Proton Conduction

Deutsche Ausgabe: DOI: 10.1002/ange.201604534
Internationale Ausgabe: DOI: 10.1002/anie.201604534

Hydrogen-Bonded Organic Frameworks (HOFs): A New Class of Porous Crystalline Proton-Conducting Materials

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Abstract: *Two porous hydrogen-bonded organic frameworks (HOFs) based on arene sulfonates and guanidinium ions are reported. As a result of the presence of ionic backbones appended with protonic source, the compounds exhibit ultra-high proton conduction values (σ) $0.75\times10^{-2}\,\mathrm{S\,cm^{-1}}$ and $1.8\times10^{-2}\,\mathrm{S\,cm^{-1}}$ under humidified conditions. Also, they have very low activation energy values and the highest proton conductivity at ambient conditions (low humidity and at moderate temperature) among porous crystalline materials, such as metal–organic frameworks (MOFs) and covalent organic frameworks (COFs). These values are not only comparable to the conventionally used proton exchange membranes, such as Nafion used in fuel cell technologies, but is also the highest value reported in organic-based porous architectures. Notably, this report inaugurates the usage of crystalline hydrogen-bonded porous organic frameworks as solid-state proton conducting materials.*

Over the past decade, scientific research on porous architectures has skyrocketed leading to significant advancement and development of novel materials.[1] Of them, metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) have been forerunners in this aspect showing versatile applications in the fields of gas storage, separation, sensing, catalysis, and fuel cells.[2] Very recently, a new class of materials named hydrogen-bonded organic frameworks (HOFs) has emerged as an exciting class of compounds constructed purely from organic moieties and stabilized by non-covalent hydrogen-bonding interactions.[3] Although frameworks based on hydrogen-bonding interactions were already known it was not until very recently that HOFs have attracted a significant deal of attention especially because of their promising potential as porous crystalline functional materials.[4] However, for a material to be put at on an equal footing with other conventional porous materials, such as zeolites, MOFs, or COFs, several other applications need to be scrutinized. Fuel-cell technology is one such field which has spurred a tremendous amount of interest among the people working in alternative sources of energy.[5] The proton-exchange membrane fuel cell (PEMFC) is of particular interest owing to fast transportation and ease of handling. Most of the porous crystalline PEMs that have been tried and tested are either inorganic materials, MOFs, or more recently covalent organic frameworks.[6] However, a new class of porous crystalline proton conducting materials which has easy syntheses, solution processability, and the possibility of reconciling its structure with the proton conduction mechanism could be a rational alternative for Nafion which is currently used in fuel-cell industries.

HOFs have emerged as a new class in the porous crystalline materials regime in which advantages in the ease of their synthesis, structural elucidation via single-crystal X-ray diffraction, low energy consuming regeneration processes, and good thermal stability.[3d,7] Hydrogen bonds play a pivotal role in the formation of such frameworks, and can be utilized to give important functionalities, such as tunable host guest interactions.[8] Another prominent aspect in such cases is that if a HOF material is decorated with Brønsted acid base pairs which can form intermolecular hydrogen bonding between them, then a network of hydrogen-bonding interactions may result, which can lead to proton conduction pathways. HOFs therefore can represent a new class of porous materials where the advantage of atomic level insight helps to predict the mechanism of transport phenomenon. Moreover, porosity may allow the incorporation of suitable ion carriers which can result in an ordered arrangement within the confined channels. Thus, rationally choosing such a supramolecular architecture can lead to fabrication of new materials for PEMs.

Arene disulfonates and guanidinium ions are very competent hydrogen-bonded host frameworks. The scope of tunability in either quasihexagonal or ribbon-like motif arises from the favorable H-bonding interactions between the guanidinium proton donors and sulfonate lone pairs and result in the formation of wide variety of structures.[9] The hydrogen-bonding interactions between guanidinium sulfonate (GS) moieties forms the roof and the arene groups form the pillar of such supramolecular architectures (Scheme 1). Judicious choice of a hydrophobic pillar (arene group) can improve the water stability of such GS sheets. Two-dimensional (2D) hydrogen-bonded GS sheets with porous channels, high carrier concentration, and structural robustness are

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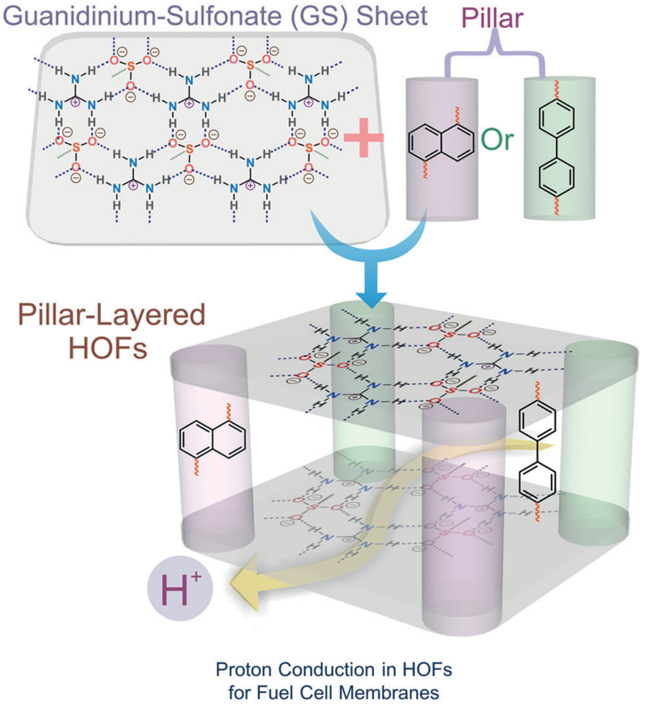
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201604534.



Scheme 1. Schematic representation of hydrogen-bonded frameworks based on arene sulfonates and guanidinium ions showing the proton-conduction pathway.

ideal candidates for proton conduction and can be modulated to give light-weight solid-state proton-conducting materials.

Herein, we report two porous two-dimensional (2D) HOFs based on arene sulfonic acid, that is, 4,4′-biphenyldisulfonic acid and 1,5-Napthalenedisulfonic acid, non-covalently bonded to guanidinium ions to form infinite pillar-brick type arrangement (Figure 1). As a result of the presence of a proton source, that is, the guanidinium cation, and a proton acceptor, that is, the sulfonate groups, these non-covalent organic frameworks exhibit very high proton conduction values in the range of $10^{-2}\,\mathrm{S\,cm^{-1}}$ under humidified conditions. Strategic control of hydrophobicity has been employed to improve on the water stability along with such high proton conduction values. Although porous materials, such as zeolites, MOFs, and COFs, have been investigated as proton-conducting materials, porous hydrogen-bonded organic frameworks have not been examined so far for solid-state PEMs. Herein we report the first examples of porous non-covalent organic frameworks as proton-conducting materials.

Simple room-temperature reaction between 1,5-napthalenedisulfonic and guanidine hydrochloride in acetone/MeOH solvent system affords single crystals of a hydrogen bonded framework, HOF-GS-10 (see the Supporting Information). Single crystal X-ray analysis of HOF-GS-10 revealed that the compound crystallized in triclinic system with space group *P*1. The hydrogen-bonding complementarity of the guanidinium cation and the sulfonate groups result in the formation of 2D framework in which the naphthalene groups serve as a pillar and the roof is formed by the GS sheets (Figures S2–S6 in the Supporting Information). This results in the formation of 1D channels along crystallographic *a* axis which are occupied by guest molecules (Figure S7). On a similar line, another 2D H-bonded framework based on 4,4′-biphenyldisulfonic acid and guanidine hydrochloride was prepared.[10] The 2D framework, HOF-GS-11 which has a bilayer arrangement composed of biphenyl units and extended H-bonded network of GS sheet (Figures S10–S12) with a shifted ribbon motif (Figure S16?) in the clathrates, results in a bilayer height of 11.23 Å. The resulting channels of the 2D framework are occupied by *p*-xylene guest molecules. IR spectra of both the compounds show characteristic peak of the sulfonate and guanidinium groups (Figures S21,S29). PXRD pattern of both compounds HOF-GS-10 and HOF-GS-11 confirmed phase purity of the bulk sample (Figures S16,S22). Thermogravimetric analysis of the compounds HOF-GS-10 and HOF-GS-11 showed an initial loss due to solvent guest molecules after which the compounds are stable up to about 320 °C (see Figure 3 a). Variable-temperature PXRD analysis of both the compounds revealed high degree of crystallinity even heating at temperature range 30–320 °C (Figures S18 and S25). For HOF-GS-11 the subtle changes in PXRD pattern occur due to loss of the large guest molecule that is, *p*-xylene as a result of the conformational freedom associated with such architectures, resulting in the formation of dense structure. The framework however reverts back to its original structure when exposed to mother liquor (Figure S23). Such structural dynamism is quite common in porous flexible frameworks upon removal of guest molecules.[11] Field-Emission scanning electron microscopy (FE-SEM) images of both the compounds in dispersed phase revealed crystalline nature of such frameworks (Figure 2 a,b), whereas atomic force microscopy images indicate uniform morphology of such 2D frameworks (Figures 2 c,d). CO_2 adsorption isotherm showed (Figures S30,31) that both these H-bonded frameworks are porous in nature.

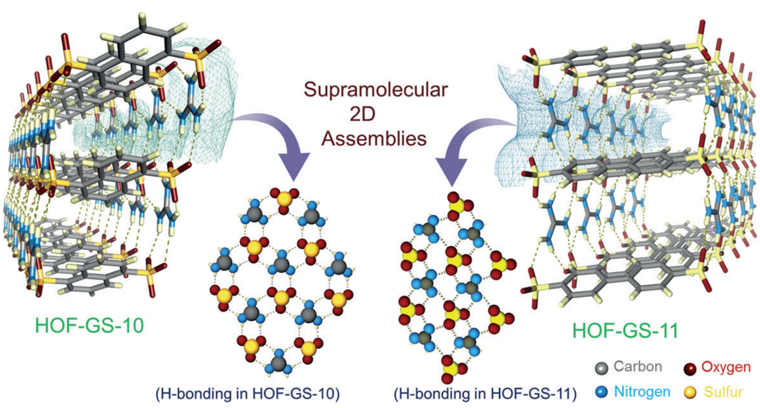


Figure 1. Hydrogen-bonded 2D frameworks of HOF-GS-10 and HOF-GS-11 showing the hydrogen-bonding interaction between the sulfonate groups and the guanidinium cations in both the compounds.

For any solid-state proton conducting material performing at humid conditions, one of the important aspects is having extended H-bonding net-

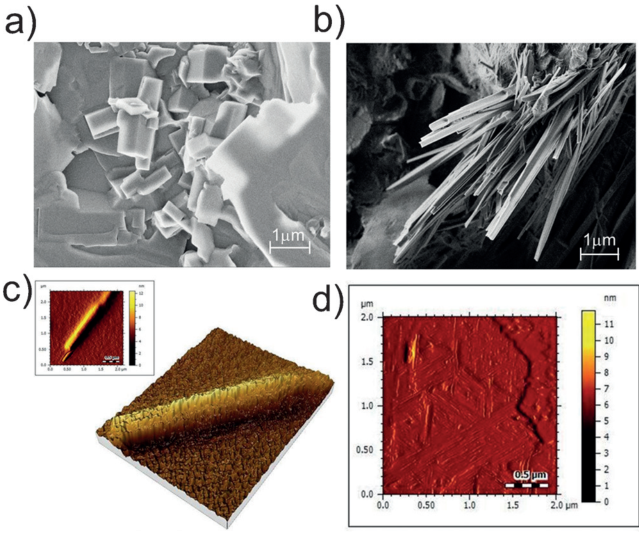


Figure 2. SEM images of a) HOF-GS-10 and b) HOF-GS-11 showing crystalline morphology c) AFM image of single crystal of HOF-GS-10 and d) AFM images of HOF-GS-11 showing uniform morphology.

work. Since both compounds have proton donor and acceptor sites, we speculated they may be suitable candidates for proton conduction. The high thermal stability and structural insight prompted us to investigate the proton conduction properties of these H-bonded frameworks. Electrochemical impedance spectroscopy (EIS) technique was employed to pelletized sample with controlled humidity and temperature to analyze the proton conduction behavior of the HOF compounds. At low humidity conditions, approximately 60 % (30 °C) HOF-GS-10 showed proton conduction of $1.78\times10^{-4}\,\mathrm{S\,cm^{-1}}$, whereas HOF-GS-11 showed proton conduction of $2.6\times10^{-4}\,\mathrm{S\,cm^{-1}}$. PEMs working at low humidity and ambient temperatures are desired because they inhibit cathode flooding and maintain unhindered proton transport required for practical applications in fuel cell industries and/or renewable energy storage devices. Notably, this is highest report of proton conduction value at low humidity and at ambient temperature in the domain of porous materials (Table S1). Upon gradually increasing the relative humidity, a clear increase in the proton conduction value is observed (HOF-GS-10 showed $1.3\times10^{-3}\,\mathrm{S\,cm^{-1}}$ and HOF-GS-11 showed $9.1\times10^{-3}\,\mathrm{S\,cm^{-1}}$ at 80 % RH) and reached a maximum value $0.75\times10^{-2}\,\mathrm{S\,cm^{-1}}$ for HOF-GS-10 and $1.8\times10^{-2}\,\mathrm{S\,cm^{-1}}$ for HOF-GS-11 at 95 % RH and at 30 °C (Figure 3 f). The reproducibility of these resulted was consistent up to three experiments. Notably, this reports the highest value of proton conduction exhibited by organic based porous materials and the values are comparable to the porous materials, such as MOFs (Table S3). This clearly indicates that water plays a significant role in proton conduction pathway. The disappearance of the typical semi-circle at high RH (Figures S37,S42) is accounted for the decrease in the time constant value which depends on the bulk resistance of the sample as previously explained by Kitagawa et al.[12]

We also performed H_2O adsorption isotherm where HOF-GS-10 being comparatively more hydrophobic due to the presence of naphthalene group showed a water uptake of $3.47\,\mathrm{mmol\,g^{-1}}$ whereas the less hydrophobic HOF-GS-11 showed a relatively more uptake of $11.6\,\mathrm{mmol\,g^{-1}}$ (Figures S34,35). Also, at higher RH/relative pressure both the structures show gate opening behavior probably to accommodate more number of H_2O molecules inside the framework correlating to the fact that we observe higher conductivity value at higher RH. The PXRD pattern of the pellet used for proton conduction measurements for HOF-GS-10 showed almost negligible changes confirming the structural integrity in presence of water vapor (Figure S17). This result is in good

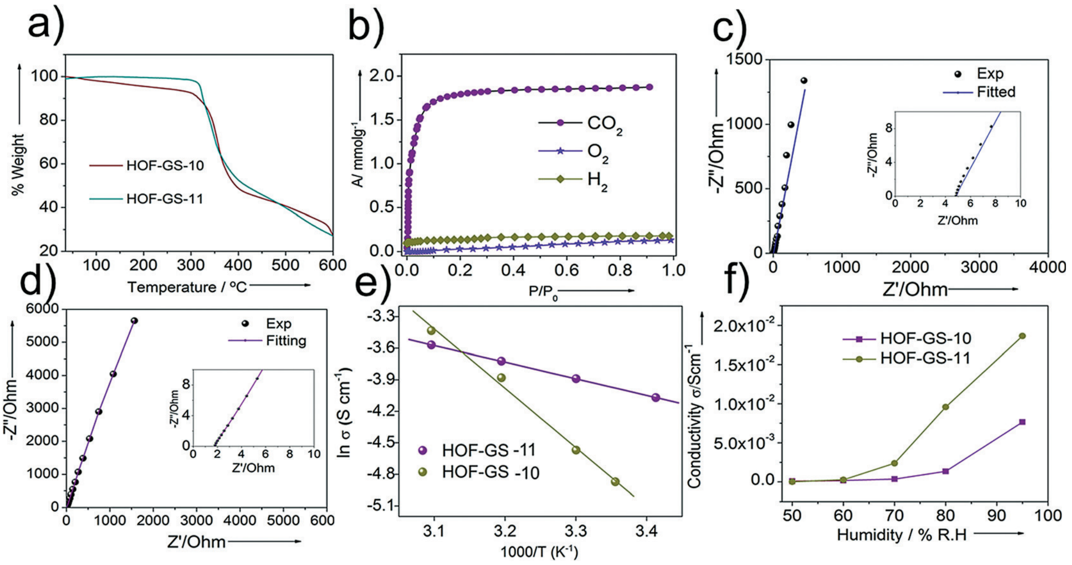


Figure 3. a) TGA pattern of the desolvated phases of HOF-GS-10 and HOF-GS-11, b) CO_2 (dots), O_2 (stars), and H_2 (diamonds) adsorption isotherms of HOF-GS-10 at 195 K (CO_2 and O_2) and at 77 K (H_2), c) Nyquist plot of HOF-GS-10 at 95 % RH and 30 °C, d) Nyquist plot of HOF-GS-11 at 95 % RH and 30 °C, e) Arrhenius plot of HOF-GS-10 and HOF-GS-11 and f) proton conduction values of HOF-GS-10 and HOF-GS-11 at varying humidity and at 30 °C.

agreement to the fact that HOF-GS-10 is comparatively more hydrophobic thereby unperturbed by water vapor and consequently showed lesser uptake in the adsorption profile of H_2O.

However, for HOF-GS-11 subtle changes in PXRD are observed after PC measurement which upon dehydration reverts back to the desolvated phase confirming of the flexible nature of the HOFs (Figure S24). For any PEM operating in fuel cells it is imperative to ascertain the proton conduction mechanism. Therefore we resorted to calculate the activation energy (E_a) values from temperature dependent conductivity at 95% RH. The least-square fit of the Arrhenius plots for HOF-GS-10 and HOF-GS-11 gave E_a values of 0.489 eV and 0.135 eV respectively (Figure 3e). Such low activation energy values are confirmation of the fact that a Grotthuss type mechanism is prevalent in these cases and these values are comparable to the lowest activation energy values reported in literature (Table S2). The difference in E_a values of these two compounds are accounted to the difference in the hydrophobic nature of these two compounds. HOF-GS-10 having a comparatively more hydrophobic naphthalene residue would inhibit more number of H_2O molecules to be accommodated in the pores thereby accounting for higher E_a and lower conductivity values. For HOF-GS-11, accommodation of more number of water molecules occur due to lesser hydrophobic biphenyl units and facilitate fast and efficient proton transfer pathway resulting in such high proton conduction values and consequently lower E_a values. Also presence of Brønsted acid base pairs in the pillar brick arrangement serves as a continuous network resulting in low E_a values in these two compounds. Differential scanning calorimetry (DSC) measurement confirms that there are no phase transitions in HOF-GS-10 (Figure S20), whereas in HOF-GS-11 we get an endotherm at about 110 °C due to loss of solvent guest molecules (Figure S27) resulting in crystal to crystal transition (also evident from VT-PXRD), thereby negate the fact of transformation of these compounds to any super protonic phase. Also in the cooling cycle of HOF-GS-11 we observe an exothermic peak at about 160 °C, which may be attributed to the solidification of the melted phase of the compound with the retention of crystallinity. When DSC measurement for the desolvated sample of HOF-GS-11 was taken at lower heating range (ca. 200 °C) no such exothermic peak was observed (Figure S28). Such type of behavior has been observed before in crystalline frameworks.[6h] The potential of this type of materials as PEM prompted us to measure the H_2 and O_2 gas adsorption isotherm both at low and room temperatures which showed negligible uptake (Figure 3b, Figure S32,S33). However further studies to check the permeability of such gases along PEMs for practical applications are required.

In our efforts for finding novel crystalline materials for solid-state PEMs we have reported two porous 2D HOF materials based on arene sulfonates and guanidinium cations, which exhibit high proton conduction. These materials not only show a high value at high RH but also present the highest value of proton conduction at moderate RH for a porous crystalline compound. The low activation energy and high proton-conduction values are not only comparable to the highly proton conducting MOFs operating under humid conditions but is also in the range of the commercialized Nafion membranes. These materials have an intrinsic advantage of having low density, thermal stability, ordered crystalline nature, and easy syntheses, which may result in a concoction of new lightweight materials for fuel-cell technologies. Design of such porous crystalline solids for PEM is a key theme, and if achieved in a targeted fashion could hold great promise for the future in the field of alternative sources of energy.

Acknowledgements

R.M and B.A. are thankful to CSIR for research fellowship. P.S. is thankful to UGC for research fellowship. We are thankful to IISER Pune, MHRD-FAST for funding and DST-FIST (SR/FST/CSII-023/2012) for micro-focus SC-XRD facility.

Keywords: guanidinium · hydrogen-bonded organic frameworks · porous crystalline frameworks · proton conduction · sulfonates

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 10667–10671
Angew. Chem. **2016**, *128*, 10825–10829

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Received: May 10, 2016
Revised: June 15, 2016