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Solvent-free synthesis of magnesium phosphite-oxalates showing second-harmonic generation responses

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Synthesis

$Mg(OAc)_2·4H_2O$ (99%, Aladdin), ethylenediamine (98%, Aladdin), N,N,N',N'-tetramethyl-1,3-propanediamine (97%, Aladdin), H_3PO_3 (99%, MACKLIN), $H_2C_2O_4·2H_2O$ (≥99.5%, Aladdin) were commercially available and used without further processing.

Synthesis of $C_2H_{10}N_2·Mg(H_2PO_3)_2(C_2O_4)$ (**1**): A mixture of $Mg(OAc)_2·4H_2O$ (0.428 g), H_3PO_3 (0.410 g), ethylenediamine (200 μL), and $H_2C_2O_4·2H_2O$ (0.252 g) was sealed in a 25 mL Teflon-lined steel autoclave and heated at 130 °C for 3 days, and then cooled slowly to room temperature at a rate of 6 °C h^{-1}. The solid products consist of colourless block crystals of compound **1** and some unknown powder. Colourless block crystals of compound **1** were separated from the resulting products by sonication, washed with distilled water, and then dried in air (60% yield based on magnesium).

Synthesis of $C_7H_{20}N_2·Mg_2(H_2PO_3)_2(C_2O_4)_2·H_2O$ (**2**): A mixture of $Mg(OAc)_2·4H_2O$ (0.428 g), H_3PO_3 (0.328 g), N,N,N',N'-tetramethyl-1,3-propanediamine (335 μL), and $H_2C_2O_4·2H_2O$ (0.504 g) was sealed in a 25 mL Teflon-lined steel autoclave and heated at 150 °C for 7 days, and then cooled slowly to room temperature at a rate of 6 °C h^{-1}. The solid products consist of colourless block crystals of compound **2** and some unknown powder. Colourless block crystals of compound **2** were separated from the resulting products by sonication, washed with distilled water, and then dried in air (41% yield based on magnesium).

Single crystal X-ray diffraction

Single crystal X-ray diffraction data were collected on a on a New Gemini, Dual, Cu at zero, EosS2 diffractometer at room temperature. 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 X-ray diffraction data were obtained using a Shimazu XRD-6100 diffractometer with Cu-Kα radiation (λ = 1.5418 Å), in the angular range of 2θ = 5-50° (step width: 0.02°).

Thermogravimetric analysis

The thermogravimetric analyses of compounds **1** and **2** were performed on a Netzsch STA 409 PC thermal analyzer, with a heating rate of 10 ºC /min and in the range of RT-800 ºC at 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 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, α is the absorption coefficient, and S is the scattering coefficient.[3, 4]

Second-harmonic generation tests

A Q-switched Nd: YAG lasers was used to measure the SHG signals of compound **1**, compound **2**, and KDP under 1064 nm radiation based on Kurtz-Perry method.[5] Crystalline compounds **1** and **2** and KDP were ground and sieved into the following particle size: 25-45, 45-58, 58-75, 75-106, 106-150, and 150-212 μm owing to that the SHG efficiency mainly depends on the particle size.

Computational descriptions

The first-principles calculations were carried out on compounds **1** and **2** by using the CASTEP.[6] The gradient-corrected functional (GGA) with Perdew-Burke-Ernzer (PBE) was used for all the calculations.[7] All the atoms were performed by Norm-conserving pseudopotentials (NCP), with H 1s, C $2s^22p^2$, N $2s^22p^3$, O $2s^22p^4$, P $3s^23p^3$, Mg $3s^2$ treated as valence electrons.[8] The kinetic energy cutoff of 900 eV and the k-point sampling of 2 × 1 × 3 were chosen for compound **1** and the k-point sampling of 1 × 1 × 3 were chosen for compound **2**.[9] All other parameter settings are CASTEP default values.

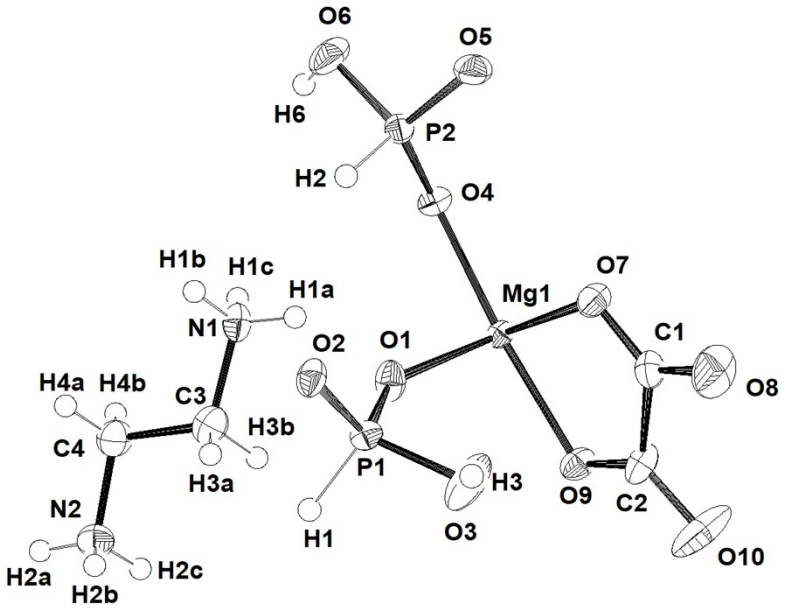

Fig. S1 ORTEP plot of the asymmetric unit of compound **1**, showing the labeling scheme and the 50% probability displacement ellipsoids.

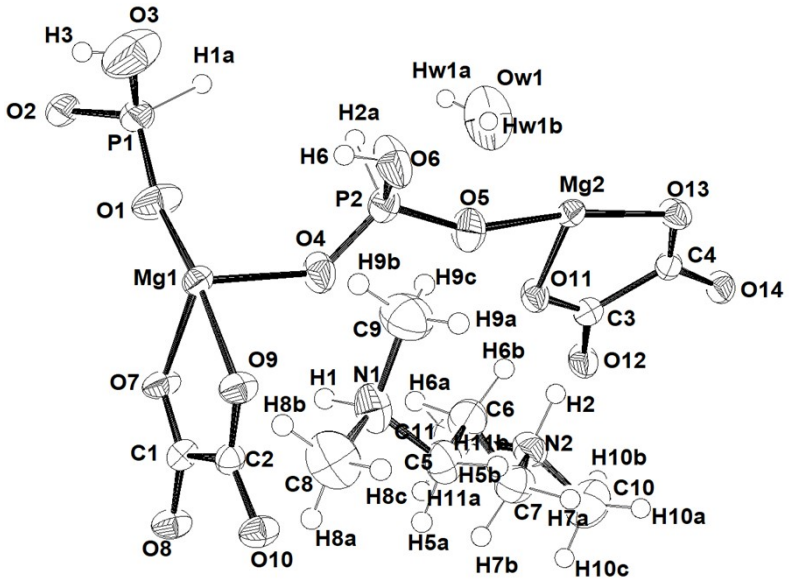

Fig. S2 ORTEP plot of the asymmetric unit of compound **2**, showing the labeling scheme and the 50% probability displacement ellipsoids.

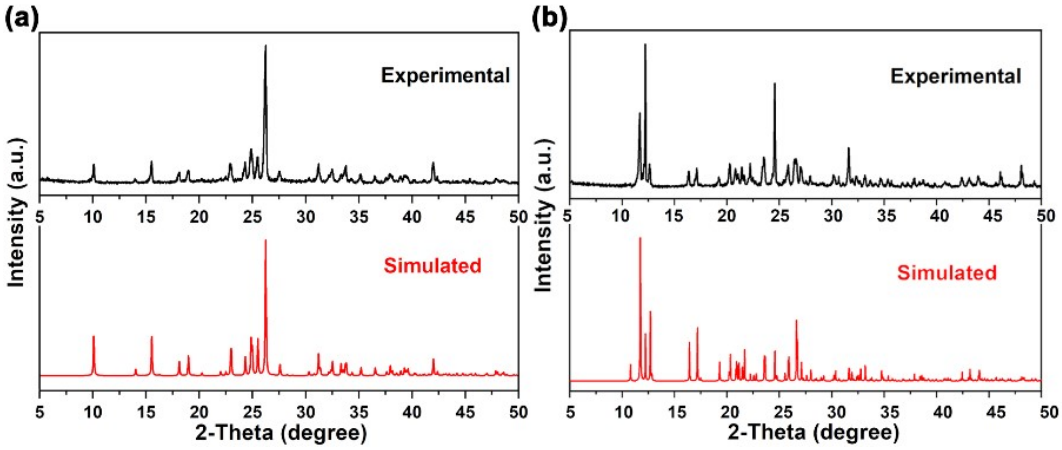

Fig. S3 Experimental and simulated XRD patterns for compound **1** (a) and compound **2** (b).

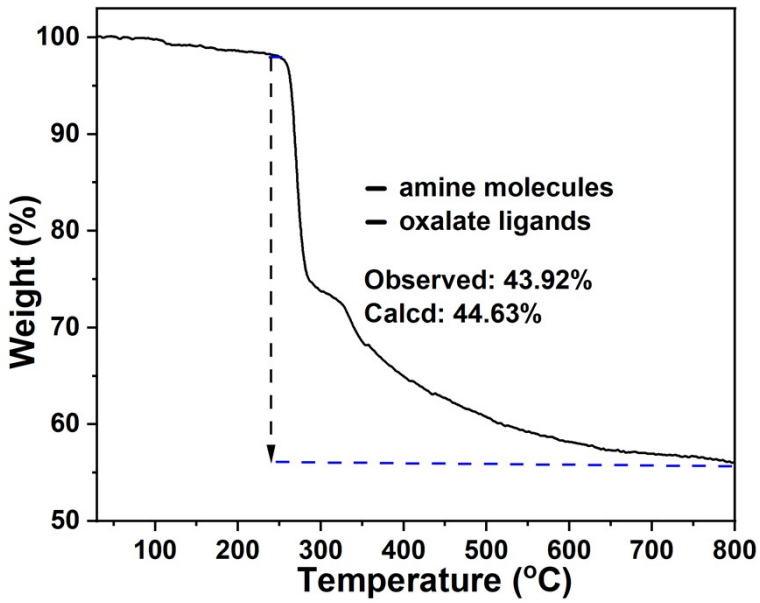

Fig. S4 TGA analysis of compound **1** under N_2 atmosphere.

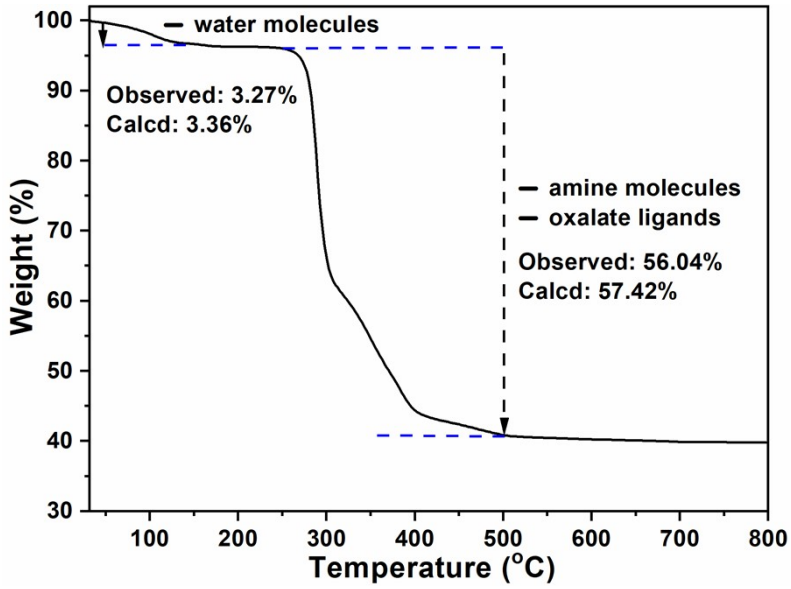

Fig. S5 TGA analysis of compound **2** under N_2 atmosphere.

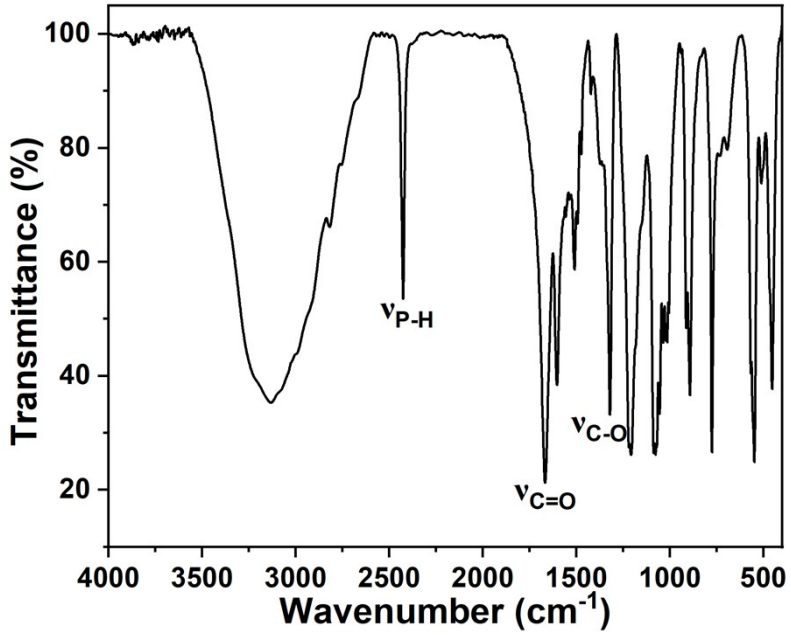

Fig. S6 The IR spectrum of compound **1**.

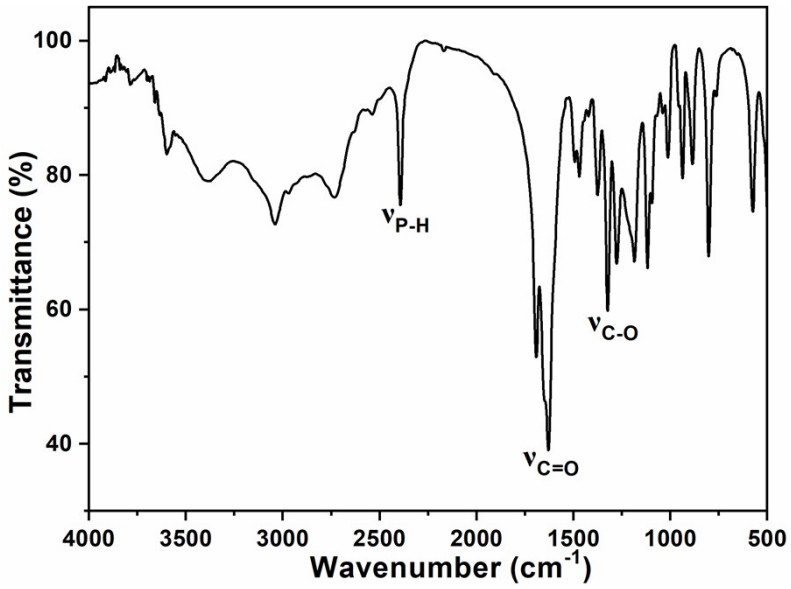

Fig. S7 The IR spectrum of compound **2**.

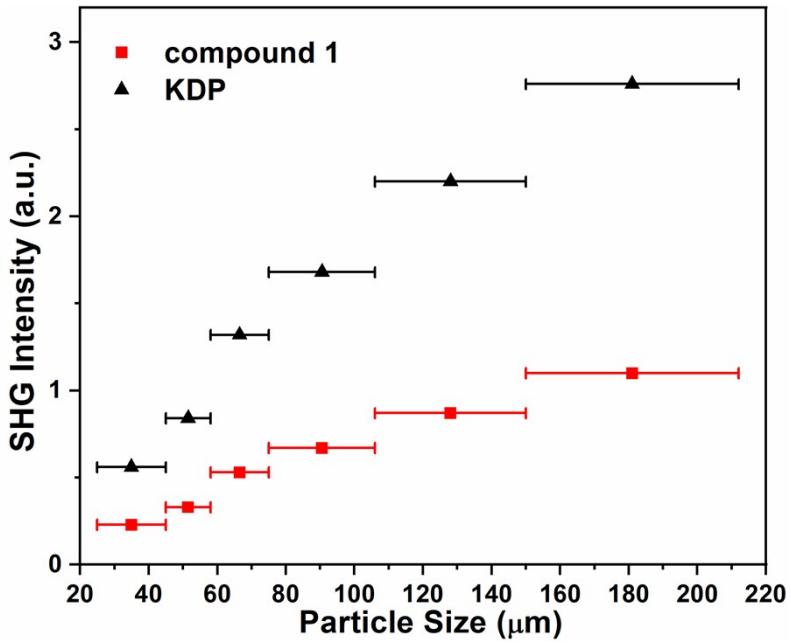

Fig. S8 SHG intensity versus particle size at 1064 nm for compound **1**.

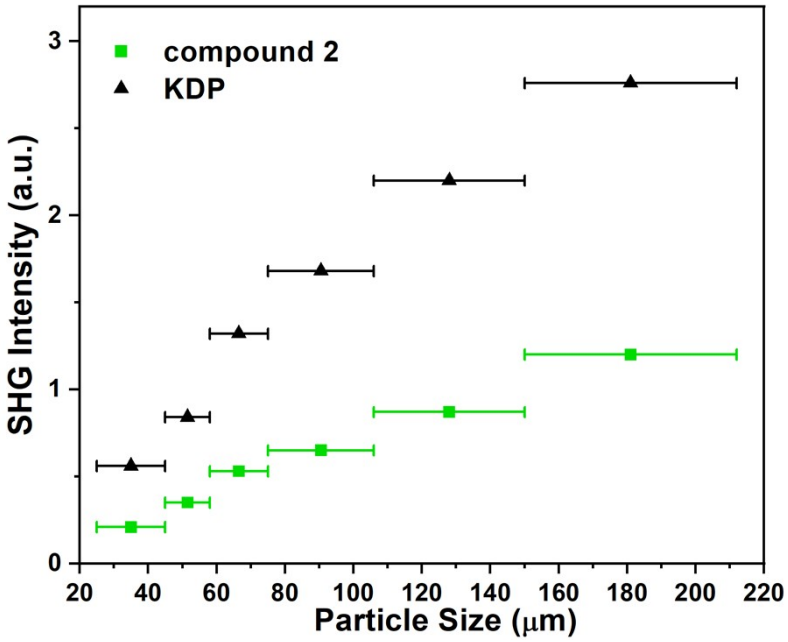

Fig. S9 SHG intensity versus particle size at 1064 nm for compound **2**.

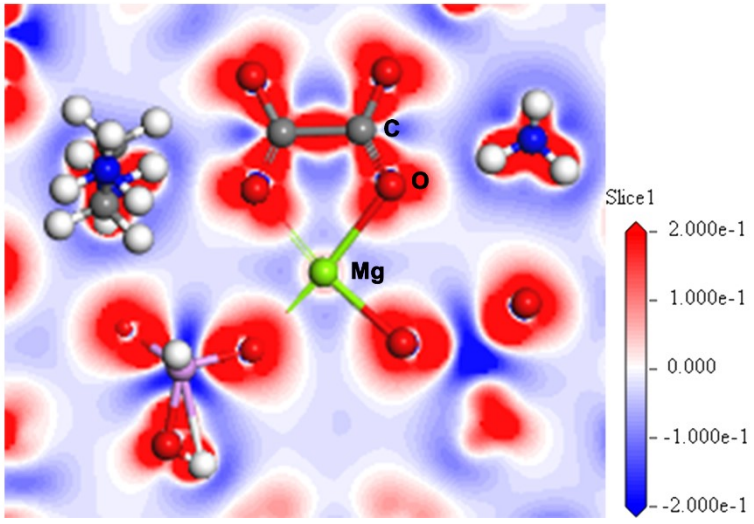

Fig. S10 Electron-density difference map of compound **1**.

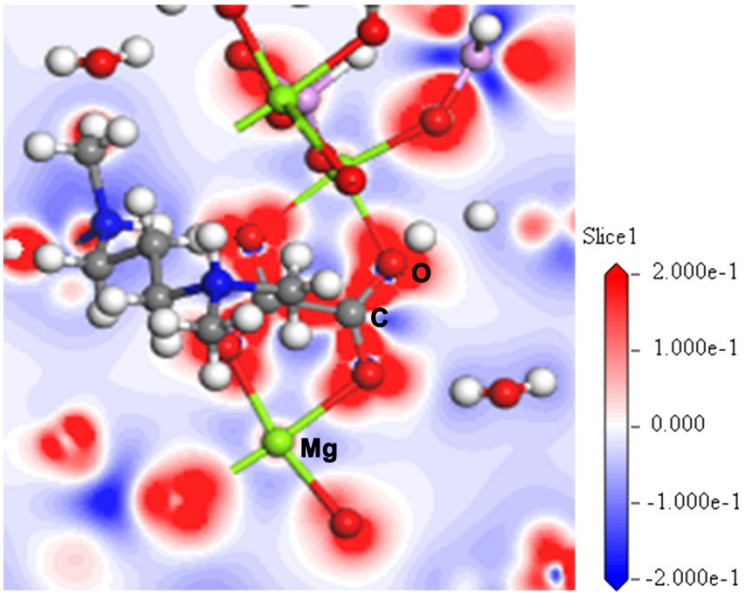

Fig. S11 Electron-density difference map of compound **2**.

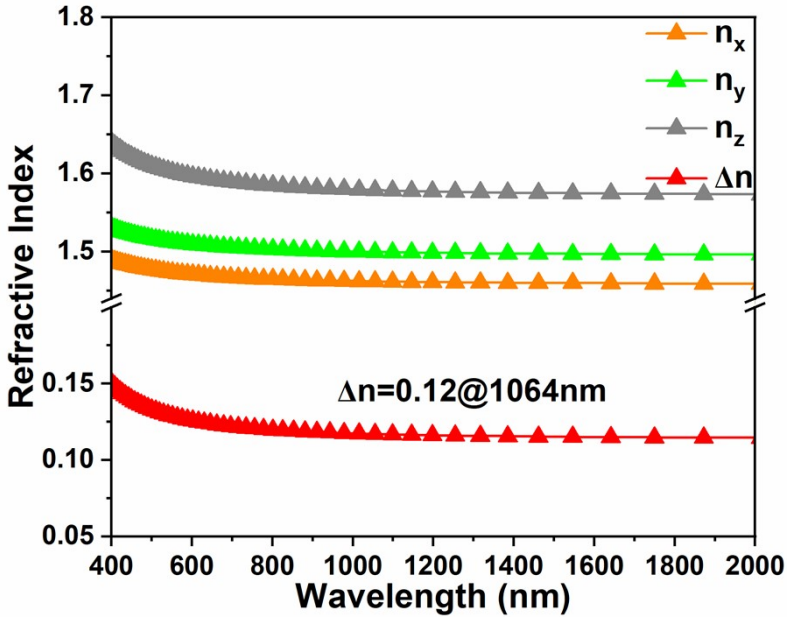

Fig. S12 Calculated refractive indexes for compound **1**.

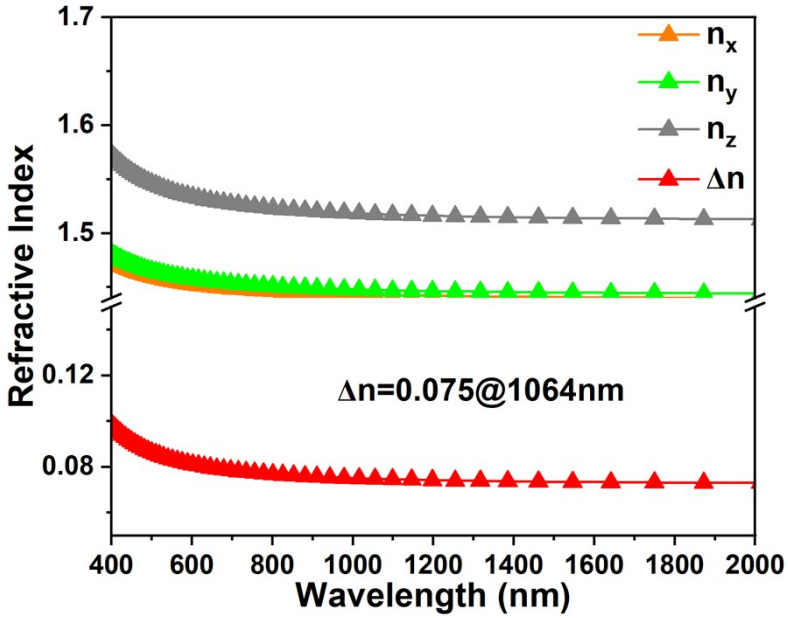

Fig. S13 Calculated refractive indexes for compound **2**.

References

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