Two amino acid-templated metal phosphates: surfactant-thermal synthesis, water stability, and proton conduction

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Physical measurements:

Powder X-ray diffraction (XRD) data were obtained using a Rigaku D/MAX-rA diffractometer with Cu-Kα radiation (λ = 1.5418 Å). The elemental analysis was carried out on an Elementar Vario EL III analyzer. IR spectra (KBr pellets) were recorded on a Nicolet Impact 410 FTIR spectrometer. The thermogravimetric analyses were performed on a Netzsch STA 449c analyzer in a flow of N_2 with a heating rate of 10 ºC/min. The fluorescent spectrum was collected on a Fluorolog-3 fluorescence spectrometer (Horiba JobinYvon) equipped with a 450 W xenon lamp. Alternating current impedance measurements were carried out with a Solartron SI 1260 impedance/gain-phase analyzer over the frequency range from 0.1 Hz to 10 MHz with an applied voltage of 10 mV. The relative humidity was controlled by a STIK Corp. CIHI-150B incubator. The sample was pressed to form a cylindrical pellet of crystalline powder sample (~2 mm thickness ×5 mm ϕ) coated with C-pressed electrodes. Two silver electrodes were attached to both sides of pellet to form four end terminals (quasi-four-probe method). Single crystal X-ray diffraction data were collected on a New Gemini, Dual, Cu at zero, EosS2 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]

Reference

1. G. M. Sheldrick, Acta Cryst., Sect. A, 2008, 64, 112.

Synthesis

Synthesis of $Zn(HPO_4)(C_6H_{11}NO_2)$ (1): Compound **1** was prepared by heating a mixture of ZnO (0.082 g), L-homoproline (0.261 g), H_3PO_4 (85%, 0.135 mL), and PEG-200 (2.0 mL) in a Teflon-coated steel autoclave at 150 °C for 7 days. The autoclave was subsequently allowed to cool to room temperature. Colourless crystals of compound **1** were separated from the resulting product by filtration, washed with ethanol, and dried in air (31% yield based on zinc). This compound can't be prepared

without L-homoproline in the reactions. Instead, a hydrated zinc phosphate $Zn_3(PO_4)_2 \cdot 4H_2O$ (hopeite, JCPDS: 37-465) was often obtained as the resulting product.

Synthesis of $(C_5H_{10}NO_2)Ga_4(PO_4)_4F \cdot 3H_2O$ (2): Compound **2** was prepared by heating a mixture of Ga_2O_3 (0.187 g), L-proline (0.115 g), H_3PO_4 (85%, 0.135 mL), HF (40%, 88 μL), and PEG-200 (2.0 mL) in a Teflon-coated steel autoclave at 160 °C for 7 days. The autoclave was subsequently allowed to cool to room temperature. Light-yellow crystals of compound **2** were separated from the resulting product by filtration, washed with ethanol, and dried in air (46% yield based on gallium). This compound can't be prepared without L-proline in the reactions. Instead, a dense gallium phosphate $GaPO_4$ with a quartz-type structure was often obtained as the resulting product.
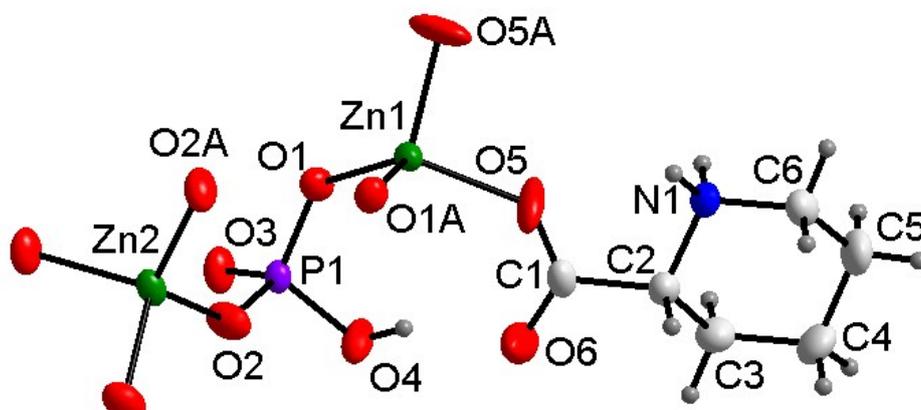
Fig. S1. View of the tetrahedral coordination environments for Zn and P in the asymmetric unit of compound **1**, showing the atom-labeling scheme and 50% thermal ellipsoids. Atom labels having "A" and "B" refer to symmetry-generated atoms.
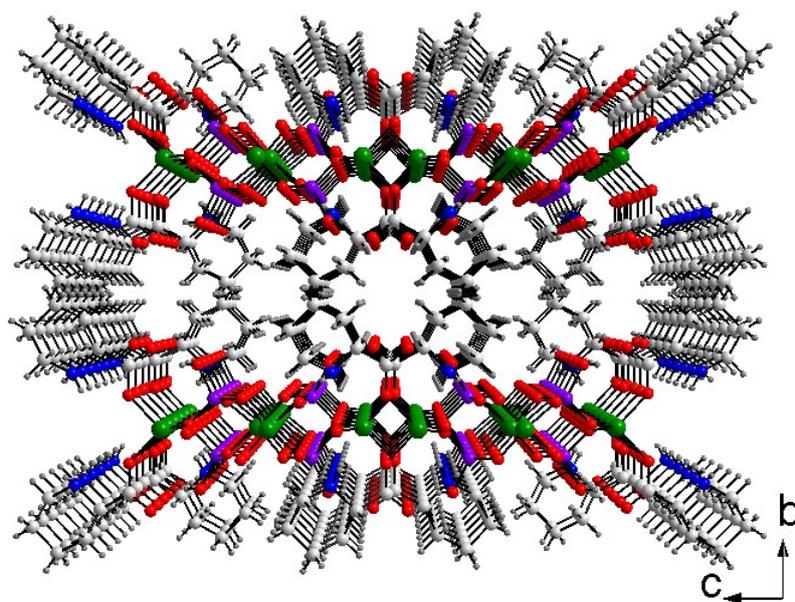
Fig. S2. Pack structure of compound **1** along the [100] direction.
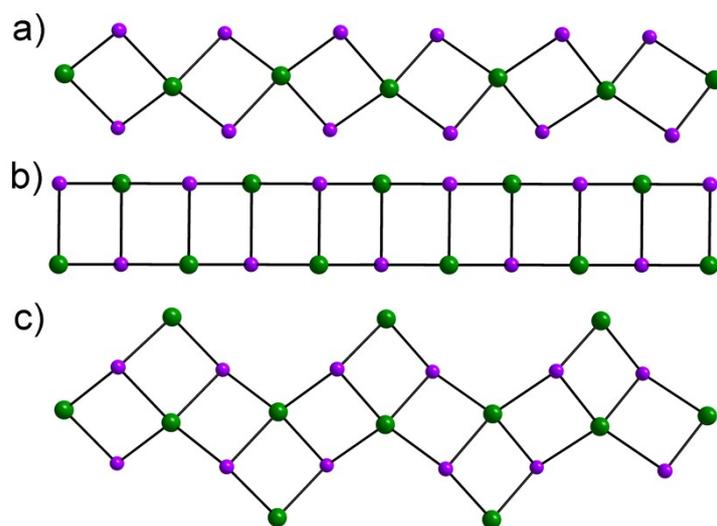
Fig. S3. Schematic representation of three chain-like structures found in metal phosphates: (a) corner-sharing 4-MR chain; (b) edge-sharing 4-MR chain; (c) zigzag edge-sharing 4-MR chain. Oxygen atoms are omitted for clarity.
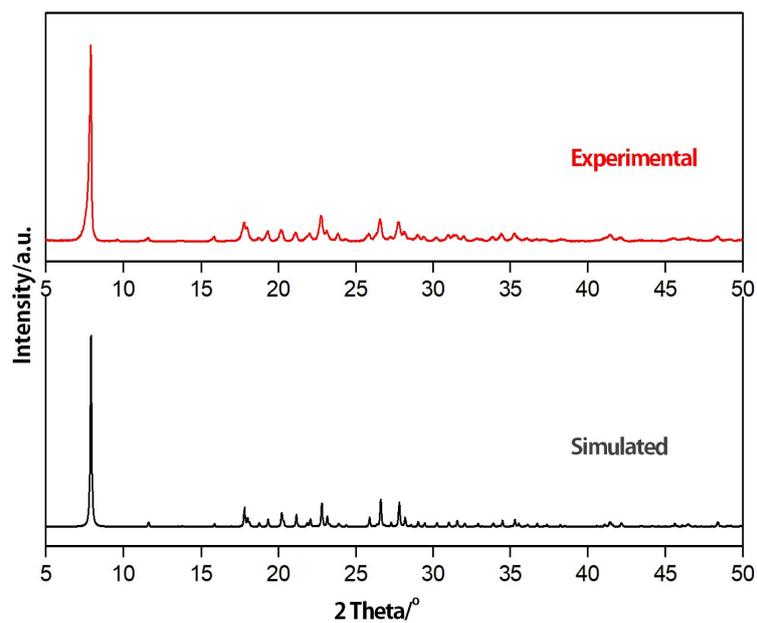
Fig. S4. Experimental and simulated powder XRD patterns of compound **1**.
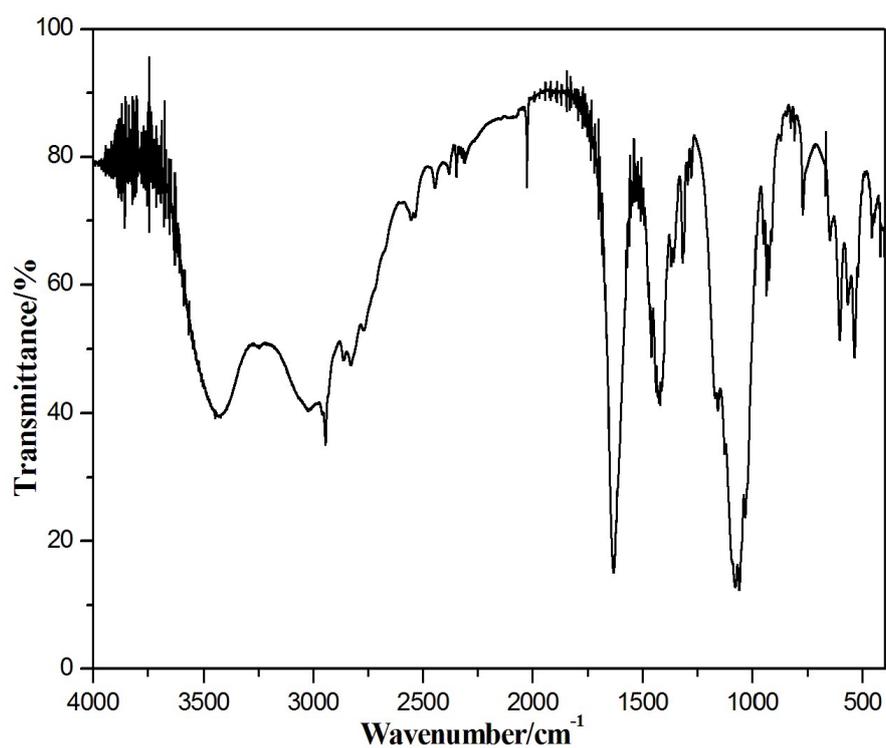
Fig. S5. IR spectrum of compound **1**.
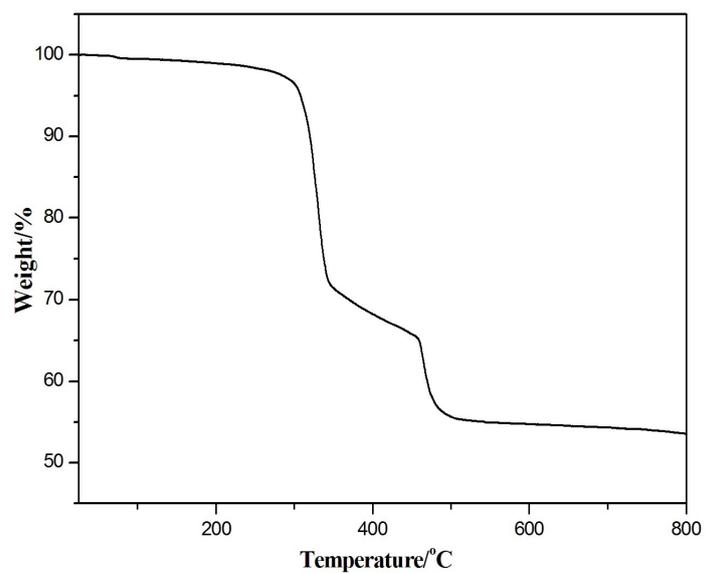
Fig. S6. TGA curve of compound **1**.

Fig. S7. Crystal photo of compound **1** on a thin glass fiber.
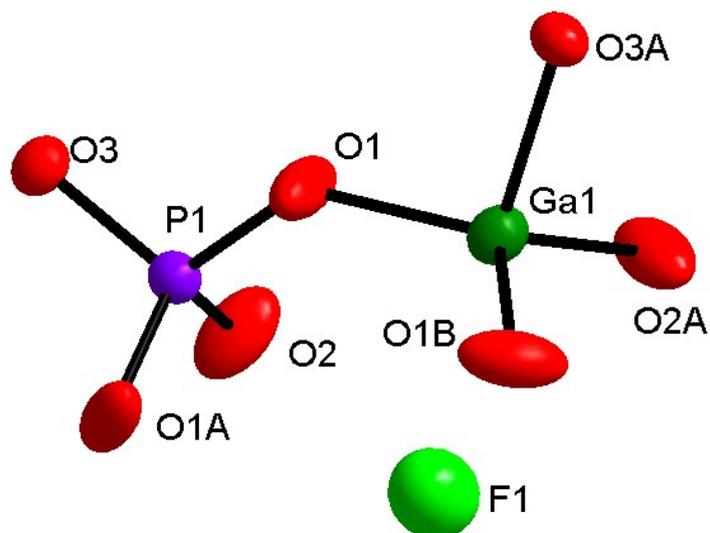
Fig. S8. View of the tetrahedral coordination environments for Ga and P in the asymmetric unit of compound **2**, showing the atom-labeling scheme and 50% thermal ellipsoids. Atom labels having "A" and "B" refer to symmetry-generated atoms.
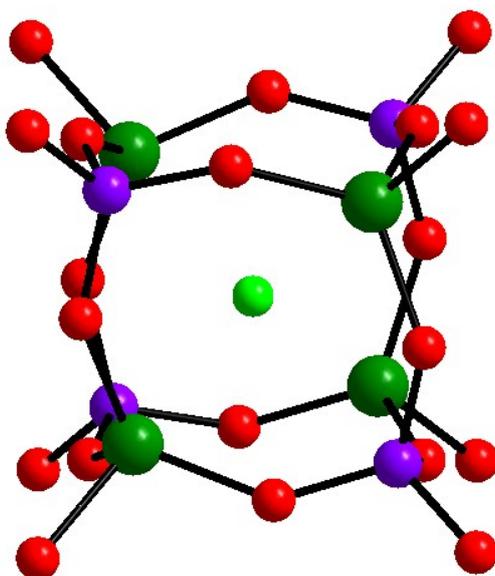
Fig. S9. View of the d4r cage encapsulating F$^-$ ions within its center.
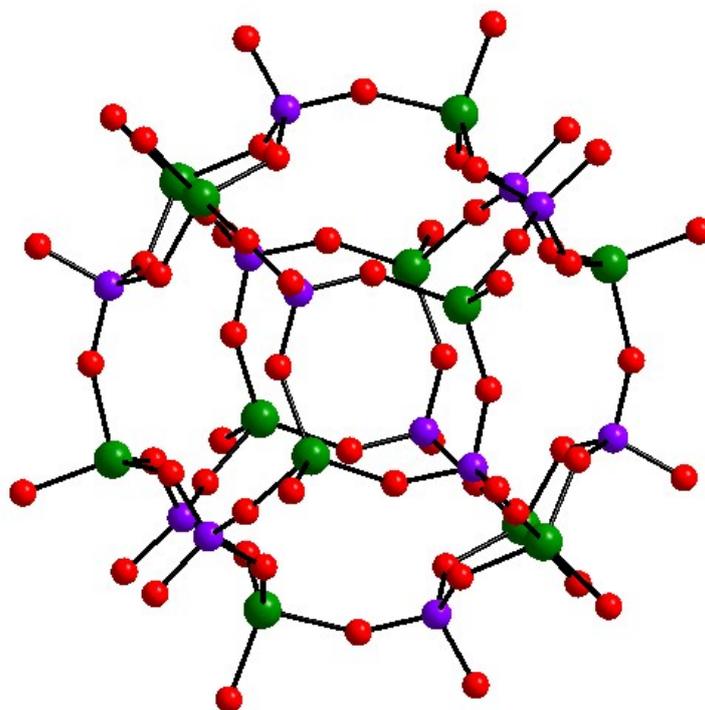
Fig. S10. View of the β cage in compound **2**.
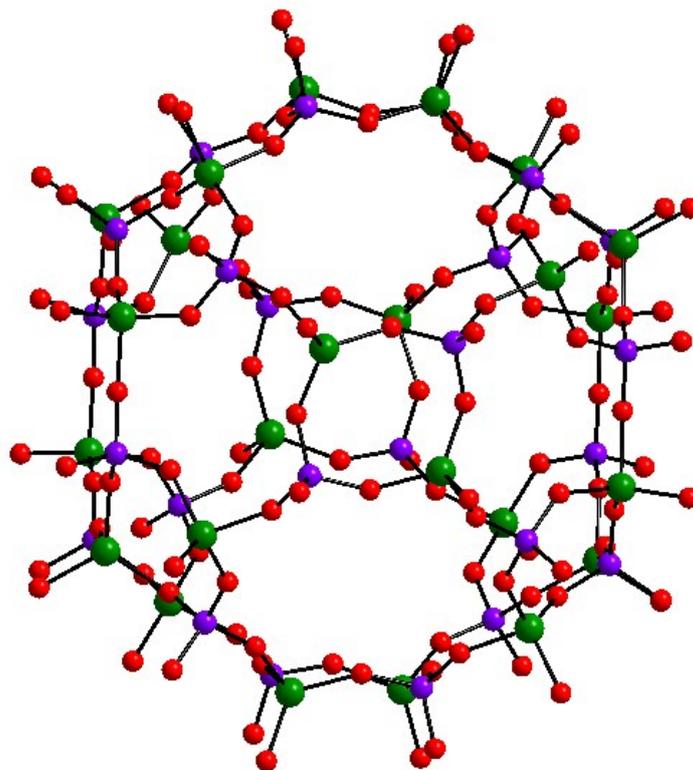
Fig. S11. View of the α cage in compound **2**.
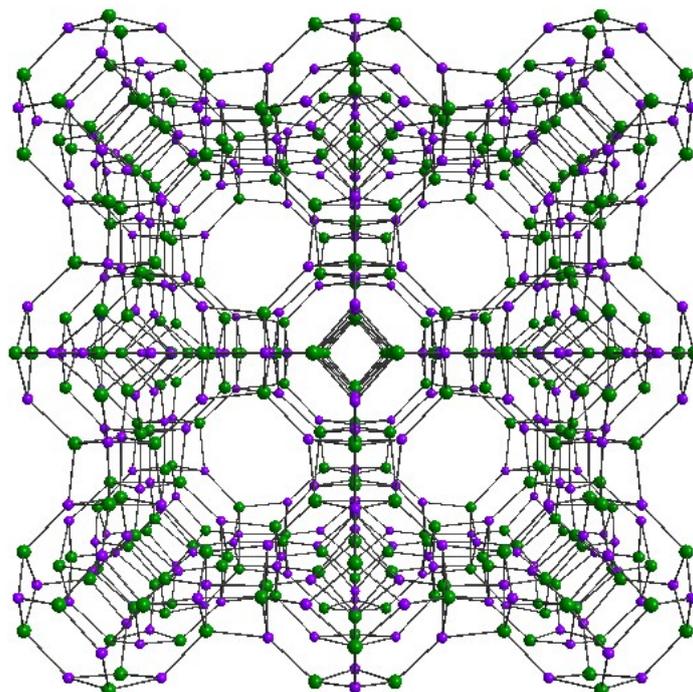
Fig. S12. The zeolitic LTA topology of compound **2**.
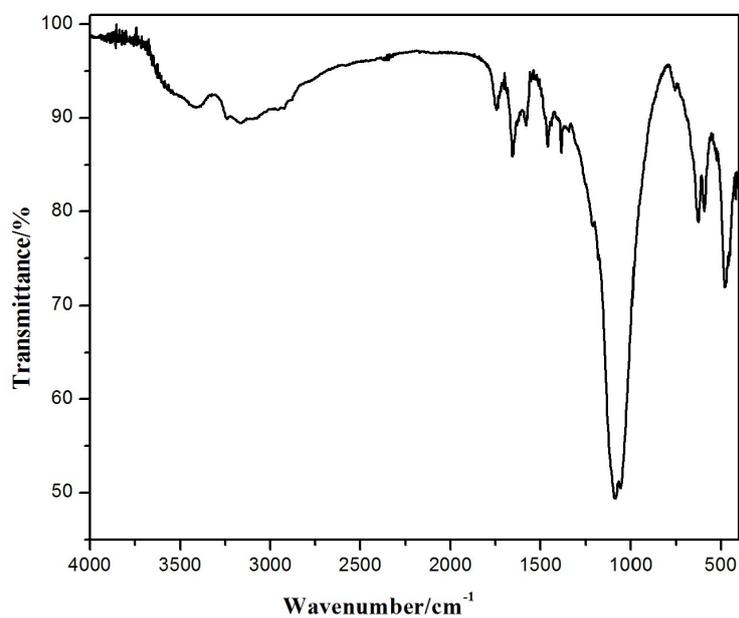
Fig. S13. IR spectrum of compound **2**.
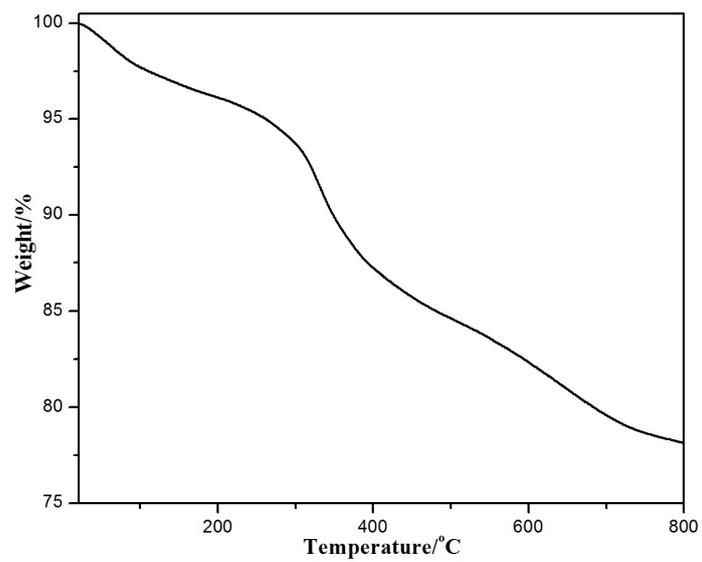
Fig. S14. TGA curve of compound **2**.
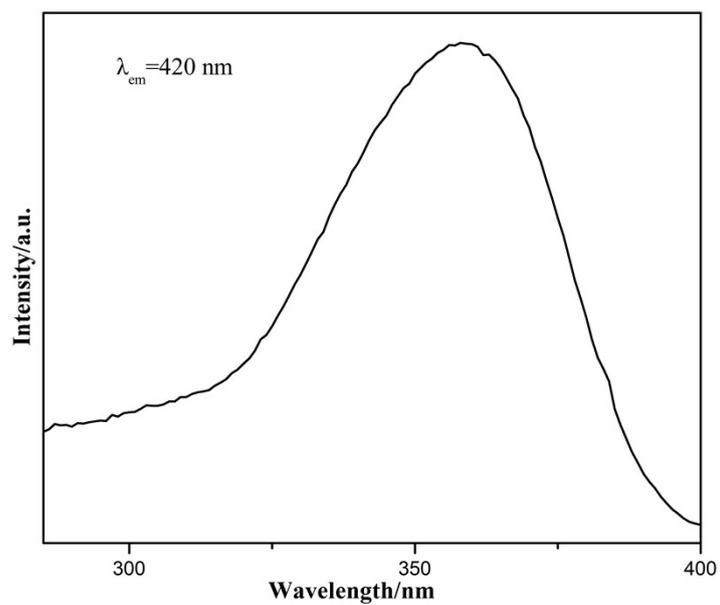
Fig. S15. The excitation spectrum of compound **2**.
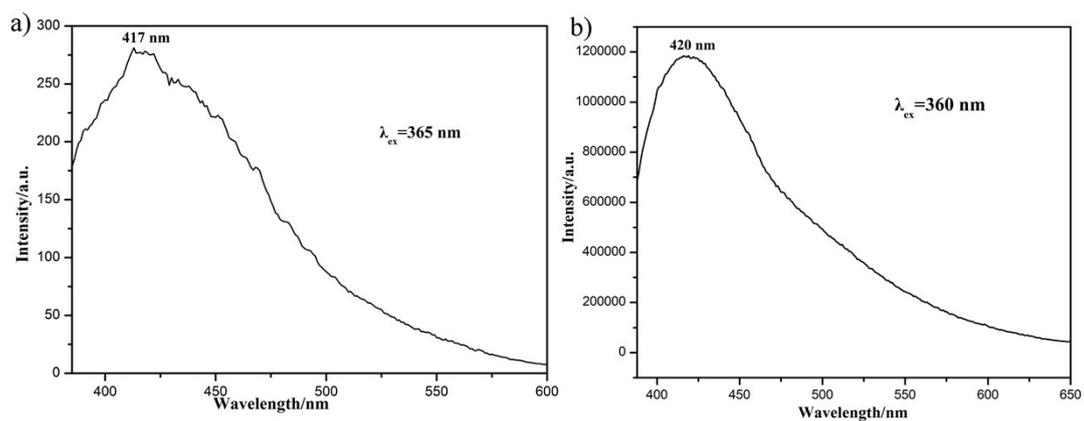
Fig. S16. Room-temperature emission spectra of (a) L-proline molecules and (b) compound **2**.

$\tau = 2.08$ ns
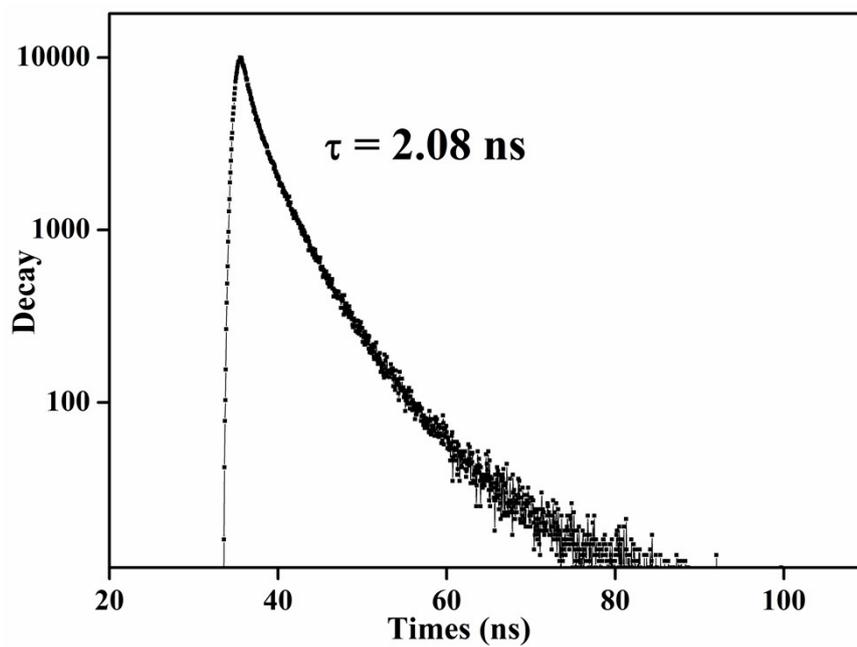
Fig. S17. The lifetime of compound **2**.
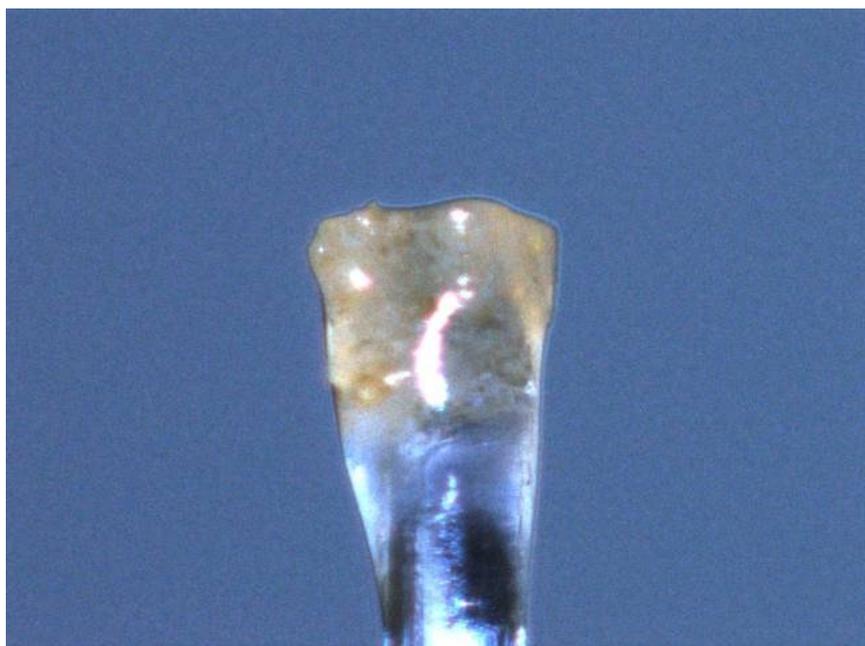
Fig. S18. Crystal photo of compound **2** on a thin glass fiber.
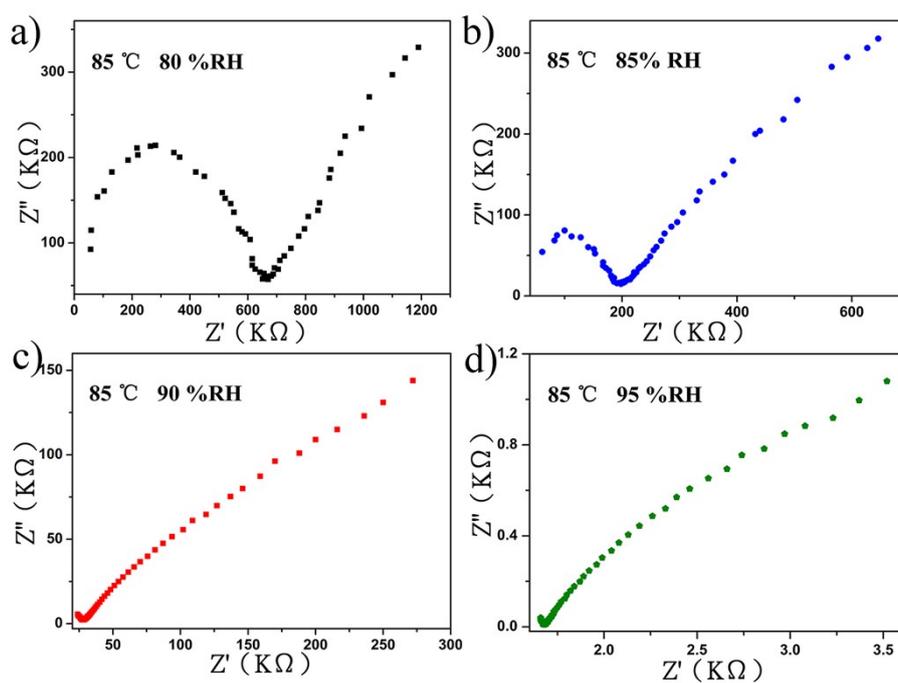
Fig. S19. Nyquist plots of compound **2** at 85 °C under different humidity conditions. The conductivity is 2.29×10^{-6} S·cm^{-1} (80% RH), 7.54×10^{-6} S·cm^{-1} (85% RH), 4.43×10^{-5} S·cm^{-1} (90% RH), and 8.89×10^{-4} S·cm^{-1} (95% RH).