Achieving Superprotonic Conduction with a 2D Fluorinated MOF

Paulo G.M. Mileo, Karim Adil, Louisa Davis, Amandine Cadiau, Youssef Belmabkhout, Himanshu Aggarwal, Guillaume Maurin, Mohamed Eddaoudi, and Sabine Devautour-Vinot

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.8b06582 • Publication Date (Web): 18 Sep 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
Achieving Superprotonic Conduction with a 2D Fluorinated MOF

Paulo G.M. Mileo, ⁸, † Karim Adil, ⁸, † Louisa Davis, ‡ Amandine Cadiau, ‡ Youssef Belmabkhout, ‡ Himanshu Aggarwal, ‡ Guillaume Maurin, ‡ Mohamed Eddaoudi*, † and Sabine Devautour-Vinot*†

† Institut Charles Gerhardt Montpellier, UMR 5253 CNRS, UM, ENSCM, Université Montpellier, Place E. Bataillon, 34095 Montpellier cedex 5, France
‡ Functional Materials Design, Discovery & Development Research Group (FMD⁵), Advanced Membranes & Porous Materials Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

Supporting Information Placeholder

ABSTRACT: A hydrolytically stable MOF material, named KAUST-7, was derived from a structural phase change of KAUST-7 upon exposure to conditions akin to protonic conduction (363 K / 95% Relative Humidity). KAUST-7 exhibited a superprotonic conductivity as evidenced by the impedance spectroscopic measurement revealing an exceptional conductivity up to $2.0 \times 10^{-2} \text{ S cm}^{-1}$ at 363 K and under 95% RH, a performance maintained over 7 days. 

* † Amandine Cadiau, ‡ Guillaume Maurin, ‡ Mohamed Eddaoudi*, † and Sabine Devautour-Vinot*†

Fuel cell technology is recognized as a powerful source of energy for a large variety of applications. Electolyte allowing fast proton conduction is a key component in fuel cells development.¹ Besides the standard solid electrolyte Nafion, the search for alternative proton conductive solids that incorporate a high concentration of proton sources and highly mobile proton carriers is of growing interest.

Metal organic frameworks (MOFs),² a relatively new class of solid-state materials, have received great attention as solid-state proton conductors because of i) their tunable functionality for the creation of diverse proton sources and ii) their crystalline nature that allows a regular spatial distribution of mobile proton carriers such as water, amphiprotic organic molecules or acid molecules contained in the pores.² Recently, a series of water stable fluorinated MOFs has been reported with outstanding separation performances for gas mixtures of great interest in oil and gas industry.³ Typically, the 3D- pcu KAUST-7, based on the 2-periodic square grid, Ni-(pyrazine)₆, bridged by the (NbO₅)₂⁻ pillars via the axial oxygen and fluorine centers, has shown great promise for the selective molecular exclusion of propane from propylene.⁴e

Investigation of the stability of KAUST-7 in operating condition pertaining to protonic conduction, i.e. 363 K / 95% Relative Humidity (RH), revealed a structural phase change leading to a 2D-MOF, named KAUST-7', that has dense and periodic arrays of water coordinated to the Ni²⁺ Lewis acid sites in a highly confined environment. Fortunately, this novel KAUST-7' is potentially an efficient water-mediated proton conductor owing to: i) the presence of acidic coordinated water as proton sources; ii) a crystal-line tunnel-like architecture associated with an ultra-small porosity, to favor the formation of an orientated hydrogen-bonded network of the guest water molecules; and iii) a good hydrolytic stability to ensure that the proton conductivity performances can be maintained over cycles. Impedance spectroscopy measurements confirmed that KAUST-7' shows a superprotonic conductivity up to $2.0 \times 10^{-2} \text{ S cm}^{-1}$ at 363 K and under 95% RH with the crystal structures maintained over 7 days of experiments. The combination of an exceptional performance and very good water stability makes this material as a solid alternative to the commercial benchmark Nafion for further applications as proton-exchange membranes,⁶ key components in diverse energy and environmental related technologies including water electrolyzers, fuel cells, redox flow batteries and humidity sensors. This experimental finding is further supported by an in-depth exploration of the proton migration mechanism using advanced molecular simulations.

KAUST-7 was initially prepared following the reported procedure⁵ in a hydrofluoric acid aqueous solution containing a mixture of Ni(NO₃)₂·6H₂O, Nb₂O₅ and pyrazine. This material was further treated under 95% RH and at different temperatures. Powder X-ray diffraction (PXRD) patterns showed that KAUST-7 is irreversibly transformed into a new material, named KAUST-7'. They also revealed that a structural change appears at 348 K leading to a new phase that is present with only a negligible amount of the starting material at 363 K (Figure 1c). The structure of the new phase, called KAUST-7', has been solved from PXRD data. The indexation, conducted using Mc Maille software⁶ and confirmed by applying the Le Bail methodology,⁷ led to a monoclinic unit cell (a=11.1827(1)Å, β=123.36(1)°) with the C2/m space group (see Table S1).
This material was found to be isostructural to a fluorinated pyrazine based analogue i.e CuNbOF$_2$(H$_2$O)$_2$(pyz). Accordingly, the atomic positions of this material were taken as structure solution by replacing Cu$^{2+}$ by Ni$^{2+}$ cations and a Rietveld refinement was performed (Fig. 1d) leading to good reliability factors ($R_{b}$agg$= 4.79\%$, $R_f= 3.68\%$). The structure can be described as two-dimensional sheets resulting from the connection of one-dimensional Ni-pyrazine chains pillared by (NbOF)$_3$ octahedra. The coordination sphere of Ni$^{2+}$ cations is completed with two water molecules (Figure 1a and Figure 1b) leading to the chemical formula NiNbOF$_2$(H$_2$O)$_2$(pyr) as deduced from the elemental analysis (see ESI).

Impedance measurements were recorded on this material in a powdered form from 363 to 298 K at 95\% Relative Humidity (RH), after 24 hours equilibration time between temperatures. The Nyquist plots are shown in Figure 2a. They correspond to very low impedances and result in a linear tail end of semicircles at high frequency and a subsequent capacitive tail due to the ionic-blocking electrodes at lower frequencies at low temperature. The total impedance was extrapolated from the linear region to the real axis. The corresponding conductivity values increase from 6.7 x 10$^{-5}$ S cm$^{-1}$ to 2.0 x 10$^{-2}$ S cm$^{-1}$ upon heating from 298 K to 363 K. KAUST-7$'$ exhibits conductivity values at least five times higher than KAUST-7 in the temperature range 298 K - 323 K (see Table S3). Interestingly, KAUST-7$'$ surpasses the benchmark of 10$^{-2}$ S cm$^{-1}$ proton conductivity and further competes with the best water-mediated proton conducting MOFs. Moreover, this remarkable performance is maintained over one week (Figure S4), while the solid preserves its crystal structure integrity under the operating conditions, as confirmed by the inspection of the PXRD pattern collected on the sample after the conductivity measurements (Figure S1). These findings further support the robustness and high water stability of KAUST-7$'$. The Arrhenius plot ($\ln(\sigma/T) = f(1/T)$) is illustrated in Figure 2b and leads to an activation energy $E_a$ of 0.19 eV. This value lies within the range of $E_a < 0.4$ eV, which suggests a Grotthus like mechanism$^{10}$ involving the proton transfer through a hydrogen-bond network, while water is expected to assist the proton displacement.

To further evidence the key role of water in the proton transport mechanism, impedance measurements were equally carried out at room temperature under different humidity conditions. Figure S5 clearly demonstrates the conductivity dependence on RH, since $\sigma$ drastically increases from 2.9 x 10$^{-7}$ S cm$^{-1}$ to 6.7 x 10$^{-5}$  S cm$^{-1}$ for RH raising from 40 \% to 95 \%. This evolution follows the increasing of the water uptake as a function of the relative water pressure as shown by the adsorption isotherm (Figure S6). This further confirms that protons are involved in the water assisted conductivity process.$^{11}$

More interestingly, a Bode representation of the electrical response, i.e. $\sigma_{ac} = f(f)$, where $f$ is the frequency of the electrical field (see ESI) allowed us to reveal that KAUST-7$'$ switches from a superionic conductor behavior towards an insulator one under dehydration as illustrated by the change of the $\sigma_{ac}$ profile depicted in Figure 2c$^\text{\prime}$. The electrical conductivity profile of the hydrated sample is dominated by the dc plateau associated with the long-range transport of the proton species. It is accompanied by the Maxwell Wagner Sillars polarization present at low frequency, due to the accumulation of the ionic charge carriers at the sample/electrodes interface. The later corresponds to the capacitive tail observed in the Nyquist plot (Figure 2a).

![Figure 1](image1.png)

**Figure 1.** (a) Crystal structure of KAUST-7' along [001] and (b) along [101]. (c) Variable temperature of KAUST-7 under 95\% RH showing that KAUST-7' appears at 348 K (d) Rietveld refinement of KAUST-7'.

![Figure 2](image2.png)

**Figure 2.** a) Nyquist plot from ac impedance data recorded at 95\% RH from 363 to 298 K for KAUST-7'. b) Corresponding Arrhenius type plot of the conductivity of KAUST-7'. The line corresponds to the linear least-square fit. c) Real part of the conductivity as a function of temperature, recorded at 298 K for the hydrated (RH = 95\%) and the anhydrous (RH = 0\%) KAUST-7'.

The Nyquist plots are shown in Figure 2a. They correspond to very low impedances and result in a linear tail end of semicircles at high frequency and a subsequent capacitive tail due to the ionic-blocking electrodes at lower frequencies at low temperature. The total impedance was extrapolated from the linear region to the real axis. The corresponding conductivity values increase from 6.7 x 10$^{-5}$ S cm$^{-1}$ to 2.0 x 10$^{-2}$ S cm$^{-1}$ upon heating from 298 K to 363 K. KAUST-7' exhibits conductivity values at least five times higher than KAUST-7 in the temperature range 298 K - 323 K (see Table S3). Interestingly, KAUST-7' surpasses the benchmark of 10$^{-2}$ S cm$^{-1}$ proton conductivity and further competes with the best water-mediated proton conducting MOFs. Moreover, this remarkable performance is maintained over one week (Figure S4), while the solid preserves its crystal structure integrity under the operating conditions, as confirmed by the inspection of the PXRD pattern collected on the sample after the conductivity measurements (Figure S1). These findings further support the robustness and high water stability of KAUST-7'. The Arrhenius plot ($\ln(\sigma/T) = f(1/T)$) is illustrated in Figure 2b and leads to an activation energy $E_a$ of 0.19 eV. This value lies within the range of $E_a < 0.4$ eV, which suggests a Grotthus like mechanism$^{10}$ involving the proton transfer through a hydrogen-bond network, while water is expected to assist the proton displacement.

To further evidence the key role of water in the proton transport mechanism, impedance measurements were equally carried out at room temperature under different humidity conditions. Figure S5 clearly demonstrates the conductivity dependence on RH, since $\sigma$ drastically increases from 2.9 x 10$^{-7}$ S cm$^{-1}$ to 6.7 x 10$^{-5}$  S cm$^{-1}$ for RH raising from 40 \% to 95 \%. This evolution follows the increasing of the water uptake as a function of the relative water pressure as shown by the adsorption isotherm (Figure S6). This further confirms that protons are involved in the water assisted conductivity process.$^{11}$

More interestingly, a Bode representation of the electrical response, i.e. $\sigma_{ac} = f(f)$, where $f$ is the frequency of the electrical field (see ESI) allowed us to reveal that KAUST-7' switches from a superionic conductor behavior towards an insulator one under dehydration as illustrated by the change of the $\sigma_{ac}$ profile depicted in Figure 2c$^\text{\prime}$. The electrical conductivity profile of the hydrated sample is dominated by the dc plateau associated with the long-range transport of the proton species. It is accompanied by the Maxwell Wagner Sillars polarization present at low frequency, due to the accumulation of the ionic charge carriers at the sample/electrodes interface. The later corresponds to the capacitive tail observed in the Nyquist plot (Figure 2a). For the
The behavior is typical of an extremely poor conductor, i.e., an insulator, consistent with the low values of $\sigma'(\omega)$ ($<10^{-10}$ S cm$^{-1}$). It equally turns out that the conductivity recorded at 5000 Hz and 298 K drastically drops by 9 orders of magnitude when RH decreases from 95 to 0%, i.e., $\sigma = 6.7 \times 10^{-3}$ S cm$^{-1}$ and $\sigma = 4.0 \times 10^{-12}$ S cm$^{-1}$ for the hydrated and anhydrous solids respectively.

In summary, we presented a new water stable lamellar Ni$^{2+}$-based MOF, called KAUST-7', with exceptional proton conductivity performances exceeding $10^{-2}$ S cm$^{-1}$ at 363 K and 95% RH. This makes this novel material one of the most practical alternative materials to the commercial benchmark Nafion for further ion-exchange membrane applications. The origin of this remarkable conductivity was elucidated by molecular simulations, which showed that the acidic protons were issued from the coordinated water and further transferred within the material through an extended and efficient water H-bonded network along the inter-layer. Moreover, KAUST-7' shows a spectacular behavior by switching from a superconductor towards an insulator upon dehydration, with a huge conductivity drop, i.e. 9 orders of magnitude, beneficial for candidate humidity sensor materials.

ASSOCIATED CONTENT

Supporting Information. Supporting Information contains some details on the solid characterization, impedance measurements and modeling (pdf). The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

* sabine.devautour-vinot@umontpellier.fr
* mohamed.eddaoudi@kaust.edu.sa

Author Contributions

§ These authors contributed equally.

ACKNOWLEDGMENT

The research leading to these results has received funding from the King Abdullah University of Science and Technology (KAUST) under Center Partnership Fund Program (CPF 2910). P.G.M. thanks the National Counsel of Technological and Scientific Development (CNPQ) for the scholarship. G.M. thanks the Institut Universitaire de France for its support. The authors declare no competing financial interest.

Figure 3. Illustration of the hydrogen-bond network rearrangement after 0.009 ps (a), 1.072 ps (b) and 1.879 ps (c) of the AIMD calculation run. The atoms are represented as follows: F, green; C, gray; O, red; N, blue; Ni, Nb, brown and H, white. The representation is provided along [101].

This sharp conductivity change with RH suggests that KAUST-7' may have great potential as an active sensing material for the design of impedance-type humidity sensors, with sensitivity even surpassing that of MOFs based devices already reported in the literature.\textsuperscript{15} Quantum-based molecular simulations were further performed to shed light on the water-mediated proton transport mechanism at the atomistic scale. The fully hydrated KAUST-7' structure, containing 2 water molecules per unit formula, consistent with the water adsorption uptake determined at saturation from the adsorption isotherm (see figure S6) was first geometry optimized at the DFT-D3 level using the PBE GGA functional\textsuperscript{13} combined with a Gaussian basis set,\textsuperscript{14} the GTH pseudopotentials\textsuperscript{15} and the Grimme’s DFT-D3 semi-empirical dispersion corrections\textsuperscript{16} as implemented in the CP2K package\textsuperscript{17} (see SI for details). The corresponding DFT-optimized structure (Figure S7) clearly evidences the formation of a hydrogen-bonded network highly orientated along the layer that involves water adsorbed between the layers (H$_2$O$_x$), fluorine atoms (F) of the inorganic node and water coordinated to Ni$^{2+}$ (H$_2$O) with separating distances for the pairs F…H$_x$, F…H$_y$ and O…H$_z$ below 1.9 Å (see Figure S8). \textit{Ab initio} Molecular Dynamics (AIMD) simulations were further performed to explore the dynamics of the fully hydrated KAUST-7' using the same functional/basis set as mentioned above. These simulations were run with a time step of 1 fs for 20 ps at 298 K, in order to collect enough statistics to describe the main features of the microscopic proton conduction mechanism. This calculation revealed that the H-bonded network is characterized by a continuous evolution that implies ever-changing cleavage/formation of hydrogen-bond interactions between H$_2$O$_x$, F and H$_2$O$_z$ species. An illustration of the local dynamics of this H-bonded network is provided in Figure 3. Typically, H$_2$O$_x$ which initially interacts with the 2 fluorine atoms labelled as F1 and F2 (Figure 3a), can rotate to form an extra-interaction with H$_2$O$_y$ and another fluorine atom labelled as F3, while keeping the hydrogen-bond with F1 (Figure 3b). This local rearrangement of H$_2$O$_x$ can further induce a reorientation of H$_2$O$_z$ in such a way to create an H-bond with a fluorine atom labelled as F4 that belongs to another inorganic node (Figure 3c). Such a global H$_2$O$_x$-assisted reorganization of the H-bond network generates favorable pathways for the proton propagation at the origin of the excellent conduction properties of this material.
REFERENCES
