Designing of UiO-66 Based Super Protonic Conductor with Highest MOF Based Proton Conductivity

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ABSTRACT: MOF based proton conductors have received immense importance recently. The present study endeavors to design two post-synthetically modified Uio-66 based MOFs and study the effects of their structural differences on their proton conductivity. UiO-66-NH$_2$ is modified by reaction with sultones to prepare two homologous compounds i.e., PSM 1 and PSM 2, which have SO$_3$H groups in comparable extent (Zr:S ≈ 2:1) in both. But the pendant alkyl chain holding the –SO$_3$H group is of different length. PSM 2 has longer alkyl chain attachment than that of PSM 1. This difference in length of side arm results in huge difference in proton conducting behavior of the two compounds. PSM 1 is observed to have highest MOF based proton conductivity (1.64 x 10$^{-3}$ Scm$^{-1}$) at 80 °C, which is comparable to commercially available Nafion while PSM 2 shows significantly lower conductivity. Again, the activation energy for proton conductivity is one of the lowest among all MOF based proton conductors in case of PSM 1 while, PSM 2 requires larger activation energy (almost three times). This profound effect of variation of chain length of side arm by 1 carbon atom in case of PSM 1 and PSM 2 was rather surprising and never documented before. This effect of length of side arm can be very useful to understand proton conduction mechanism of MOF based compounds and also to design better proton conductors. Besides, PSM 1 showed proton conductivity as high as 1.64 x 10$^{-3}$ Scm$^{-1}$ at 80 °C temperature, which is the highest reported value till date among all MOF based systems. The lability of the –SO$_3$H proton of the post synthetically modified Uio-66 MOFs has theoretically been determined by molecular electrostatic potential (MEP) analysis and theoretical pK$_a$ calculation of models of functional sites along with relevant NBO analyses.

INTRODUCTION

Transportation of protons plays a key role in photophosphorylation to harvest solar energy via ADP to ATP conversion.$^{13}$ Concentration gradient regulated proton transport through channels in cellular membrane is essential in energy transfer processes of organisms.$^2$ Apart from this fundamental function, efficient proton transport is also crucial for development of fuel cells, which can be one potential source of alternative energy in recent future. Different light and heavy vehicles are major reason behind high consumption of fossil fuels and environmental pollution too. Replacement of conventional engines by fuel cells is the best potential solution to this problem. Designing of novel fuel cell requires efficient proton conducting solid electrolyte.$^{4,5}$ All these factors make the study of proton conducting materials and proton transport very important for fundamental as well as applied science.$^{16}$

Plenty of reports on new and efficient proton conductors in last five years, clearly establishes the increasing importance of this field in recent times.$^7$-$^{27}$ Meanwhile, a lot of effort has also been devoted within last decade to contribute to the understanding of proton conduction mechanism.$^{38}$-$^{36}$ The most common method of proton conduction is solvent assisted proton transfer.$^{1,2}$ Similar mechanism has been found to operate in most of the Brønsted acids, common protonic solvents and functionalized polymers.$^{29}$-$^{33}$-$^{34}$ Apparently, protonic solvents and Brønsted acids have the simplest structures among all; but, on the contrary, they are found to follow complicated conductive mechanism.$^{32}$-$^{33}$ Since the last few decades, organic polymeric compounds (e.g., Nafion) are well established as the supreme proton conductors. They possess conductivity of the order of 10$^{-3}$ Scm$^{-1}$ under humidification.$^6$ The problem associated with their practical usage is, their high manufacturing cost and lack of scope to tune their conductivities. On the other hand, detailed structural information is available for the mixed metal oxides and inorganic cluster containing compounds as they are crystalline in nature. But they are less popular as proton conductors due to low efficiency at ambient conditions.$^{30}$-$^{32}$

In this scenario, metal organic frameworks (MOFs) stand as a connecting bridge between inorganic cluster containing compounds and organic polymers in terms of detailed structural information from crystal structure and
efficiency of proton conduction. These MOFs, being polymeric hybrid of organic linker molecule and metal ions, cultivate some of the useful properties of both. They have high thermal stability, tunable dimensionality of channels, provision to modify the organic linkers to impart selective functionality, scope of loading charge carrier ion and also the provision to incorporate Brønsted acidity inside the MOF cavity. UiO-66, a renowned subclass of MOFs, has emerged as a high potential material to prepare highly efficient proton conductors. Uio-66 consists of cationic \( \{\text{Zr}_x\text{O}_y\} \) nodes connected to each other by BDC (benzenedicarboxylic acid)-based ligands. Different derivatives of UiO-66 type MOFs have been reported in literature, where the BDC ligand was functionalized by different groups e.g., amines, carboxylic acids, sulphonic acids, anhydrides, halogens etc. Suitable water adsorptivity, existence of empty hydrophilic channels and scope to modify the pores by post synthetic modifications are some of the major reasons behind the notable domination by UiO-66 derivatives in the field of MOF based proton conductors. Plenty of reports on UiO-66 based proton conductors are available in literature with conductivity values varying in a wide range of \( 10^{-1} \text{Scm}^{-1} \) to \( 10^{3} \text{Scm}^{-1} \). Researchers have tried to explore different structural properties and synthetic modifications to design more efficient UiO-66 based functional materials. For quite a long time, isomorphous ligand replacements, organic linker modifications, enhancement of crystal defects and loading of different guest molecules (e.g., histamine, triazole, etc.) have served as well-known paths to prepare MOF based proton conductors. A very recent report by Shimizu and co-workers has demonstrated that the bulk conductivities of two MOF materials, PCMOF2\(^{12}\)(Pz) and PCMOF2\(^{12}\)(Tz) (Pz = 1H-pyrazole and Tz = 1H-1,2,4-triazole), are over \( 10^{1} \text{S cm}^{-1} \) at 85 °C and 90% relative humidity. Earlier, Yang et al. showed a sulphonic acid rich flexible MOF, BUT-8(Cr)A to have conductivity of \( 1.27 \times 10^{-3} \text{Scm}^{-1} \) (at 80 °C under 100% relative humidity), the highest reported proton conductivity, exhibited by any MOF material except PSM reported in this work. Few years ago, Hong and coworkers showed UiO-66(SO\(_3\)H)\(_2\) to possess conductivity of \( 8.4 \times 10^{-3} \text{Scm}^{-1} \). High loading of pendant sulphonic acid groups played crucial role behind this observed proton conductivity. Li and coworkers developed another UiO-66 based proton conductor by its functionalization. It was established from the same work that Brønsted acidic groups, dangling inside from the walls of the channels, helps the protonation and deprotonation steps required for proton flow through the preformed aqua-chain under high humidity. It was also shown that, the proton conduction was directly related with the water sorptivity of UiO-66 derivative. In a complete different approach, Kitagawa and co-workers showed that, controlling the mobility of proton can also be fundamentally important apart from enhancing Brønsted acid concentration to control the proton conductivity of a MOF. Focusing on the contemporary works on UiO-66 based proton conductors, our attention was drawn to the fact that, even though, enormous significance of the pendant Brønsted acid has been established, much efforts have been given to recognize the effect of chain length of the arm (attached to the rigid framework in one end and holding the acid group in the other end) on proton conductivity. In this present work, we have put an effort to study it and attempted to combine the missing dots in order to get the complete picture.

We prepared (Scheme 1) two post synthetically modified UiO-66 MOFs (hereafter referred as PSM 1 and PSM 2) with variation in chain length of side arm holding the Brønsted acid group. Choice of post synthetic modification (PSM) over preformed BDC derivative was crucial to nullify incorporation of any unwanted structural differences (i.e., crystal defects etc.). The choice was also influenced by recent works of Garibay,

![Scheme 1](image-url)
Cohen and co-workers, who reported various crucial post synthetic functionalizations on UiO-66 that are difficult otherwise.65

The two sister compounds, reported here i.e., PSM 1 and PSM 2, were synthesized by adapting a highly reproducible two step synthetic method, where both the steps were well established in previous reports but never combined together to prepare any MOF based proton conductors. Thus prepared, PSM 1 is found to be a MOF based super proton conductor, having the highest conductivity among all MOFs. We have also demonstrated the profound effect of chain length of side arm on efficiency of proton conductivity of the MOF.

MATERIALS AND METHODS
Synthesis of UiO-66-NH$_3$, PSM 1, PSM 2 and PSM 1-Li
To obtain the post synthetically modified compounds, first UiO-66-NH$_3$ was prepared following the procedure, reported by Farha and coworkers.64 In a typical synthesis, 5.4 mmol of ZrCl$_4$ was dissolved in 50 mL DMF in presence of 10 mL of conc. HCl by sonication. Then 6.75 mmol BDC-NH$_2$(BDC = benzene dicarboxylic acid) was added along with 100 mL of DMF. The reaction mixture was kept at 80 °C temperature for 24 hours in a sealed Teflon capped container of 250 mL. After slow cooling, the reaction mixture was filtered and washed. Subsequently, the crude UiO-66-NH$_3$ was stirred in dry ethanol for 72 hours to remove absorbed DMF molecules prior to post synthetic modifications and further characterizations. See section S2, Supporting Information for detailed synthetic procedure.

Fully activated and characterized UiO-66-NH$_3$ microcrystals were then separately treated with 1,3-propane sultone and 1,4-butan e sultone to obtain PSM 1 and PSM 2 respectively (Scheme 1). This scheme of post synthetic modification was adapted from the work of Yaghi and coworkers.63 Similar post synthetic modifications are well established in recent times.64-66 In a typical PSM procedure, UiO-66-NH$_3$ and sultone were taken in DCM in equimolar ratio at room temperature (30 °C). After 24 hours, the post synthetically modified compounds were repeatedly washed with DCM, water and ethanol to get rid of any unreacted and trapped sultone/hydrolyzed sulfonic acid from the pores. For detailed synthetic procedure, see section S2, Supporting Information.

PSM 1-Li was prepared by ion exchange between the labile protons of PSM 1 and Li$^+$ ion. PSM 1 was stirred in 0.5 M aqueous solution of LiCl for 24 hours. The modified compound i.e., PSM 1-Li was washed thoroughly with water after the completion of ion exchange.

Physical Characterization
All the four compounds, UiO-66-NH$_3$, PSM 1, PSM 2 and PSM 1-Li were thoroughly characterized by powdered XRD analysis, UV-Vis diffused reflectance spectroscopy, X-ray photoelectron spectroscopy, FT-IR spectroscopy, AES-ICP, FESEM-EDX and digestive NMR analysis. Gas and water sorption measurements, TG analysis and impedance spectroscopic measurements were done when they were required.

Proton Conductivity Measurements
Proton conductivity of UiO-66-NH$_3$, PSM 1, PSM 2 and PSM 1-Li were measured by alternating current (AC) impedance spectroscopy using 2-electrode configuration (parallel plate mode). Samples were pelletized from their powdered microcrystals and sandwiched between two carbon papers (to lower the contact resistance between the electrodes and the sample and also to minimize probable artefacts originating from the sample surface inhomogeneity) before putting inside a home-made cell with 2 electrode set up. Powdered sample was kept under a pressure of 5 ton/ cm$^2$ for 3 minutes to prepare each sample pellet. Impedance spectra were recorded in the temperature range from 10 °C to 80 °C and relative humidity (RH) range of 30% to 95%. A programmable incubator was employed to keep the sample pellet at desired temperature and humidity for proton conductivity measurement. For higher temperature measurements i.e., >250 °C a home-made set up was used to stabilize the temperature and humidity instead of the incubator. For details of electrode set up, pellet preparation, impedance measurement parameters, incubation process etc., see section S13 in Supporting Information. Impedance spectra were recorded for PSM 1 and PSM 2 during both the heating and cooling cycles. Reusability of the proton conductors was examined by recording four consecutive heating and cooling cycles for both PSM 1 and PSM 2. Long term stability of the conductors was checked by proton conductivity measurements in constant time interval, while the sample was kept in the humidified elevated temperature throughout the whole period. Conductivity calculations were done from the Nyquist plots of impedance spectra by fitting with the most suitable equivalent circuit.

RESULTS AND DISCUSSION
As shown in Figure 1, the PXRD patterns of PSM 1 and PSM 2 were found to match well with the simulated one of UiO-66 MOF. After post synthetic modifications, they possess no notable change from the parent UiO-66-NH$_3$ pattern, signifying the integrity of the UiO-66 framework to be maintained. It shows that, the employed post synthetic modification does not disturb the crystal structure of UiO-66-NH$_3$.

All the compounds were found to retain their crystalline nature even after 1 year of keeping in open air (see Section S6, Supporting Information).
The crystallinity and structure of PSM 1 and PSM 2 were not disturbed significantly under high temperature or under high temperature (see Section, S6, Supporting Information). The compounds PSM 1 and PSM 2 were found to retain their structure even after 7 days of aqua-treatment at high temperature.

From XPS spectra of PSM 1 and PSM 2, binding energy for S2p3/2 peak was found at 168.3 eV and 168.0 eV, respectively. This is a clear proof of +IV oxidation state of sulfur in both; hence the presence of SO$_3$H group is confirmed (Figure 2). Furthermore, the N1s spectrum of PSM 1 shows strong peak at 401.9 eV with a shoulder at 400.9 eV, similar to PSM 2 but distinctly different from UiO-66-NH$_3$ primary amine peak. The XPS spectra are indicative of the presence of (1) secondary amine of the type ‘-CH-NH-CH$_2$-’ (400.9 eV and 400.7 eV for PSM 1 and PSM 2 respectively) and (2) primary amine ‘-NH$_2$’ (401.9 eV) in both. The huge shift in primary amine peak in PSM 1 and PSM 2, compared to that of UiO-66-NH$_3$, can be a direct consequence of strong H-bonding with the adjacent -SO$_3$H group of dangling side arm. Such XPS spectral shift due to H-bond formation is not uncommon for metal oxides, hydroxides and organic molecules but has not been documented before for UiO-66 MOF system. Such extensive H-bonding can facilitate the aqua chain formation by fragmenting the long channel into smaller hydrophilic compartments.

The XPS spectral shift between secondary amine peak of PSM 1 and PSM 2 can be accounted qualitatively by the theoretical natural bond orbital (NBO) analysis on the

![Figure 1. Powdered XRD patterns of UiO-66-NH$_3$, PSM 1 and PSM 2 compared with simulated pattern of UiO-66.](image1.png)

![Figure 2. N1s (left), S2p3/2(right) X-ray photoelectron spectra of PSM1 and PSM 2.](image2.png)

![Figure 3. FT-IR spectra of UiO-66-NH$_3$, PSM 1 and PSM 2.](image3.png)

model dangling parts of PSM 1 and PSM 2. The core molecular orbital (which consists of 100% characteristic of N1s) of PSM 1 is found to be more stable than that of PSM 2 by ~0.0024 eV. It is noted that the calculated XPS spectral shift from NBO analysis qualitatively explains the observation obtained from the experiment as the calculations were performed on the model compounds in gas phase, while the experiment was carried out on the actual compounds in solid phase. Overall, the present theoretical prediction helps to understand the observed XPS spectral shift.

The FT-IR spectra (Figure 3) of UiO-66-NH$_3$, PSM 1 and PSM 2 are found to have notable similarities. The peak at 1565 cm$^{-1}$, because of the ‘C=O’ bond of carboxylate linkage, is present in all three spectra. In contrast, the peaks at ~3265 cm$^{-1}$ arising from the primary ‘-NH$_2$’ functional group of UiO-66-NH$_3$, is not visible in case of PSM 1 and PSM 2. This is because of the post synthetic modification of half of the ‘-NH$_2$’ functional group of UiO-66-NH$_3$, during formation of PSM 1 and PSM 2. As a result of addition of hydrophilic ‘-SO$_3$H’ group via post synthetic modification, water content increases inside PSM 1 and PSM 2 under normal aerial conditions. Extensive H bonding interactions between ‘-OH’ of ‘-SO$_3$H’ groups mask all other peaks lying in this region. Due to ‘-SO$_3$H’ group, two peaks near 1037 cm$^{-1}$ and 1150 cm$^{-1}$ can be found both in PSM 1 and PSM 2. As expected, these peaks are not present in FT-IR spectrum of UiO-66-NH$_3$(Figure 3). From both the XPS and FT-IR data, we infer successful post synthetic modification of UiO-66-NH$_3$ to prepare PSM 1 and PSM 2 while keeping the basic UiO-66 intact.

We have performed digestive NMR and ESI-MS spectral analyses. For detailed procedure see section S12, Supporting Information. Both the $^1$H NMR spectra and ESI-MS spectra of PSM 1 and PSM 2 show the presence of impurities generated due to uncontrolled fragmentation of the compound during digestion in HF. Even then, peaks due to the desired fragments i.e., the aromatic ring and alkyl side arm, can be identified from the $^1$H NMR spectra of PSM 1 and PSM2. ESI-MS spectra of PSM 1 and PSM 2 show high intensity peaks at m/z value of 303.48 and 317.02 respectively. The peak positions match well with the mass of expected fragments in each case. Thus,
digestive NMR and ESI-MS data support the structural analysis, obtained from other physical characterization techniques. ICP-AES analysis was performed to have further structural insight about the Brønsted acid loading in PSM 1 and PSM 2. It was found that, the extent of PSM was consistent with the atomic ratio of S:Zr ≈ 1:2 in both the compounds (from ICP-AES analysis) and weight percent of sulfur was found to be 5.02 % and 5.03 % in PSM 1 and PSM 2, respectively (see section S8, Supporting Information). The two factors, i.e., (i) the employment of same UiO-66-NH$_2$ microcrystals for PSM and (ii) similar Brønsted acid loading in both PSM 1 and PSM 2, are helpful to evaluate proton conductivity only on the basis of side arm length and ignore any variance in contribution from other factors. Furthermore, it could also be confirmed from ICP-AES analysis that, only half of the `-NH$_2$' groups of UiO-66-NH$_2$, are modified in both cases (PSM 1 and PSM 2). These results also enlighten the fact of low Brønsted acid loading (almost one fourth) when compared with the similar system UiO-66(SO$_3$)$_2$, reported by Phang et al.$^{44}$

As the PSM is supposed to increase steric bulk inside the cavities of PSM 1 and PSM 2 from that of UiO-66-NH$_2$ parent MOF, large variation in the permanent porosity could be expected. N$_2$ gas sorption measurement at 77 K was used as the tool to determine permanent porosity of all the MOFs (Figure 4(a)). Prior to gas adsorption studies, UiO-66-NH$_2$, PSM 1 and PSM 2 were degassed for 10 hours under vacuum at 120 °C (for details see section S9, Supporting Information). All three gas adsorption isotherms follow Type-I behavior, confirming presence of micropores. Inter-grain sorption (typical phenomenon of microporous materials) results in the rapid rise of isotherm around P/P$_0$= 0.9-1 for all the three compounds (Figure 4(a)). Brunauer-Emmett-Teller (BET) surface analysis from N$_2$ sorption studies reveal that, PSM 1 (surface area 328.5 m$^2$/g) is having slightly higher available surface area for N$_2$ sorption than that of PSM 2 (surface area 294.3 m$^2$/g). But both of them are having surface area much lower than that of UiO-66-NH$_2$ (surface area 684.5 m$^2$/g). The significant decrease in BET surface area of ≈370 m$^2$/g in PSM 1 and PSM 2 from that of UiO-66-NH$_2$, is a direct consequence of less availability of free space due to impregnation of long side arms inside the pores of PSM 1 and PSM 2. BET surface areas of PSM 1 and PSM 2 differs by 34.2 m$^2$/g, which can be attributed to the more bulkiness of the side arm of PSM 2 as well as minutely higher loading in case of PSM 2 (vide supra) than PSM 1.

As mentioned above, the BET surface area of UiO-66-NH$_2$ itself (684.5 m$^2$/g) was found to be lower than that shown in similar recent reports.$^{44}$ In order to have more insight into this surface area profile, the same UiO-66-NH$_2$ was characterized by N$_2$ sorption measurement after activating the compound at 180 °C for 6 hours. And in this case, BET surface area for the same UiO-66-NH$_2$ was recorded to be 1086 m$^2$/g. Thus, the lower surface area (684.5 m$^2$/g) obtained before was a result of activation of UiO-66-NH$_2$ in relatively lower temperature and not due to lack of crystalinity of the parent MOF, UiO-66-NH$_2$.

All the UiO-66 based MOFs have good water adsorptivity. And the post synthetically modified UiO-66-NH$_2$ derivatives show even superior water adsorptivity (Figure 4(b)) and notable aqua-stability (discussed earlier). Water adsorptivity is of immense importance in case of water assisted proton conduction, because adsorbed water molecules help the proton conductor to build continuous hydrogen-bonded network/chain along proton-propagating pathways. Under identical humidity (P/P$_0$ = 0.5), both the post synthetically modified compounds, PSM 1 and PSM 2 are found to show almost a 10-fold increase in the water uptake than that of UiO-66-NH$_2$, as shown in Figure 4(b). Slopes of water adsorption isotherms of PSM 1 and PSM 2 are found to be similar and almost 12 fold to that of pristine UiO-66-NH$_2$. High slope of water adsorption isotherms of PSM 1 and PSM 2, even in moderate humidity, indicates their enhanced hydrophilic nature. Among PSM 1 and PSM 2, PSM 2 has slightly higher water sorption capacity than PSM 1, which might be a result of slight higher loading of –SO$_3$H pendant groups in PSM 2. These results indicate that, PSM plays a vital role not only to incorporate Brønsted acidity but also to increase hydrophilicity. Thus, water
adsorption studies gave us a preliminary idea of the high potential of PSM 1 and PSM 2 to have enhanced water mediated proton conductivity in comparison to pristine UIO-66-NH$_3$.

Proton Conductivity Measurement and Related Analyses

Proton conductivity of all the compounds were measured by impedance spectroscopy using technique mentioned earlier (vide supra) (for detailed methodology, see section S13, Supporting Information). Nyquist plots were constructed on the complex plane of impedance between $Z'$ (real part of impedance) and $Z''$ (imaginary part of impedance). A semicircle of high radius of curvature and another one with low radius of curvature could be resolved in the Nyquist plots of impedance spectra of both the compounds. Inter-grain resistance and electrode-electrolyte contact resistance are responsible for the low frequency region impedance spectra while resistance of the material corresponding to proton conduction contributes for the high frequency region of impedance spectra. Li substituted PSM 1 i.e., PSM 1-Li was prepared to understand the origin of proton conductivity; whether it is a result of Brønsted acidic groups or due to participation of any other mobile charge carriers (electrons, metal ions etc), see section S13, Supporting Information. PSM 1-Li was prepared by substituting all the labile Brønsted acidic protons of PSM 1 by lithium. PSM 1-Li shows no significant conductivity (conductivity observed to be $\approx$10$^{-8}$ Scm$^{-1}$; Figure S26, Supporting Information). Such low conductivity of PSM 1-Li clearly proves that, once the labile protons are substituted in PSM 1 by Li, the conductivity decreases significantly. Thus, contribution from electronic conductivity or any other charge carriers can be neglected in case of PSM 1. The same logic can be applicable in case of PSM 2.

Temperature dependent proton conduction measurements (Figure 5(a) & (b) and 5(c) & (d)) have been carried out for both the compounds, PSM 1 and PSM 2. The samples were kept at constant temperature and humidity (relative humidity) for 4 hours before recording each data. Both the compounds, PSM 1 and PSM 2 show steady increase in proton conductivity with increase in temperature. Measurements were carried out during both the heating and cooling cycles to check the reversibility of the performance. The Nyquist plots of heating and cooling cycle are similar to each other in terms of nature of curve, but, do not superpose (which it should, ideally). This deviation can be explained as a result of difference in water content inside the pores during heating and cooling cycles (see section S13, Supporting Information). Similar observations are quite common in MOF based proton conductors. The observed proton conductivity was found to be retained for more than four consecutive heating and cooling cycles. Both PSM 1 and PSM 2 sample pellets were examined by PXRD and FT-IR analyses after proton conductivity measurements (see section S14, Supporting Information). PXRD and FT-IR spectra of the pelletized compounds showed no notable change even after 4 cycles. A lowering of $\approx$ 18m$^2$/g BET surface area is observed in case of PSM 1 after 5 cycles of measurement. Such minor lowering of surface area indicates no major change in the microstructure of PSM 1 in the end of proton conduction measurements. This lowering can be a result of the high pressure which is applied for pelletizing the compound before proton conductivity measurements. To check long term stability proton conductivity measurements were carried out for PSM 1 at 80 °C for 48 hours. The data recorded at each 12 hours interval show very little fluctuation in proton conductivity. Please see Supporting Information Section S14 for detailed discussion.

Long term proton conductivity measurement of 48 hours along with the impedance measurement during consecutive 5 cycles of heating and cooling prove the stability and reusability of PSM 1 and PSM 2 as proton conductor. The similarities between the N$_2$-sorption isotherms, PXRD patterns and FT-IR spectra between the initially recorded ones and the ones recorded after each cycle of impedance measurement (Figure S27, Figure S28, Figure S29, and Figure S30, in Supporting Information) negate the chances of any major structural change. The results, thus obtained, establish the fact that both the compounds have the potential to function as stable proton conductors.

Experimentally obtained impedance spectral data were analyzed and fitted with the most relevant circuit ($R_1/\left(Q_1+R_2Q_2\right)+Q_3$) where $R_1$, $R_2$= resistance, $Q_1$, $Q_2$, $Q_3$ =Constant phase elements (Figure6(a), inset) to calculate proton conductivity. All the experimentally obtained impedance spectral data could be fitted with the same circuit without notable error (in terms of $\chi^2$ value). By fitting with equivalent circuit, it is found that, PSM 1

![Figure 5. Nyquist plots of impedance spectra of (a) PSM 1 and (c) PSM 2. Spectra were recorded at different temperatures during heating (spheres) and cooling (sphere with line) cycles. (b) and (d) shows the proton conductivity recorded during heating cycle of PSM 1 and PSM 2 respectively. Measurements were carried out at 95% relative humidity. Plots (a) and (b) were scaled arbitrarily to magnify the high frequency region of impedance spectra of PSM 1 and PSM 2.](image-url)
shows proton conductivity ($\sigma$) of $5.83 \times 10^{-2}$ S cm$^{-1}$ at 11.5 °C with 95% relative humidity (RH), while PSM 2 has $\sigma$ value of $5.9 \times 10^{-4}$ S cm$^{-1}$ at similar condition (10.1 °C, 95% RH). The value of $\sigma$ for PSM 1 is, so far, the highest reported proton conductivity value for a MOF-like material at such a low temperature (10.1 °C), which is ~100 times of its sister compound i.e., PSM 2.

At 80 °C, the proton conductivity was all the more pronounced for both the compounds than conductivities recorded at lower temperatures. The values of $\sigma$ for PSM 1 and PSM 2 were $1.64 \times 10^{-4}$ S cm$^{-1}$ and $4.66 \times 10^{-5}$ S cm$^{-1}$ respectively. The value of $\sigma$ for PSM 1 at 80 °C is the highest among all MOF-based proton conductors (Table S2, Supporting Information). The proton conductivity of PSM 1 is even comparable to that of commercially available organic polymeric conductor Nafion.$^8$

Similar to most of the reported UiO-66 type proton conductors, PSM 1 and PSM 2 show water assisted proton conductivity$^{39,30}$ under humidified condition, as shown in Figure 6 (a) and Figure 6(b) respectively. Loading of Brønsted acidic ‘–SO$_3$H’ functionalized side arms increases the amount of hydrophilic domains. Both PSM 1 and PSM 2 show excellent water adsorptivity (vide supra) in moderate to high humidity region (P/P$_o$=0.5-0.7). Thus, proton conductivity of both the compounds was measured in wide range of relative humidity (from moderate to high), at 30 °C (Figure 6). Conductivity was found to increase rapidly in moderate RH (from 30% to 70% RH). Slow but steady increment in conductivity was observed under high RH (80% to 95%) conditions (Figure S25). The enhancement of proton conductivity with increase in humidification, confirms a water assisted proton conduction in both PSM 1 and PSM 2. Proton conduction can take place in a facile manner in these two compounds even in moderate humidity (~70% humidity).

PSM 1 has higher efficiency in terms of proton conductivity than PSM 2 under all experimental conditions. Unlike proton conduction through grain boundary or via mobile guest molecules, these post synthetically modified compounds perform proton conduction with the help of covalently bound pendant ‘–SO$_3$H’ groups via aqua channel formation (under humidification) inside the pores.

The water assisted proton conductivity of PSM 1 can be compared to that of the UiO-66(SO$_3$H)$_2$ reported by Hong and coworkers. Although, PSM 1 has only one-fourth concentration of Brønsted acid groups than that, present in UiO-66(SO$_3$H)$_2$, but almost twice efficient in comparison to UiO-66(SO$_3$H)$_2$.$^{44}$ A comprehensive assessment of the two suggests that, the extent of availability of labile protons plays the most influential role in case of PSM 1 and not the concentration of the Brønsted acid groups as, observed, in the case of UiO-66-(SO$_3$H)$_2$.$^{44}$

It is quite interesting to note that, only a slight structural difference between PSM 1 and PSM 2 gives rise to the sharp variation in their observed proton conductivity. This is a unique observation in the area of MOF-based proton conductors, which again highlights the same fact of different extent of availability of the labile ‘–SO$_3$H’ protons in PSM 1 and PSM 2. Both these compounds have almost similar ‘–SO$_3$H’ content but, show widely different proton conductivity, which can be a direct consequence of the difference in availability of labile protons and not the number of labile protons. Thus, in this present work, the effect of variation in chain-length of side arm (carrying the pendant Brønsted acid group) on proton conductivity of MOF based materials has been portrayed.

The variation in length of the dangling alky chains can result in change in several parameters e.g., (a) difference in pK$_a$ value of the Brønsted acid groups, (b) variation of hydrophobic steric bulk inside the pores among PSM 1 and PSM 2, and (c) difference in H-bonding interactions between neighboring ‘–NH$_2$’ and ‘–NH–(CH$_3$)$_2$–SO$_3$H’ groups in case of PSM 1 and ‘–NH$_2$’ and ‘–NH–(CH$_3$)$_2$–SO$_3$H’ groups in case of PSM 2 etc. All these factors might contribute to

Figure 6. (a) Nyquist plot of impedance spectra of PSM 1 under different humidification conditions at 30 °C. Inset: Equivalent circuit of impedance spectra of PSM 1 and PSM 2. (b) Nyquist plot of impedance spectra of PSM 2 under different humidification conditions at 30 °C.
the observed trend of proton-conductivity. Among all, one of the most crucial factors is the difference in $pK_a$ value of PSM 1, PSM 2 and UiO-66-NH$_2$. The theoretical $pK_a$ values of the dangling `-SO$_3$H' group of PSM 1, PSM 2 and `-NH$_2$' group of UiO-66-NH$_2$ are 3.47, 4.91 and 35.99, respectively (see section S7, Supporting Information). Lower the $pK_a$ of a proton in a compound, higher is its lability, leading to higher proton conductivity. The $pK_a$ values are in accord with the trend expected from observed proton conductivity. Along with that, the extensive compartmentalization due to H-bonding between the dangling -SO$_3$H and nearby -NH$_2$ enhances the proton conductivity of both PSM 1 and PSM 2. On the other hand, the probability of any difference in the extent of H-bonding between PSM 1 and PSM 2 can be ignored because in both cases spectral shifts of Nis XPS spectra from the parent compound UiO-66-NH$_2$ are similar. Based on this XPS analysis (vide supra) it can be said that, the extent of H-bonding is similar in both PSM 1 and PSM 2. This extensive H-bonding favours proton conduction in PSM 1 as well as in PSM 2 over UiO-66-NH$_2$, which cannot have such kind of H-bonding. Thus, negating any crucial role of factor (c) to decide the order/trend of proton conductivity among PSM 1 and PSM 2, factor (a) (difference in $pK_a$) can be considered as the most important factor that explains the observed trend of proton conductivity among PSM 1 and PSM 2. Again, we must mention that, contribution from other factors cannot be completely neglected.

![Figure 7](image)

**Figure 7.** Molecular electrostatic potential (MEP) diagram of (a) BDC-NH-CH$_2$-CH$_2$-SO$_3$H, and (b) BDC-NH-CH$_2$-CH$_2$-CH$_2$-SO$_3$H. They are the two model compounds which represent the two post synthetically modified functional units of PSM 1 and PSM 2 respectively.

Further, we confirm the lability of the `-SO$_3$H' proton of PSM 1 and PSM 2 by molecular electrostatic potential (MEP) of model compounds of functional units of PSM 1 and PSM 2. NBO (natural bond order) analyses of the dangling part of PSM 1 and PSM 2 were also performed (see section S8, Supporting Information). The MEP plots (Figure 7) indicate higher electro-positivity on the `-SO$_3$H' proton of PSM 1 (deep blue, Figure 7) as compared to the same of PSM 2 (light blue, Figure 7). While, NBO analyses indicate higher charge transfer from the `-OH' oxygen to the `-OH' hydrogen of `-SO$_3$H' proton of PSM 2 as compared to the same of PSM 1. This gives more stability to the dangling part of PSM 2 by ~1.08 Kcal/mol. Thus, the `-SO$_3$H' proton of PSM 1 becomes more labile than that of PSM 2. Thus, the theoretical studies on the model compounds of PSM 1, PSM 2 and UiO-66-NH$_2$ partly explain the observed proton conductivity on the basis of charge distribution, $pK_a$ and bond order calculations.

Activation energy ($E_a$) of proton conduction was calculated for PSM 1 and PSM 2, based on the proton conductivity calculated for heating cycle (Figure 8(a) and Figure 8(b) respectively). For detailed calculation of activation energy, see section S5, Supporting Information. Activation energy ($E_a$) was found to be 0.107 eV/atom for PSM 1 and 0.292 eV/atom for PSM 2. As the values suggest, both PSM 1 and PSM 2 follow water assisted Grotthuss mechanism for proton conduction. The activation energy for PSM 1 is one of the lowest reported till date for any MOF based proton conductors (Table S12, Supporting Information). Low activation energy of
PSM 1 indicates the profound effect of easy availability of ‘SO$_3$H’ protons. Again, $E_v$ values for PSM 2 is almost 3 times higher than that for PSM 1. This is a consequence of only the structural difference i.e., the difference in the chain length of the side arm. It is evident that (1) extensive H-bonding occurs for PSM 1 as well as PSM 2 and (2) the difference by one ‘-CH$_2$’ unit in the side arm of PSM 1 and PSM 2 leads to difference in lability of proton of PSM 1 and PSM 2 (vide supra). As a result, proton conductivity is enhanced in both PSM 1 and PSM 2 than UiO-66-NH$_2$ but, PSM 1 shows much higher conductivity and lower activation energy (mostly due to its lower $pK_a$) than PSM 2. Though, the exact reason is not yet known, but observing such huge difference in proton conductivity, just by increasing ‘-CH$_2$’ fragment by one unit, is noteworthy.

CONCLUSION

We have prepared a super-proton conductor (PSM 1) with conductivity as high as 1.64x10$^{-4}$ Scm$^{-1}$, which is the highest reported value till date among all other MOF based systems, operating below 100 °C. We also have shown that PSM 2, the homologous counterpart of PSM 1, has ~35 times lower proton conductivity than that of PSM 1. These observations clearly demonstrate the effects of length of side arm on the observed proton conductivity. We have shown by theoretical studies that, the difference in the chain length causes dramatic variation in $pK_a$ values of the two compounds. The observed proton conductivity trend matches well with the order, expected from calculated $pK_a$. This observation is highly important to understand the role of the length of the side arm and design MOF based super proton conductors with higher efficiency performing at ambient temperature. This work has also highlighted the scope of employment of post synthetic modifications to UiO-66 and other MOF systems, so that, robust and more efficient MOF based proton conductors can be designed and developed.

ASSOCIATED CONTENT

Supporting Information: The Supporting Information is available free of charge on the ACS Publications website at DOI:

Instrumentation, synthesis of compounds (UiO-66-NH$_2$, PSM 1, PSM 2 and PSM 1-Li), characterization (PXRD, TGA, FESEM-EDX analysis, Gas adsorption and water adsorption studies, FT-IR, AES-ICP, etc.), Proton conductivity measurements (impedance spectroscopy in different conditions), and supporting results( stability of pelletized sample, reusability of compounds as proton conductors etc.) are given in PDF format.

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ABBREVIATIONS

BDC, benzenedicarboxylic acid; FT-IR, Fourier Transformed InfraRed; TGA, Thermal Gravimetric Analysis; AES-ICP, Inductively Coupled Plasma Resonance Atomic Emission Spectroscopy; NMR, Nuclear Magnetic Resonance; XPS, X-Ray Photoelectron Spectroscopy; PXRD, Powdered X-Ray Diffraction; NBO, Natural Bond Order; MEP, Molecular electrostatic potential.

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Table of Contents artwork: