

Supplementary Materials

A novel heterometal–organic coordination polymer with chelidamic acid: nonlinear optical and magnetic properties

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General Procedures:

All reagents were purchased from commercial sources and used without further purification. Elemental analyses (C, H, N, and O) were carried out with an Elementar Vario EL. Optical diffuse reflectance spectrum was measured on a PE Lambda 35 UV–vis spectrophotometer equipped with an integrating sphere at 293 K, and the BaSO₄ plate was used as the reference. The absorption spectrum was calculated from reflection spectrum by the Kubelka-Munk function:¹ $\alpha/S = (1-R)^2/2R$, α is the absorption coefficient, S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm , and R is the reflectance. The energy gap was determined as the intersection point between the energy axis at the absorption offset and the line extrapolated from the linear portion of the absorption edge in the α/S versus E (eV) plot. Variable-temperature magnetic susceptibility and field dependence magnetization measurements of the title complexes on polycrystalline samples were performed on an MPMS-XL and PPMS 9T Quantum Design SQUID magnetometer. All data were corrected for diamagnetism estimated from Pascal's constants. The nonlinear optical (NLO) property is investigated under the time-dependent density functional theory (TDDFT) and the sum-over-states method (SOS) at B3LYP level in

¹ (a) Wendlandt, W. W.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966.

(b) Kortüm, G. *Reflectance Spectroscopy*; Springer-Verlag: New York, 1969.

GAUSSIAN 03 program.² The standard basis sets of 3-21G are used for C, H, O and N atoms, and basis sets of Lanl2DZ are used for Cu and Ag atoms. For the reasons of economy and computational feasibility, 1/4 of the cell is selected in the calculated model.

Synthesis of $\text{AgCu}_2(\text{C}_7\text{H}_2\text{NO}_5)(\text{C}_7\text{H}_3\text{NO}_5)\cdot 2\text{H}_2\text{O}$ (**1**):

A mixture of AgNO_3 (0.3 mmol), $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (0.15 mmol), chelidamic acid (0.25 mmol), and water (10 ml) was loaded into a 25-ml Teflon-lined autoclave, and heated at 413 K for 2 days, after which it was cooled to room temperature over 2 days. Pale blue prismatic crystals of **1** that are stable in air were obtained by filtration of the result solution. Anal. Calcd. (%) for **1**: C, 26.60; H, 1.42; N, 4.43; O, 30.37. Found (%): C, 26.64; H, 1.45; N, 4.47; O, 30.40.

Crystallographic Data Collection and Structural Refinements:

Single crystal of **1** suitable for X-ray analyses was mounted on a glass fiber, respectively. Data set of **1** were collected on a Siemens SMART CCD diffractometer equipped with a graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. Intensities were corrected for LP factors and for empirical absorption using the ω scan technique. Siemens SAINT software was used for data reduction. The structure was solved by the direct methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were located by difference Fourier maps and subjected to anisotropic refinement. All of the calculations were performed by the Siemens SHELXTL version 5 package of crystallographic software.³ All H atoms of coordinated water molecules and hydroxyl oxygen (O5) were placed in calculated positions, with O–H distances of $0.85(3) \text{ \AA}$, and refined in riding mode with $U_{\text{iso}}(\text{H})$ values of $1.5U_{\text{eq}}(\text{O})$. Other H atoms were allowed to ride on their respective parent atoms with C–H distances of 0.93 \AA , and were included in the refinement with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Nonlinear Optical Measurements:

The third order nonlinear optical properties of **1** were investigated by using Z-scan

² M. J. Frisch et al., GAUSSIAN 03, GAUSSIAN Inc., Pittsburgh, PA, 2003; B. J. Orr and J. F. Ward, *Mol. Phys.*, 1971, **20**, 513; B. M. Pierce, *J. Chem. Phys.*, 1989, **91**, 791.

³ *SHELXTL Reference Manual*, version 5; Siemens Energy & Automation Inc.: Madison, WI, 1994.

method.⁴ A Nd:YAG laser system (Continuum NP70) with pulse duration of 8 ns at wavelength of 532 nm was employed as the light source. The spatial profiles of the optical pulses were nearly Gaussian contribution. The pulse laser beam was focused onto a sample cell with a 30-cm focal-length lens. The input and output pulses' energy was measured simultaneously by precision laser detectors (818J-09B, Newport Corp), which were linked to a computer through an RS232 interface. The NLO properties of the samples were manifested by moving the samples along the axis of the incident laser irradiance beam (*z*-direction) with respect to the focal point and with incident laser irradiance kept constant. An aperture of 2 mm radius was placed in front of the detector to measure the transmitted energy.

⁴ M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan and E. W. V. Stryland, *IEEE J. Quantum Electron.*, 1990, **26**, 760.

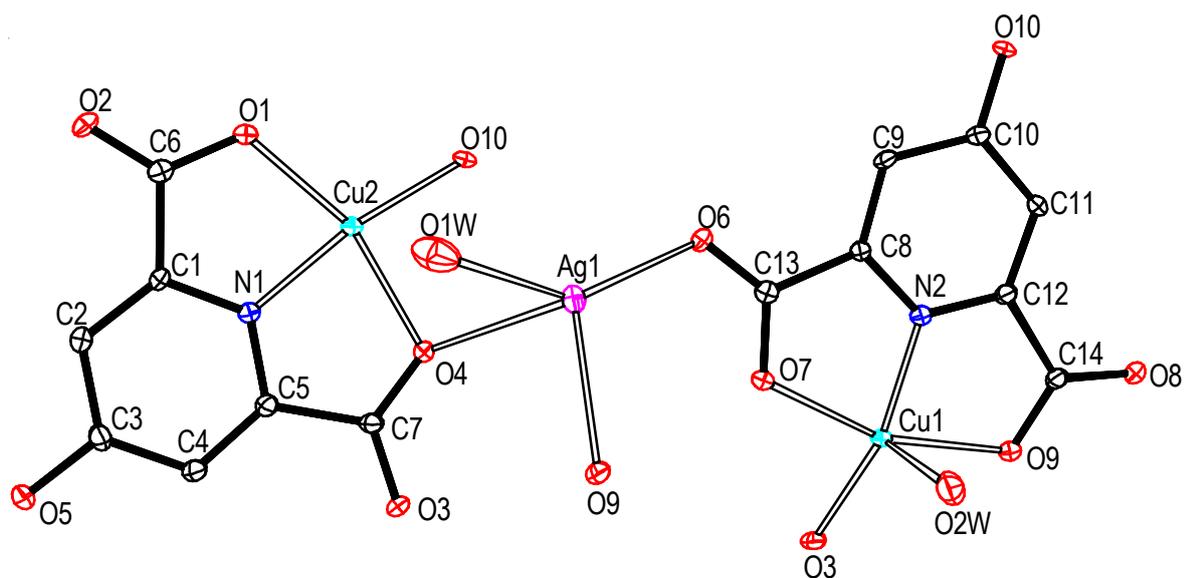


Fig. S1. Molecular structure of **1** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

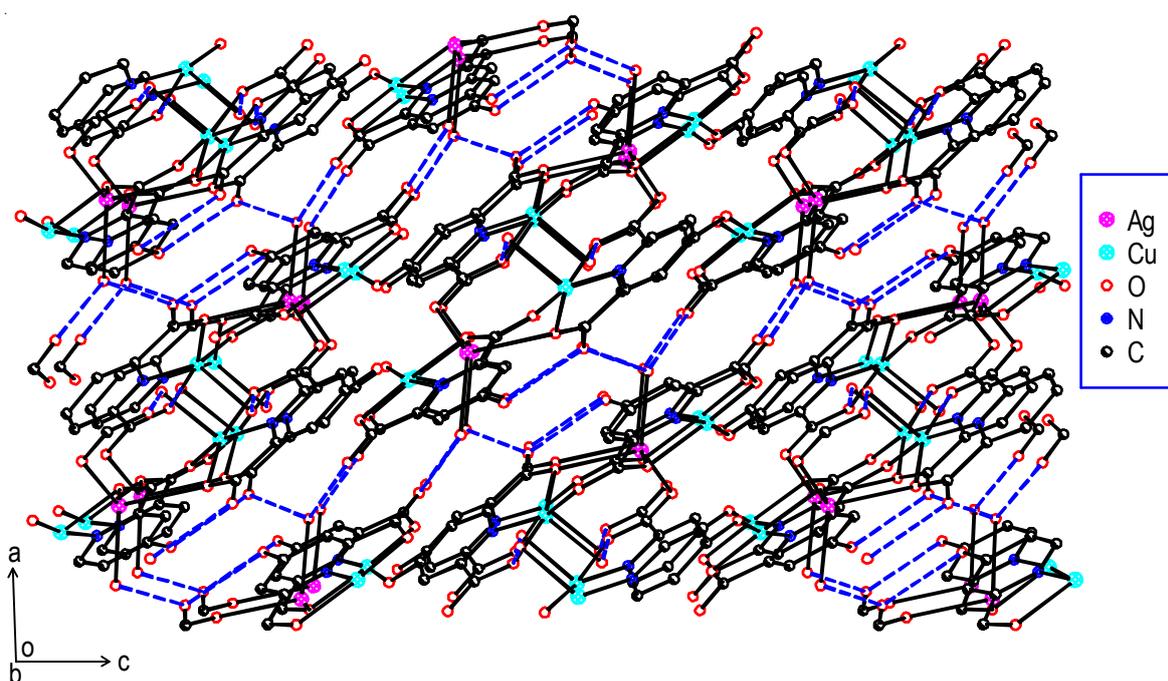


Fig. S2. A view of 3-D network of **1** along the *b* axis. The blue dashed lines represent the H bonds. Hydrogen atoms are omitted for clarity.

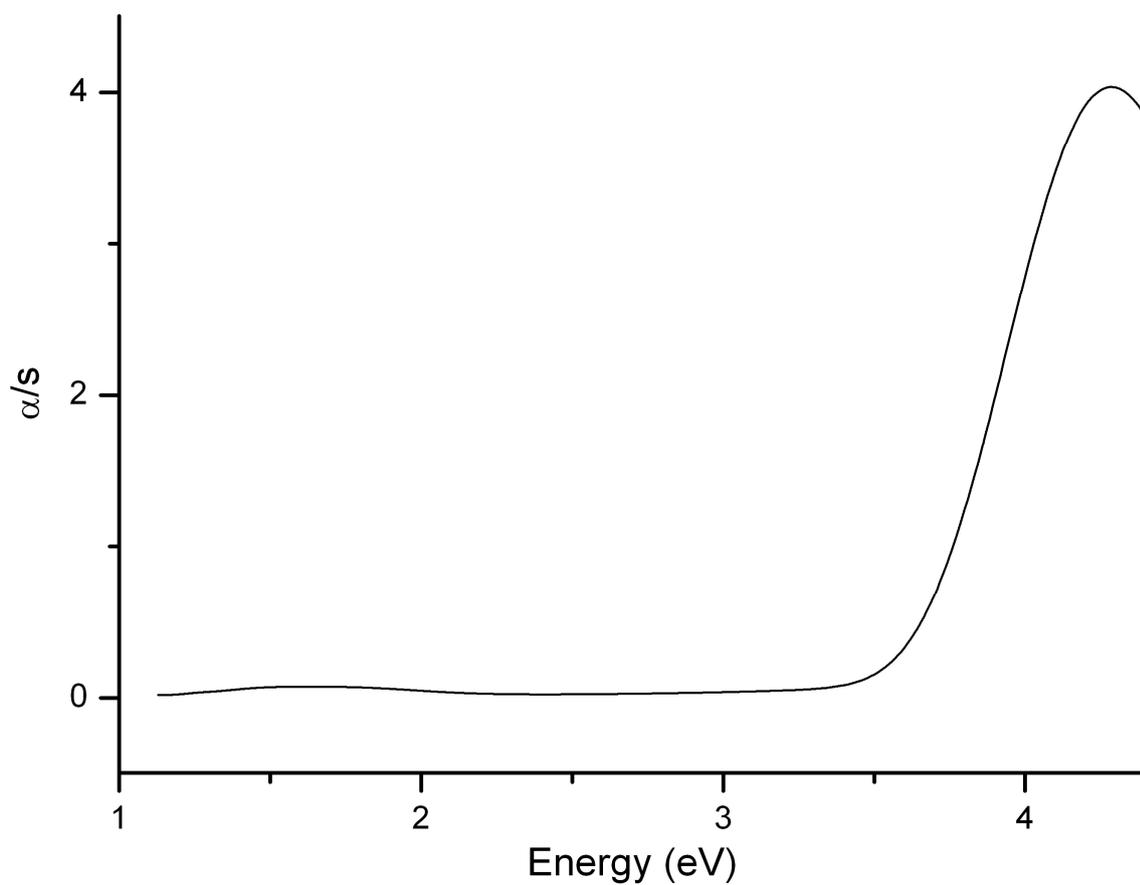


Fig. S3. Diffuse reflectance spectrum of **1**.