

## Accessory Publication

### **A new 3D metal–organic framework containing chelidamic acid with unusual (3,6)-connected topology: synthesis, crystal structure and optical properties**

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#### **General Procedures:**

All reagents were purchased from commercial sources and used without further purification. Elemental analyses (C, H and N) were carried out with an Elementar Vario EL. Optical diffuse reflectance spectrum was measured on a PE Lambda 900 UV–vis spectrophotometer equipped with an integrating sphere at 293 K, and the BaSO<sub>4</sub> plate was used as the reference. The absorption spectrum was calculated from reflection spectrum by the Kubelka-Munk function:<sup>1</sup>  $\alpha/S = (1-R)^2/2R$ ,  $\alpha$  is the absorption coefficient,  $S$  is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5  $\mu\text{m}$ , 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  $\alpha/S$  versus  $E$  (eV) plot. And photoluminescence analysis was performed on an Edinburgh FLS920 fluorescence spectrometer.

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<sup>1</sup> (a) W. W. Wendlandt, H. G. Hecht, *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966. (b) G. Kortüm, *Reflectance Spectroscopy*; Springer-Verlag: New York, 1969.

The powder XRD pattern was collected with a Rigaku DMAX 2500 diffractometer at 40 kV and 100 mA for Cu- $K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) with a scan speed of  $5^\circ/\text{min}$  at room temperature. The simulated pattern was produced using the Mercury program and single-crystal reflection data. Figure S5 gives the powder XRD patterns of **1**, which corresponds well with the simulated one, conforming the high purities of the prepared sample.

### Crystallographic Data Collection and Structural Refinements:

A light yellow single crystal of **1** was mounted on a glass fiber for the X-ray diffraction analysis. Data was collected on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293(2) K. The intensity data were collected with an  $\omega$  scan technique and corrected for  $LP$  factors as well as for absorption by the multi-scan method. 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<sup>TM</sup> version 5 package of crystallographic software.<sup>2</sup> All H atoms of coordinated water molecules 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  $0.93 \text{ \AA}$ , and were included in the refinement with isotropic displacement parameters  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

### Computational procedures:

The crystallographic data of the present compound determined by X-ray were used to calculate the electronic band structure. Calculation of the electronic band structure along with density of states (DOS) was carried out with density functional theory (DFT) using one of the three nonlocal gradient corrected exchange-correlation functionals (GGA-PBE) and performed with the CASTEP code,<sup>3</sup> which uses a plane wave basis set for the valence electrons and norm-conserving pseudopotential for the core electrons.<sup>4</sup> The number of plane waves included in the basis was determined by a cutoff energy  $E_c$  of 550 eV. Pseudoatomic calculations were performed for H-1s<sup>1</sup>,

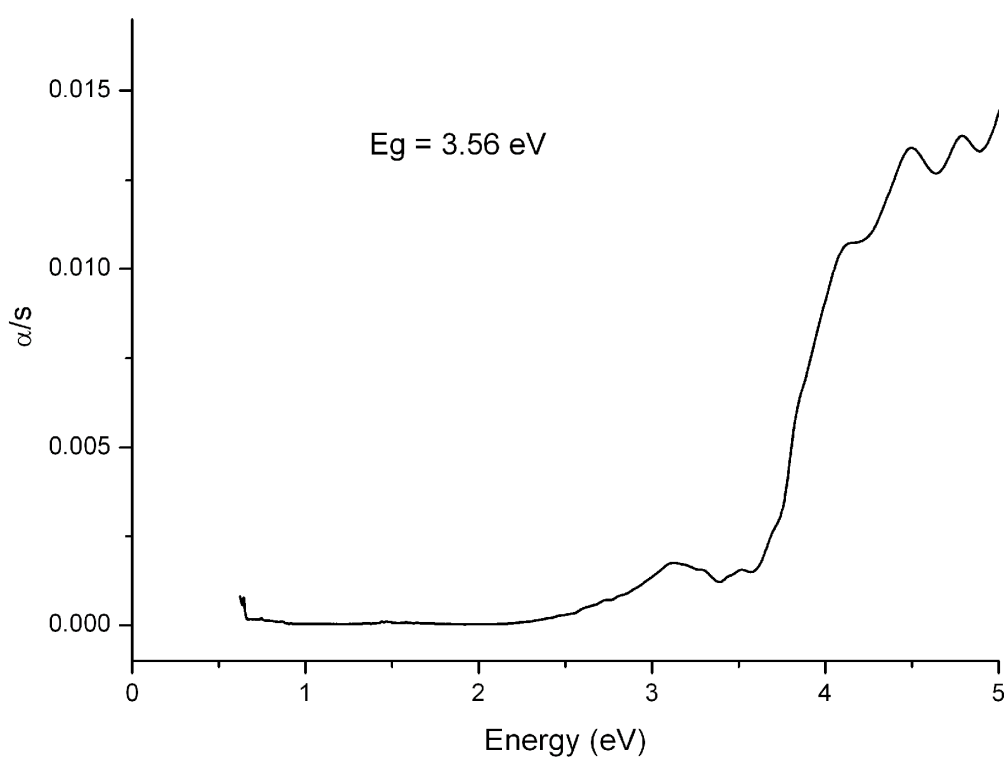
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<sup>2</sup> SHELXTL Reference Manual, version 5; Siemens Energy & Automation Inc.: Madison, WI, 1994.

<sup>3</sup> (a) M. Segall, P. Linda, M. Probert, C. Pickard, P. Hasnip, S. Clark, M. Payne, *Materials Studio CASTEP*, version 2.2; Accelrys: San Diego, CA, 2002; (b) M. Segall, P. Linda, M. Probert, C. Pickard, P. Hasnip, S. Clark, M. Payne, *J. Phys.: Condens. Matter*, **2002**, *14*, 2717.

<sup>4</sup> D. R. Hamann, M. Schluter, C. Chiang, *Phys. Rev. Lett.*, **1979**, *43*, 1494.

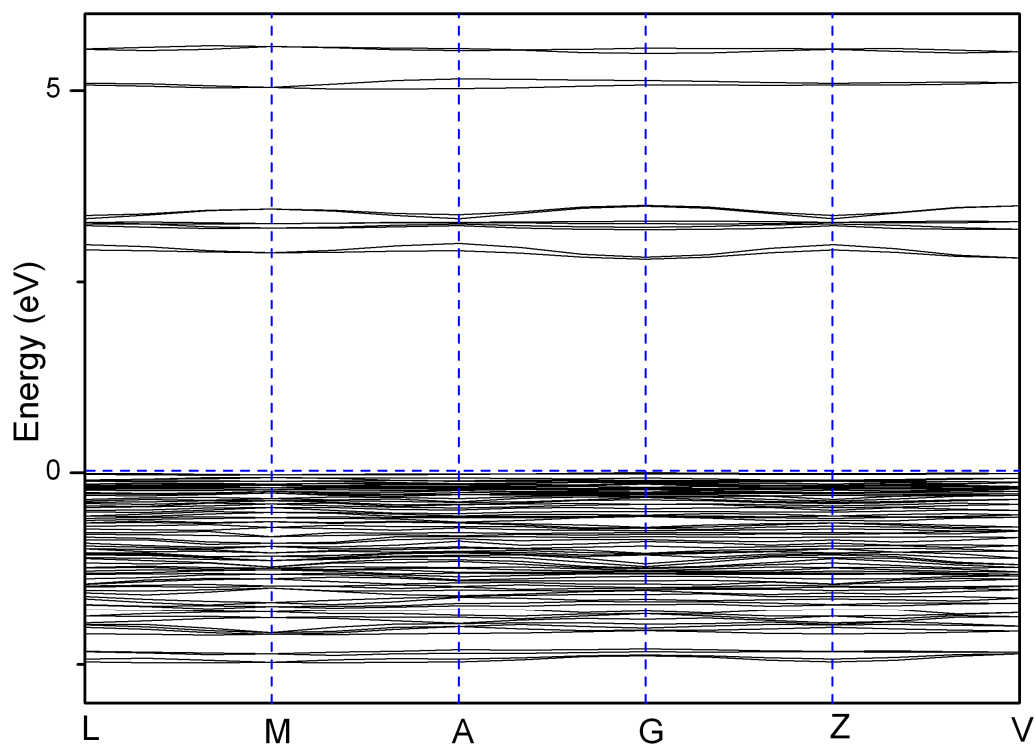
C-2s<sup>2</sup>2p<sup>2</sup>, N-2s<sup>2</sup>2p<sup>3</sup>, O-2s<sup>2</sup>2p<sup>4</sup>, and La-5d<sup>10</sup>6s<sup>1</sup>. The parameters used in the calculations and convergence criteria were set by the default values of the CASTEP code.<sup>3a</sup> The calculations of linear optical properties were also made in this work. CASTEP calculated the real  $\epsilon_1(\omega)$  and imaginary  $\epsilon_2(\omega)$  parts of the dielectric function. The  $\epsilon_2(\omega)$  can be thought of as detailing the real transitions between occupied and unoccupied electronic states. The real and imaginary parts were linked by a Kramers-Kronig transform.<sup>5</sup> This transform was used to obtain the real part  $\epsilon_1(\omega)$  of the dielectric function.



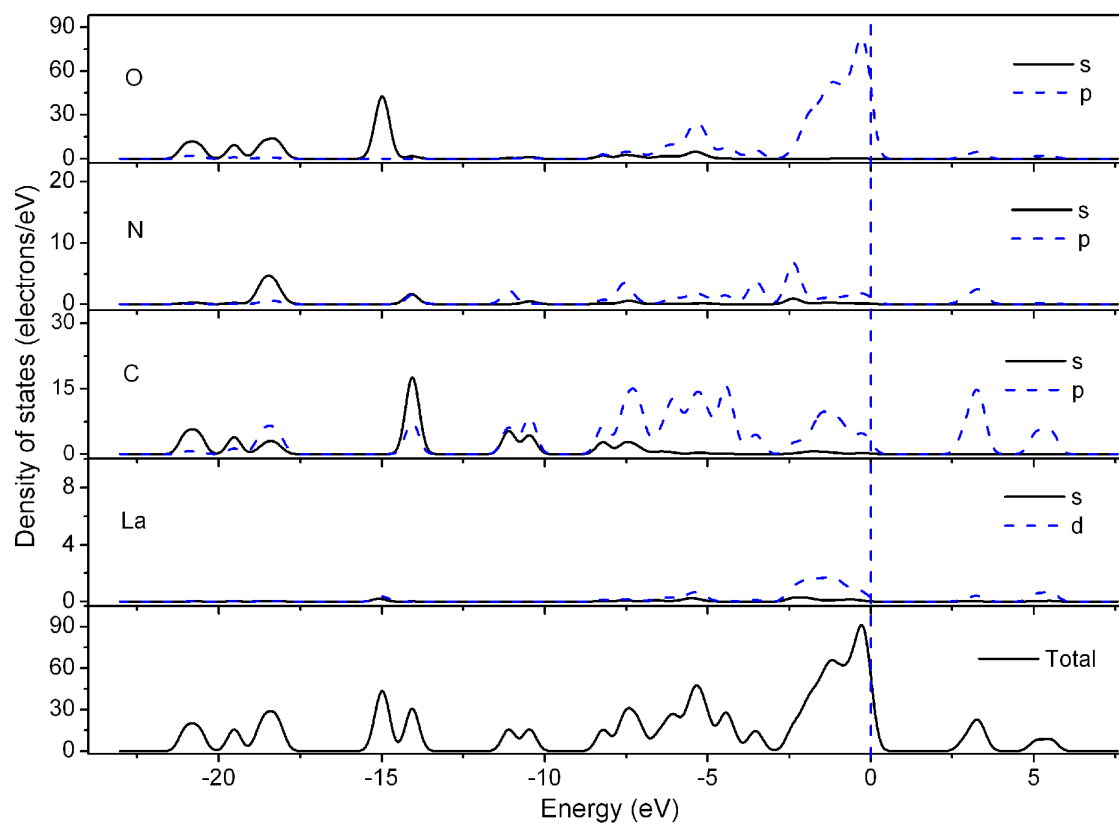
**Fig. S1.** Diffuse reflectance spectrum of **1**.

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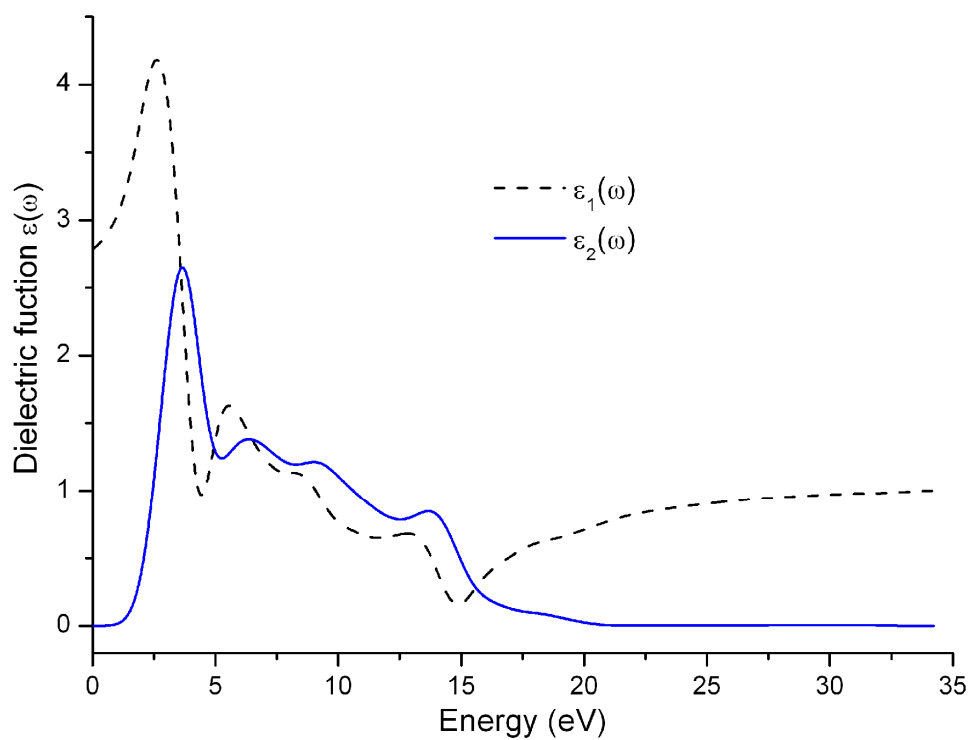
<sup>5</sup> F. Bassani, G. P. Parravicini, *Electronic States and Optical Transitions In Solids*; Pergamon Press Ltd.: Oxford, 1975, pp149.



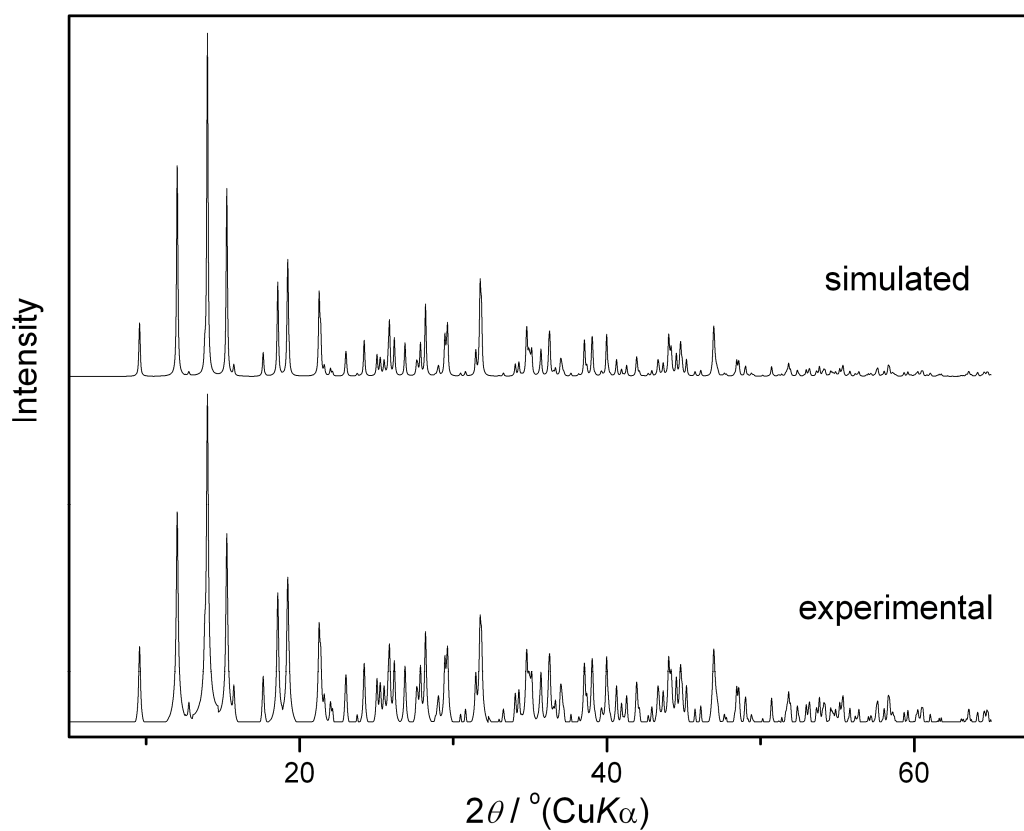
**Fig. S2.** Energy band structures of **1**. Energy bands are shown only between -3.0 and 5.5 eV for clarity, and the Fermi level is set at 0 eV.



**Fig. S3.** Total and partial DOS of **1**. The Fermi level is set at 0 eV.



**Fig. S4.** Calculated real and imaginary parts of dielectric functions in **1**.



**Fig. S5.** The simulated and experimental powder X-ray diffraction patterns of **1**.