1and other crystal details are listed in Table S1-S4.

Powder XRD (PXRD)

The powder X-ray diffraction (XRD) data were recorded on an Advance diffractometer at 40 kV and 100 mA with Cu Kα1 radiation (Bruker D8, the radiation wavenumber is 1.5406 Å) at room temperature, with a scan speed of 10°/min at the angular range of 10-70°. The phase purity was confirmed by using powder X-ray diffraction technology.

Infrared Spectrum

The IR spectra was collected on a Nicolet iS5 Fourier-transformed infrared (FTIR) spectrometer at room temperature (4000-400 cm^{-1}). The sample and dry KBr are mixed and ground in a certain proportion and pressed into flakes for measurement. (weight ratio = 1:100).

UV-vis Diffuse Reflectance Spectroscopy

The UV-vis diffuse reflectance spectra were obtained by using a Varian Cary 5000 spectrophotometer with a scan range of 200-800 nm at room temperature. The spectrally pure barium sulfate was selected as a reference (100% reflectance), and a

ground powder sample was coated on its surface for testing.

Phosphorescence

Phosphorescence excitation spectra and luminescence emission decays were measured on a Hitachi F-4700 spectrophotometer.

Thermal analysis

Thermogravimetric analysis (TGA) was carried out using a Netzsch STA 449 F5 analyzer. The specific method is to weigh a sample of about 0.8 mg and place it in a platinum crucible, heat it from room temperature to 800℃ at a rate of 10 K min^{-1} in a N_2 gas atmosphere.

Second Harmonic Generation (SHG) Measurement

The second-order NLO measurements of the powder samples were performed at room temperature, and the SHG effect of the powder samples was measured using a Q-switched 1064 nm Nd: YAG laser by using the improved Kurtz and Perry methods. Polycrystalline samples of this compound were sieved into different particle sizes (35-50, 50-74, 74-100, 100-154, 154-180 and 180-280 μm) to investigate whether its SHG response could be phase matched. The reference substance KH_2PO_4 (KDP) was selected to compare with the SHG efficiency of the sample, so as to evaluate the second-order NLO effect of the measured sample.

Refractive Index Measurements

Birefringent properties of $N_2H_4Zn(HC_3N_3O_3)$ obtained by polarized light microscopy at 589 nm. The following formula was used to calculate birefringence:
$R = \Delta n \times d$
R denotes optical path difference, Δn represents birefringence, and d means the thickness of the crystal.

Computational method

The calculation method is based on the framework of density functional theory, and the CASETEP module of Materials Studio 8.0 is used to calculate the electronic structure and optical properties of $N_2H_4Zn(HC_3N_3O_3)$.[3] In order to define the exchange correlation potential, the generalized gradient approximation of PBE functional under GGA is used to obtain a stable optimal structure.[4] The structure of the cell is optimized by BFGS algorithm, and the interaction between valence electrons and ionic solids is described by using ultra-soft pseudopotential. The valence electron states of C, N, O, H and Zn are $2s^22p^2$, $2s^22p^3$, $2s^22p^4$, $1s^1$ and $3p^63d^{10}4s^2$, respectively. The plane wave truncation energy is set to 850 eV, and the numerical integration of the Brillouin region is performed using the Monkhorst-Pack grid k point 2×2×2 grid. The geometric optimization is carried out by considering convergence criteria: the total energy, the

force acting on the atom, the maximum stress and the atomic displacement are 1.0×10-5 eV/atom, 0.03 eV/A, 0.05 GPa and 0.001 A.

Results and Discussion

TableS1. Crystal data and structure refinement for $N_2H_4Zn(HC_3N_3O_3)$.

Empirical formula	$N_2H_4Zn(HC_3N_3O_3)$
Formula weight	233.50
Temperature/K	296.15
Crystal system	monoclinic
Space group	*Cc*
a/Å	9.4696(5)
b/Å	9.4104(4)
c/Å	7.9944(4)
α/°	90
β/°	113.333(2)
γ/°	90
Volume/Å^3	645.46(3)
Z	4
ρ_{calc}g/cm^3	2.269
μ/mm^{-1}	3.721
F(000)	448.0
Crystal size/mm^3	0.11 × 0.11 × 0.10
Radiation	Mo Kα (λ = 0.71073)
2*Θ* range for data collection/°	8.662 to 55.178
Index ranges	$12 \le h \le 12$, $-12 \le k \le 12$, $-10 \le l \le 10$
Reflections collected	4648
Independent reflections	1404 [R_{int} = 0.0303, R_{sigma} = 0.0410]
Data/restraints/parameters	1404/2/111
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0174, wR_2 = 0.0468
Final R indexes [all data]	R_1 = 0.0175, wR_2 = 0.0469
Largest diff. peak/hole / e Å^{-3}	0.28/-0.25
Flack parameter	0.077(17)

$R_1 = \Sigma||Fo|-|Fo||/\Sigma|Fo|$. $wR_2 = [w(Fo^2-Fc^2)^2]/[wFo^4]^{1/2}R_1$

Table S2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $N_2H_4Zn(HC_3N_3O_3)$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	*U(eq)*
Zn1	2327.8(5)	5888.5(3)	4801.5(5)	16.53(17)
O3	4191(3)	8121(3)	7513(4)	26.3(6)
O1	4993(4)	3705(3)	5875(4)	31.1(7)
N4	1787(4)	4054(3)	3285(4)	17.3(6)
N2	7014(3)	5163(3)	7306(5)	26.4(7)
N3	6632(3)	7452(3)	8149(4)	18.6(6)
N1	4498(3)	5939(3)	6537(4)	18.2(6)
O2	9026(3)	6615(3)	8699(4)	32.4(7)
N5	992(3)	4186(3)	1316(4)	17.4(6)
C1	5466(4)	4785(4)	6542(5)	19.2(7)
C3	5084(4)	7191(3)	7392(5)	15.3(7)
C2	7631(4)	6439(4)	8084(5)	20.3(7)

Table S3. Selected bond lengths (Å) for $N_2H_4Zn(HC_3N_3O_3)$.

Bond	Lengths (Å)	Bond	Lengths (Å)
Zn1-N4	2.055(3)	N2-C1	1.374(4)
Zn1-N3[1]	1.982(3)	N2-C2	1.982(5)
Zn1-N1	1.973(3)	N3-C3	1.368(4)
Zn1-N5[2]	2.070(3)	N3-C2	1.358(4)
O3-C3	1.247(5)	N1-C1	1.357(2)
O1-C1	1.228(4)	N1-C3	1.365(4)
N4-N5	1.457(2)	O2-C2	1.225(4)

[1]-1/2+X, 3/2-Y, -1/2+Z; [2]+X, 1-Y, 1/2+Z

Table S4. Selected bond angles (°) for $N_2H_4Zn(HC_3N_3O_3)$.

Bond	Angles (°)	Bond	Angles (°)
N4-Zn1-N5[1]	104.44(12)	C1-N1-C3	119.7(3)
N3[2]-Zn1-N4	109.25(13)	C3-N1-Zn1	118.5(2)
N3[2]-Zn1-N5[1]	107.30(11)	N4-N5-Zn1[4]	117.1(2)
N1-Zn1-N4	112.48(11)	O1-C1-N2	120.8(3)
N1-Zn1-N3[2]	115.38(11)	O1-C1-N1	122.1(3)
N1-Zn1-N5[1]	107.27(13)	N1-C1-N2	117.2(3)
N5-N4-Zn1	117.86(18)	O3-C3-N3	118.7(3)
C2-N2-C1	124.2(3)	O3-C3-N1	119.4(3)
C3-N3-Zn1[3]	116.8(2)	N1-C3-N3	121.9(3)
C2-N3-Zn1[3]	121.7(2)	N3-C2-N2	117.0(3)
C2-N3-C3	119.8(3)	O2-C2-N2	117.0(3)
C1-N1-Zn1	119.9(2)	O2-C2-N3	123.1(3)

[1]+X, 1-Y, 1/2+Z; [2]-1/2+X, 3/2-Y, -1/2+Z; [3]1/2+X, 3/2-Y, 1/2+Z; [4]+X, 1-Y, -1/2+Z

Table S5. Hydrogen Bonds for $N_2H_4Zn(HC_3N_3O_3)$.

D-H…A	d(D-H)/ Å	d(H-A)/ Å	d(D-A)/ Å	D-H-A/ °
N-HA…O1[1]	0.89	2.50	3.296(4)	149.8
N-HA…O3	0.89	2.27	2.938(4)	131.5
N-HB…O2[2]	0.89	2.07	2.832(4)	142.6
N4-H4…O1[3]	0.86	1.92	2.775(4)	173.6
N1-H1A…O1[4]	0.89	2.65	3.398(4)	142.0
N1-H1A…O2[5]	0.89	2.39	3.160(4)	144.2
N1-H1B…O1[6]	0.89	2.53	3.008(4)	114.3
N1-H1B…O1[7]	0.89	2.09	2.856(4)	144.1

[1]+X,1-Y,-1/2+Z; [2]-1+X,1-Y,-1/2+Z; [3]1/2+X,-1/2+Y,+Z; [4]-1/2+X,3/2-Y,-1/2+Z; [5]-1+X,+Y,-1+Z; [6]-1/2+X,-1/2+Y,-1+Z; [7]-1/2+X,1/2-Y,-1/2+Z

Table S6. The results of bond valence sum (BVS) calculations.[5]

Compound	Atom	Z	Bond length r_{ij}(Å)	R_0	B	Bond Valence s_{ij}
$N_2H_4Zn(HC_3N_3O_3)$	Zn	30				2.05
	N1	7	1.973	1.77	0.37	-0.58
	N3[1]	7	1.982	1.77	0.37	-0.56
	N4	7	2.055	1.77	0.37	-0.46
	N5[2]	7	2.07	1.77	0.37	-0.44

Table S7. The birefringence of cyanurates and isocyanurates.[6-11]

Compounds	Birefringence	Reference
$RbLi(HC_3N_3O_3)\cdot 2H_2O$	0.186@514 nm	6
$Pb_3(HC_3N_3O_3)_2(OH)_2$	0.342@800 nm	7
$Pb_2Cd(HC_3N_3O_3)_2(OH)_2$	0.291@800 nm	7
$SrHC_3N_3O_3\cdot 2H_2O$	0.184@532 nm	8
$SrHC_3N_3O_3\cdot 2.5H_2O$	0.341@532 nm	8
$KLi(HC_3N_3O_3)\cdot 2H_2O$	0.186@514 nm	9
$K_2(C_3N_3O_3H)$	~0.35@800nm	10
$Li_2HC_3N_3O_3\cdot 2H_2O$	0.345@532 nm	11
$Rb_2HC_3N_3O_3$	0.4@532 nm	11
$LiRbHC_3N_3O_3\cdot 2H_2O$	0.259@532 nm	11
$NaRb_{0.84}Cs_{0.16}HC_3N_3O_3\cdot 2H_2O$	0.238@532 nm	11
$N_2H_4Zn(HC_3N_3O_3)$	**0.294 @ 589 nm**	**This work**

Table S8. The SHG of cyanurates and isocyanurates

Compounds	SHG	
$K_6Cd_3(C_3N_3O_3)_4$	3 × KDP	12
$Y_5(C_3N_3O_3)(OH)_{12}$	2.5× KDP	13
$Yb_5(C_3N_3O_3)(OH)_{12}$	3.8× KDP	13
$Lu_5(C_3N_3O_3)(OH)_{12}$	4.2 × KDP	13
$KLi(HC_3N_3O_3)\cdot 2H_2O$	5.3× KH2PO4	9
$RbLi(HC_3N_3O_3)\cdot 2H_2O$	2.1 × KDP	6
$RbNa(HC_3N_3O_3)\cdot 2H_2O$	5.3 × KDP	14
$LiRbHC_3N_3O_3\cdot 2H_2O$	2.7 × KDP	11
$NaRb_{0.84}Cs_{0.16}HC_3N_3O_3\cdot 2H_2O$	3 × KDP	11
$K_2Pb(H_2C_3N_3O_3)_4(H_2O)_4$	2.6 × KDP	15
$Rb_3Na(H_2C_3N_3O_3)_4\cdot 3H_2O$	0.2 × KDP	16
$Cs_3Na(H_2C_3N_3O_3)_4\cdot 3H_2O$	0.67 × KDP	17
$N_2H_4Zn(HC_3N_3O_3)$	13 × KDP	**This work**

Table S9. The phosphorescence lifetime of organozinc compounds.[7]

Compounds	Phosphorescent lifetime	Reference
$[Zn_4(HEDP)_2(TIMB)]\cdot H_2O$	201 ms	18
$(Ph_3S)_2ZnCl_4$	263.17 ms	19
$(Ph_3S)_2MnCl_4$	2.84 ms	19
$[NH_3Me]\cdot[Zn_2(HEDP)(TPA)_{0.5}(H_2O)_2]\cdot 2H_2O$	163.7 ms	20
$[Zn_5(BIPA)_4MIM(OH)_2(H_2O)_2]$	7.041 ms	21
$[Zn_3(BIPA)_2(MIM)_3(OH)_2]\cdot 2H_2O$	3.155 ms	21
$Zn(HCOO)_2$(4,4'-bipy)	185.26 ms	22
$ZnCl_2\cdot$R -2-MP	167.16 ms	23
$ZnCl_2\cdot$S-2-MP	91.07 ms	23
$Na_2Zn_2(C_9H_3O_6)_2(H_2O)_8\cdot 3H_2O$	351 ms	24
$N_2H_4Zn(HC_3N_3O_3)$	**448 ms**	**This work**

Table S10. d_{11} and Δn after retaining a certain primitive element

	N_2H_4	$C_3N_3O_3H$	Zn
d_{11}	0.98 pm·V^{-1}	7.88 pm·V^{-1}	1.04 pm·V^{-1}
Δn	0.049@589 nm	0.34@589 nm	0.079@589 nm

Figure S1. As-synthesized single-crystal photo of $N_2H_4Zn(HC_3H_3N_3O)$.

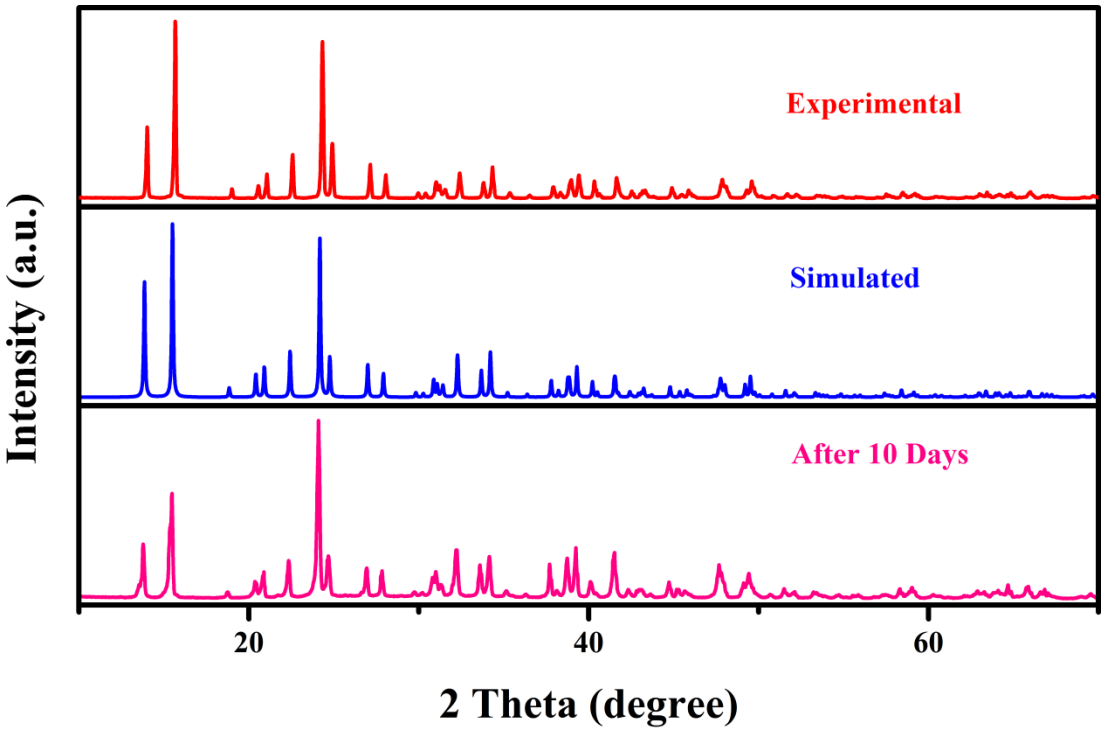

Figure S2. Experimental, simulated and soaked in water after 10 days XRD patterns for $N_2H_4Zn(HC_3N_3O_3)$.

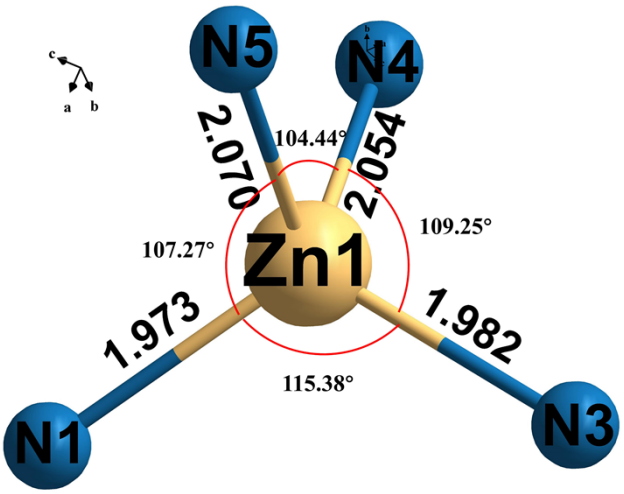

Figure S3. Zn atoms Coordination environment of the Zn atom.

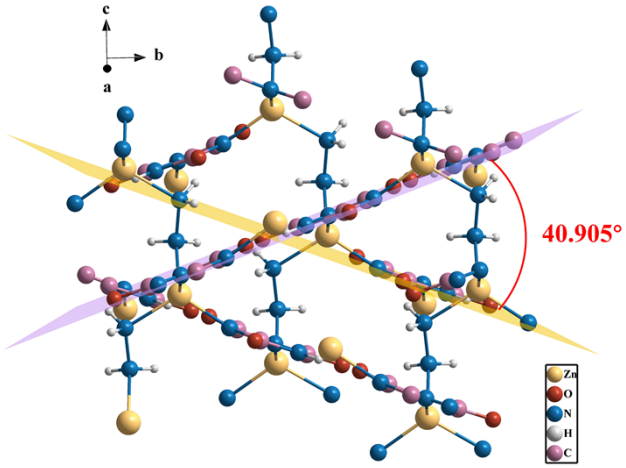

Figure S4. Two different arrangements of $HC_3N_3O_3^{2-}$ and the Angle between them.

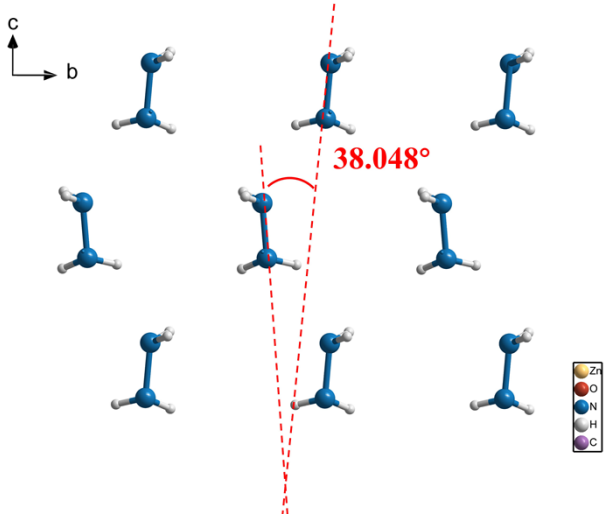

Figure S5. The intersection angle between two $[N_2H_4]$ molecules.

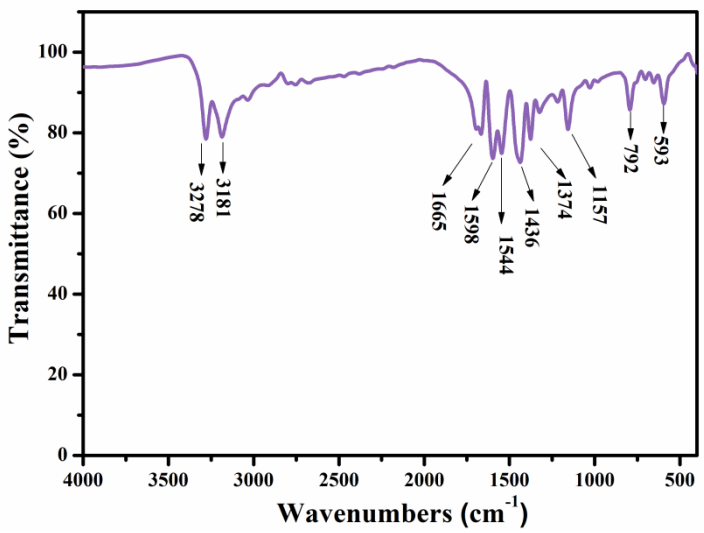

Figure S6. IR spectra of $N_2H_4Zn(HC_3N_3O_3)$.

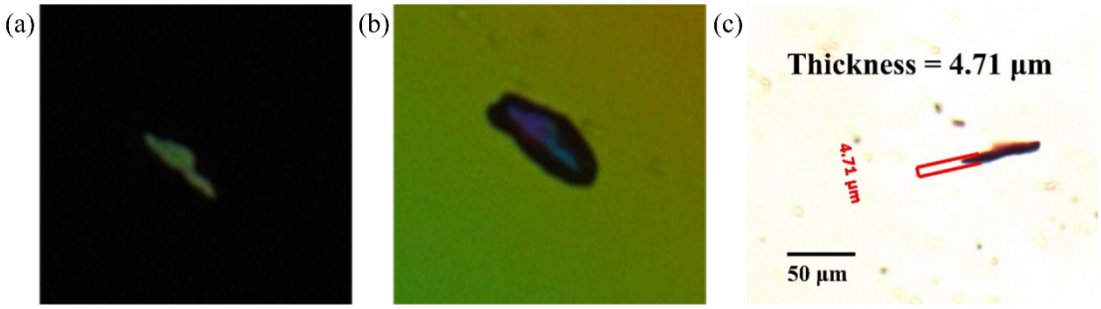

Figure S7. $N_2H_4Zn(HC_3N_3O_3)$ single crystals achieve complete extinction (a, b) in cross-polarized light and crystal thickness (c).

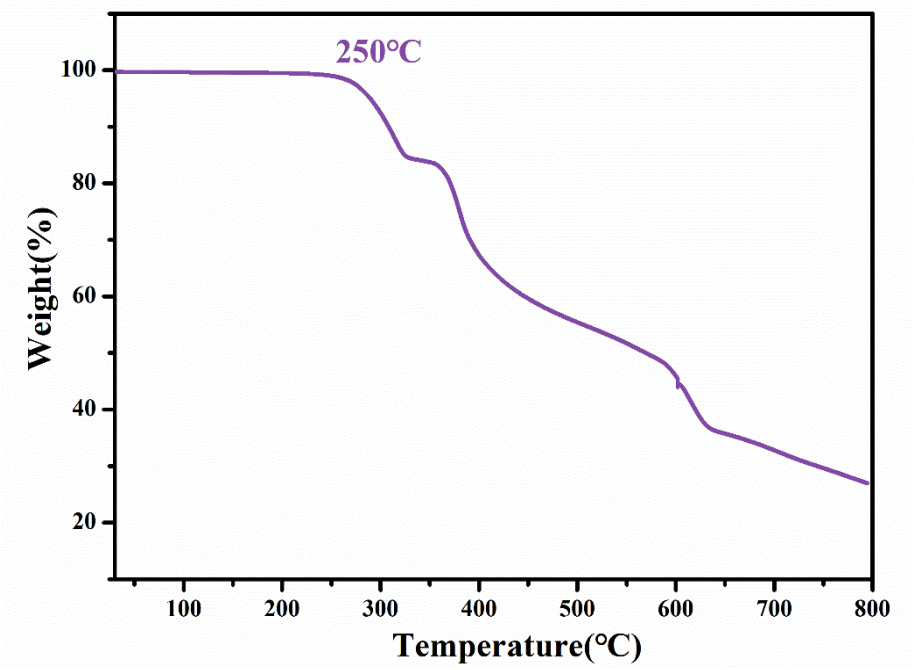

Figure S8. Thermogravimetric curve of $N_2H_4Zn(HC_3N_3O_3)$.

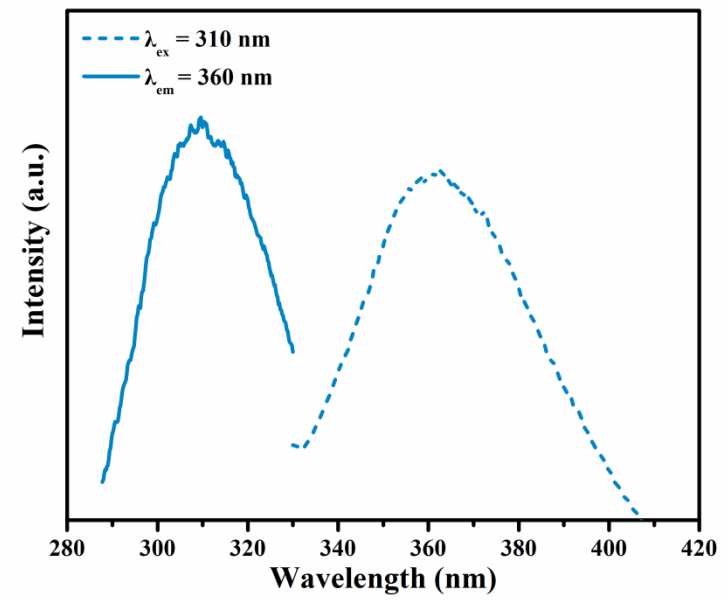

Figure S9. Fluorescence spectra of $N_2H_4Zn(HC_3N_3O_3)$.

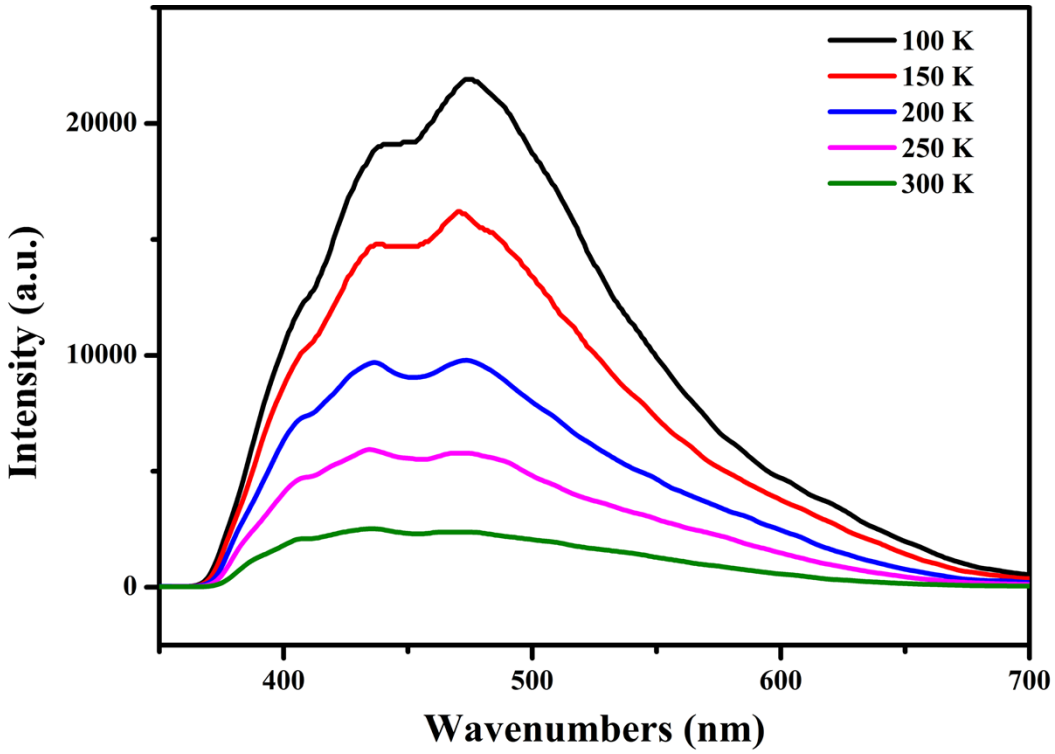

Figure S10. Phosphorescence spectra of $N_2H_4Zn(HC_3N_3O_3)$ recorded in the temperature range of 100-300 K.

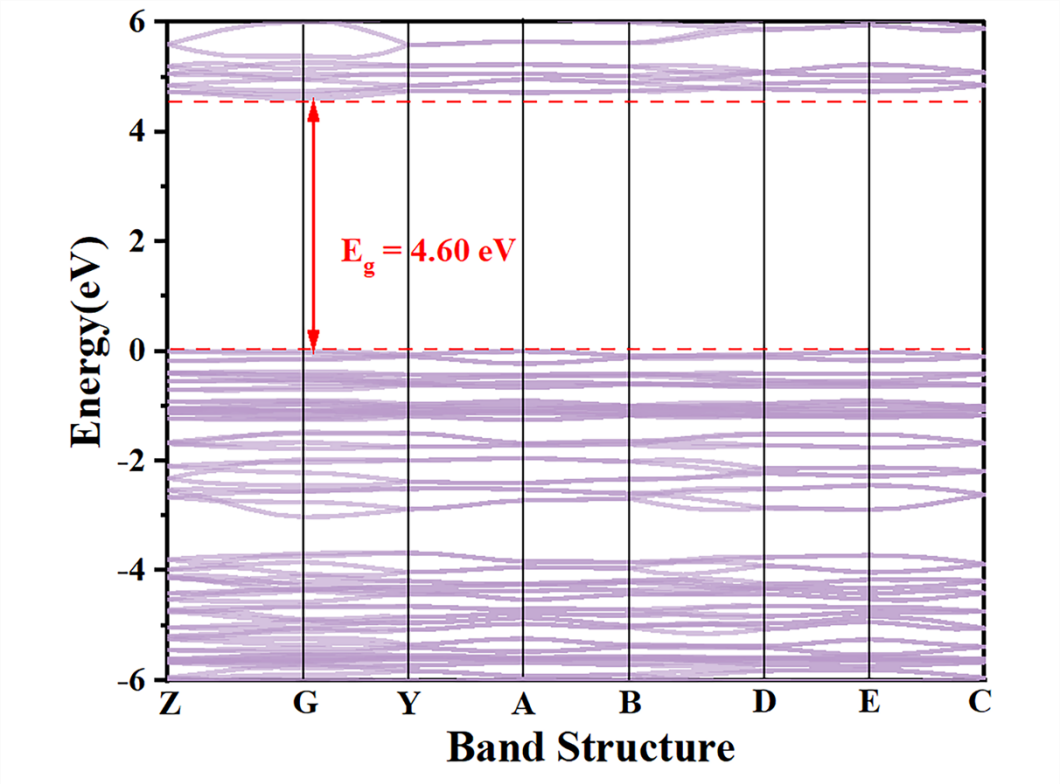

Figure S11. Calculated band structure of $N_2H_4Zn(HC_3N_3O_3)$.

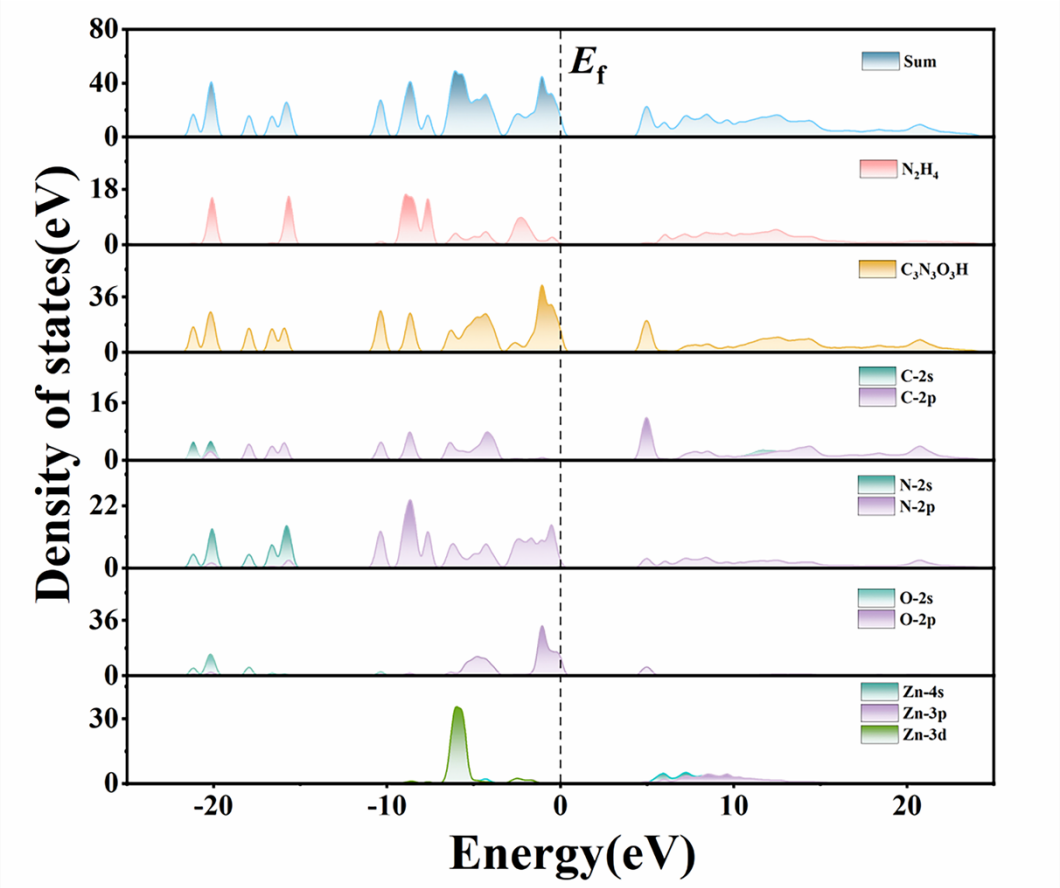

Figure S12. Calculated full and partial densities of states $N_2H_4Zn(HC_3N_3O_3)$.

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