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Journal Name

ARTICLE

Engineering the Proton Conductivity of Metal-organic Hybrid Materials by Varying Coordination Mode of the Ligand

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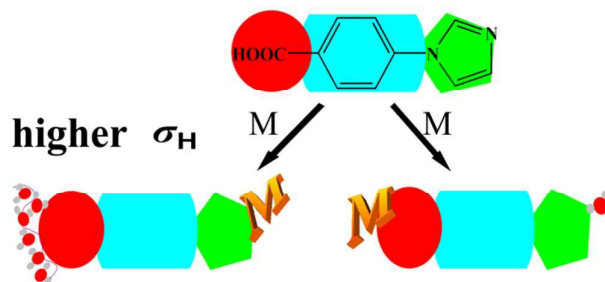
The report of design and synthesis of adjustable proton-conducting metal–organic coordination hybrids is still rare. Herein, we synthesised and characterized two coordination compounds: $\text{Cu}(\text{HL})\text{L}$ (**1**) and $\text{H}_4\text{Mo}_8\text{O}_{24}\text{L}_4 \cdot 3\text{H}_2\text{O}$ (**2**) (L = 4-(1H-imidazolyl) benzoic acid). In addition, we firstly reported that adjusting the proton conductivity of metal-organic hybrids via varying the coordination mode of a specific ligand L (L = 4-(1H-imidazolyl) benzoic acid). Compound **1** has proton conduction of $1.08 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at 97%RH at room temperature, while under the same condition, **2** has obviously lower proton conduction of $1.09 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$. Proton conduction of the two hybrids varied with nearly one thousand fold.

Introduction

Environmental pollution and fast depletion of fossil fuels force researchers to develop new technology to produce clean and renewable energy. Fuel cell technology is the solution to the two problems, which is one of the most promising energy conversion devices with high conversion efficiency and low pollution^{1,2}. The proton conducting electrolyte is one of key parts in fuel cells which greatly influences efficiency and commercialization of fuel cells. However, the widely used Nafion membrane shows profound drawbacks such as low water retention capacity above 100 °C or under low humidity for extended period³, complicated and toxic synthetic process as well as expensive price, which limit the development of fuel cells^{3,4}. This becomes the driving force for the exploration of a wide variety of compounds as potential solid electrolyte materials, such as ceramic oxides, polyoxometalates, polymers and their blends or adducts.

Metal-organic frameworks (or metal-organic coordination polymers) have emerged as an outstanding class of designed and tunable crystalline proton conductors⁵. Proton-conducting MOFs (PCMOFs) are broadly classified as two categories: i) water-mediated PCMOFs whose conductivities are humidity-dependent; ii) anhydrous PCMOFs that operate at high

temperature under low humidity. The precise structural features and functional groups may provide profound clues for understanding the mechanism of proton conductivity.



Scheme 1 Schematic representation of varying coordination mode of the ligand to adjust proton conduction of metal-organic hybrids (The big red circle represents the carboxyl group, the bright green part represents the imidazole group, the turquoise part represents benzene group, M represents transition metals and the small red circle with grey circles decoration represents water molecules).

Researchers are currently focusing on synthesizing PCMOFs with high conductivity, for example, $\text{Mg}_2(\text{H}_2\text{O})_4(\text{H}_2\text{J}) \cdot \text{H}_2\text{O}$ (J = 2,5-dicarboxy-1,4-benzene-diphosphonic acid)⁶, $\{[(\text{Me}_2\text{NH}_2)_3(\text{SO}_4)]_2[\text{Zn}_2(\text{ox})_3]\}_n$ ⁷, $\text{UiO-66}(\text{SO}_3\text{H})_2$ ⁸, poly(4-styrene sulfonate) threaded in MIL-101⁹, $\text{H}_2\text{SO}_4@\text{MIL-101}$ ¹⁰ etc. These materials are good proton conductors but some are not water stable¹¹. Moreover, the relationship between the structure features and proton conduction activity has not been widely investigated yet¹². It is necessary to develop a set of materials which are water stable and proton conduction adjustable by varying structure features.

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[†]Electronic Supplementary Information (ESI) available: XRPD, TGA, UV-vis absorption spectrum, Tables, X-ray crystallographic files in CIF format. See DOI:10.1039/b000000x/

To date, there have been some reports about proton conductors based on either imidazole¹³ or carboxylic acid/phosphoric acid¹⁴. However, there has been no investigation on the MOF system containing both imidazole and carboxyl groups, not to mention adjusting proton conduction by varying the coordination mode. Additionally, although some of MOFs with high conductivity in the range of 10^{-2} S·cm⁻¹ have been demonstrated, there have seldom discussion about the nature of proton conduction and features of crystal structures.

Herein, we hope to reveal the relationship between the nature of proton conduction and structural features. We chose a bi-proton-conducting-group ligand L (L = 4-(1H-imidazolyl)benzoic acid) to coordinate with different transition metals. The imidazole group and carboxyl group have distinct adorable coordination modes to transition metals and so we can adjust the corresponding coordination-free group which acts as the proton conduction carrier (Scheme 1). A copper (I) cation tends to form a linear coordination mode with the imidazole group, resulting in the protonated and coordination-free carboxylate group as the proton carrier. While when the ligand meets molybdenum, the carboxyl group tends to coordinate to the molybdenum atom with the imidazole group being free. The two metal-organic materials showed good water stability. The proton conductivity of the compound with carboxylate groups as proton carriers increases 1000 times higher than that of the one with imidazole groups as proton carriers¹⁵.

Experimental section

Materials and Methods

All chemicals and solvents (of analytical grade) were purchased from commercial sources (Aldrich, POCh, Polmos) and were used as supplied unless otherwise stated. The organic ligand 4-(1H-imidazolyl)benzoic acid was purchased from Jinan Comolai Trading company and used without further purification.

Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 2400 CHN elemental analyzer. IR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrophotometer equipped with an iD5 diamond ATR attachment. Electronic diffuse reflectance spectra were measured in BaSO₄ pellets as a reference using UV-3600 UV-VIS-NIR spectrophotometer equipped with ISR-260 attachment. Powder X-ray diffraction measurement was recorded radiation at room temperature on a Siemens D5005 diffractometer with Cu-K α ($\lambda = 1.5418$ Å). Rigaku Miniflex 600 diffractometer with Cu-K α radiation ($\lambda = 1.5418$ Å) in a 2θ range from 5° to 50° with a 0.02° step at a scan speed of 1° min⁻¹. The CCDC numbers for the two compounds are 1421602-1421603. Thermogravimetric analyses (TGA) were performed on a Mettler-Toledo TGA/SDTA 851e instrument, coupled with a quadrupole mass spectrometer (QMS) ThermoStar GSD 300 T Balzers, with a heating rate of 10°C min⁻¹ in a temperature range of 25–600°C.

Synthesis of Compound 1 Cu(HL)L: Cu(NO₃)₂·3H₂O (0.0604 g, 0.25 mmol) and organic ligand L (L = 4-(1H-imidazolyl)benzoic acid (0.047 g, 0.25 mmol) were dissolved into 10 mL distilled water¹⁶. The pH of mixed solution was adjusted by 0.02 mL of 1M

hydrochloric acid to 6.5. The mixture was transferred and sealed into a 23 mL polytetrafluoroethylene (PTFE)-lined stainless steel autoclave, heated at 165°C for 5 days and then was cooled to room temperature. Black block crystals were isolated, purified with dry ethanol and then vacuum-dried with the yield 0.026g, 11.8% based on L ligand. Elemental analysis (%): Calc. for C₂₀H₁₅CuN₄O₄ (Mr: 438.9 g/mol): C, 49.71; N, 11.59; H, 3.13; Found: C, 49.75; N, 11.63; H, 3.06. IFT-IR (KBr) ν /cm⁻¹: 3133(br), 1602(vs), 1545(vs), 1408(s), 1338(s), 943(m), 781(s), 730(s), 641(w), 542(w), 439(w).

Synthesis of Compound 2 [H₄Mo₈O₂₄L₄]·3H₂O: (NH₄)₆(Mo₇O₂₄) (0.12g, 0.25mmol), and organic L ligand (0.047g, 0.25 mmol) were dissolved into a 10 mL distilled water. PH value of the mixed solution was adjusted with 1M HCl to 3.5. The mixture was sealed into a 23 mL polytetrafluoroethylene (PTFE)-lined stainless steel autoclave, heated at 165°C for 5 days and then was cooled to room temperature. Yellow block crystals were obtained by filtration, washed with dry ethanol and vacuum-dried with the yield 0.041g, 33.5% based on L ligand. Elemental analysis (%): Calc. for C₄₀H₃₈Mo₈N₈O₃₅ (Mr: 1958.30 g/mol): C, 1.64; H, 1.05; N, 0.47; Mo, 35.00; Found: C, 1.20; H, 1.14; N, 0.44; Mo, 36.86. FT-IR (KBr) ν /cm⁻¹: 3122(br), 1616(wk), 1554(wk), 1408(s), 943(m), 916(wk), 770(s), 560(m), 512(m), 463(m).

Physical characterization

Impedance measurement of the samples was performed on an IVIUM (Netherland) electrochemical workstation. The sample was compressed to a pellet under a pressure of 15 MPa at room temperature. The pellet was attached to the surface of platinum electrode. The proton conductivity was measured using AC impedance measurement. The relative humidity and temperature were controlled by using an HDHWHS-50 incubator. ZSimpView software was used to simulate impedance data to complete the Nyquist plot and obtain the resistance value. The proton conductivity is calculated as

$$\sigma = L/AR$$

Where σ is the ionic conductivity, R is the resistance, L is the thickness, and A is the area of the pellet. Activation energy linear fitting of the plot was obtained from the equation given below:

$$\sigma T = \sigma_0 \exp(-E_a / K_B T)$$

Where σ_0 is the pre-exponential factor, K_B is the Boltzmann constant, and T is the temperature¹⁷.

Results and discussion

Description of Crystal Structures

Compound 1 was composed of rigid L ligands and Cu cations. Single-crystal X-ray diffraction analysis shows that this is a discrete mononuclear copper complex crystallizes in the monoclinic space group $C2/c$ with one copper coordinating with two L ligands forming a linear molecule (Fig. 1a& S1). The Cu (I) center is surrounded by two nitrogen atoms (N1) from two different L ligands and lies at the symmetric centre of the molecule. Cu-N bond lengths are 1.855(3) and 1.870(3) Å, respectively, and N-Cu-N bond angles are 172.1°. The imidazole ring and benzene ring of the L ligand are not in the same plane

with the dihedral angles range from 19.428° to 33.138°. The carboxyl group of one coordination L ligand was not deprotonated during the reaction. In this complex, the carboxyl groups did not coordinate to any transition metal cations with only imidazole group connecting to Cu.

Reversely, we planned to obtain compounds with only carboxyl groups coordinating to transition metal cations whereas the imidazole group being free. We have tried many transition metal cations such as Cu²⁺, Co²⁺, Fe³⁺ etc, however, both carboxyl and imidazole groups coordinate to transition metal cations. According to the HSAB theory, hard acid prefers to hard base and soft acid prefers to soft base. N atom can be regarded as soft base and it is easier for Cu⁺ coordinating to N. Similarly, hard acid Mo⁶⁺ will prefer to coordinate with O atoms.

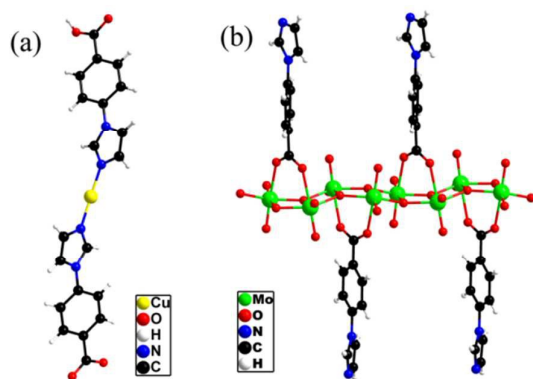
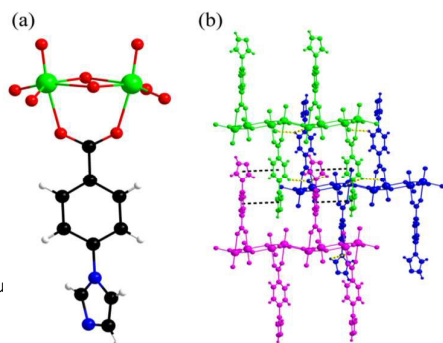


Fig. 1 Ball-and-stick representation of compounds **1** (a) and **2**(b).

Then we chose MoO₄²⁻ as the transition metal source to induce the assembly process and a molybdenum-oxo cluster based inorganic-organic compound **2** was synthesized (Fig.1b). Each Mo atom is six coordinated by oxygen atoms containing two terminal oxygen atoms O_t (Mo=O_t= 1.691-1.699 Å), three bridging μ₃-O atoms (Mo-O = 1.950-2.313 Å) and one oxygen atom from the carboxyl group. In this compound, the imidazole group was free and protonated, while the carboxyl group bridged two Mo atoms resulting in a basic repeating unit {HMo₂O₈L} (Fig.2a). X-ray single-crystal crystallography shows that the asymmetric unit contains two {HMo₂O₈L} units. The adjacent {HMo₂O₈L} unit was upturned and connected via μ-O to form an infinite 1D chain which can also be regarded as the inorganic backbone decorated with protonated L ligands. The adjacent 1D chains form a 3D supramolecule via π-π stacking and hydrogen bonds (Fig. 2b). The distance of π-π interactions between the imidazole rings from one chain and the benzene ring from the adjacent 1D chain ranges from 3.65~3.71 Å and that of the C-H...O hydrogen bonds ranges from 2.35~2.83 Å.



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Fig. 2 (a) The {Mo₂O₆L} unit of **2**; (b) The 3D supramolecular structure via π-π interaction.

Table 1. Crystal data and structure refinement for **1** and **2**

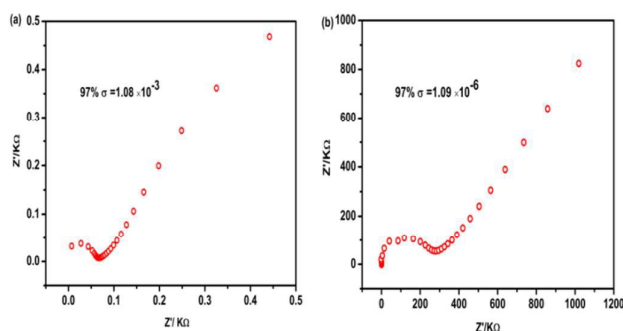
Compound	1	2
Formula	C ₂₀ H ₁₅ Cu N ₄ O ₄	C ₄₀ H ₃₈ Mo ₈ N ₈ O ₃₅
Mr	438.90	1958.30
Cryst. Syst.	Monoclinic	Monoclinic
space group	C2/c	P2(1)/c
a(Å)	24.513(5)	7.3598(15)
b(Å)	18.922(4)	14.818(3)
c(Å)	17.238(3)	26.434(5) A
α(deg)	90 deg	90 deg
β(deg)	119.74(3) deg	94.94(3) deg
γ(deg)	90 deg	90 deg
V(Å ³)	6943(3) Å ³	2872.1(10) Å ³
Z	16	2
Calculated density	1.680 Mg/m ³	2.264 Mg/m ³
F(000)	3584	1900
R(int)	0.0445	0.0379
R indices [I>]	0.0502	0.0365
wR2(all data)	0.1502	0.0928
GOF on F ²	1.079	0.945
CCDC No	1421602	1421603

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$. ^b $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$

Characterizations

Thermogravimetric analysis (TGA) of **1** shows one step of weight loss (75.7%) starting at 250 °C, corresponding to the decomposition of organic ligands (Fig.S6). Compound **2** shows two-step weight loss: the first step of weight loss ~4.01% (ranging from 20 to 250 °C) corresponds to the release of lattice water molecules; the second step of weight loss ~37.48% (ranging from 300 to 420 °C) corresponds to the decomposition of organic ligands (Fig.S7). The TGA results indicate that the two compounds have good thermal stability below 200 °C, which exhibits the potential application in fuel cells. X-ray photoelectron spectroscopy (XPS) analysis was

carried out to determine the elemental composition of the as-prepared materials. The Cu 2p spectra were obtained for compound **1** (Fig. S8). The results exhibit two peaks at 932.57 eV and 952.57 eV in the Cu 2p spectrum, attributed to the Cu 2p_{3/2} and 2p_{1/2} binding energies for Cu⁺³⁰. Additionally, we used PXRD to investigate the bulk phase purity. The experimental PXRD profiles of the two compounds match well with the corresponding simulated curves of **1** and **2** (Fig. S9 & S10). A potential proton-conducting material should be stable and not soluble under humid conditions, and so we used PXRD to investigate the water stability of the as-prepared samples. There is no peak shift or pattern change according to the respective PXRD pattern, which indicates the good stability of two compounds under humidified condition (RH 97% at room



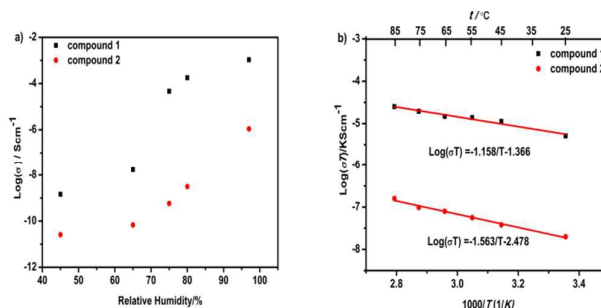
temperature) or in boiling water (refluxed for 10 hours).

Fig. 3. (Left) Nyquist plot of compound **1** at 298 K under relative humidity 97%, $\sigma = 1.08 \times 10^{-3} \text{ S cm}^{-1}$; (Right) Nyquist plot of compound **2** at 298 K under relative humidity 97%, $\sigma = 1.09 \times 10^{-6} \text{ S cm}^{-1}$.

Proton conduction measurement

A few portable fuel cells that work at low temperatures and humidified conditions are on the stage regarded as clean energy devices. It is necessary to obtain water stable proton conductors. To inspect the proton conductivity (σ), AC impedance analysis was employed to evaluate the proton conductivities of **1** and **2** using the corresponding compacted pellet of the powdered crystalline sample at 25°C in the relative humidity range from 45% to 97%. The proton conductivity of as-prepared **1** is found to be $1.45 \times 10^{-9} \text{ S cm}^{-1}$ from the Nyquist plot at room temperature under 45% RH. With the increase of RH%, the proton conductivity value continues to rise and reach $1.08 \times 10^{-3} \text{ S cm}^{-1}$ at 97% RH (Fig. 3 & S13). While under the same condition, the proton conductivity of **2** changes from 2.56×10^{-11} to $1.09 \times 10^{-6} \text{ S cm}^{-1}$ in the RH range from 45% to 97%. The proton conductivity of **1** is nearly one thousand times higher than that of compound **2** at room temperature 97% RH (Fig. 3), which is probably due to converse coordination of the ligand to transition metal ions. The rise of proton conductivity of **1** and **2** with the increase of relative humidity suggests that the proton conductivity of two compounds is humidity-dependent. These results are supported by water-adsorption profiles as shown in Fig. S11

and S12. The samples for water adsorption isotherms were pre-heated at 150°C for 1h in vacuum to remove most water molecules before the measurement. The two compounds can absorb water vapor and the absorption ability of **1** is higher than that of **2** which are in consistent with the difference of the proton conductivity between the two compounds. It is supposed that water-mediated conduction occurs more easily along carboxylate groups and hydrogen bonds as shown in Fig. 3. Activation energy (E_a) is another vital factor to evaluate proton conducting materials and a type of materials with low



E_a is in pursuit in the field of fuel cells.

Fig. 4. (a) RH dependence of the conductivity (σ) for **1** and **2** at 298 K. (b) Arrhenius-type plot of the conductivity of **1** and **2** at various temperatures and under ~65% RH condition.

The E_a value of the two compounds were respectively extracted by utilizing the linear correlation in the plot of $\ln(\sigma T)$ versus $1000/T$. E_a of **1** is 0.23 eV and that of **2** is 0.31 eV, implying that the proton conduction process of **1** follows the Grotthuss mechanism (0.1–0.4 eV)³⁴. This value is comparable to that of Nafion (0.22 eV)³⁵ and lower than other proton conducting MOFs^{36–39}. Compound **1** is a new type of good intrinsic proton conductor.

Conclusions

In conclusion, we have designed and synthesized two novel proton-conducting metal-organic hybrid materials based on 4-(1H-imidazolyl)benzoic acid, which are stable and insoluble in water. The proton conductivity of metal-organic hybrids can be adjusted by varying the coordination mode of the ligand. The impedance data shows that the type of proton carrier and hydrogen bonds are key factors for proton conducting property. In compound **1**, the carboxyl group is coordination-free and provides a quicker proton hopping pathway via hydrogen bonds. Consequently, the proton conductivity of **1** is nearly 1000 times higher than that of **2**. The proton conduction mechanism of compound **1** follows the Grotthuss mechanism. This work provides a new strategy to design and adjust proton conducting materials and even to understand the influence of different proton carriers on proton conduction.

Acknowledgements

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