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Modulating proton diffusion and conductivity in metal–organic frameworks by incorporation of accessible free carboxylic acid groups†

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Three multi-carboxylic acid functionalised ligands have been designed, synthesised and utilised to prepare the new barium-based MOFs, MFM-510, -511, and -512, which show excellent stability to water-vapour. MFM-510 and MFM-511 show moderate proton conductivities (2.1×10^{-5} and 5.1×10^{-5} S cm⁻¹, respectively) at 99% RH and 298 K, attributed to the lack of free protons or hindered proton diffusion within the framework structures. In contrast, MFM-512, which incorporates a pendant carboxylic acid group directed into the pore of the framework, shows a two orders of magnitude enhancement in proton conductivity (2.9×10^{-3} S cm⁻¹). Quasi-elastic neutron scattering (QENS) suggests that the proton dynamics of MFM-512 are mediated by “free diffusion inside a sphere” confirming that incorporation of free carboxylic acid groups within the pores of MOFs is an efficient albeit synthetically challenging strategy to improve proton conductivity.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) are a promising technology for the use of hydrogen-based energy in applications such as transport.¹ A key factor for its success is the development of materials which can move protons efficiently across the cell. The most commonly used PEM material is the polymer Nafion, which consists of a perfluorinated polyethylene backbone with sulfonic acid terminated side chains.² The acidic nature of this polymer facilitates proton conduction in the order of 10^{-2} S cm⁻¹ below 85 °C in the presence of water. However, the lack of long range order in polymers restricts the in-depth understanding of the mechanism of proton conductivity, thus inhibiting the development of new materials with higher conductivity and/or wider temperature range for operation.

In recent years, hybrid MOF materials have emerged as potential candidates as a new class of proton conductors owing to a number of unique features.^{3–7} For example, the functionalisation of organic constituents allows the periodic introduction of acidic groups (*e.g.*, –COOH, –PO₃H₂, –SO₃H), which can facilitate efficient proton transfer pathways.^{8–14} However, the synthesis of MOFs bearing free acid groups is very challenging, primarily due to the favoured deprotonation of these acids and their subsequent coordination to the metal nodes under solvothermal conditions. The crystalline nature of MOFs provides an opportunity to understand further the dynamics of proton diffusion, which can be used to inform future materials design. Quasi-elastic neutron scattering (QENS) has been shown recently to be a powerful technique for gaining insights into the mechanism of proton conduction in crystalline MOFs.^{15,16} However, such studies remain very rare to date. Current research into proton conducting MOFs (PCMOFs) can be separated into low temperature (<100 °C) and high temperature (>100 °C) materials.¹⁷ Low temperature PCMOFs are much more common, and, similar to Nafion, rely on the presence of water to mediate proton transfer through the framework. The hydrogen bonding network of water molecules is usually dictated by the structure and dimensionality of the framework itself and high water-stability is often a critical requirement for PCMOFs.¹⁸

Herein, we report the progressive design and synthesis of three organic linkers, H₃L¹ ([1,1':3',1''-terphenyl]-2',4,4''-tricarboxylic acid), H₄L² ([1,1':3',1''-terphenyl]-4,4',4'',6'-tetracarboxylic acid) and H₅L³ ([1,1':3',1''-terphenyl]-2',4,4',4'',6'-

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pentacarboxylic acid) containing multi-carboxylic acid functionality. The ligands combine with $\text{Ba}(\text{NO}_3)_2$ to form three MOFs, MFM-510 $[\text{Ba}_2(\text{L}^1)(\text{H}_2\text{O})_{1.5}(\text{CO}_2)(\text{DMF})_{1.5}]$, MFM-511 $[\text{Ba}(\text{H}_2\text{L}^2)(\text{H}_2\text{O})(\text{DMF})]$ and MFM-512 $[\text{Ba}_2(\text{HL}^3)(\text{H}_2\text{O})_4]$ which are stable to water vapour. MFM-510, in which all carboxylic acids are bound to the metal node, exhibits only moderate proton conductivity ($2.1 \times 10^{-5} \text{ S cm}^{-1}$) at 99% RH and 298 K. Although MFM-511 contains two monodentate carboxylic acid groups which remain protonated, their mobility is highly restricted by strong intramolecular hydrogen bonding to a neighbouring carboxyl oxygen atom, leading to a moderately enhanced conductivity of $5.1 \times 10^{-5} \text{ S cm}^{-1}$ at 99% RH and 298 K. In comparison, MFM-512, which retains pendant carboxylic acid functionality directed into the unrestricted framework void, shows two orders of magnitude enhancement on proton conductivity ($2.9 \times 10^{-3} \text{ S cm}^{-1}$) under the same conditions. Considering the similar metal–ligand coordination of these three MOFs, these improvements on proton conductivity can be considered as a direct result of the incorporation of free and accessible carboxylic acid groups into MOFs.^{13,19,20} We also report an investigation of the proton diffusion and dynamics in MFM-512 *via* QENS, which confirms the proton conduction in MFM-512 is mediated by the “free diffusion inside a sphere” mechanism.

Experimental section

Materials and characterisations

Starting materials were purchased from Sigma Aldrich and used without further purification. Full experimental details of syntheses and techniques used can be found in the ESI.†

Results and discussions

Synthesis and structural characterisation

H_3L^1 , H_4L^2 and H_5L^3 were obtained *via* a two-step synthesis, involving an initial Suzuki–Miyaura cross-coupling reaction between an aryl-dibromo compound with [4-(ethoxycarbonyl)phenyl]boronic acid (Fig. 1). This was followed by oxidation of the methyl groups situated on the central aromatic ring and subsequent hydrolysis of the terminal ester functionalities. MFM-510, -511 and -512 were synthesised under solvothermal conditions by combining the respective ligand with $\text{Ba}(\text{NO}_3)_2$ and 2 M HCl in a mixture of DMF, ethanol and water before heating in a 5 mL screw top vial at 85 °C for 72 h. All MOFs were obtained as colourless single crystals in a single phase, enabling

their structure determination *via* single crystal X-ray diffraction. The synthesis of MFM-510, -511 and -512 can be readily scaled up using an open reaction vessel, and the phase purity of the scaled-up materials has been confirmed by PXRD (Fig. S1–S3†).

MFM-510 crystallises in the $P2_1/c$ space group (Table S1†) and contains two types of mononuclear $\text{Ba}(\text{II})$ node with trigonal prismatic coordination (Fig. 2). The type I $\text{Ba}(\text{II})$ center is bound to three monodentate carboxylates (O1), two terminal aquo ligands (O2) and two formate molecules (O3) which bridge to adjacent type II nodes, the formic acid being formed *via* the thermal decomposition of DMF during the synthesis. The type II $\text{Ba}(\text{II})$ nodes are bound by three monodentate carboxylates (O4), one bidentate carboxylate (O5), one bridging formate (O3) and a terminal DMF molecule (O6). The structure of MFM-510 results in H_3L^1 being fully deprotonated and bound to $\text{Ba}(\text{II})$ centers by all three carboxylic acid groups, leaving no pendant –COOH groups. The extended framework of MFM-510 is constructed with tightly packed 2D metal–ligand sheets running along the *a*-axis.

The 4-fold COOH-functionalised ligand H_4L^2 was targeted to synthesise MFM-511 in an attempt to create pendant carboxylic acid sites. This molecule has two carboxylic acid moieties on its central ring compared to one in H_3L^1 . It was hypothesised that the steric bulk created by chelation to the highly coordinated $\text{Ba}(\text{II})$ metal centres would lead to at least one of the carboxylic acid groups being retained as a pendant functional group upon formation of a MOF structure. MFM-511 crystallises in the $P\bar{1}$ space group and contains interconnected pores which build to form a 3D open structure (Table S1† and Fig. 3). MFM-511 has one type of $\text{Ba}(\text{II})$ node which consists of a 9-coordinated metal centre with mono-capped square anti-prismatic coordination geometry. Each $\text{Ba}(\text{II})$ is chelated by three monodentate carboxylates (O1, O2, O3), two bidentate carboxylates (O1', O4), one terminal aquo (O5) and one terminal DMF ligand (O6). Two nodes combine *via* two bridging carboxylates (O1) to form a $\{\text{Ba}_2\text{O}_{16}\}$ moiety (Fig. 3c). Eight bi-metallic units $\{\text{Ba}_2\text{O}_{16}\}$ connect *via* six linkers to give four small voids which surround a larger central pore (Fig. 3a). The smaller voids ($8.7 \times 3.5 \text{ \AA}$) are decorated by two bound carboxylate groups. The large central pore ($14 \times 12 \text{ \AA}$) is decorated by terminal water molecules which are 10 Å apart for the $\text{O}\cdots\text{O}$ separation. Unfortunately, as with MFM-510, all of the carboxyl groups in MFM-511 are coordinated to $\text{Ba}(\text{II})$ centres with no free pendant carboxylic acid groups present. However, two monodentate carboxyl O atoms adjacent to O2 and O3 remain protonated, but their accessibility is severely hindered as they point into the smaller void of the



Fig. 1 Synthesis of H_3L^1 , H_4L^2 and H_5L^3 .





Fig. 3 View of (a) the crystal structure in MFM-511 along the a -axis, highlighting restrictive hydrogen bonding of carboxyl proton ($a = 1.79 \text{ \AA}$); (b) the Ba(II) metal node in MFM-511 showing monocationic square antiprismatic coordinate geometry; (c) the binuclear Ba(II) moiety in MFM-511 viewed along the a -axis. Carbon, grey; oxygen, red; hydrogen, white; nitrogen, blue; barium, teal.

range of 1.93–2.51 Å. The hydrogen bonding interactions in MFM-512 are considerably weaker than those in MFM-511 meaning that the mobility of the carboxyl protons is less

restricted (Fig. 5). This increases the possibility of an effective hydrogen bonding network being formed for proton conductivity in the presence of free water.



Fig. 4 View of (a) the crystal structure of MFM-512 along the a -axis; (b) type I and (c) type II Ba(II) nodes in MFM-512 showing distorted octahedral and trigonal prismatic square face monocationic coordination, respectively. H-atoms are omitted for clarity; (d) View of the tetranuclear Ba(II) cluster in MFM-512. Carbon, grey; oxygen, red; hydrogen, white; barium, magenta (type I) and cyan (type II).





Fig. 6 (a) Adsorption isotherms for water in MFM-510, -511, and -512. Desorption isotherms are shown in ESI† for clarity. (b) Relationship between water capacity and proton conductivity for MFM-510, -511, and -512 and a selection of MOFs in literature. ^aImpedance measurements at high humidity and room temperature, full details in Table S4.† ^bWater capacity at the RH of the impedance data. ^cWater uptake assessed by volumetric or gravimetric analysis.

99% RH and 298 K in these MOFs (Fig. 6b). The hysteresis present in desorption cycles in all cases indicates the presence of hydrophilic channels in these MOFs (Fig. S21–S23†). All three MOFs show negligible N₂ sorption uptake (Fig. S24–S26†) consistent with the larger kinetic diameter of N₂ compared to water, the uptake of water being enhanced further by internal hydrogen bonding interactions within the MOF.

QENS study of proton diffusion in MFM-512

To gain an understanding of the mechanism of proton dynamics in MFM-512, QENS spectra of MFM-512 were recorded between 248 and 423 K. In a QENS experiment, diffusional dynamics are probed by studying changes in inelastic scattering near the elastic signal at zero energy transfer. Such processes manifest themselves in QENS spectra as a decrease in the elastic intensity corresponding to coherent scattering, accompanied by a broadening of the linewidth associated with incoherent scattering of individual atoms. As the neutron coherent scattering cross-section is notably larger for hydrogen compared to other elements, the observed broadening can be assigned mainly to hydrogen atoms from the MOF. The crystal structure of MFM-512 suggests that the mobile hydrogen atoms are from water molecules bound to the metal and from the pendant carboxylic acids, as the hydrogen atoms on the phenyl rings are tightly bound.

The elastic incoherent structure factor (EISF) measures the contribution of the elastic scattering to the total scattering, with different diffusive modes possessing different Q -dependence (where Q is momentum transfer). It is thus possible to investigate the geometrical information of the free protons in MFM-512 by calculating the EISFs. For MFM-512, the EISF plots show obvious Q -dependence (Fig. 7) and can be successfully fitted using the “free diffusion inside a sphere” model (eqn (1)).¹⁵

$$\text{EISF} = p + (1 - p)[3j_1(Qr)/(Qr)]^2 \quad (1)$$

where j_1 is the first-order spherical Bessel function, r is the radius of the sphere, and p and $(1 - p)$ are the immobile and mobile fraction involved in the diffusion process, respectively. The fitting resulted in $r = 1.8995 \text{ \AA}$ (Table S5†) which is in

excellent agreement with the approximate hydrogen bond distances observed crystallographically for MFM-512 (Fig. 5a). This emphasises the need for an effective hydrogen bonding network within the framework structure which becomes increasingly viable as increasing amounts of water are adsorbed under high humidity conditions. Overall, this result is consistent with the activation energy measurement from impedance spectroscopy data that suggested a Grotthuss ‘proton-hopping’ mechanism, which necessitates short distances between adjacent sites.

It is worth noting that whilst both NMR methods and QENS probe diffusional dynamics within molecular systems, they are complementary techniques in that different time- and space-scales are probed. QENS focusses on shorter time lengths at the atomic scale. The complementary nature of such techniques has been highlighted when looking at hydrated Nafion membranes, where QENS data have been used to probe in more depth the dynamics of water, with highly consistent diffusion coefficients as those obtained from the macromolecular-scale



Fig. 7 Plots of elastic incoherent structure factor (EISF) for MFM-512. Solid curves represent the simulated EISF (eqn (1)) using the model of “free diffusion inside a sphere” at the corresponding temperatures.



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