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Assembly of Three Coordination Polymers Based on a Sulfonic-carboxylic Ligand Showing High Proton Conductivity

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Three new coordination polymers (CPs)/metal-organic frameworks (MOFs) with different structures have been synthesized by using 4,8-disulfonyl-2,6-naphthalenedicarboxylic acid (H_4L) and metal ions, Cu^{2+}, Ca^{2+} and Cd^{2+}. Cu compound features a one-dimensional chain structure, further extending into a 2D
10 layer network through H-bond interactions. Ca and Cd compounds both show 3D frameworks with (4, 4)-connected **PtS**-type topology and (3, 6)-connected **bct**-type topology, respectively. These CPs/MOFs all exhibit proton conduction behavior, especially for Cu compound with proton conductivity of 3.46×10^{-3} $S\cdot cm^{-1}$ at 368 K and 95% relative humidity (RH). Additionally, the activation energy (Ea) has been also investigated to deeply understand the proton-conduction mechanism.

Introduction

The design of soild-state proton conductors has been an attractive challenge in many areas of chemistry, from battery-related technologies to biological systems.[1-3] Proton conductivity has long been investigated in a wide range of materials such as
20 organic polymers, oxo acids and their salts, ceramic oxides and carbon nanotubes.[4] Recently, metal-organic frameworks (MOFs) or called coordination polymers (CPs) are an emerging class of crystalline porous materials assemblied of inorganic metal ions and clusters and polydentate organic linker ligands. They have
25 been extensively studied for their structural diversity and potential applications in gas storage and separation,[5] heterogeneous catalysis,[6] drug delivery,[7] energy stroage and conversion,[8] and chemical sensing.[9] Meanwhile, based on their ion-conducting behavior, CPs/MOFs begun receiving more
30 attention due to the easy construction and the dynamic motion of the ionic components in the structures.[10-11]

   In these compounds, the conductivity generally arises from guest molecules such as acid, water molecules/clusters or counter-ions: H^+, NH_4^+ and imidazolium cations as proton-carrier
35 sources; alternatively, it could also arise from hydrogen-bonded networks as proton-conduction pathways.[12] In comparison with other proton-conducting materials, the main advantage of CPs/ MOFs is their highly crystallized structures, providing a useful insight into the conduction pathway and mechanism.[13]
40 Furthermore, the designable architecture, the ease with which functional ligands can be introduced into framework design, and the capability to incorporate different guest species provide numerous opportunities to improve the proton conduction property by materials design.
45 Recently, our group has reported a series of intterelated work about proton conductivity. The proton conductivities were measured in humidity condition and concretised by means of incorporating the moving $[(CH_3)_2NH_2]^+$ ions[14] and the free carboxylic groups in the framework[15]. Based on the work they
50 have done, the sulfonic-carboxylic ligands as the appealing candidates for synthesizing excellent proton-conducting materials capture our eyes for the strong coordination carboxylic groups and acidic sulfonic groups.[16] Particularly, owing to the three oxygen atoms of sulfonic group, the sulfonic group can ligate
55 metal ions into multidimensional framework, while the oxygen atoms may still be available to further act as H-bond acceptors.[17] These sites could assist in anchoring carrier molecules or directly transferring protons as part of a conduction pathway. However, MOFs based on sulfonic-carboxylic ligands are still relatively
60 few and have rarely been explored extensively as proton-conducting materials.

   Herein, we employ the 4,8-disulfonyl-2,6-naphthalenedicarboxylic acid (H_4L) as a sulfonic-carboxylic ligand to construct CPs/MOFs, looking forward to exploring high
65 proton-conducting materials. In this work, we successfully obtained three different structural CPs/MOFs with Cu^{2+}, Ca^{2+} and Cd^{2+} ions, namely $[Cu(H_2L)(DMF)_4]_n$ (**1**) , $[CaL_{0.5}(DMF)_{2.5}]_n$ (**2**), $[CdL_{0.5}(DMF)_2]_n$ (**3**). These CPs/MOFs all exhibit proton conduction behavior, especially for Cu compound with proton
70 conductivity of 3.46×10^{-3} $S\cdot cm^{-1}$ at 368 K and 95% relative humidity (RH). In addition, the Ea has been also investigated to further understand the proton-conduction mechanism.

Experiment Section

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Materials and Physical Measurements

The 4,8-disulfonyl-2,6-naphthalenedicarboxylic acid (H_4L) was synthesized according to the literature.[18] All the other starting

materials employed were purchased from commercial sources and used as received without further purification. Elemental analyses were determined with a VarioEL analyzer. Fourier transform infrared (FT-IR) spectroscopy was obtained with a
5 Bruker TENSOR 27 Fourier transform infrared spectrometer with the KBr pellet technique and operating in the transmittance mode in the 4000-400 cm⁻¹ region. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 449F3 TG/DTA instrument under air atmosphere. The samples were heated from about 40 °C
10 to 800 °C with a heating rate of 10 °C/min. The experimental powder X-ray diffraction data (PXRD) were collected on a Bruker D8-FOCUS diffractometer equipped with Cu Kα1 (λ = 1.5406 Å; 1600 W, 40 kV, 40 mA) with the step of 0.02°. The simulated PXRD patterns were calculated by using single-crystal
15 X-ray diffraction data and processed by the free *Mercury v1.4* program provided by the Cambridge Crystallographic Data Center.

Synthesis of [Cu(H₂L)(DMF)₄]ₙ (1)

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A mixture containing H₄L (0.0188 g, 0.05 mmol), Cu(NO₃)₂·3H₂O (0.0241 g, 0.10 mmol) in 1.5 mL of DMF was sealed in a Teflon-lined autoclave and heated at 65 °C under autogenous pressure for eight hours and then allowed to cool to
25 room temperature. The crystals were washed with DMF, ethanol and air-dried. Yield: 65% (based on Cu²⁺). Anal. Calcd for C₂₄H₃₂N₄O₁₄S₂Cu (Mr: 728.20): C, 39.59%; H, 4.43%; N, 7.69%. Found: C, 39.37%; H, 4.35%; N, 8.07%. IR (cm⁻¹): 3425(w), 3084(w), 2928(m), 1713(s), 1643(s), 1431(s), 1381(s), 1242(s),
30 1172(s), 1047(s), 712(m), 611(s), 534(w).

Synthesis of [CaL₀.₅(DMF)₂.₅]ₙ (2)

A mixture containing H₄L (0.0188 g, 0.05 mmol),
35 Ca(NO₃)₂·4H₂O (0.0236 g, 0.10 mmol) in 1.5 mL of DMF was sealed in a Teflon-lined autoclave and heated at 120 °C under autogenous pressure for three days and then allowed to cool to room temperature. The crystals were washed with DMF, ethanol and air-dried. Yield: 57% (based on Ca²⁺). Anal. Calcd for
40 C₂₆H₄₂N₅O₁₅S₂Ca₂ (Mr: 808.93): C, 38.60%; H, 5.23%; N, 8.66%. Found: C, 39.03%; H, 5.11%; N, 8.24%. IR (cm⁻¹): 3437(m), 2941(w), 2822(w), 1664(s), 1624(s), 1508(w), 1419(s), 1356(s), 1256(m), 1192(m), 1040(m), 941(w), 821(w), 687(w), 621(m), 532(w).

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Synthesis of [CdL₀.₅(DMF)₂]ₙ (3)

A mixture containing H₄L (0.0188 g, 0.05 mmol), Cd(NO₃)₂·4H₂O (0.0308 g, 0.10 mmol) in 1.5 mL of DMF was
50 sealed in a Teflon-lined autoclave and heated at 100 °C under autogenous pressure for three days and then allowed to cool to room temperature. The crystals were washed with DMF, ethanol and air-dried. Yield: 53% (based on Cd²⁺). Anal. Calcd for C₁₃H₁₆N₂O₇SCd (Mr: 456.74): C, 34.19%; H, 3.53%; N, 6.13%.
55 Found: C, 34.37%; H, 3.35%; N, 6.07%. IR (cm⁻¹): 3450(w), 3102(w), 2945(w), 1654(s), 1561(s), 1410(s), 1369(s), 1253(m), 1160(s), 1107(m), 1032(m), 927(w), 793(m), 701(w), 619(s), 520(w).

60 ### X-ray Crystallography

The X-ray intensity data for the three compounds were collected on a Bruker SMART CCD diffractometer with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å, 45 kV, 35
65 mA). Data integration and reduction were processed with SAINT software.[19] Multiscan absorption corrections were applied with the SADABS program.[20] The crystal structure was solved by means of Direct Methods and refined employing full-matrix least-squares on F² (SHELXTL-97).[21] All the hydrogen atoms except
70 for those of coordinated DMF molecules were generated geometrically and refined isotropically using the riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

75 ### Proton conductivity measurement

The powder for alternating-current (AC) impedance measurements was prepared by grinding the sample into a homogeneous powder with a mortar and pestle. The powder of
80 compounds **1-3** were then added to a standard 8 mm die, sandwiched between two stainless steel electrodes and pressed at 16 MPa for 2 min. All of the pellets were 8 mm in diameter and 1.3-1.5 mm in thickness with about 100 mg samples. Proton conductivity measurements of the compounds were determined
85 using an impedance and gain-phase analyzer (PARSTAT 4000, Ametek, USA) over frequency range 0.1 Hz to 4 MHz with an input voltage amplitude of 100 mV and the conventional quasi-four-probe method. Measurements were taken in the temperature range of 298-368 K with varying relative humidity (controlled by
90 using an HDHWHS-50 incubator). ZsimpWin software was used to fit impedance data sets by means of an equivalent circuit (Scheme S1) simulation to complete the Nyquist plot and obtain the resistance values (Table S3-S5). Proton conductivity was calculated by the following equation:

95 $$\sigma = L/(RA)$$

Where σ = proton conductivity, L = thickness of the pellet, R = resistance of the pellet, and A = area of the pellet = $4\pi r^2$ where r = radius of the pellet.
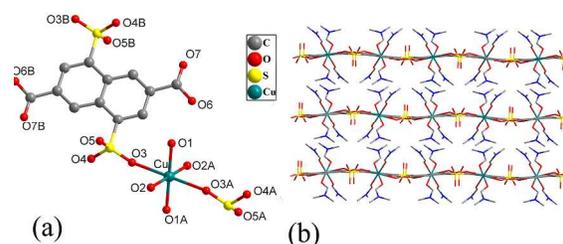

Fig. 1 (a) Local coordination environment of the Cu²⁺ ions in **1**. Hydrogen atoms attached to carbon atoms are omitted for clarity. Symmetry codes: A, 2-x, -y, 2-z; B, 2-x, 1-y, 1.5-z; C, 2-x. (b) The crystal structure of **1**.

100 ## Results and Discussion
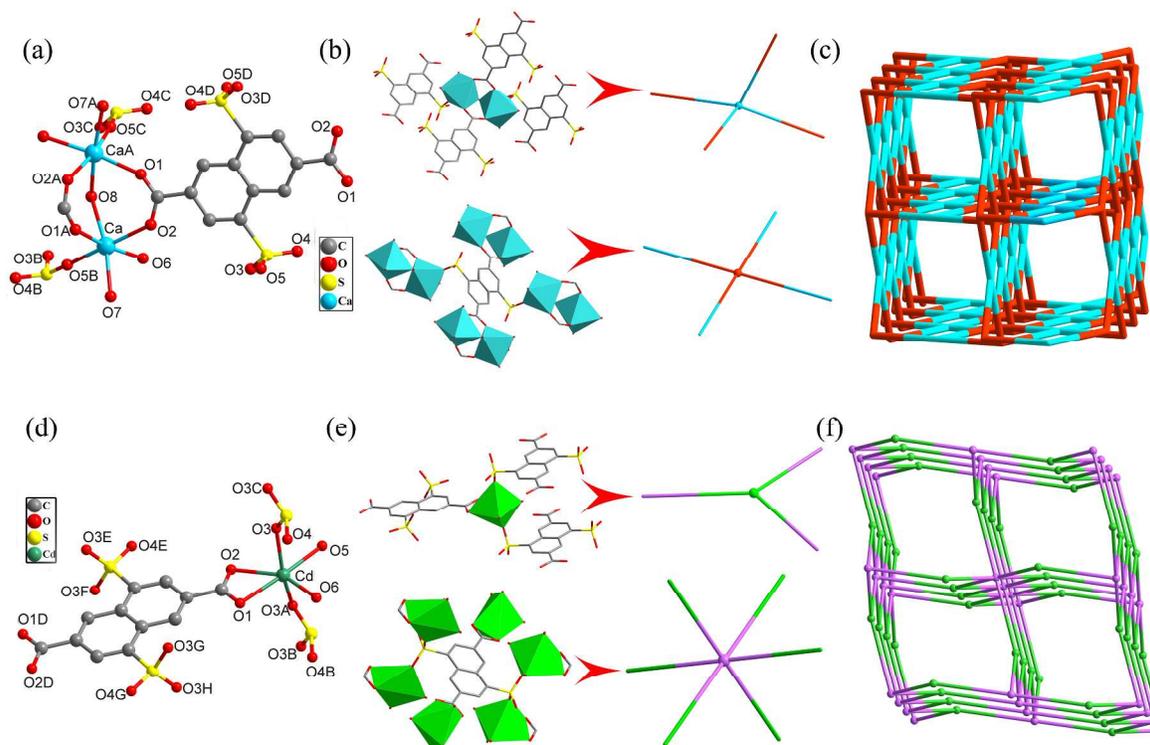
Structure description

Fig. 2 (a) Local coordination environment of the Ca^{2+} ions in **2**. Hydrogen atoms attached to carbon atoms are omitted for clarity. Symmetry codes: A, 2-x, y, 1.5-z; B, 1.5-x, 0.5+y, 1.5-z; C, 0.5+x, 0.5+y, z; D, 1.5-x, 0.5-y, 1-z. (b) Scheme illustrating that the binuclear unit of Ca^{2+} can be reduced to a 4-connected node and the L^{4-} ligand can be reduced to a 4-connected node. (c) Topological representation of **2**. (d) Local coordination environment of the Cd^{2+} ions in **3**. Symmetry codes: A, x, y, 2-z; B, x, y, 1+z; C, x, y, 1-z; D, 2-x, 1-y, z; E, 1.5-x, 0.5+y, 1.5-z; F, 1.5-x, 0.5+y, 0.5+z; G, 0.5+x, 0.5-y, 1.5-z; H, 0.5+x, 0.5-y, 0.5+z.(e) Scheme illustrating that the Cd^{2+} center can be reduced to a 3-connected node and the L^{4-} ligand can be reduced to a 6-connected node. (f) Topological representation of **3**.

Solvothermal reaction of $Cu(NO_3)_2$ and H_4L in N, N-methylformamide (DMF) produces blue block crystals of $[Cu(H_2L)(DMF)_4]_n$. Single-crystal X-ray analysis reveals that Compound **1** crystallizes in the $P2_1/n$ space group and features a

5 one-dimensional chain based on Cu^{2+} ions and H_2L^{2-} ligands. The asymmetric unit of compound **1** consists of a half crystallographically independent Cu^{2+} ion, one half H_2L^{2-} ligand, and two coordinated DMF molecules (Fig. 1a). Each Cu^{2+} center is coordinated with six oxygen atoms, including two sulfonic

10 oxygen atoms at its axial sites, and four oxygen atoms from four DMF molecules at its equatorial sites to form a distorted octahedral geometry. All Cu-O bond lengths are within the expected ranges.[22] The adjacent Cu^{2+} centers are linked *via* H_2L^{2-} ligands to form an infinite 1D chain along the *b* direction, further

15 extending into a 2D layer network through H-bond interactions which is probably the pathway for proton conductivity (Fig. S1).

When Ca^{2+} is utilized instead of Cu^{2+} in compound **1**, compound **2** is obtained and it crystallizes in the monoclinic space group $C2/c$ with one crystallographically independent Ca^{2+}

20 ion, a half L^{4-} ligand, two and a half coordinated DMF molecules in the asymmetric unit. Ca^{2+} ion adopts a six-coordinated octahedral geometry, defined by six oxygen atoms from two monodentate carboxylic groups, one sulfonic group, and three DMF molecules (Fig. 2a). The Ca-O distances vary from 2.270(5)

25 to 2.417(4) Å, in accordance with reported values in other calcium-oxygen compounds.[23] Furthermore, two Ca^{2+} ions are held together by two carboxylic groups to yield a binuclear $[Ca_2(COO)_2]^{2-}$ unit. Each binuclear unit is linked by four L^{4-}
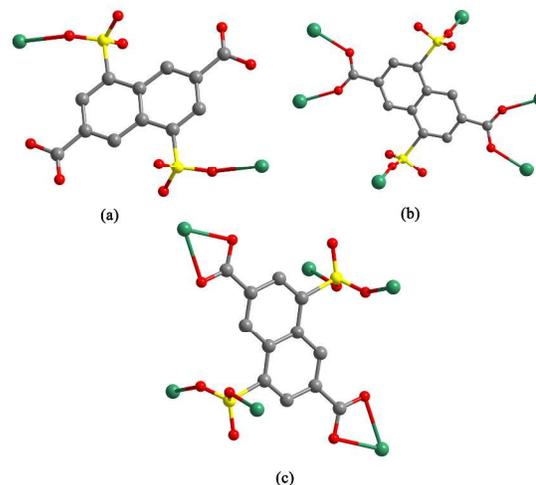
Scheme 1. Observed coordination modes of the sulfonic-carboxylic ligand H_4L.

ligands, each L^{4-} ligand connects with four binuclear units (Fig.
30 2b). Thus, the binuclear units are connected by the L^{4-} ligands to generate a 3D framework. With consideration of the binuclear, L^{4-} ligand as four-connecting nodes, the overall structure of compound **2** topologically possesses a binodal (4, 4)-connected **PtS**-type topology calculated with TOPOS program[24] (Fig. 2c).

35 Compound **3** crystallizes in the orthorhombic space group *Pnnm* revealing a three-dimensional MOF. The asymmetric unit contains a half crystallographically independent Cd^{2+} ions, one quarter of L^{4-} ligand and one coordinated DMF molecule. As
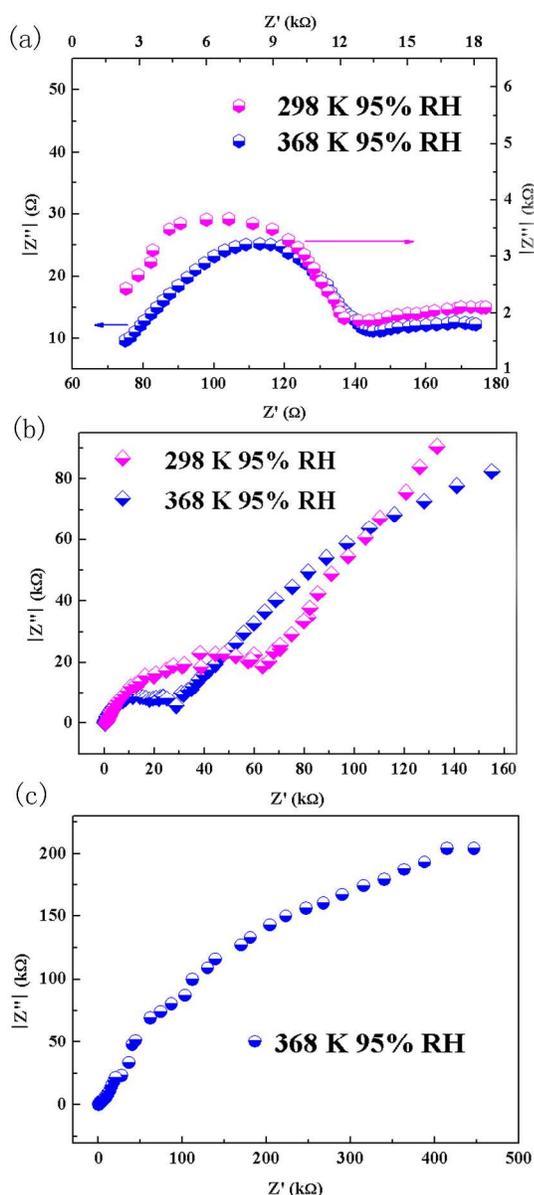
Fig.3 The Nyquist plots for proton conductivity at 95% RH for **1, 2** and **3** at given conditions
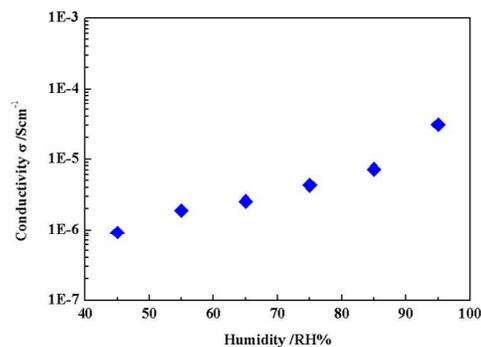

Fig. 4 RH dependence of conductivity for **1** at 298 K

centers in the monodentating fashion (Scheme 1a). However, in other two compounds, the sulfonic-carboxylic ligand adopts multitudinous coordination motifs. For compound **2**, full

20 deprotonated sulfonic-carboxylic ligand exhibits a hexadentate coordination mode with two bidentate carboxylic groups and two monodentate sulfonic groups (Scheme 1b). Similar to compound **2**, the sulfonic-carbxylic ligand in compound **3** deprotonates completely and also displays a hexadentate fashion but with two

25 chelate carboxylic groups and two bidentate sulfonic groups (Scheme 1c). Therefore, the coordination modes of the sulfonic-carboxylic ligand play important roles for the structural diversity of the compounds. Furtehrmore, the more strongly polarized oxygen atoms and the free carboxylic groups of the sulfonic-

30 carboxylic ligands indicated that the compounds can be potentially applied as proton-conducting materials.
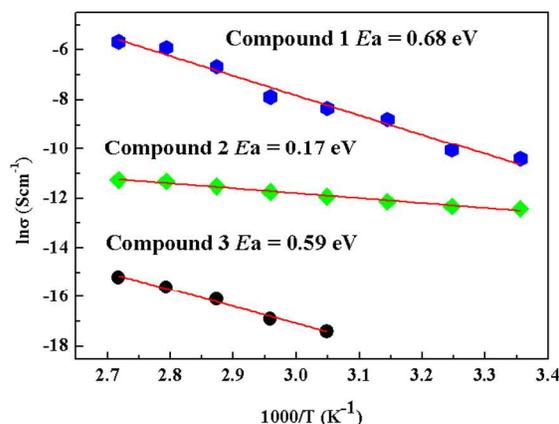

Fig. 5 Arrhenius-type plots of the conductivity for **1** (blue), **2** (green), **3** (black) at various temperatures and 95% RH

Structural stability

35 We evaluated the structural stability of compounds **1-3** against humidity because high water stability is widely required for various applications, especially for proton conductivity.[26] The powders of three compounds were exposed to 95% RH at ambient temperature for 48 h. The PXRD patterns after

40 humidified are identical as the initial ones, indicating that the crystal structures of compounds **1-3** are stable under the high humid condition (Fig. S2-S4). Thermogravimetric analyses are investigated for the thermal stability, revealing that the crystal structures of **1** and **3** are retained until 200 °C, while the crystal

45 structure of **2** is intact up to 120 °C (Fig. S5). Meanwhile, the IR

illustrated in Fig. 2d, the Cd^{2+} ion is six-coordinated representing a distorted octahedral geometry with two oxygen atoms from a chelating carboxylic group, two oxygen atoms from two monodentate sulfonic groups and two oxygen atoms from two

5 DMF molecules. The Cd-O bond distances range from 2.170(5) to 2.357(4) Å, which are comparable to those reported for other Cd-O donor compounds.[25] From the topological point of view, each center Cd^{2+} ion is ligated by three ligands, which can be considered as a 3-connected node; each L^{4-} ligand connects with

10 six Cd centers defining as a 6-connected node (Fig. 2e). On the basis of this simplification, compound **3** possesses a (3, 6)-connected **bct**-type topology calculated by TOPOS[24] (Fig. 2f).

In compound **1**, the sulfonic-carboxylic ligand behaves as a dianion with two protonated carboxylic groups forming strong H-

15 bond with the adjacent sulfonic groups and DMF molecules. While only two sulfonic oxygen atoms coordinated with Cu^{2+}

spectra of compounds **1-3** exhibit an obvious increse of the characteristic band of water molecules (*ca.* 3450 cm^{-1}), indicating that compounds **1-3** can effectively enrich and absorb water molecules.(Fig. S6-S8)

Proton conductivity

The proton conductivity of compounds **1-3** were measured by alternating current (AC) impedance spectroscopy with varying temperature and RH. Representative Nyquist plots are shown in Fig. 3. The semi-circle in the high-frequency region deals with bulk and grain boundary resistance, whereas the tail at low frequency is consistent with mobile ions that are blocked by the electrode-electrolyte interface. The proton conductivity of **1** gradually increases with increase of humidity at ambient temperature (298 K) by about 2 orders of magnitude from 9.09×10^{-7} S·cm^{-1} at 40% RH to 3.05×10^{-5} S·cm^{-1} at 95% RH, suggesting that water molecules play an important role in creating the proton-conducting pathways (Fig. 4). As the temperature increases, the conductivity increases and reaches a maximum value of 3.46×10^{-3} S·cm^{-1} at 368 K (95% RH) (Fig. 3a) which is comparable with those of Cu-DSOA (1.9×10^{-3} S·cm^{-1} at 98% RH and 85 °C)[16a] and PCMOF-5 (2.5×10^{-3} S·cm^{-1} at 98% RH and 60.1 °C)[27]. In compound **2**, the conductivity value is 4.04×10^{-6} S·cm^{-1} at 298 K. At 368 K, the conductivity increases to 1.27×10^{-5} S·cm^{-1} (Fig. 3b). However, compound **3** fails to exhibit conductive property at ambient temperature. With increasing temperature, it begins to show conductive property at 328 K with 2.77×10^{-8} S·cm^{-1}. Even at 368 K, the conductivity is just 2.49×10^{-7} S·cm^{-1} (Fig. 3c). Recently, Kitagawa's group reported three rare examoles of CPs with free non-coordinating sulfonic acid groups, showing higher proton conductivity 3.9×10^{-4} S·cm^{-1} at 298 K and 60% RH. This can be ascribed to the more easy ionization of the non-coordinating sulfonic acid groups.[16c] Shimizu's group reported a β-PCMOF2 that conducted proton in regular one-dimensional pores lined with sulfonate groups.[12a] Proton conduction in this MOF was modulated by the controlled loading of 1*H*-1,2,4-triazole (Tz) guests within the pores and reached 5×10^{-4} S·cm^{-1} at 150 °C in anhydrous H$_2$. Take these work and our work into consideration, we can speculate that the free non-coordinating sulfonic acid groups and their regular pattern in the pores are the most critical factors which can influence the proton conductivity.

Compared with different structures of compounds **1-3**, it is to be note that the free carboxylic groups can easily ionizes in contact with water, making great contributions to conductive property of compound **1**. Furthermore, although the sulfonic acid groups are coordinated in the 3D frameworks, the strongly polarized and non-coordinated oxygen atoms still can increase the conductive property. In compound **1**, the H on free carboxylic oxygen forms a hydrogen bond with oxygen in sulfonic groups and DMF molecules to make an extended hydrogen-bonding network in the *ab* plane (Fig. S1). The free water molecules accepts protons which are dissociated from free carboxylic groups and/or coordinated DMF molecules, forming H$_3$O$^+$. Then, the proton is transferred by the formation and breaking of hydrogen bonds at appropriated positions for fast proton hopping across the extended hydrogen-bonding network. However, the

activation energy (*E*a) estimated by the Arrhenius plots is 0.68 eV (Fig. 5), indicating that the proton transfer for compound **1** is governed by the Grotthuss mechanism along with some other processes such as direct diffusion of additional protons with water molecules (Vehicle mechanism).[28] Although compound **2** shows lower *E*a (0.17 eV) followed the Grotthuss proton hopping mechanism, the fact that compound **1** exhibits higher proton conduction than compound **2** is indicative of a high carrier concentration, especially originating from the free carboxylic groups. Compound **3** shows not only lower proton conduction but also higher *E*a (0.59 eV). Since there are less non-coordinated oxygen atoms from sulfonic groups than compounds **1** and **2**, the proton conduction for compound **3** mainly controls by Vehicle mechanism. So the conductive property follows the trend **1** >> **2** >> **3**, which is in accord with the experimental research.

Conclusions

In conclusion, we have successfully synthesized three CPs/MOFs with a sulfonic-carboxylic ligand and metal ions Cu^{2+}, Ca^{2+} and Cd^{2+}, exhibiting amusing structures and distinct binding motifs. Interestingly, these three CPs/MOFs show significant difference in their proton conductivity, especially for compound **1** with proton conductivity of 3.46×10^{-3} S·cm^{-1} at 368 K and 95% RH. This strategy of employing sulfonic-carboxylic ligands as linkers to construct CPs/MOFs with free acid groups as superior conductive materials for applications has potential to explore.

Acknowledgement

Notes and references

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