Supporting Information

Multifunctional proton-conducting and sensing pillar-layer framework based on [24-MC-6] heterometallic crown clusters

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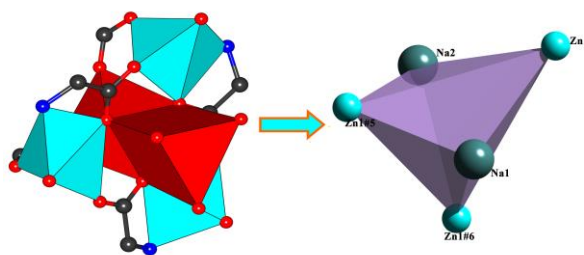[b]University of Chinese Academy of Sciences, Beijing, 100049, China
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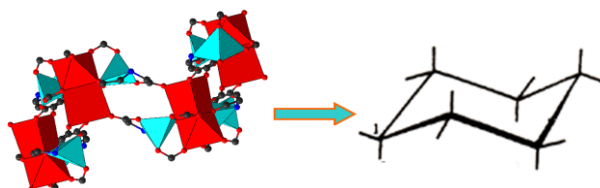
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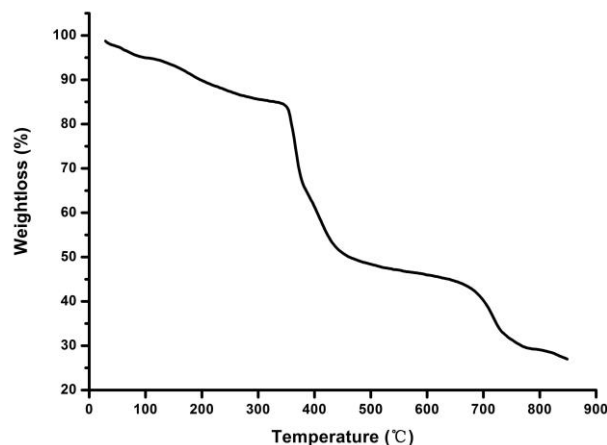Email: hongjie@ciac.jl.cn (Hong-Jie Zhang)

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Fig. S1 A heterometallic cluster with distorted trigonal bipyramidal environment. (Symmetry code: #5 1-y, x-y, z; #6 1-x+y, 1-x, z).

Fig. S2 Chair conformation of [24-MC-6] metallacrown in compound **1**.

Fig. S3 The TGA curve of compound **1**.

Experimental Section

Materials and Measurements

All starting materials and solvents were reagent grade, commercially available and used without further purification. H_3cpida was synthesized according to the reported procedures.[1] Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. TG analyses were performed on a Perkin−Elmer Thermal Analysis Pyris Diamond heated from room temperature to 850 ℃ under a N_2 atmosphere at a rate of 10 ℃ min^{-1} (Fig. S3).

Synthesis of **1**: $Zn(NO_3)_2 \cdot 6H_2O$ (0.5 mmol), H_3cpida (0.12 g), NaOH (0.06g) and

DMF (5 mL) was sealed in a 15 mL Teflon-lined stainless-steel autoclave under autogenous pressure and heated at constant 90 °C for 3 days and then was cooled to room temperature slowly. The resulting hexagonal-shaped crystals were collected. Elemental analysis for $C_{42.50}H_{49.50}N_{6.50}Na_2O_{20.50}Zn_3$ (**1**) (1221.48) (%): calcd. C 41.79, H 4.08, N 7.45; found C 41.72, H 4.15, N 7.39.

Crystal data for **1**: $C_{42.50}H_{49.50}N_{6.50}Na_2O_{20.50}Zn_3$, $M_r = 1221.48$, Trigonal, space group *P-3*, $a = 14.700(3)$ Å, $b = 14.700(3)$ Å Å, $c = 13.252(3)$ Å, alpha = 90, beta = 90, gamma = 120, $V = 2480.0(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.636$ g cm^{-3}, final $R_1 = 0.0530$ and $wR_2 = 0.1257$ ($R_{int} = 0.0920$) for 2962 independent reflections [$I>2\sigma(I)$]. CCDC 932848.

Proton conductivity measurements

The powders were prepared by grinding the sample into a homogeneous powder with a mortar and pestle. The powders were then added to a standard 11 mm die, sandwiched between two stainless steel electrodes and pressed at 8 MPa for 3 min. the pellet was 11 mm in diameter and 1.063 mm in thickness. The impedances were measured with a frequency response analyzer/potentiostat (Princeton Applied Research PAR 2273, EG&GPARC, Princeton, NJ) over a frequency range from 0.1 Hz to 1 MHz, with a quasi-four probe electrochemical cell and an applied ac voltage of 100 mV. Measurements were taken in the temperature range of 25–95 °C with 97% relative humidity (controlled by using an HDHWHS-50 incubator). ZSimpWin software was used to extrapolate impedance data results by means of an equivalent circuit simulation to complete the Niquist plot and obtain the resistance values. Conductivity was calculated using the following equation:

$$\sigma = L / RS$$

where σ is the conductivity (S cm^{-1}), L is the measured sample thickness (cm), S is the electrode area (cm^2) and R is the impedance (Ω).
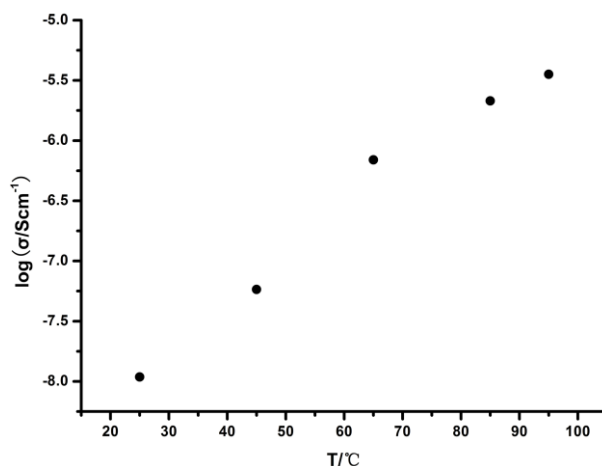
**Fig. S4** Log(σ/S cm^{-1}) versus temperature plot of compound **1** at 25-95°C under 97% RH.
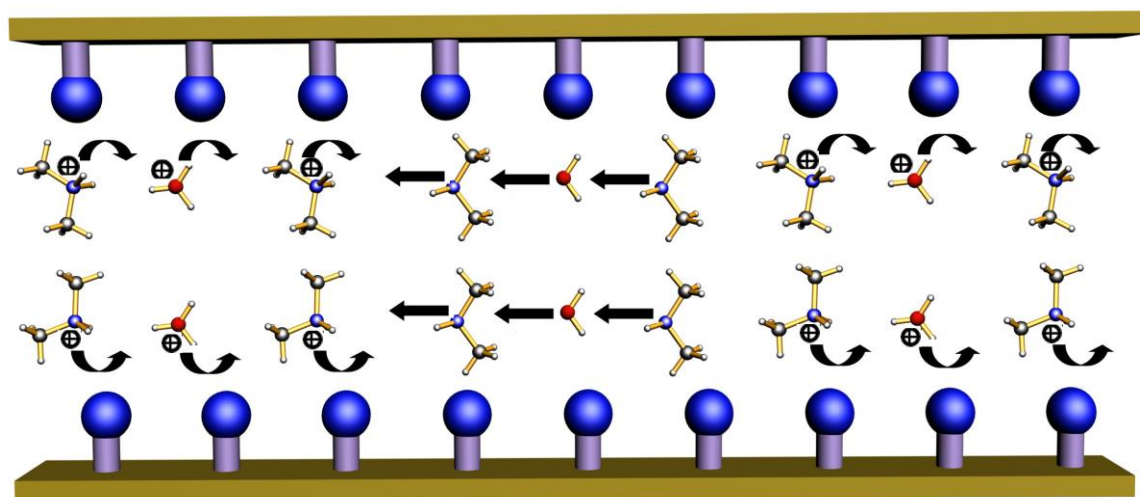
Fig. S5 The possible mechanism of proton transport in compound **1**.

Luminescent measurements

The luminescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer equipped with a 150W xenon lamp as the excitation source. The strongest emission wavelengths were located at 368 nm when excited at 323 nm. For the experiment of sensing small organic molecules (Fig. S6 and Fig. S7a), the **1**-solvent emulsions were prepared by introducing 5.5 mg of **1** powder into 5.00 mL of acetone, benzene, DMF, dichloromethane, toluene, methanol, chloroform, THF, ethanol, acetonitrile, aether and ethyl acetate, and the width of the excitation slit was 2.5 nm and the emission slit was 2.5 nm; for the experiment of sensing metal ions (Fig.

S7b), the **1**-M^{2+} emulsions were prepared by introducing 5.5 mg of **1** powder into 5.00 mL of $M(NO_3)_x$ (M = Zn^{2+}, Cd^{2+}, Na^+, Ni^{2+}, Co^{2+}, or Cu^{2+}) solution, the width of the excitation slit was 5.0 nm and the emission slit was 10.0 nm; for the experiment of sensing various concentration acetone (Fig. S8), the **1**-solvent emulsions were prepared by introducing 5.5 mg of **1** powder into 5.00 mL of DMF solvent containing different amounts of acetone, the width of the excitation slit was 10.0 nm and the emission slit was 5.0 nm; for the experiment of sensing different concentration of Cu^{2+} (Fig. S9), the **1**-Cu^{2+} emulsions were prepared by introducing 5.5 mg of **1** powder into 5.00 mL different concentration of $Cu(NO_3)_2$ solution (0, 10^{-4}, 10^{-3}, 10^{-2} mol/L), the width of the excitation slit was 10.0 nm and the emission slit was 5.0 nm. After sonication treatment 2 h, the luminescence spectra were measured.

To elucidate the possible mechanism for the luminescent quenching effect by metal ions, N1s X-ray photoelectron spectroscopy (XPS) studies were carried out on **1** and M^{2+}-incorporated **1** (M^{2+} = Cu^{2+} or Co^{2+}). The N1s peak from amide nitrogen atoms at 399.50 eV in **1** is shifted to 399.75/400.15 eV on the addition of Cu^{2+}/Co^{2+} (Fig. S11). There may be the weak binding of amide nitrogen atoms to M^{2+} in M^{2+}-incorporated **1** (M^{2+} = Cu^{2+} or Co^{2+}), which has been confirmed by the result of Chen.[2] Such binding reduces the intraligand luminescent efficiency and results in the quenching effect. The enhancing effect may be caused by a weak binding between the Zn^{2+}/Cd^{2+} and the organic linker of compound **1**. The weak binding resulted in a ligand-centered charge transfer, which may lead to the enhancing effect.[3]
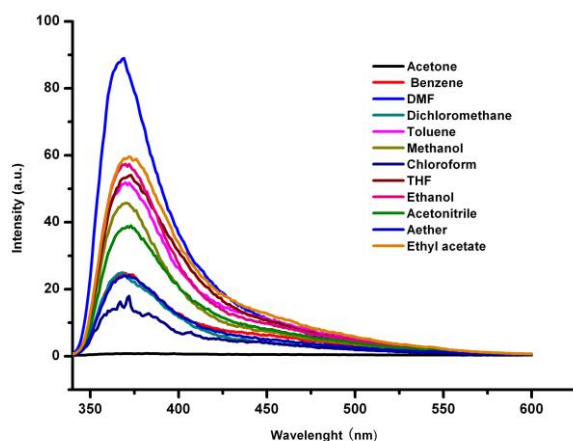
Fig. S6 PL spectra of compound **1** introduced into Acetone, Benzene, DMF, Dichloromethane, Toluene, Methanol, Chloroform, THF, Ethanol, Acetonitrile, Aether and Ethyl acetate.
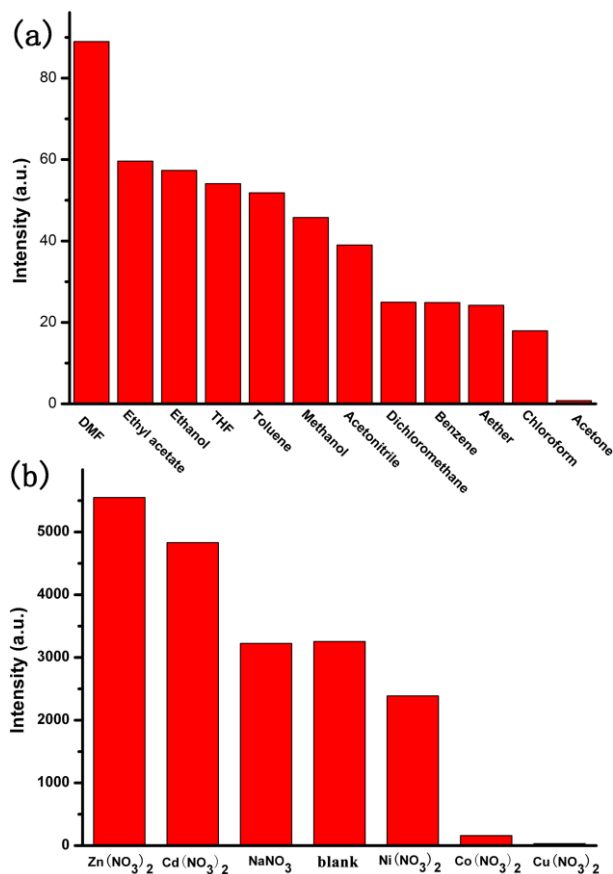

Fig. S7 Comparisons of the luminescence intensity of the **1** introduced into various pure solvents (a), and incorporating different metal ions, activated in 5 mL DMF solution containing 0.01 M M(NO$_3$)$_x$ (b).
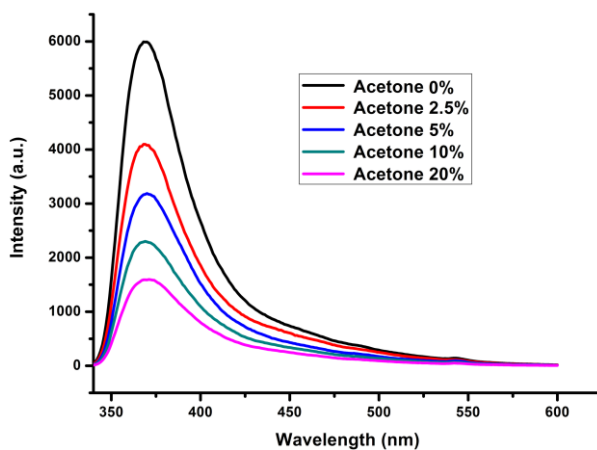
Fig. S8 The PL spectra of compound **1** DMF emulsion in the presence of various content of acetone.
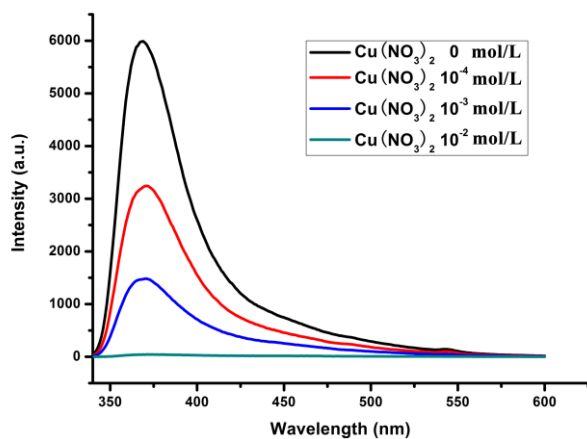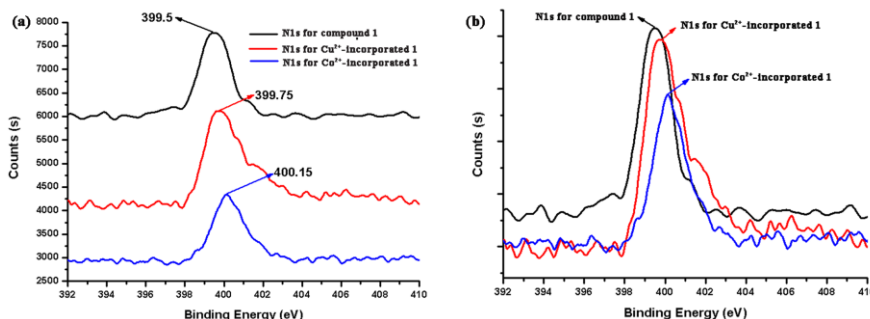

Fig. S9 The PL spectra of compound **1** in $Cu(NO_3)_2$ DMF solution at different concentrations.
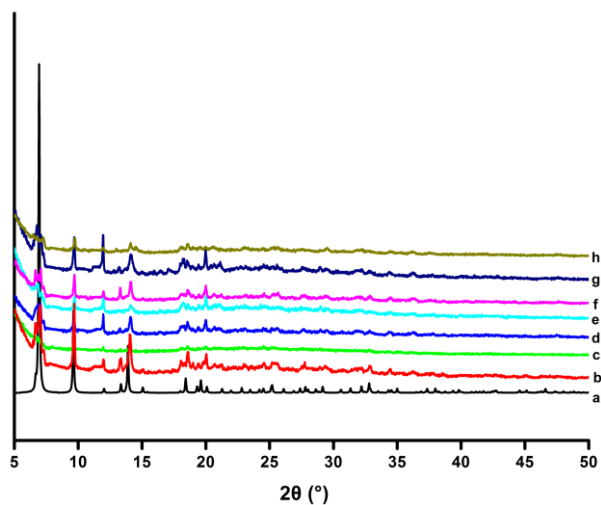
Fig. S10 Powder X-ray diffraction patterns of a) simulated from the X-ray single

structure of **1**, b) as-synthesized **1**, and diffraction patterns obtained after the introduction of various metal ions: c) Cd^{2+}, d) Co^{2+}, e) Cu^{2+}, f) Na^{2+}, g) Ni^{2+} and h) Zn^{2+}.

Fig. S11 N1s X-ray photoelectron spectroscopy (XPS) spectra (a) and move up/down (b) for clarity.

1 G. P. Yong, Z. Y. Wang and Y. Cui, *Eur. J. Inorg. Chem.*, 2004, 4317.

2 B. L. Chen, L. B. Wang, Y. Q. Xiao, F. R. Fronczek, M. Xue, Y. J. Cui and G. D. Qian, *Angew. Chem. Int. Ed.*, 2009, **48**, 500.

3. (*a*) S. Liu, Z. H. Xiang, Z. Hu, X. P. Zheng and D. P. Cao, *J. Mater. Chem.*, 2011, **21**, 6649; (*b*) Q. Tang, S. X. Liu, Y. W. Liu, J. Miao, S. J. Li, L. Zhang, Z. Shi and Z. P. Zheng, *Inorg. Chem.*, 2013, **52**, 2799.