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Supporting Information

Second-harmonic generation in two hybrid organic–inorganic metal chlorides based on L-thioproline ligand

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Synthesis

All starting reagents were used without further purification: L-thioproline (98%), $ZnCl_2$ (AR, 98%), CuCl (AR, 98%), and H_3PO_2 (AR, 50%) were purchased from Shanghai Macklin Biochemical Co., Ltd. HCl (AR 38%) were purchased from Chengdu Chron Chemical Co., Ltd.

(L-$C_4H_8NO_2S$)$CuCl_2$ (**1**) was prepared by mixing CuCl (0.099 g, 1 mmol), L-thioproline (0.268 g, 2 mmol), HCl (38%, 1 mL), and H_3PO_2 (50%, 0.2 mL) in a glass vial. The mixture was stirred for 30 min at room temperature. The resulting clear solution was slowly evaporated at room temperature to give colorless crystals of compound **1** (55% yield based on copper).

(L-$C_4H_7NO_2S$)$_2ZnCl_2$ (**2**) was prepared by mixing $ZnCl_2$ (0.136 g, 1 mmol), L-thioproline (0.268 g, 2 mmol), HCl (38%, 0.063 mL), and H_2O (1.0 mL) in a glass vial. The mixture was stirred for 30 min at room temperature. The resulting clear solution was slowly evaporated at 45 ℃ to give colorless crystals of compound **2** (65% yield based on zinc).

Structural determination

Single crystal X-ray diffraction data were collected on Bruker D8 Venture diffractometer 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 XRD analysis

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°, and with a scan step width of 0.02° and a fixed time of 0.2 s.

Thermal Stability Analysis

Thermal analysis was performed in a dynamic nitrogen atmosphere using a Shimadzu DTG-60H thermal analyzer with a heating rate of 10 ºC/min in the range of 30 to 800 ºC.

IR Spectroscopy

IR spectra of compounds **1** and **2** were obtained on a Nicolet Impact 4100 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 title 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[3, 4] was used to calculate the absorption spectra from the reflection spectra: $F(R) = \alpha/S = (1-R)^2/2R$, where R is the reflectance, α is the absorption coefficient, and S is the scattering coefficient.

Birefringence Measurements

The birefringences of compounds **1** and **2** were characterized by using the polarizing microscope equipped (ZEISS Axio Scope. A5) with a Berek compensator.

Second-Harmonic Generation Tests

The Kurtz and Perry method was used to measure powder second harmonic generation (SHG) signals at room temperature.[5] The SHG efficiency mainly depends on the particle size, and the crystalline compound was ground and divided into the following particle sizes: 25–45, 45–58, 58–75, 75–106, 106–150 and 150–212 μm. Microcrystalline KH_2PO_4 (KDP) with the same particle size was used as a reference. The measurements were performed using Q-switched Nd: YAG lasers with visible light at 1064 nm, and a cut-off filter was used to limit the background flash light on the sample, and the SHG signal is recorded by a photomultiplier tube.

Computational Methods

In order to understand the relationship between structure and properties of compounds **1**, **2**, the first-principles calculations were carried out by using the CASTEP software package.[6] The band structure, density of states (DOS) / partial density of states (PDOS), and optical properties of compounds **1** and **2** were calculated. The generalized gradient approximation (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 $1s^1$, C $2s^22p^2$, N $2s^22p^3$, O $2s^22p^4$, S $3S^23P^4$, Cl $3s^23p^5$,Zn $3d^{10}4s^2$, Cu $3d^{10}4s^1$ treated as valence electrons.[8] The kinetic energy cutoff of 750 eV and the k-point sampling of 5 × 5 × 3 were chosen for the compound **1**. The k-point sampling of 4 × 3 × 2 were chosen for the compound **2**.[9] All other parameter settings are CASTEP default values. In addition, the scissors operators were adopted when calculating the birefringence, and the values are 0.9 eV for compound **1** and 0.0 eV for compound **2**.

To obtain the linear optical properties, the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ has been determined in the random phase approximation from the PBE wavefunctions. The imaginary part of the dielectric function due to direct inter-band transitions is given by the expression,

$$\varepsilon_2(\hbar\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{k,v,c}\left|\left\langle\psi_k^c\left|u\cdot r\right|\psi_k^v\right\rangle\right|^2\delta(E_k^c - E_k^v - E) \qquad \text{(equation S1)}$$

where Ω, ω, u, v and c are the unit-cell volume, photon frequencies, the vector defining the polarization of the incident electric field, valence and conduction bands, respectively. The real part of the dielectric function is obtained from ε_2 by a Kramers-Kronig transformation,

$$\varepsilon_1(\omega) = 1 + (\frac{2}{\pi})\int_0^{+\infty} d\omega' \frac{\omega'^2 \varepsilon_2(\omega)}{\omega'^2 - \omega^2}$$

(equation S2)

In calculation of the static $\chi^{(2)}$ coefficients, the so-called length-gauge formalism derived by Aversa and Sipe [10] and modified by Rashkeev *et al* [11] is adopted, which has been proved to be successful in calculating the second order susceptibility for semiconductors and insulators.[12, 13] In the static case, the imaginary part of the static second-order optical susceptibility can be expressed as:

$$\chi^{abc} = \frac{e^3}{\mathrm{h}^2\Omega}\sum_{nml,k}\frac{r^a_{nm}(r^b_{ml}r^c_{ln} + r^c_{ml}r^b_{ln})}{2\omega_{nm}\omega_{ml}\omega_{ln}}[\omega_n f_{ml} + \omega_m f_{ln} + \omega_l f_{nm}] + \frac{ie^3}{4\mathrm{h}^2\Omega}\sum_{nm,k}\frac{f_{nm}}{\omega^2_{mn}}[r^a_{nm}(r^b_{mn;c} + r^c_{mn;b}) + r^b_{nm}(r^a_{mn;c} + r^c_{mn;a}) + r^c_{nm}(r^a_{mn;b} + r^b_{mn;a})]$$

(equation S3)

where r is the position operator, $\hbar\omega_{nm} = \hbar\omega_n - \hbar\omega_m$ is the energy difference for the bands m and n, $f_{mn} = f_m - f_n$ is the difference of the Fermi distribution functions, subscripts a, b, and c are Cartesian indices, and $r^b_{mn;a}$ is the so-called generalized derivative of the coordinate operator in k space,

$$r^b_{nm;a} = \frac{r^a_{nm}\Delta^b_{mn} + r^b_{nm}\Delta^a_{mn}}{\omega_{nm}} + \frac{i}{\omega_{nm}} \times \sum_l (\omega_{lm} r^a_{nl} r^b_{lm} - \omega_{nl} r^b_{nl} r^a_{lm})$$

(equation S4)

where $\Delta^a_{nm} = (p^a_{nn} - p^a_{mm}) / m$ is the difference between the electronic velocities at the bands n and m.

Table S1 Selected hydrogen bonds for compound **1**.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<(DHA) (deg)
O(2)−H(2)···Cl(1)#1	0.67(12)	2.41(13)	3.006(6)	150(19)
N(1)−H(1A)···Cl(2)#2	0.89	2.30	3.175(7)	166.0
N(1)−H(1B)···Cl(1)#3	0.89	2.43	3.035(7)	125.3

Symmetry transformations used to generate equivalent atoms: #1 *1-x,-1/2+y,1-z*; #2 *+x,-1+y,+z*; #3 *1+x,-1+y,+z*.

Table S2 Selected hydrogen bonds for compound **2**.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<(DHA) (deg)
N(1)−H(1A)···O(2)#1	0.89	1.80	2.673(5)	167.7
N(1)−H(1B)···Cl(1)#1	0.89	2.72	3.344(4)	128.2
N(1)−H(1B)···O(2)	0.89	2.09	2.609(5)	116.1
N(2)−H(2A)···Cl(2)#2	0.89	2.57	3.417(5)	160.5
N(2)−H(2B)···S(2)#3	0.89	2.71	3.339(4)	128.4
N(2)−H(2B)···O(3)	0.89	2.05	2.579(5)	117.1

Symmetry transformations used to generate equivalent atoms: #1 *1-x,1/2+y,-z*; #2 *1-x,1/2+y,1-z*; #3 *-x,1/2+y,1-z*.

Table S3. Bond lengths [Å] for compounds **1** and **2**.

compound **1**		compound **2**	
Cu1-Cl	2.2610(18)	Zn1-Cl1	2.2528(14)
Cu1-Cl2#1	2.392(2)	Zn1-Cl2	2.2546(13)
Cu1-Cl2	2.3521(19)	Zn1-O1	1.966(4)
Cu1-S1	2.2984(16)	Zn1-O3	1.955(3)
S1-C3	1.815(8)	S1-C3	1.796(6)
S1-C4	1.809(7)	S1-C4	1.764(5)
O1-C1	1.194(10)	S2-C7	1.799(5)
O2-C1	1.312(9)	S2-C8	1.790(6)
N1-C2	1.510(9)	O1-C1	1.258(5)
N1-C4	1.492(11)	O2-C1	1.234(6)
C1-C2	1.525(9)	O3-C5	1.271(5)
C2-C3	1.507(9)	O4-C5	1.213(6)
		N1-C2	1.503(5)
		N1-C4	1.489(6)
		N2-C6	1.487(6)
		N2-C8	1.469(6)
		C1-C2	1.512(7)
		C2-C3	1.506(7)
		C5-C6	1.529(6)
		C6-C7	1.517(6)

Symmetry transformations used to generate equivalent atoms: #1 *1-x,-1/2+y,2-z*.

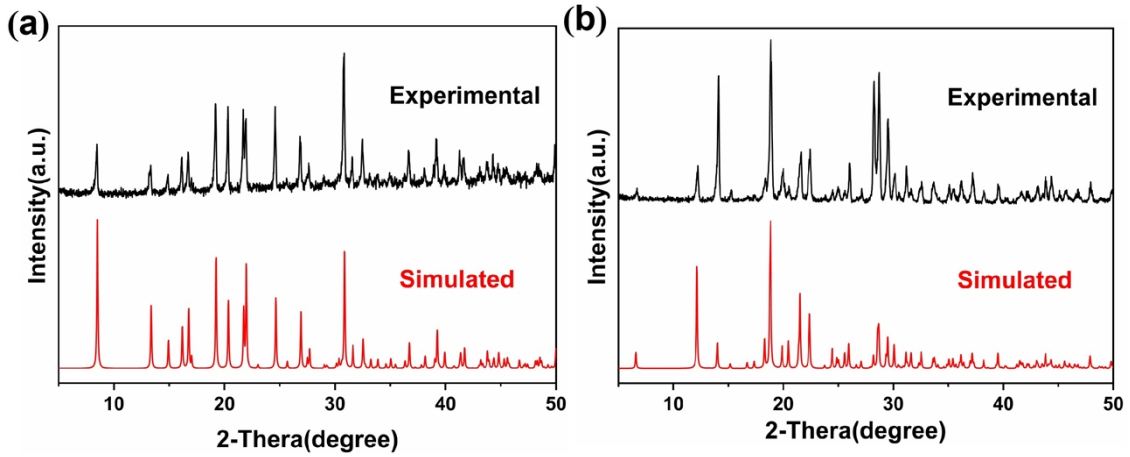

Fig. S1 Simulated and experimental powder XRD patterns for compounds **1** (a) and **2** (b).

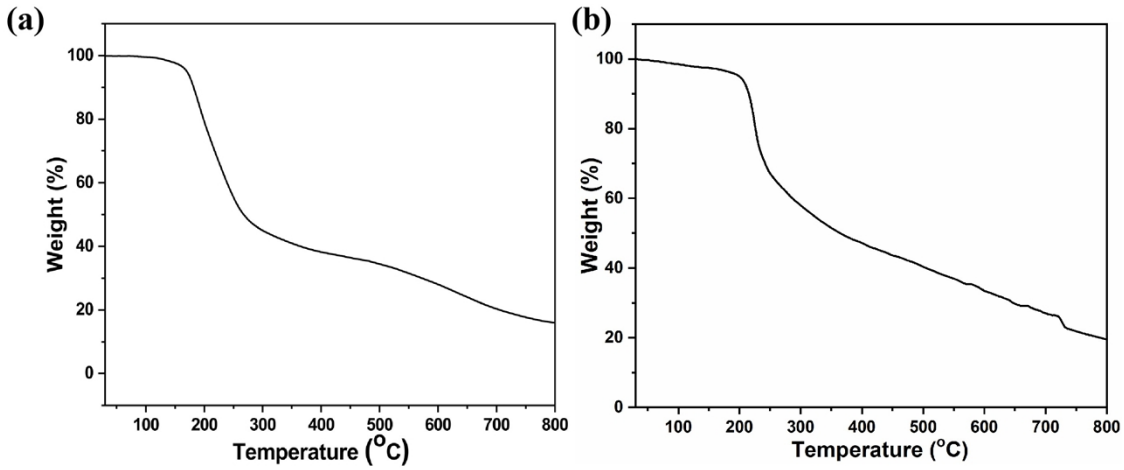

Fig. S2 TGA curves of compounds **1** (a) and **2** (b).

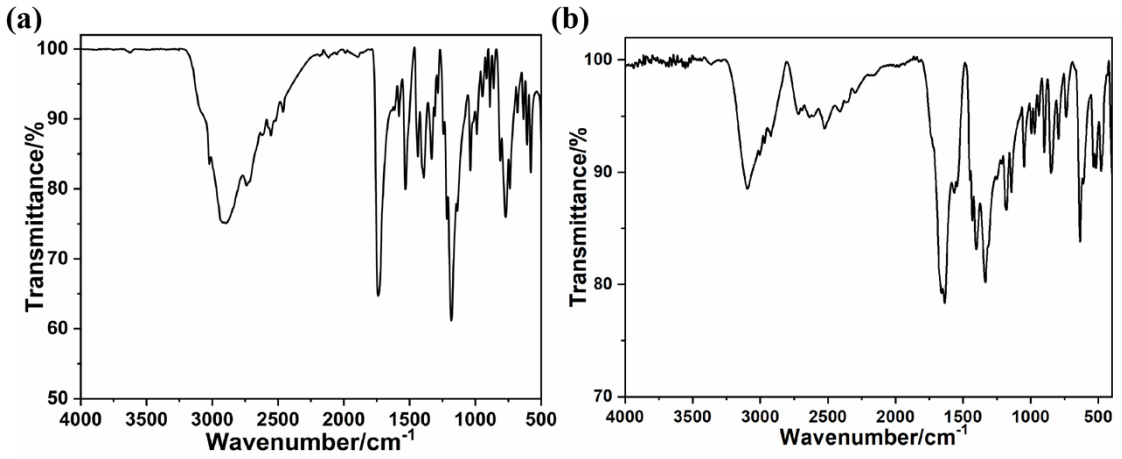

Fig. S3 IR spectra of compounds **1** (a) and **2** (b).

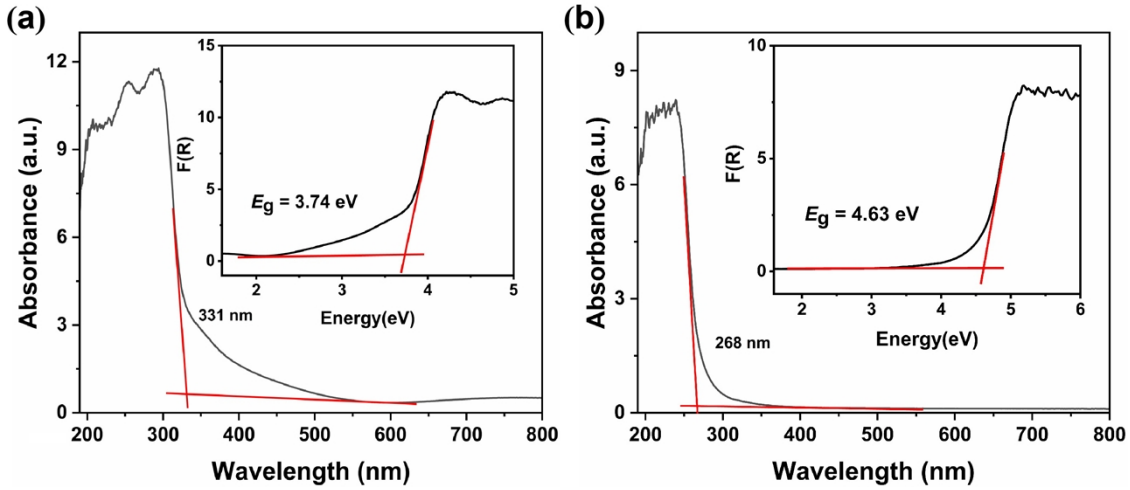

Fig. S4 UV-vis absorption spectra for compounds **1** (a) and **2** (b).

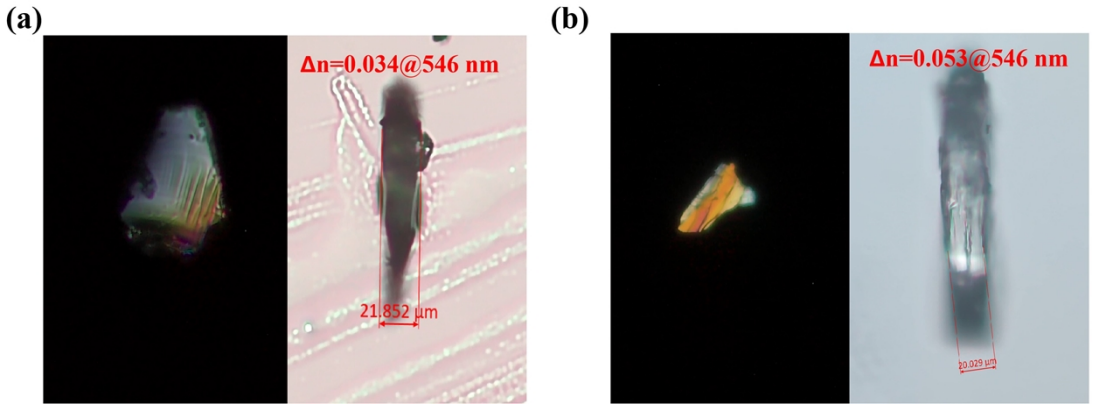

Fig. S5 Birefringence measurements for compounds **1** (a) and **2** (b) performed using a polarizing microscope.

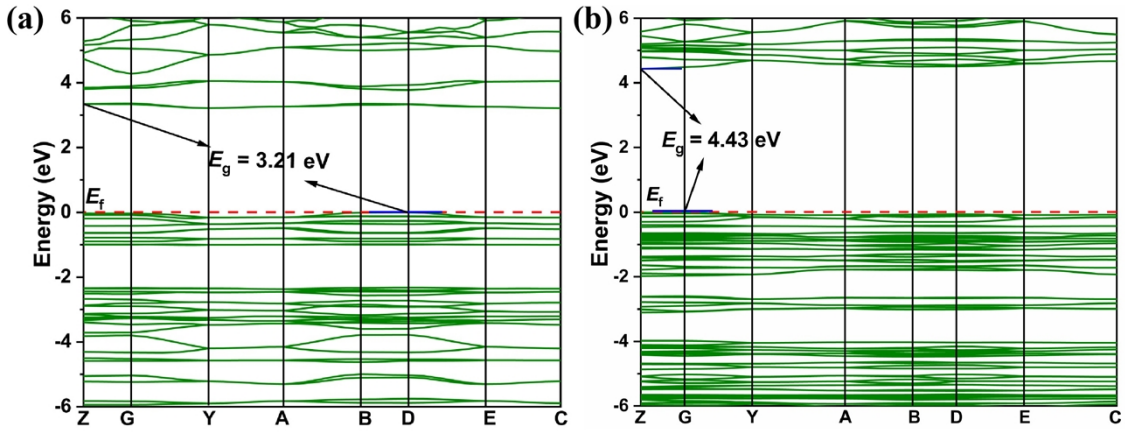

Fig. S6 Calculated band structures for compounds **1** (a) and **2** (b) (the Ferm level is set at 0 eV).

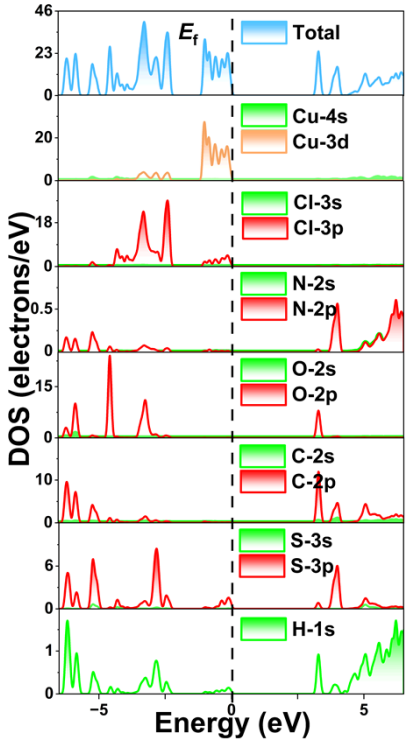

Fig. S7 Total and partial DOS of compound **1**.

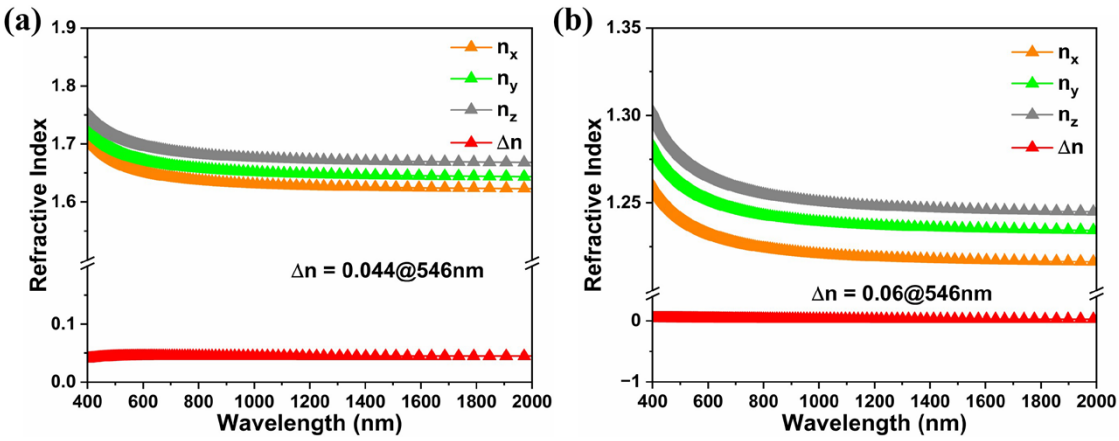

Fig. S8 The calculated linear refractive indices of compounds **1** (a) and **2** (b).

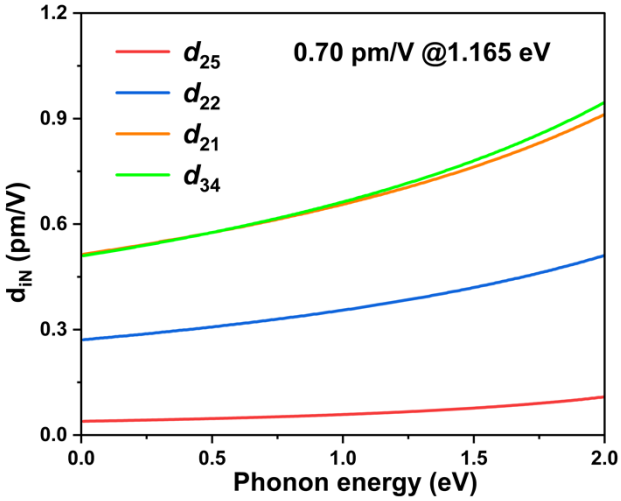

Fig. S9 Calculated frequency-dependent SHG coefficients for compound **2.**

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