Supplementary Information (SI) for CrystEngComm.

A novel sandwich Ni-added polyoxometalate with nonlinear optical properties and photothermal conversion performance

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Content

1. Experimental section

FT-IR spectrum were measured by using a Nicolet iS10 FT-IR spectrometer in the range of 400–4000 cm^{-1} with KBr pallets. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance XRD diffractometer with Cu Kα radiation (λ = 1.54056 Å). Thermogravimetric analyses were conducted in under N_2 flowing on a Shimadzu DTG-60H with the heating rate of 10 °C min^{-1} from 40 to 1000 °C. UV-Vis absorption spectra were obtain using a SP-1901 UV-Vis spectrophotometer. Conmpound **1** was irradiated using a near-infrared (808 nm) VCL-808nmM1-7W laser. A Fotric 326C+#L25 thermal imaging camera was employed to monitor the sample, collecting real-time temperature data during the process.

2. Supporting Figures

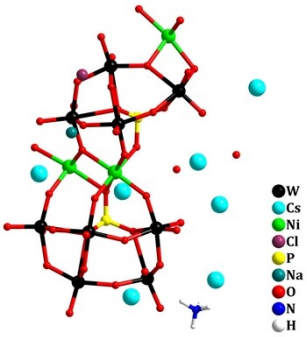

Figure S1 Asymmetric unit of **1**.

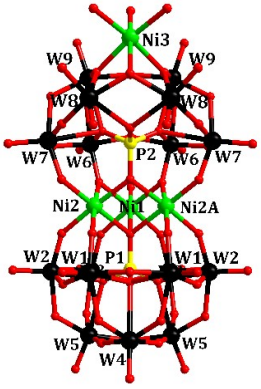

Figure S2 Ball-and-stick view of **1.**

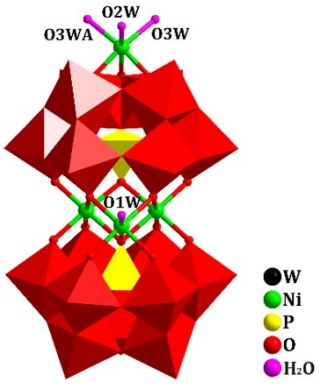

Figure S3 Polyhedral view of **1**.

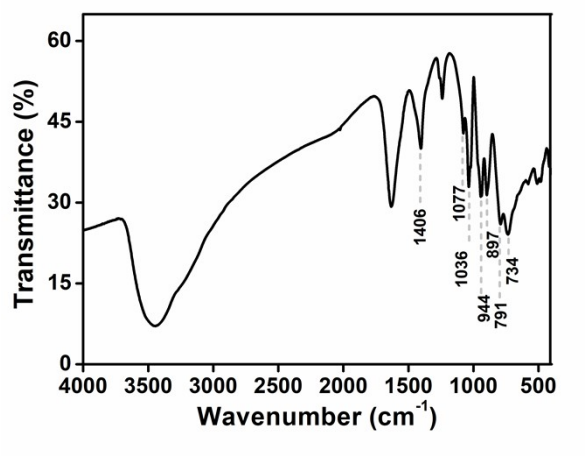

Figure S4 The FT-IR of **1**.

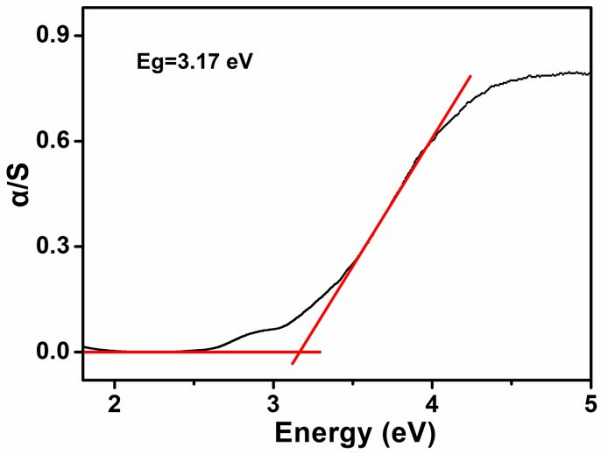

Figure S5 Relationship between Kubelka -Munk function and Energy (eV).

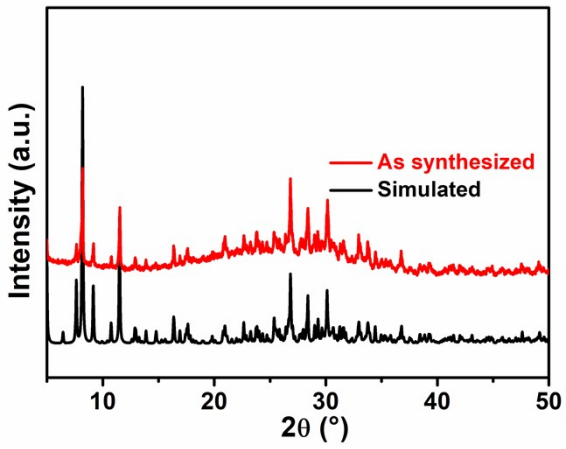

Figure S6 Synthesized and simulated PXRD pattern of **1**.

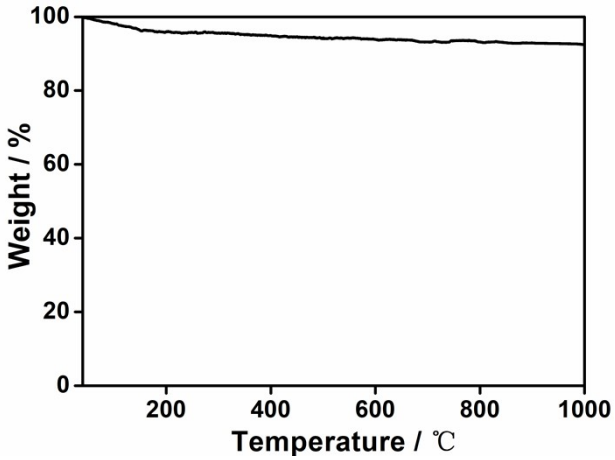

Figure S7 Thermogravimetric analysis curve of **1**.

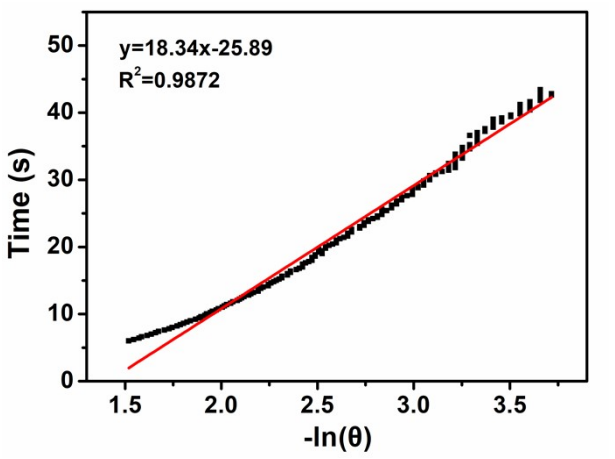

Figure S8 The corresponding time $-ln\theta$ linear curve of **1**.

Table S1 Temperature increase (*ΔT*) corresponding to the power density for various photothermal materials.

Photothermal materials	Light source	Power density	*ΔT* (℃)	conversion efficiency	Ref.
$(NH_4)Cs_{7.5}Na_{0.5}H_2[Ni(H_2O)_3Ni_3(H_2O)(PW_8O_{31})(PW_9O_{34})]Cl{\cdot}9H_2O$	808 nm laser	1 W cm^{-2}	70 ℃	20.5%	**This work**
$[Ag_{29.78}Cu_{1.22}Br_2(FUR)_{20}(TPP)_{10}]^{3+}$	808 nm	1 W cm^{-2}	88 ℃	-	1
DTC cocrystals	808 nm	0.7 W cm^{-2}	42.3 ℃	18.8%	2
$\{[La_3(bcbp)_3(NO_3)_6O][La(NO_3)_6]_{1/3}\}_n$	808 nm	1.5 W cm^{-2}	88 ℃	77%	3
PT-B-COF	808 nm	1.8 W cm^{-2}	43	31.2%	4
PT-N-COF	808 nm	1.8 W cm^{-2}	94	66.4%	

3. Calculation for the photothermal conversion efficiency

The conversion efficiency was evaluated using the approach detailed in previous studies[5,6]. A comprehensive explanation is provided below:

The photothermal conversion efficiency (η) is obtained according to Equation (1):

$$\eta = \frac{hS(T_{max} - T_{sur})}{I(1-10^{-A})} \quad \text{* MERGEFORMAT (1)}$$

Here, T_{max} represents the maximum temperature (97.1 °C), T_{surr} represents the initial temperature (27.1 °C), I denotes the incident laser power (1 W cm^{-2}), and A refers to the absorbance of the sample at 808 nm (0.09).

According to the total energy balance for this system:

$$\sum_i m_i C_{pi} \frac{dT}{dt} = Q_s - Q_{loss} \quad \text{* MERGEFORMAT (2)}$$

Here, m_i (0.0126 g) and $C_{p,i}$ (0.8 J^{-1} °C^{-1}) represent the mass and specific heat capacity of the system components (compound **1** and quartz glass), respectively. Q_s represents the thermal energy generated by **1** under NIR laser irradiation, while Q_{loss} represents the thermal energy lost to the surrounding environment.

$$\Delta T = \int_0^t dT \quad \text{* MERGEFORMAT (3)}$$

$$Q_{loss}(T) = hS\Delta T \quad \text{* MERGEFORMAT (4)}$$

At the maximum temperature, the system reaches thermal equilibrium, expressed as:

$$Q_s = Q_{loss} = hS\Delta T_{max} \quad \text{* MERGEFORMAT (5)}$$

To determine hS, a dimensionless driving temperature θ is introduced, defined as follows:

$$\theta = \frac{T - T_{surr}}{T_{max} - T_{surr}} = \frac{\Delta T}{\Delta T_{max}} \quad \text{* MERGEFORMAT (6)}$$

$$d\theta = \frac{dT}{T_{max} - T_{surr}} = \frac{dT}{\Delta T_{max}} \quad \text{* MERGEFORMAT (7)}$$

The sample system time constant τ_s:

$$\tau_s = \frac{\sum_i m_i C_{p,i}}{hS} \quad \text{* MERGEFORMAT (8)}$$

By combining equations (2), (7), and (8), the following can be derived:

$$\frac{d\theta}{dt} = \frac{1}{\Delta T_{max}} \cdot \frac{Q_s - Q_{loss}}{\sum_i m_i C_{p,i}} = \frac{Q_s - Q_{loss}}{hS\tau_s \Delta T_{max}} \quad \text{* MERGEFORMAT (9)}$$

$$\frac{Q_{loss}}{hS\tau_s \Delta T_{max}} = \frac{hS\Delta T}{hS\tau_s \Delta T_{max}} = \frac{\theta}{\tau_s} \quad \text{* MERGEFORMAT (10)}$$

When the laser is off, $Q_s = 0$, therefore:

$$\frac{d\theta}{dt} = \frac{1}{\tau_s} \cdot \frac{Q_s}{hS\Delta T_{max}} - \frac{\theta}{\tau_s} \quad \text{* MERGEFORMAT (11)}$$

$$\frac{d\theta}{dt} = -\frac{\theta}{\tau_s} \quad \text{* MERGEFORMAT (12)}$$

$$t = -\tau_s ln\theta \quad \text{* MERGEFORMAT (13)}$$

So hS could be calculated from the slope of cooling time (t) vs $-ln\theta$. Therefore, τ_s is 18.34 s (Fig. S8) and the photothermal conversion efficiency η is 20.5%.

References

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