

Electronic Supporting Information

**Solvent-free synthesis and optical properties of two open-framework  
metal oxalates with zeolitic ABW and diamondoid topologies†**

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## Synthesis

The starting material  $\text{Sc}_2\text{O}_3$ ,  $\text{In}(\text{OAc})_3$ , N,N,N',N'',N''-pentamethyldiethylenetriamine (pmdeta) and  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  were commercially available with analytical grade and used without further processing.

Colourless bulk crystals of compound **1** were obtained by heating a mixture of  $\text{Sc}_2\text{O}_3$  (0.138 g),  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (0.504 g), and pmdeata (210  $\mu\text{L}$ ) at 150 °C for 7 days (43% yield based on scandium). Following a similar synthetic procedure, colourless bulk crystals of compound **2** were obtained by heating a mixture of  $\text{In}(\text{OAc})_3$  (0.292 g),  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (0.378 g), and pmdeata (210  $\mu\text{L}$ ) at 150 °C for 7 days (58% yield based on indium).

## Single crystal X-ray diffraction

Single crystal X-ray diffraction data were collected on a Bruker APEX-II CCD diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. The structures were refined on  $F^2$  by full-matrix least-squares methods using the SHELXTL program package.<sup>1,2</sup>

## Powder X-ray diffraction

Powder X-ray diffraction data were obtained using a Shimadzu XRD-6100 diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), in the angular range of  $2\theta = 5\text{-}50^\circ$  (step width:  $0.02^\circ$ ).

## Thermogravimetric analysis

The thermogravimetric analyses of compounds **1** and **2** were performed on a METTLER TOLEDO TGA/DSC 2/1600 thermal analyzer, with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  and in the range of RT-800 °C at  $\text{N}_2$  atmosphere.

## IR spectroscopy

IR spectra of compounds **1** and **2** were obtained on a Nicolet Impact 410 FTIR spectrometer by using KBr pellets, with transmission mode from 4000 to  $400 \text{ cm}^{-1}$ .

## UV-vis diffuse reflectance spectroscopy

UV-vis diffuse reflectance spectra of compounds **1** and **2** were recorded by using Shimadzu UV-2600 UV-vis spectrophotometer at room temperature. The Kubelka-Munk function is used to calculate the absorption spectrum from the reflection

spectrum:  $F(R) = \alpha/S = (1-R)^2/2R$ , where  $R$  is the reflectance,  $\alpha$  is the absorption coefficient, and  $S$  is the scattering coefficient.<sup>3,4</sup>

### **Fluorescence spectroscopy**

The photoluminescence (PL) properties and photoluminescence quantum yield (PLQY) of compound **2** were measured using an Edinburgh FS-5 fluorescence spectrometer with a calibrated integrating sphere system.

### **Second-harmonic generation tests**

A Q-switched Nd:YAG laser was used to measure the SHG signals of compounds **1** and **2** and  $\text{KH}_2\text{PO}_4$  (KDP) under 1064 nm radiation based on the Kurtz–Perry method.<sup>5</sup>

### **Birefringence measurement**

The birefringence of compounds **1** and **2** was characterized by using the polarizing microscope equipped (ZEISS Axio Scope. A1) with a Berek compensator. The light source of the polarizing microscope is white light. Since the boundaries of the first-order, second-order and third-order interference colors are clear and the range is only fifth-order, the relative error is small enough. Before the scanning, the small and transparent crystals were chosen to be measured and scanned to improve the accuracy of the birefringence. The formula for calculating the birefringence is

$$R = |N_e - N_o| \times T = \Delta n \times T$$

Where  $R$  represents the optical path difference,  $\Delta n$  is the birefringence, and  $T$  denotes the thickness of the crystal.

### **Computational descriptions**

The first-principles calculations were carried out on compounds **1** and **2** by using the CASTEP software.<sup>6</sup> The generalized gradient approximation (GGA) with Perdew-Burke-Ernzer (PBE) was used for all the calculations.<sup>7</sup> All the atoms were performed by Norm-conserving pseudopotentials (NCP), with H 1s, C 2s<sup>2</sup>2p<sup>2</sup>, N 2s<sup>2</sup>2p<sup>3</sup>, O 2s<sup>2</sup>2p<sup>4</sup>, Sc 3d<sup>1</sup>4s<sup>2</sup>, In 5s<sup>2</sup>5p<sup>1</sup> treated as valence electrons.<sup>8</sup> Moreover, the kinetic energy cutoff for compounds **1** and **2** was chosen as 750 eV. The k-point sampling of  $3 \times 3 \times 2$  was chosen for compound **1** and the k-point sampling of  $4 \times 2 \times 4$  was chosen for compound **2**.<sup>9</sup> All other parameter settings are CASTEP default values.

Table S1. Crystal Data and Structure Refinement for compounds **1** and **2**

	compound <b>1</b>	compound <b>2</b>
Empirical formula	C <sub>17</sub> H <sub>29</sub> Sc <sub>2</sub> N <sub>3</sub> O <sub>18</sub>	C <sub>17</sub> H <sub>24</sub> In <sub>2</sub> N <sub>3</sub> O <sub>16</sub>
Formula weight	651.35	757.04
Crystal system	orthorhombic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (no. 19)	<i>P</i> 2 <sub>1</sub> (no. 4)
<i>a</i> , Å	10.8154(8)	8.4592(5)
<i>b</i> , Å	13.2068(8)	16.8623(5)
<i>c</i> , Å	18.3845(7)	8.8757(4)
<i>α</i> , degree	90	90
<i>β</i> , degree	90	99.942(5)
<i>γ</i> , degree	90	90
Volume, Å <sup>3</sup>	2626.0(3)	1247.03(10)
<i>Z</i>	4	2
<i>D</i> <sub>c</sub> , g/cm <sup>3</sup>	1.653	2.016
<i>μ</i> , mm <sup>-1</sup>	0.606	1.933
Radiation	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)
Reflections collected	37443	20821
Independent reflections	5891	5717
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0321, 0.0814	0.0179, 0.0435
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [all data]	0.0408, 0.0846	0.0188, 0.0438

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

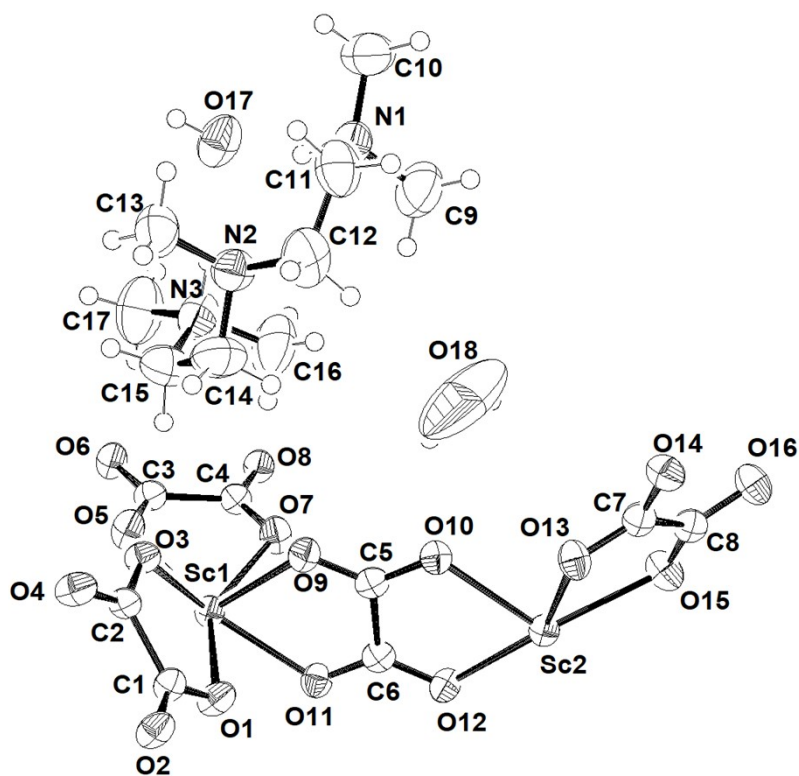
Table S2. Hydrogen bonds information for compound **1**

D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (deg)
N1-H1...O17	1.00	1.86	2.820(4)	159.4
N3-H3...O17	1.00	1.97	2.920(4)	157.8

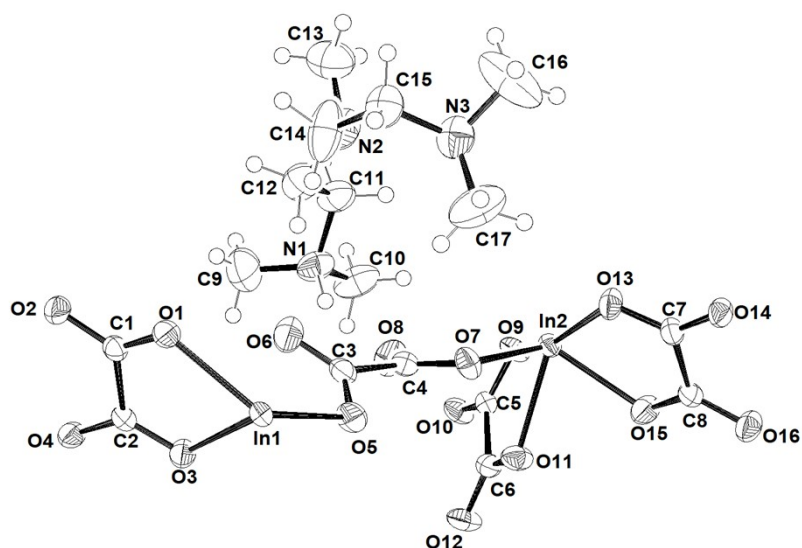
Table S3. Hydrogen bonds information for compound **2**

D-H...A <sup>a</sup>	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (deg)
N1-H1...O8	0.98	1.91	2.808(5)	150.2
N3-H3...O4#1	0.98	2.49	3.249(6)	133.7
N3-H3...O3#1	0.98	2.48	3.246(6)	134.9

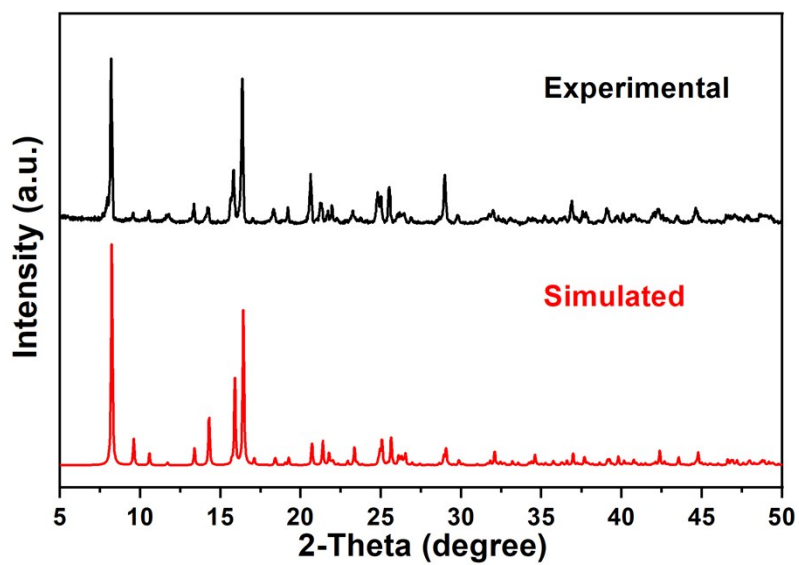
<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1 1-x, 1/2+y, 1-z.



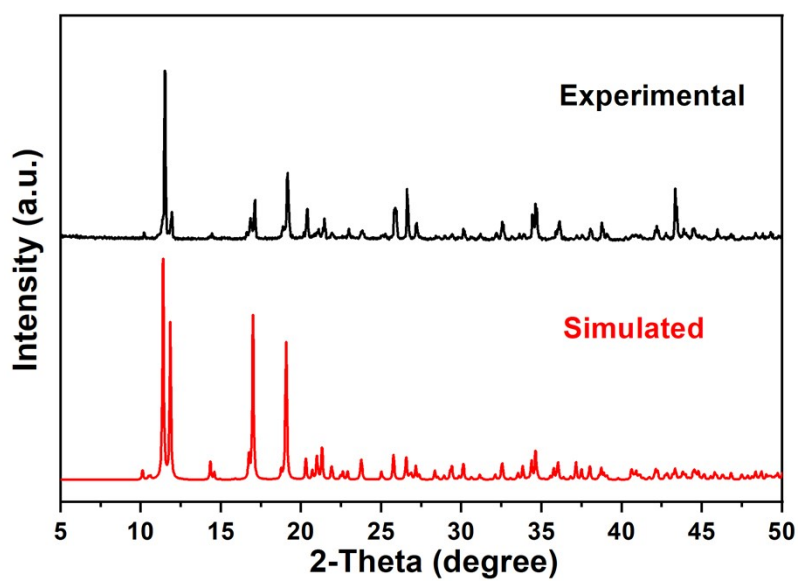
**Fig. S1** ORTEP plot of the asymmetric unit of compound **1**, showing the labeling scheme and the 50% probability displacement ellipsoids.



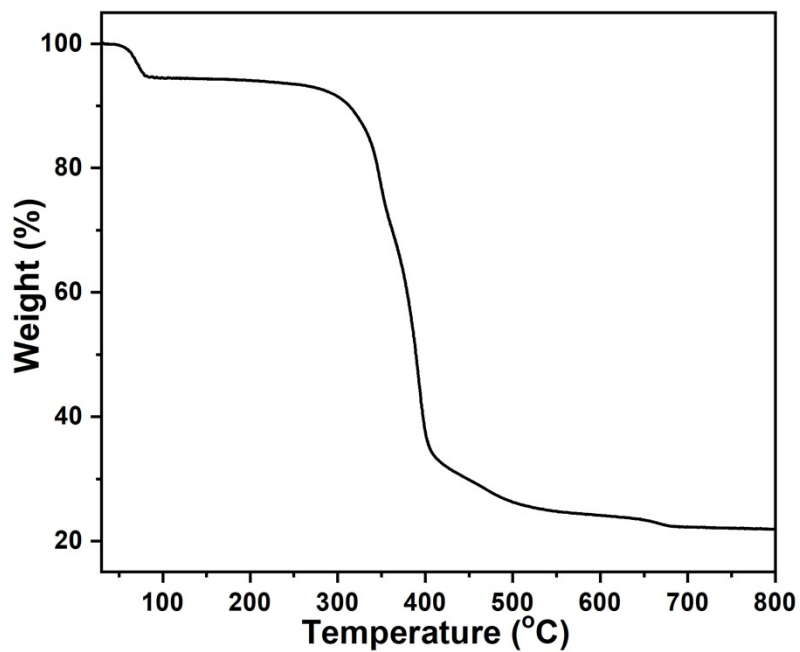
**Fig. S2** ORTEP plot of the asymmetric unit of compound **2**, showing the labeling scheme and the 50% probability displacement ellipsoids.



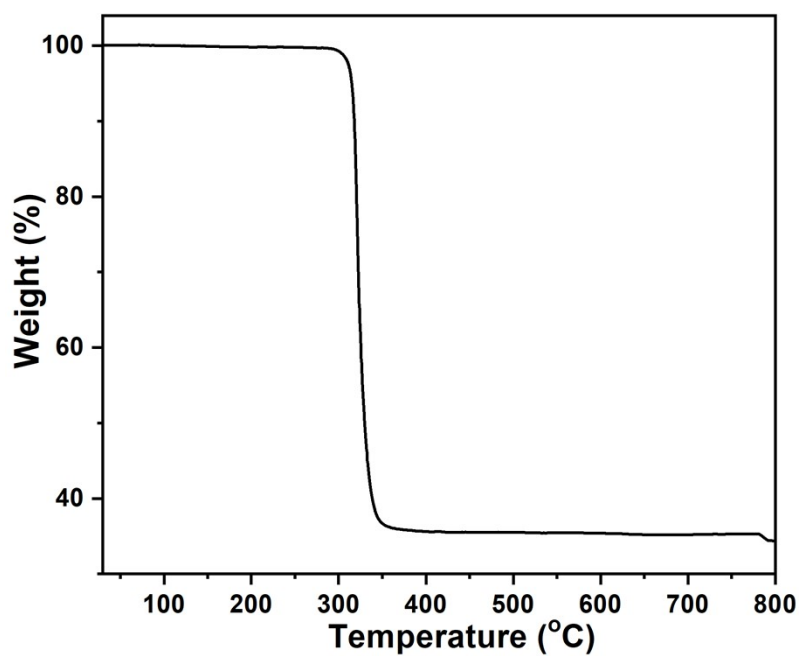
**Fig. S3** Experimental and simulated XRD patterns for compound 1.



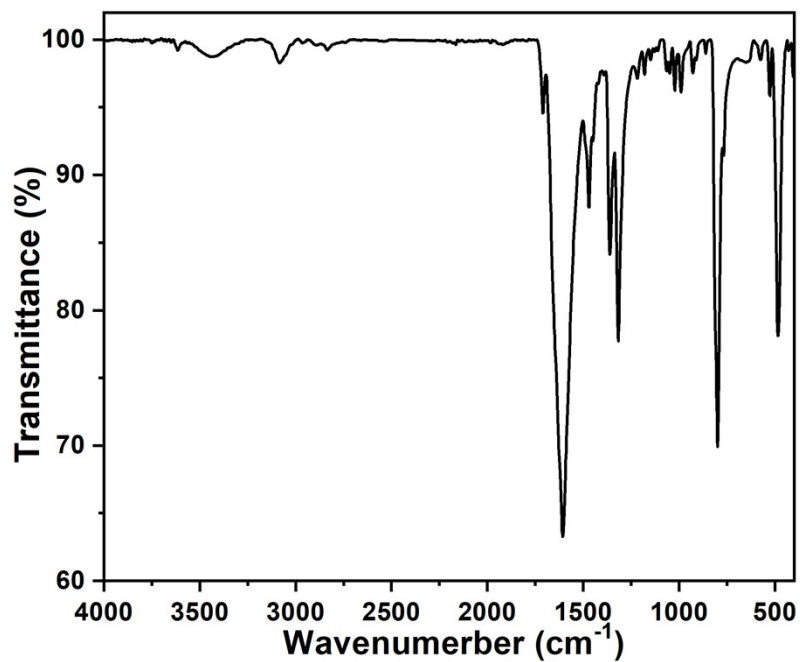
**Fig. S4** Experimental and simulated XRD patterns for compound 2.



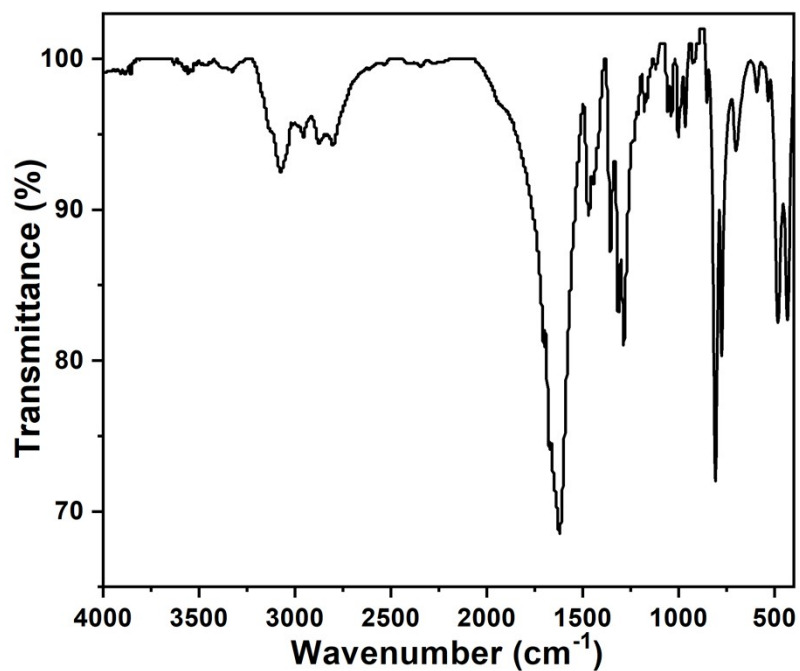
**Fig. S5** TGA analysis of compound **1** under N<sub>2</sub> atmosphere.



**Fig. S6** TGA analysis of compound **2** under N<sub>2</sub> atmosphere.



**Fig. S7** The IR spectrum of compound 1.

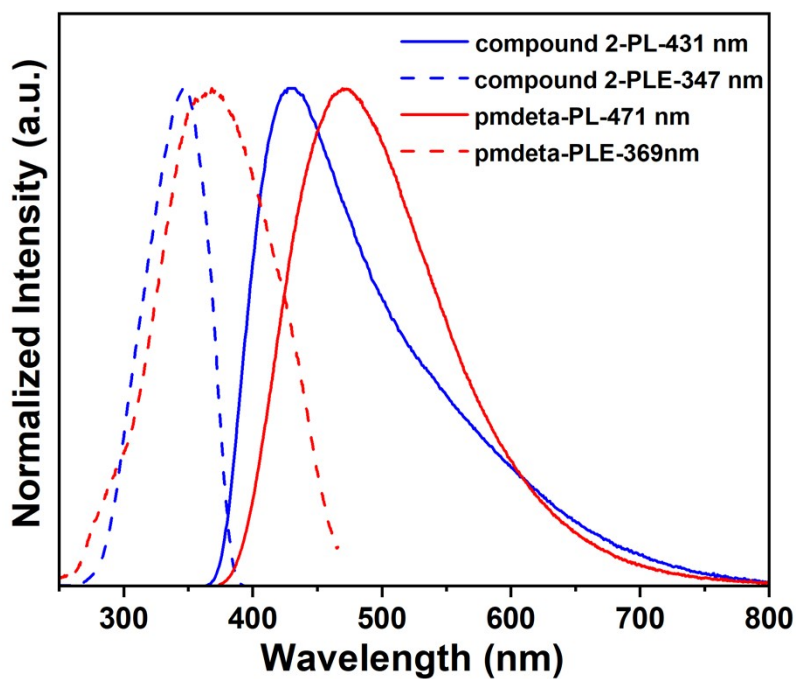


**Fig. S8** The IR spectrum of compound 2.

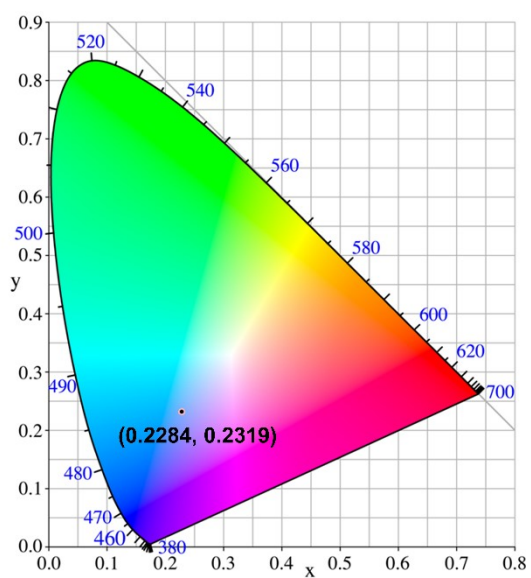




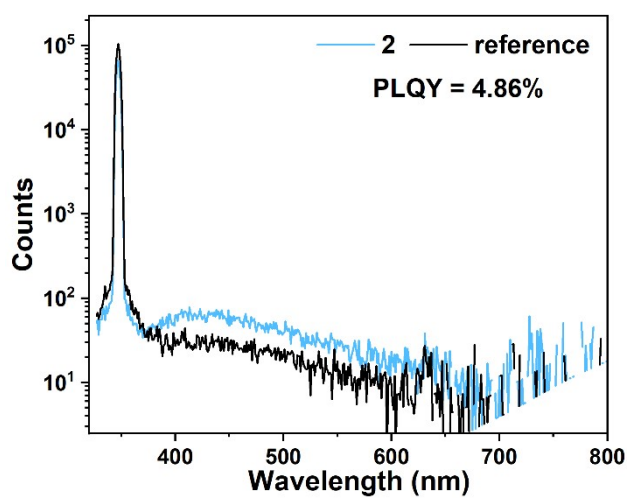
**Fig. S9.** Images of compound **2** crystals under natural light (left) and 365 nm UV light excitation (right).



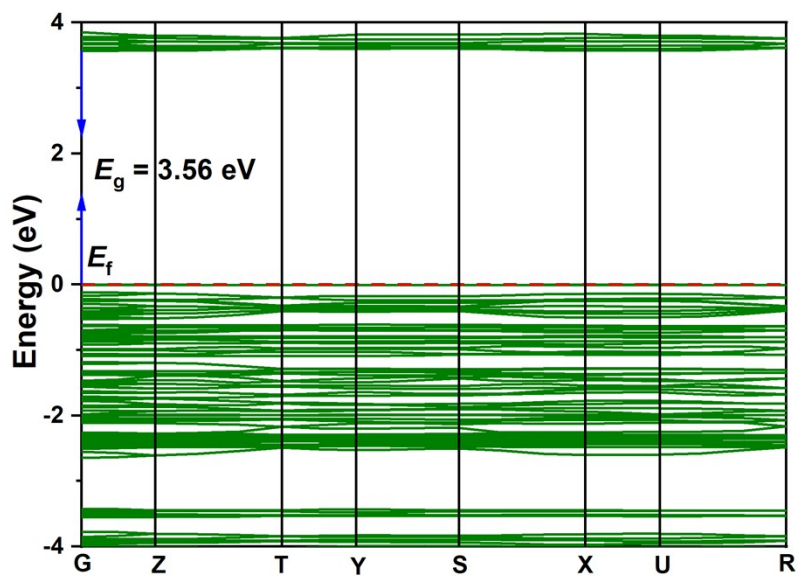
**Fig. S10.** PL and PLE spectra of compound **2** and pmdeta.



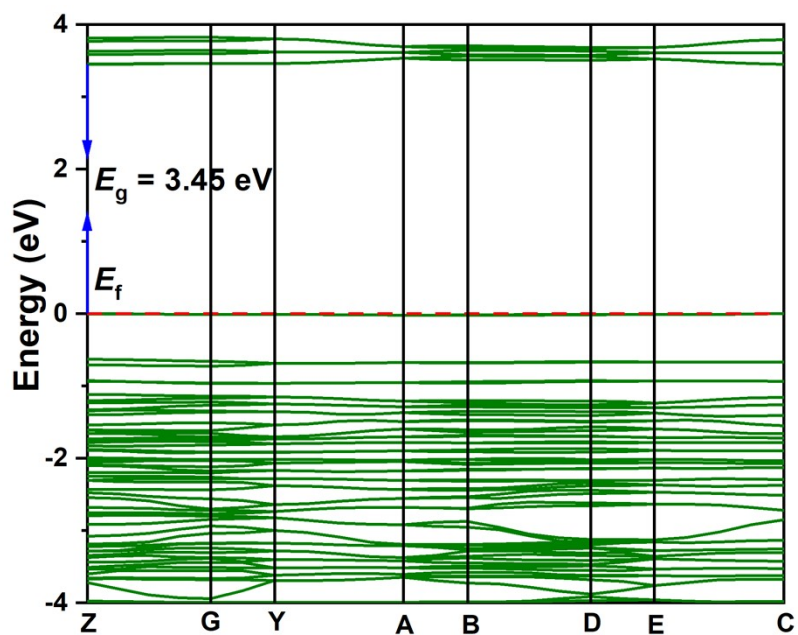
**Fig. S11.** CIE chromaticity coordinates of compound **2**.



**Fig. S12.** The photoluminescence quantum yield (PLQY) diagram of compound **2**.



**Fig. S13** Calculated band structure of compound **1** (the Fermi level is set at 0 eV).



**Fig. S14** Calculated band structure of compound **2** (the Fermi level is set at 0 eV).

## References

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