Electronic Supporting Information

# Histidine-directed synthesis and optical properties of two indium phosphite-oxalates with three-dimensional structures†

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## Synthesis

The starting material In(OH)$_3$, L-histidine, H$_3$PO$_3$, and H$_2$C$_2$O$_4$·2H$_2$O were commercially available with analytical grade and used without further processing.

In$_2$(C$_6$H$_{10}$N$_3$O$_2$)(HPO$_3$)$_2$(C$_2$O$_4$)$_{1.5}$·0.5H$_2$O (**1**) was prepared by heating a mixture of In(OH)$_3$ (0.166 g, 1 mmol), L-histidine (0.155 g, 1 mmol), H$_3$PO$_3$ (0.082 g, 1 mmol), and H$_2$C$_2$O$_4$·2H$_2$O (0.378 g, 3 mmol) in a 25 mL Teflon-lined stainless steel autoclave at 150 °C for 10 days. After cooling to room temperature, plate crystals of compound **1** were separated from the resulting product by filtration, washed with distilled water, and dried in air (43% yield based on Indium).

(C$_6$H$_{11}$N$_3$O$_2$)·[In$_4$(C$_6$H$_{10}$N$_3$O$_2$)(HPO$_3$)$_5$(H$_2$PO$_3$)(C$_2$O$_4$)$_2$] (**2**) was prepared by heating a mixture of In(OH)$_3$ (0.166 g, 1 mmol), L-histidine (0.155 g, 1 mmol), H$_3$PO$_3$ (0.205 g, 2.5 mmol), and H$_2$C$_2$O$_4$·2H$_2$O (0.378 g, 3 mmol) in a 25 mL Teflon-lined stainless steel autoclave at 150 °C for 10 days. After cooling to room temperature, prismatic crystals of compound **2** were separated from the resulting product by filtration, washed with distilled water, and dried in air (48% 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-Kα radiation ($\lambda$ = 0.71073 Å) at room temperature. The crystal structures were solved by direct methods. The structures were refined on $F^2$ by full-matrix least-squares methods using the SHELXTL program package.[1,2]

## Powder X-ray diffraction

Powder XRD data were obtained using a Shimazu XRD-6100 diffractometer with Cu-Kα radiation

($\lambda$ = 1.5418 Å), in the angular range of 2θ = 5-50°, and with a scan step width of 0.02° and a fixed time of 0.2 s.

## 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 cm$^{-1}$.

## UV-vis diffuse reflectance spectroscopy

The UV-vis diffuse reflectance spectra of the two compounds were recorded at room temperature on a Shimadzu UV-2600 UV-vis spectrophotometer in the wavelength range of 200-800 nm. BaSO$_4$

powder was used as 100% reflectance reference. The Kubelka-Munk function was used to calculate the absorption spectra from the reflection spectra: $F(R) = \alpha/S = (1-R)^2/2R$, where $R$ is the reflectance, $\alpha$ is the absorption coefficient, and $S$ is the scattering coefficient.[3,4]

## SHG tests

A Q-switched Nd:YAG laser was used to measure the SHG signals of the sieved samples under 1064 nm radiation based on Kurtz–Perry method.[5]

## Birefringence measurement

The birefringences of compounds **1** and **2** were characterized by using the polarizing microscope equipped (ZEISS Axio Scope. A1) with a Berek compensator.

## Luminescence performance measurement

The photoluminescence (PL) properties and PLQY of compounds **1** and **2** were characterized using an Edinburgh FS-5 fluorescence spectrometer with a calibrated integrating sphere system. The time-resolved PL decay was measured on a Fluoromax-3 fluorescence spectrometer.

## Computational methods

In order to understand the relationship between structure and properties of the two compounds, the first-principles calculations were carried out by using the CASTEP.[6] The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) was used for all the calculations.[7] All the atoms were performed by Norm-conserving pseudopotentials (NCP), with H $1s$, C $2s^2 2p^2$, N $2s^2 2p^3$, O $2s^2 2p^4$, P $3s^2 3p^3$, In $5s^2 5p^1$ treated as valence electrons.[8] The kinetic energy cutoff of 750 eV and the k-point sampling of $4 \times 4 \times 3$ were chosen for compound **1** and the k-point sampling of $4 \times 1 \times 4$ were chosen for compound **2**.[9] All other parameter settings are CASTEP default values.
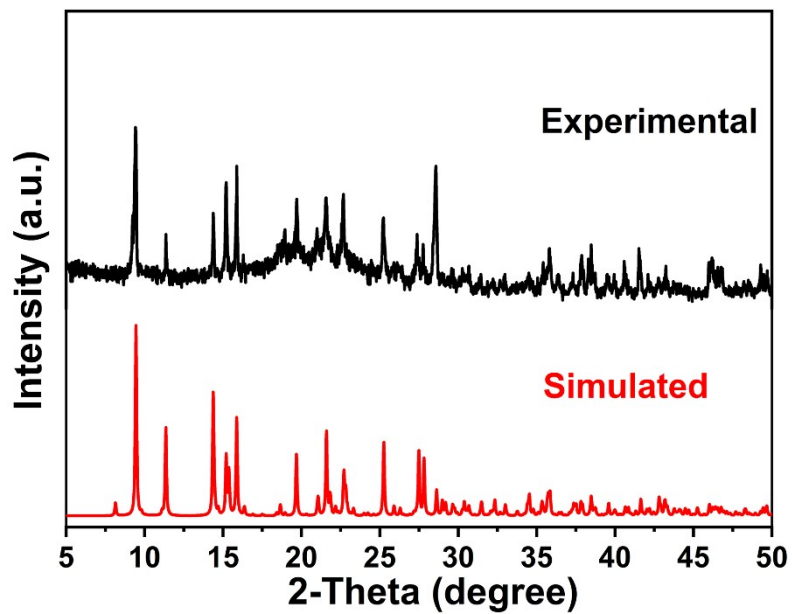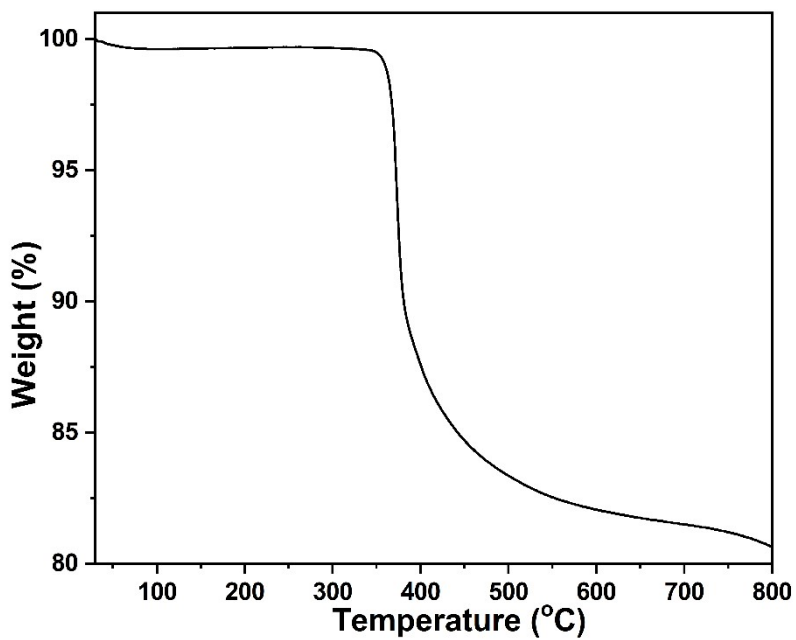
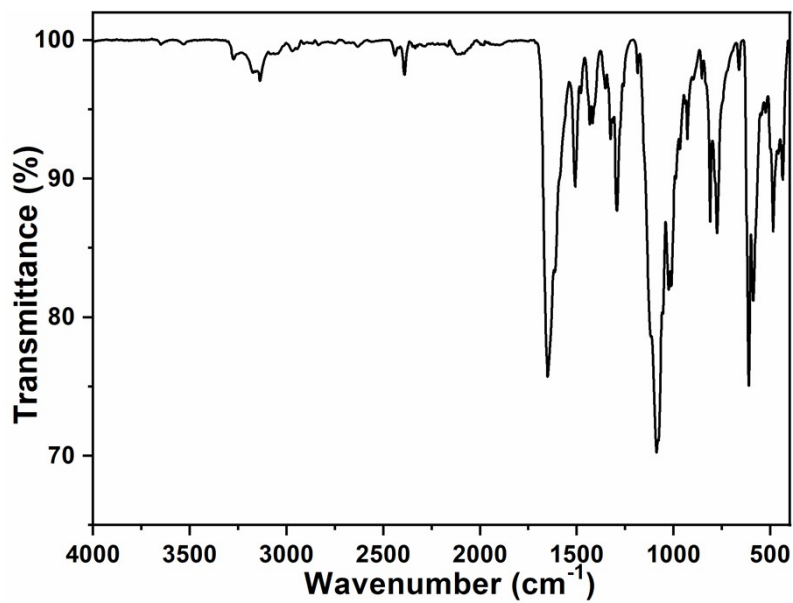**Fig. S1** Experimental and simulated XRD patterns for compound **1**.
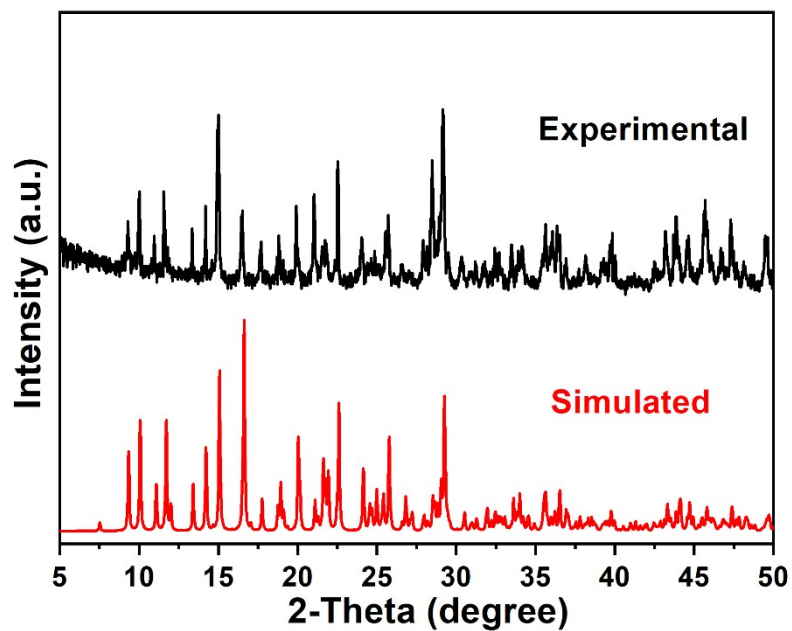


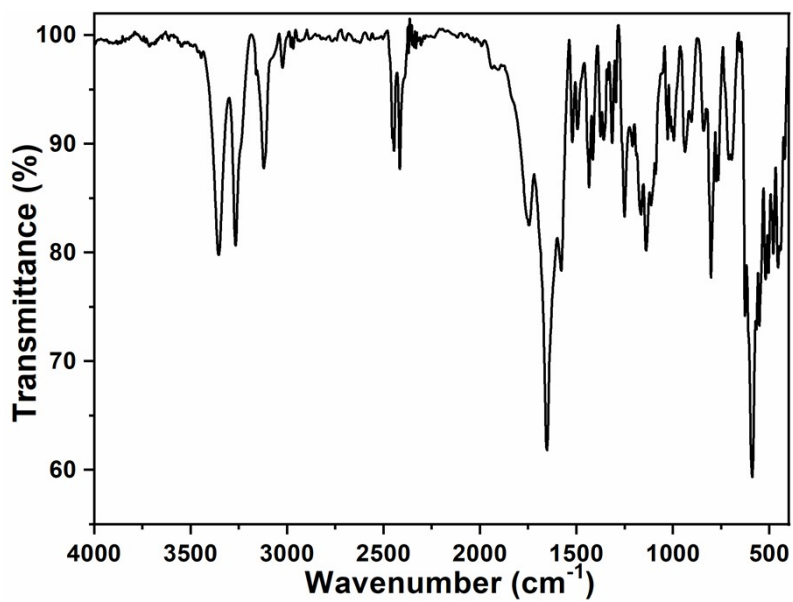**Fig. S2** Experimental and simulated XRD patterns for compound **2**.
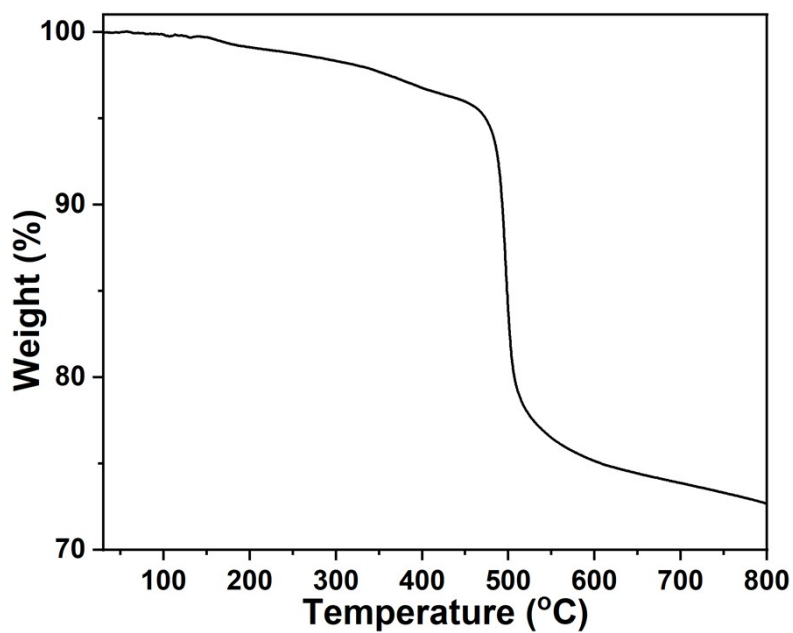
**Fig. S3** TGA analysis of compound **1** under $N_2$ atmosphere.
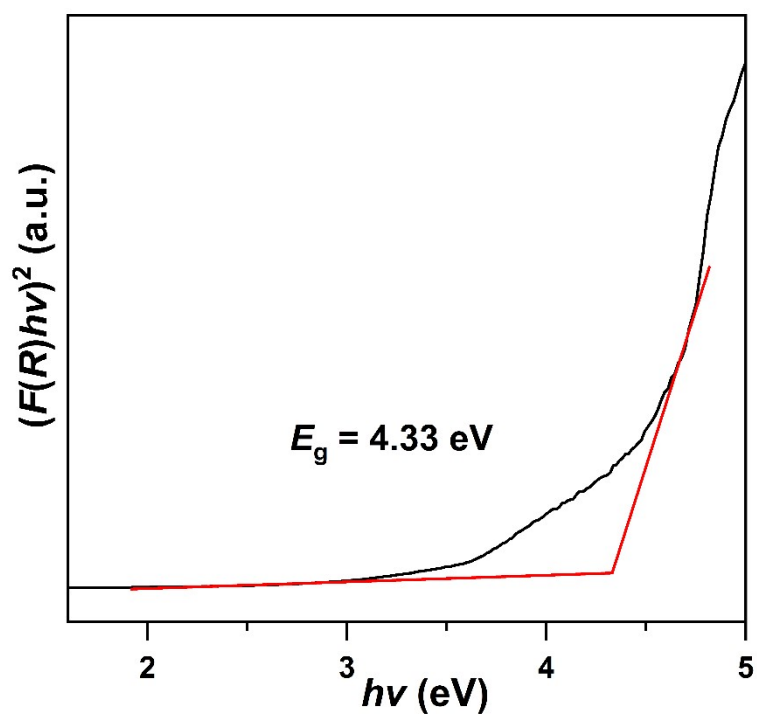


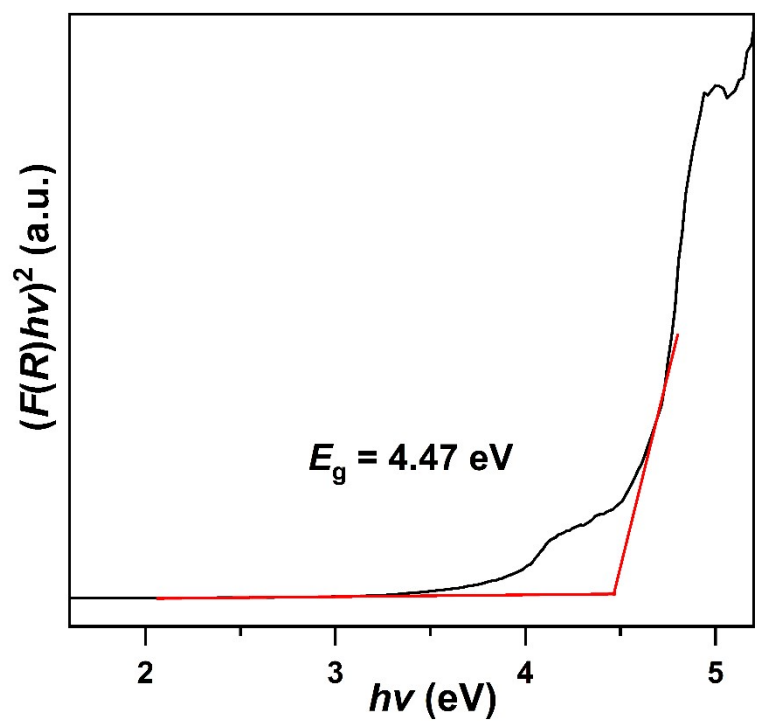**Fig. S4** TGA analysis of compound **2** under $N_2$ atmosphere.

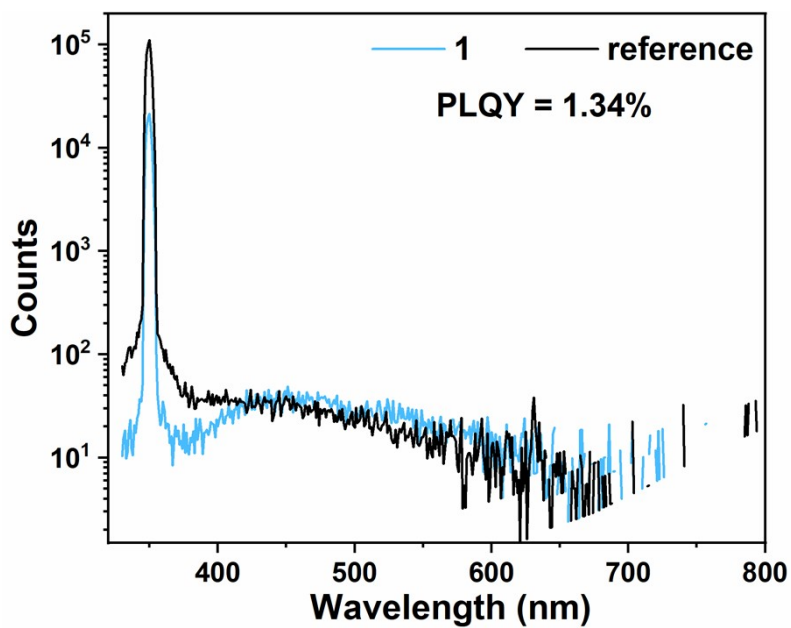**Fig. S5** The IR spectrum of compound **1**.



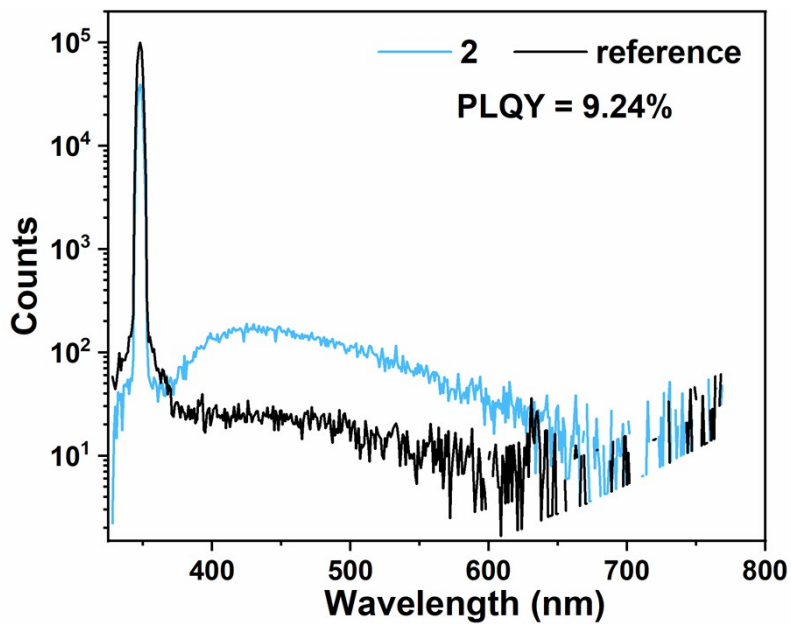**Fig. S6** The IR spectrum of compound **2**.

**Fig. S7** Tauc plot of $[F(R)hv]^2$ versus *hv* for the optical band gap of compound **1**.



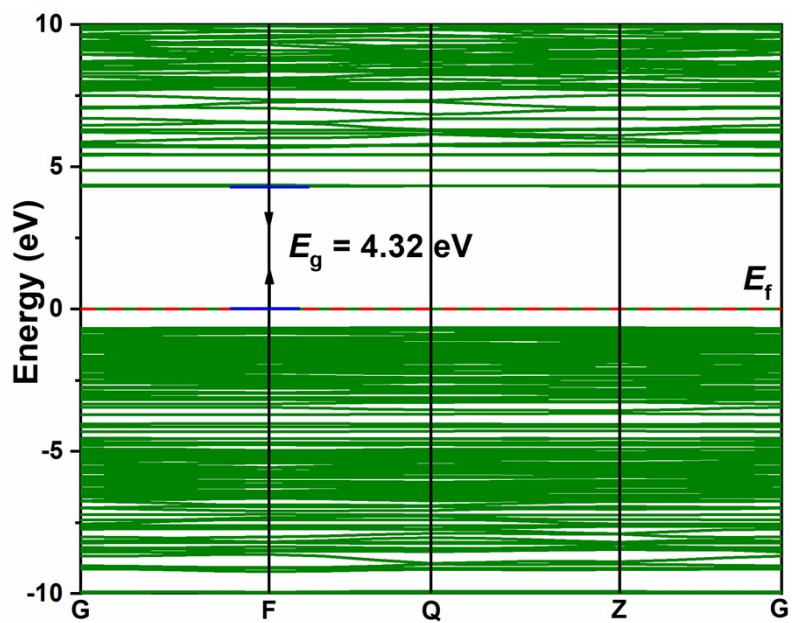**Fig. S8** Tauc plot of $[F(R)hv]^2$ versus *hv* for the optical band gap of compound **2**.

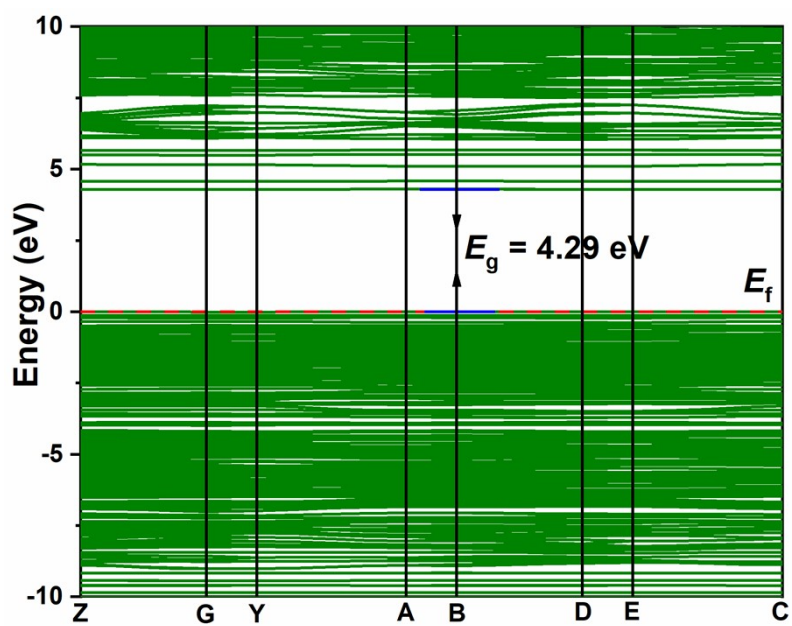**Fig. S9** The photoluminescence quantum yield (PLQY) diagram of compound **1**.



**Fig. S10** The photoluminescence quantum yield (PLQY) diagram of compound **2**.

**Fig. S11** Calculated band structure of compound **1** (the Fermi level is set at 0 eV).



**Fig. S12** Calculated band structure of compound **2** (the Fermi level is set at 0 eV).
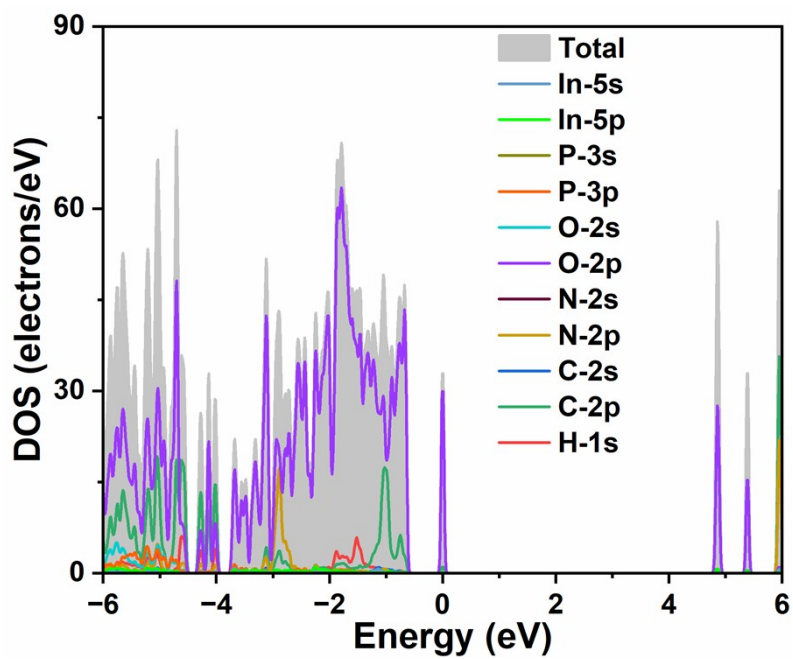
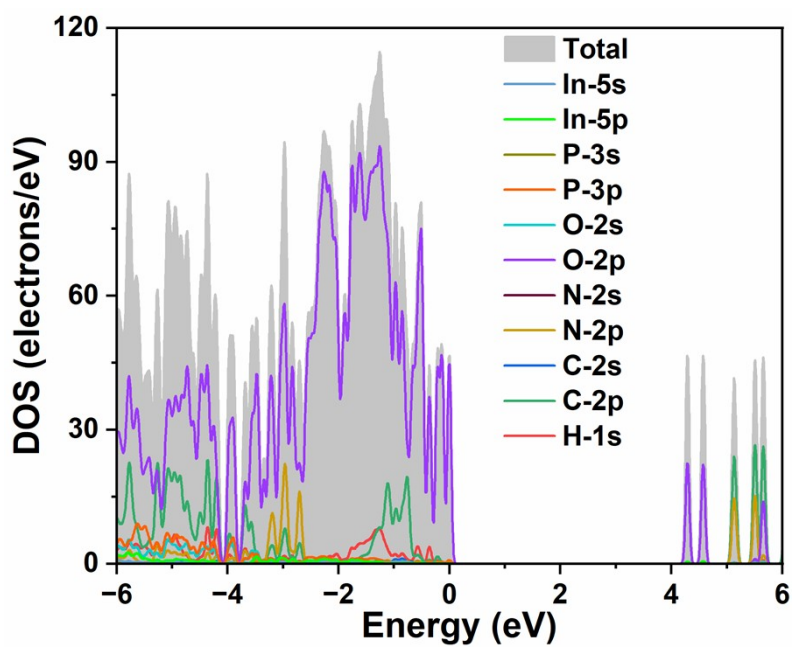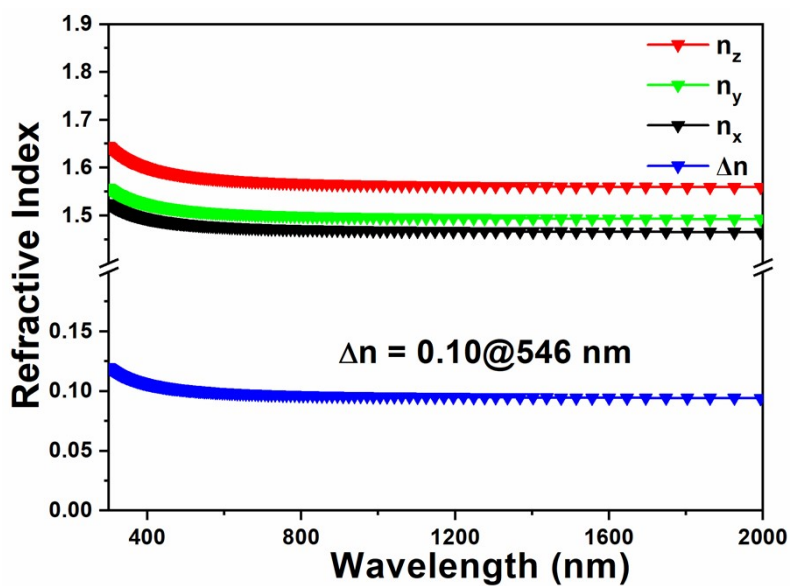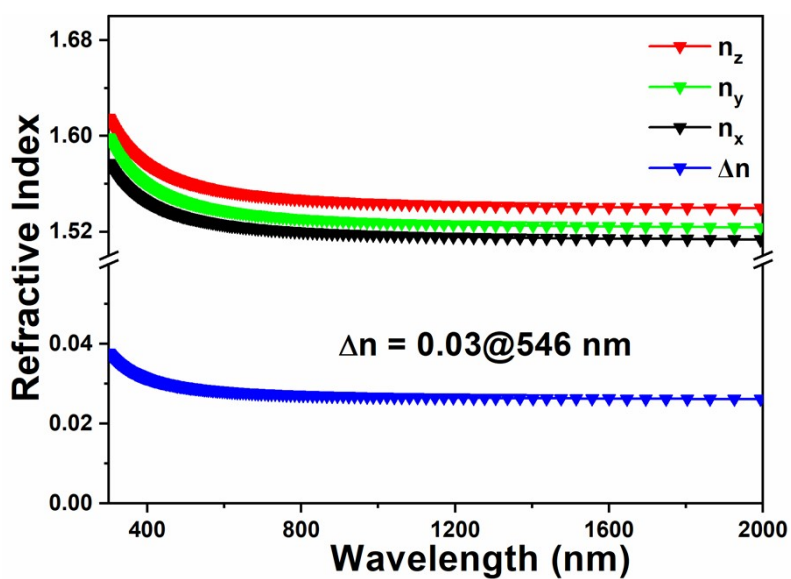**Fig. S13** Total and partial DOSs for compound **1**.



**Fig. S14** Total and partial DOSs for compound **2**.

**Fig. S15** Calculated dispersion of refractive index curves and birefringence of compound **1**.



**Fig. S16** Calculated dispersion of refractive index curves and birefringence of compound **2**.

# References

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