Facile crystallization of 2-phenyl benzimidazole-5-sulfonic acid: Characterization of lattice water dependent zwitterionic supramolecular forms, with modulation in proton conductivities

D SARAVANABHARATHI^{a,*}, M OBULICHETTY^b and M KUMARAVEL^a

^aDepartment of Chemistry, PSG College of Technology, Coimbatore 641 004, Tamilnadu, India

^bDepartment of Applied Science, PSG College of Technology, Coimbatore 641 004, Tamilnadu, India

E-mail: dsbharathi@yahoo.com

MS received 10 January 2019; revised 10 April 2019; accepted 19 May 2019

Abstract. A facile aqueous medium crystallization strategy has been found for this water insoluble title compound. Two crystalline forms, differing in the number of lattice water molecules (mono hydrated; *form I* & di-hydrated; *form II*), have been obtained, depending on the duration of crystallization. X-ray structural studies reveal that the compound crystallizes in the zwitterionic state in both the forms, due to the protonation of one imidazole nitrogen by $-\text{SO}_3\text{H}$ group, are engaged in hydrogen bonded interactions, involving lattice water molecule(s), and thus the supramolecular arrangements of the forms are influenced by lattice waters. Additional water molecules in the form II make it more hydrophilic, as confirmed using contact angle measurements. Procedures were optimized for better crystalline yields, and the bulk purity were ascertained by TGA, elemental and PXRD analysis. AC impedance measurements prove that both the crystalline forms are indeed proton conducting electrolytes, with magnitudes of $1 \times 10^{-5} \text{ S cm}^{-1}$ and $5 \times 10^{-5} \text{ S cm}^{-1}$ for form I & II, respectively under humidified conditions at 25 °C. Proton conducting performance of II has been found to be greater than I and could be correlated with its higher hydrophilicity and enriched hydrogen bonds for Grotthuss mechanism.

Keywords. 2-Phenyl benzimidazole-5-sulfonic acid; aqueous crystallization; lattice water dependent supramolecular structures; proton conduction.

1. Introduction

Crystalline non-covalent organic frameworks,¹⁻⁶ parallel to those of metal-organic frameworks,⁷ have attracted a great deal of interest in the recent literature, owing to their intriguing and complementary structural possibilities and functional characteristics. Particularly, the materials, which are stable under aqueous environments, possessing Lewis acidic charge carriers, with extensive hydrogen bonded networks in their structures, are expected to be functional alternates^{8,9} for fluorinated ionomers, like Nafion,^{8,9} for fuel cell applications, and thus are being investigated for their proton transport characteristics.^{2-5,7-12} The inherent advantages of crystalline frameworks, such as wide scope for intuitive designs, accurate structure determinations, possibility of loading different guests within the frameworks, etc., have fueled the scope of such materials as proton

electrolytes in the academic research.^{2-5,7-12} Recently we also have reported the proton transporting performances of some simple, easily accessible, and environmentally benign coordination polymers to highlight the relevance of biomimetic materials in this perspective.¹³⁻¹⁵

However, it is to be noted that the proton conducting reports on the purely crystalline organic frameworks,²⁻⁵ unlike those of the coordination polymers,^{7,10-12} are still scanty,¹⁻⁶ and hence are worth exploring.

In this context, we have chosen the 2-phenyl benzimidazole-5-sulfonic acid, as a material, to develop newer proton conducting crystalline frameworks. The simultaneous presence of imidazole and sulfonated moieties in the compound, as hydrogen bond donor and acceptor groups, are generally expected to yield well-ordered supramolecular frameworks in the solid state,^{16,17} and thus it is envisaged to be very suitable for the chosen

*For correspondence

objective. In addition, it is well known that the title compound is extremely insoluble in water,¹⁸ which is a much sought after requirement in fuel cell electrolyte applications, and thus gains merit in this perspective. Similarly, the title compound is generally regarded as an environmentally less hazardous system, and even finds application as sun screen lotions.¹⁹

However, it is to be realized that the water insoluble nature of the title compound, which is a boon for the proton conduction applications, on the other hand, poses extreme difficulty for the crystallization of the title compound, under environmentally benign aqueous medium at room temperature conditions. Hence its crystallization itself, is noticeably a challenging task, and is addressed in this work.

We have hypothesized that the difficulty of crystallizing the title compound, due to its water insolubility, could be readily overcome by the salt formation and re-acidification route, and would become as a facile method for the present objective.

Indeed we have found that the sodium salt of the title compound, which is prepared by reacting it with the calculated amount of sodium carbonate in the aqueous medium, upon simple re-acidification with the hydrochloric acid readily yields X-ray quality fine single crystals at room temperature conditions itself, without any need for hydrothermal or other type of harsh conditions and organic solvents. We have also observed that different organic acids can also be used instead of hydrochloric acid, but the tartaric acid is much handier for the acidification process. Hence we have realized that our hypothesis is indeed useful for the crystallization of the title compound, which is otherwise difficult to achieve under plain conditions.

After witnessing the crystallization by tartaric acid method, a few of them were picked up in two weeks, for carrying out single crystal X-ray structural determination, while the remaining crystalline products were left in the mother liquor itself for few more months till the arrival of structural results for the picked-up crystals. Surprisingly, it has been observed that the analytical, TGA and PXRD outcome of the months-long, mother liquor-soaked samples are not coinciding with the calculated patterns of the structural results of the single crystals, which were picked up in the first two weeks itself. Hence the crystals that were preserved in the mother liquor were also subsequently submitted for X-ray structure determinations. The structural results revealed that there are differences only in the number of lattice water molecules, but not in the molecular composition of the title compound per se, which crystallizes in the zwitterionic configuration^{20–27} in both the forms, with the concurrent exhibition of sulfonate

and protonated imidazole fragments, due to the proton transfer from the $-\text{SO}_3\text{H}$ to one of the imidazole nitrogen.^{22–26} The early crystalline form (I) has been found to possess only one lattice water molecule, whereas two water molecules have been identified in case of the matured form (II). Thus it has been realized that the hydration of the forms changes depending upon the duration of crystallization, and consequently the lattice water molecule strongly influence⁶ the overall hydrogen bonded self assemblies of the title compound, which is otherwise nearly identical. Attempts have been made in the work to harvest both the forms in pure and bulk manner with better yields. Hence the present work represents some of the early examples^{1–5} of environmentally benign crystalline organic frameworks for solid electrolyte applications and gains significance in this context.

2. Experimental

2.1 Materials and instruments

The 2-phenyl benzimidazole-5-sulfonic acid monohydrate has been sourced from Alfa Aesar and used as such for crystallization. L-tartaric acid, methanol and sodium carbonate were obtained locally. IR spectra of the samples were recorded on a Shimadzu 8400S FT-IR spectrophotometer as KBr pellets. For conductivity measurements, the powdered samples, pressed into pellets of 1.3 cm diameter under a pressure of 100 kg/cm^2 , were used (pellet thickness: form I = 0.139 cm, II = 0.148 cm). The pellets were coated with silver paint on both sides and sandwiched between two conducting surfaces of a pellet sample holder, with a screw load (SRS innovative solutions, Bangalore). Pellets sandwiched in the cell were then suspended inside a closed vessel, containing distilled water, in order to expose to 100% relative humidity (RH) conditions. The impedance measurements were carried out by using two – probe method in a BioLogic SP-200 instrument in the frequency range of 1 MHz – 10 mHz. The conductivity of the sample was calculated using the equation $\sigma = L / (Z \times A)$ where, σ , L , Z and A are respectively the conductivity (S cm^{-1}), thickness (cm), observed impedance (Ω) and the electrode area (cm^2) of the sample. The impedance (Z) of the materials was evaluated by fitting the depressed semi circle with the real axis at the low frequency range. The impedance data analyses were carried out using EC-Lab V10.37 and analysis were performed using Z-Fit & Sim. The C, H, N analyses were performed on Thermo finnigan, Flash EA 1112 CHN. Thoroughly powered samples of the complexes were used for the PXRD measurements in the Shimadzu Lab Model 6000 XRD instrument. Thermal analyses were carried out in a Perkin Elmer, Diamond TG/DTA instrument. Contact angles were measured using DMs – 200 (Kyowa Japan) model.

2.2 Crystallization of form I

The commercially available semi crystalline powder of 2-phenyl benzimidazole-5-sulfonic acid (0.290 g) was suspended in 10 mL of distilled water, taken in a boiling tube, and was allowed to react with 0.053 g of sodium carbonate, which was added directly. The contents were thoroughly shaken for 45 min, to dissolve the entire quantity of the substances during which a very clear aqueous solution was obtained. Then, a methanolic solution of L-tartaric acid (0.075 g in 30 mL), was slowly added along the walls of the tube, such that the alcohol layer was gently layered over the aqueous solution. During this process, a white turbidity was observed between the solvent layers at first, and descended later. The system was then firmly covered with a polyethylene sheet, with few tiny holes on the top, and kept without any disturbance at room temperature. Needle shaped X-ray quality crystals were obtained in nearly around fifteen days. The crystals were subsequently washed with water, and allowed to dry under open air. Yield: 45%. Anal. Calc. for $C_{13}H_{12}N_2O_4S$: C, 53.36; H, 4.10; N, 9.58; S, 10.94. Found: C, 53.25; H, 3.69; N, 9.59; S, 10.94. Whenever the crystalline samples are required in gram scale, multiple numbers of tubes were used for crystallization, using the above mentioned stoichiometry.

2.3 Crystallization of form II

The crystalline samples of form I was grown as before, and after ensuring that the needle shaped crystals are formed in substantial quantities, the entire batch of the single crystals present in the boiling tube was gently transferred to a 100 mL beaker completely, along with the mother liquor (35 mL), and was covered with a filter paper, and left as such at room temperature. During the time of subsequent crystallization, only distilled water was periodically added, in order to retain the original quantity of liquid in the beaker, and was ensured that the crystals are always well soaked. The shape of the crystals was found to gradually change from needle to transparent cubic blocks, and such transformation was found to be complete in about three months. The bulk lots of the cubic shaped crystals were then harvested, washed with water and then dried under open air. Yield: 84%. Anal. Calc. for

$C_{13}H_{14}N_2O_5S$: C, 50.27; H, 4.51; N, 9.02; S, 10.31. Found: C, 50.24; H, 5.13; N, 9.07; S, 9.75.

2.4 X-ray crystallography

X-ray diffraction and data collection was performed on a Bruker Axs Kappa Apex 2 CCD Diffractometer. The structure was solved by direct method with SHELXS-97 and refined using SHELXL-97.²⁸ The non-hydrogen atoms were refined with anisotropic displacement parameters. The C bound hydrogen atoms were placed at calculated positions and were treated as riding on their parent atoms. A summary of crystallographic data and refinement parameters are given in Table S1 (Supplementary Information).

3. Results and Discussion

3.1 Single crystal growth

As stated previously, the solubility of the title compound in common solvents is extremely limited,¹⁸ and thus the possibility of growing the single crystals of the title compound, through direct solvent based methods, is considered to be a difficult task to achieve under normal conditions. In this context, it could be realized that the present methods provide facile routes of crystallizing the title compound into well-developed X-ray quality single crystals, in two different hydration dependent forms. As illustrated in Scheme 1, the compound, which is suspended in water, is first converted into its clear solution as its sodium salt, with the action of sodium carbonate. This solution, upon acidification readily yields single crystals of the title compound. At the beginning, only hydrochloric acid was attempted for crystallization. However, in order to optimize the crystallization strategies, the procedure was experimented with different acids, including organic acids, and as a result, it was realized that the L-tartaric acid is ideally suited for this purpose. The role of tartaric acid in producing good quality crystals may not be within

Scheme 1. Optimized crystallization route for the forms I & II.

the scope of the present study, but it is believed that its inherent supramolecular structural features (such as $-\text{OH}$, $-\text{COOH}$ functional groups) might be very effective in causing the onset of nucleation and subsequent crystallization of the title compound. In fact the procedure allows us to harvest the single crystals in bulk, such that it facilitates the proton conduction studies on the title compound as compact pellets.^{2–5,7,10–15} In other words, the crystalline materials could be made available in substantial quantities, and thus the optimized strategies of the present work are indeed very useful in the context of solid transport evaluation studies.

3.2 X-ray structural characterizations and non-covalent interactions

It is to be noted that both the forms I & II are highly crystalline, and thus are well-suited for the X-ray structural analysis. Structural analyses further reveal that the asymmetric units of I is composed of a complete zwitterionic molecule and a lattice water, whereas in II, the complete zwitterionic unit is accompanied with two lattice water molecules (Figure 1).

As found in many other similar systems, the title compound, exist in the zwitterionic state in both the forms,^{20–27} due to the transfer of proton from the sulfonic acid group to one of the basic imidazole nitrogen atom, with the resultant exhibition of sulfonate and protonated imidazolium groups respectively. Such proton transfer is not surprising, as it is well known that when the ΔpK_a between the interacting groups become greater than 3, it usually results in proton transfer.^{29–31} In fact, even during the absence of a basic moiety, it still prefers to protonate at least lattice water to hydronium ion, and thereby become as a negatively charged ion.^{21,27} Hence the crystallization of the title compound in the zwitterionic form is not totally surprising. Noticeably, the near identicalness of C7–N1 and C7–N2 bonds of both

in I and II (in the range between 1.331 Å–1.337 Å), confirm the protonated and resonance stabilized nature of the imidazole rings (Tables S2 and S3, Supplementary Information).³² Similarly all the S–O bond lengths of both I & II are found to be nearly equal (Tables S2 and S3, Supplementary Information) (in the range of 1.427 Å–1.452 Å), as known in several zwitterionic sulfonates,^{20–27} exemplifies the fact that the pi electrons of the moiety are fully delocalized in the solid state. No unusual feature has been found in the planarity details of the aromatic rings of the zwitterionic system in both cases (Tables S4 and S5, Supplementary Information).

3.2a Supramolecular arrangements of form I: In the supramolecular arrangement of form I, the neighboring zwitterionic compositions (Figure 2) interact with each other in a head-tail manner through the N2–H...O1 hydrogen bond between the protonated nitrogen cations-sulfoante anion pairs. Sets of such zwitterionic compositions are further knitted by the lattice water molecule (O4), through the hydrogen bonding interactions involving sulfonate oxygen atoms of stacked layers (O4...O2 & O4...O3) in one side, and simultaneously, with the imidazole N1–H moieties (O4...H–N1) of a nearby unit (Table 1), from the other side (Figure 2 and Figure S1, Supplementary Information). As a result, a 3D infinite arrangement is well obvious in the solid state structure of I (Figure S1, Supplementary Information).

3.2b Supramolecular arrangements of form II: The compound II, which has been identified as a dihydrate, seem to exhibit additional hydrogen bonding arrangements (Table 2), and hence the supramolecular features of the form II are more enriched⁶ than the form I (Figure 3 and Figure S2, Supplementary Information). Both the lattice water molecule are connected themselves through the hydrogen bonds (O4...O5). Both of these water molecules engage with the zwitterionic

Figure 1. ORTEP diagrams of form I (left) and form II (right) shown at 40% ellipsoid levels.

Figure 2. Hydrogen bonding contacts of the form I along 'a' axis. (Lattice water [O4] is rendered in a different style for clarity).

Table 1. Hydrogen bonds for form I [Å and °].

D-H... A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(4)	0.88(2)	1.77(3)	2.641(2)	173(2)
N(2)-H(2A)...O(1)#1	0.87(3)	1.95(3)	2.809(2)	172(2)
N(2)-H(2A)...S(1)#1	0.87(3)	2.88(2)	3.618(18)	144(2)
O(4)-H(4B)...O(3)#2	0.901(17)	1.88(17)	2.773(3)	167(3)
O(4)-H(4B)...S(1)#2	0.901(17)	2.84(2)	3.630(19)	148(3)
O(4)-H(4A)...O(2)#3	0.892(17)	1.83(17)	2.722(2)	175(3)
O(4)-H(4A)...S(1)#3	0.892(17)	2.88(2)	3.730(17)	160(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y+1, -z+1$ #2 $-x+1/2, y-1/2, -z+3/2$ #3 $-x-1/2, y-1/2, -z+3/2$.

compositions of II (Figure 3), which are arranged in layers in a head-tail manner. While one of the lattice water (O4) interlinks two discrete zwitterionic molecules through its interaction with a sulfonate oxygen (O4---O2) on one side, and with the imidazole moiety (O4---N1-H) on the other side, the second lattice water molecule (O5) interlaces two other zwitterionic layers through the (O5---O1 & O5---O2) interactions. Thus, while O1 of the sulfonate interacts only with one of the water (O5) molecule, the O2 of sulfonate, binds with both of the lattice water molecules (O4---O2 & O5---O2). The third oxygen (O3) of the sulfonate engages

with another N-H unit, of a neighboring imidazole layer, through O3---H-N2 interaction, and complements the network formation (Figure 3). Overall there exists an alternating zigzag intermolecular hydrogen bonded arrangements in the solid state structure of form II (Figure 3 and S2, Supplementary Information).

From this discussion on the supramolecular features, it is clear that both I & II, although are chemically single entities, they could be regarded as lattice water directed hydrogen bonded crystalline organic frameworks. As discussed in the introductory sections, the water molecules strongly influence the supramolecular

Figure 3. Hydrogen bonding contacts of the form II along 'b' axis. (Lattice waters [O4 & O5] are rendered in a different style for clarity).

Table 2. Hydrogen bonds for form II [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(4)	0.91(2)	1.75(2)	2.654(2)	173(2)
N(2)-H(2A)...O(3)#1	0.88(2)	1.83(2)	2.675(2)	159(2)
O(4)-H(4A)...O(5)#2	0.895(18)	1.77(19)	2.659(3)	172(3)
O(4)-H(4B)...O(2)#3	0.886(18)	1.89(19)	2.776(3)	175(3)
O(4)-H(4B)...S(1)#3	0.886(18)	3.03(2)	3.844(2)	154(3)
O(5)-H(5A)...O(2)	0.874(18)	1.91(19)	2.770(3)	168(3)
O(5)-H(5A)...S(1)	0.874(18)	3.02(2)	3.787(2)	147(3)
O(5)-H(5B)...O(1)#4	0.876(18)	1.93(19)	2.813(3)	177(3)
O(5)-H(5B)...S(1)#4	0.876(18)	2.83(2)	3.611(2)	150(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2$, $y-1/2$, $-z+1/2$ #2 $-x+1$, $-y+2$, $-z$ #3 $x-1/2$, $-y+3/2$, $z-1/2$ #4 $-x+3/2$, $y-1/2$, $-z+1/2$.

outcome of the crystallization.^{1,6} These water insoluble non-covalent organic frameworks, possessing the required features of proton conducting materials, could be foreseen as proton electrolytes^{2-5,7,10-15} and thus are explored in the following sections.

3.3 FT-IR, Analytical and PXRD studies

As the molecular compositions of both the forms are nearly identical, the FT-IR spectra of them too are almost indistinguishable from each other (Figure S3, Supplementary Information). However, in the case of form II, it could be observed that the band in the region between 1150 cm^{-1} to 1240 cm^{-1} , corresponding to the asymmetric stretches of the sulfonate group, is not sharp,

and instead exhibits little splitting with line broadening (Figure 4).

This could be attributed to loss of local symmetry around the SO_3^- group in the form II,³³⁻³⁶ when compared to form I, due to the enriched hydrogen bonding interactions of the sulfonate group of the form II,^{6b} as seen in its supramolecular structure. The symmetric stretching vibrations of the group, for both the forms occur in the region from 1025 cm^{-1} to 1090 cm^{-1} . The broad peaks between 2950 cm^{-1} to 3550 cm^{-1} could originate from the combined presences of the hydrogen bonded N-H and O-H stretching vibrations of the imidazolium and water molecules of the forms.³³⁻³⁷ The sharp peaks around 500 cm^{-1} to 600 cm^{-1} could very well be attributed to the presence of lattice water molecules.³⁷

Figure 4. Overlay of FT-IR of forms I & II (expanded at the sulfoante region).

Figure 5. Overlay of the TGA profiles of forms I & II.

Similarly, the TGA analysis as well, distinguishes the lattice water molecules of both the forms in their respective thermograms, through their percentage weight loss. As shown in the Figure 5, the 6.06% loss in weight for form I (Calculated: 6.15% for one H₂O) at 90 °C and 11.60% of loss for II (calculated 11.6% for two H₂O) at 109 °C exemplify the fact that the crystalline form are indeed distinguishable through the TGA studies.¹⁵ Furthermore, it could also be observed that the water loss from the II is a rather gradual process, and it requires slightly elevated temperature than form I, which might be attributed to the entanglement of the water molecules, by more robust non-covalent forces, when compared to the form I.

The elemental analysis (C,H,N,S) of the bulk products coincide with the calculated values based on their

respective X-ray structures, and highlight the reliability of the procedures in obtaining the respective forms, in pure manner, without any cross product formation during crystallizations.

The bulk homogeneity of the samples has also been examined using the PXRD experiments as well (Figure 6). The PXRD traces of the crystalline forms, matching^{5,38} with those of their respective calculated patterns, demonstrate the bulk purity of the individual forms, thus highlighting the reliability of the present crystallization strategies in harvesting X-ray quality fine single crystals, for proton conduction studies. Moreover, randomly collected single crystals of the respective forms have also been rechecked again for their cell parameter details, and have been found to fully correspond to those of their individual parameters, ensuring the fact the probability of obtaining single crystals of additional (polymorphic) phases are significantly lower under the specified experimental conditions. PXRD traces are also useful in examining the stabilities of the compound under various common environmental conditions, in relevance to the proton conductivity studies.^{2-5,7,10-15} Usually, the pressed pellets are exposed to higher level of humidity conditions during impedance measurements, and subsequently they are recycled.^{2-5,7,10-15} Hence in the present study as well, the materialistic worthiness of the crystalline forms has been explored using the PXRD studies under those conditions. As compiled in Figure 6, the patterns of the powdered samples that are exposed to 100% humidity conditions, and similarly the patterns of the air dried samples (Figure S4, Supplementary Information), obtained after exposing the wet samples to open air for three hours under room temperature, matching^{5,38} with those of the as-synthesized pattern in their respective 2-theta positions, illustrate that the samples are indeed stable under such environments and hence are reliable for impedance measurements. The slight broadening of the peaks,^{5,38} when compared to the calculated patterns, are quite common in case of framework materials and are possibly attributed to factors such as reduction in particle size by grinding,⁵ or filling of glassy liquid (humidity in this case) into the pores^{38d,e} during sample preparations and also at the time of X-ray diffraction. However, in order to ensure that the experimental diffraction pattern, really correspond to the respective simulated traces, a thorough curve fitting analysis³⁹ of the diffraction patterns of the as-synthesized and humidity exposed samples of the forms has been performed, and the results (Table S6, Supplementary Information), significantly correlating with those of the simulated values, indeed highlight the reliability of the experimental PXRD profiles (Figure 6) of the respective forms.

Figure 6. PXRD traces of forms I & II; (A) simulated, (B) as-synthesized and (C) after humidifying under 100% RH for 48 h. (Y axis is arbitrary).

In this perspective, it is also to be noted that the PXRD of the commercially pure sample does not match with any of these two individual forms (Figure S5, Supplementary Information), and the determination of the actual structural phase of the commercial sample is rather difficult to establish through single crystal X-ray methods, due to its micro-crystalline nature. These facts point out that the as-received commercially pure micro-crystalline sample could not be directly used for any of the impedance investigations and thus the present crystallization methods indeed are worth considering.

3.4 AC impedance and proton conductivity studies

The proton conductivities of the crystalline samples were studied using the AC impedance experiments and evaluated from their Nyquist plots. In general, the solid ionic electrolytes, which are sandwiched between two electronically conducting parallel plates, are known to exhibit a semicircle at higher frequencies and a characteristic spur or tail at lower frequencies in their Nyquist plots.⁴⁰ Hence, similar features are expected in the present cases too, as the pellets are precisely packed between two metallic plates. Although the samples have not shown (Figure S6, Supplementary Information) such bench mark characteristics under inherent conditions, at 25 °C, and at open room humidity (~50% RH), the required characteristics have become immediately evident once they were exposed to 100% RH in a closed container, at room temperature. It has also been observed that the characteristic events in the Nyquist plots, and the magnitudes of the proton conductivities of the samples were kept improving with respect to the increase in the duration of the exposure to humidity, and therefore they were periodically monitored, till the samples stops exhibiting any further improvement in their performances, indicating the completion of the humidity

Figure 7. Nyquist plots of forms I & II after humidifying under 100% RH for 48 h at room temperature.

saturation processes (Figure 7). As a result, it has been found that the form I requires nearly 48 h for humidity saturation, whereas the form II attains the completion in 30 h itself. Nonetheless, in order to evaluate their performances in a parallel manner, both of them have been equally allowed for 48 h of moisture exposure at 25 °C under 100% RH, during the impedance measurements (Figure 7).

The observed Nyquist plots of both the forms required the use of an additional grain boundary resistance,^{41–45} in addition to the usual equivalent circuit^{2–5,7,10–15} and hence the circuit, $[R + (Q_b/R_b) + (Q_{gb}/R_{gb}) + Q]$ (where b = bulk or crystalline, and gb = grain boundary, total resistivity = $b + gb$), has been used for getting best fits of the results (Figure S7, Supplementary Information). It is very clear that both the crystalline forms indeed function as efficient proton conductors under 100% RH conditions (Figure 7), and the magnitudes of their

Figure 8. Contact angle results of the forms.

Figure 9. Overlay of Nyquist plots of form I & II; (A) original profile under 100% RH for 48 h at room temperature and (B) after air drying and recycling under identical conditions.

conductivities ($1 \times 10^{-5} \text{ S cm}^{-1}$ and $5 \times 10^{-5} \text{ S cm}^{-1}$ for form I and II) respectively 25°C , evaluated from their total resistivity, do compare well with the level of various other efficient solid electrolytes reported in the literature.^{2–5} Comparison of proton conductivities of the forms ($\sim 10^{-5} \text{ S cm}^{-1}$) with those of the state of the art hydrogen bonded frameworks, ranging from the order of $10^{-6} \text{ S cm}^{-1}$ in case of HOF-6²⁸ to the order of $10^{-2} \text{ S cm}^{-1}$ shown by HOF-GS11⁴ are summarized in (Table S7, Supplementary Information). Although the ionic conductivities of the present forms are not very high, still it can be considered appreciable, and thus gain merit in terms of other advantages of the materials. It is to be pointed out that the performance of form II, both in terms of the duration for humidity saturation, and also in the level of proton conductivity, is better than the form I, and is worth exploring further.

Interestingly, it has been observed during the PXRD experiments that the moisture droplets, particularly on the surface of the powered sample of form I, always tend to skid away, indicating that the form I is slightly less hydrophilic than the II. These visible observations

have been verified through contact angle measurements as well,⁴⁶ using the surfaces of the pelletized samples (Figure 8). The results (Contact angle for I; 45.5° and for II; 16.6°), parallel to those of the visual observations, confirm that the form II is definitely more hydrophilic⁴⁶ than I, which could be attributed to the presence of additional lattice water molecule, in case of the crystalline form II. Consequently, the similar rationale might also be regarded as the reason for the early attainment of humidity saturation, and also for the enhanced proton conducting performance of II than the form I.

In the follow-up experiments, when the moist pellets were kept out of the closed humidifying chamber, and exposed to open air, the levels of their proton conductivities have been found to decrease^{13–15} gradually with time, and nearly after three hours, the level of proton conduction has been found to decrease to the order of $10^{-9} \text{ S cm}^{-1}$, with noticeable changes in their Nyquist plots (Figure S8, Supplementary Information). However, when the samples were re-exposed to moisture in a closed 100% RH container, the events have been

Figure 10. The Arrhenius plot for the E_a calculation for forms I & II; (A) considers the total conductivity and (B) considers only the grain contribution.

found to become reversible in their respective Nyquist plots, with the subsequent increase in their conductivities, such that after 48 h of moisture exposure, the level of proton conductivities have been found to nearly match with their respective original magnitudes (Figure 9).

These observations clearly suggest the fact that the presence of moisture is very crucial in establishing the conductivity characteristics in both the systems,^{2-5,7,10-15} and therefore it could be realized that the protons are the charge carriers during the conduction processes.

3.4a Effect of Temperature: Temperature dependent impedance experiments also have been carried out (Figure 10 and S9, Supplementary Information) in order to estimate the energy of activation (E_a) of the materials.

As presented in the Figure 10, the E_a of the forms, whether in terms of the total conductivity or only in terms of the grain interiors (bulk), represent a value of 0.19 eV and 0.27 eV for the forms I and II respectively, thus indicating the Grotthuss mechanism of proton conduction (Figure 11) in both the cases.^{1-7,10-15}

The enhanced performance of form II, in line with its improved hydrophilicity, could also be correlated with its supramolecular architecture as well. The form II, in which the zwitterionic compositions are linked with two lattice waters on either side, leading to enriched^{6b} and parallel hydrogen bonding interactions (Figures 3 and 11 and Table 2), might provide additional opportunity for Grotthuss migration than form I, and thus the supramolecular features could also be possibly accounted for the observed results. It is also to be noted that the conductivity of form II, despite its slightly higher activation energy, is better than the form I. Such observations, though rare, are not totally unprecedented in the literature,^{5,47,48} and are accounted on the basis of the higher carrier concentrations in the electrolyte systems. It is also to be mentioned that all these observations are reproducible in two different batches as well.

Hence it could be realized that these lattice water directed crystalline organic frameworks, are undoubtedly function as solid proton electrolytes as anticipated, and therefore are worthwhile for further evaluations.

4. Conclusions

Present study highlights the facile crystallization strategies for the title compound, despite its limited solubility in common solvents, and demonstrates the influence of

Figure 11. Possible pathways for Grotthuss mechanism: (Parallel and enriched network of form II, is plausibly accounted for its efficient charge migration).

lattice water molecules in the supramolecular outcome of the structures. Two different forms of the title compound that are differing only in the number of lattice water molecule, but are nearly identical with respect to the basic molecular units, have been found. The crystallization procedures were optimized at the aqueous medium itself, using ordinary apparatuses, without invoking any sophisticated equipments, and only at room temperature conditions. The phase purities of the individual forms have been ascertained through physical methods. The basic molecule has been found to crystallize in the zwitterionic configuration in both the forms. The number of lattice water molecules was realized to be dependent upon the duration of crystallization. The ionic moieties, along with the influence of the lattice water molecules, form 3D hydrogen bonded organic frameworks. Hence the lattice water molecules potentially influence the outcomes of the supramolecular structures. The AC impedance studies prove that both the crystalline forms are efficient proton conducting electrolytes in the solid state, under humid conditions, and similarly the E_a studies have shown that the Grotthuss mechanism of conduction is followed during the process. However, the performance of form II is considered to be definitely better than I and could be attributed to its higher hydrophilicity and enriched hydrogen bonded networks. The moisture based proton conductivities of the forms are reversible, and shuttles between wet and dry conditions quite readily. As the reports on hydrogen bonded crystalline organic frameworks, showing the proton conduction characteristics are only rare, the present work involving these water stable and environmentally benign materials does indeed represent one of the early examples in this field, and hence further explorations in this direction are being carried out in our laboratory.

Supplementary Information (SI)

CCDC 1847629 and CCDC 1847630 for the forms I & II respectively contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033). Figures S1–S9 and Table S1–S7 are given in the electronic supplementary information available at <http://www.ias.ac.in/chemsci>.

Acknowledgements

This work was initially supported by the Start up Research Grant of the Science and Engineering Research Board (SERB), New Delhi that ended on 13.08.2016. Corresponding author gratefully acknowledge the SERB for providing the

financial assistance (SB/FT/CS-184/2011 dated 10.07.2013). Authors wish to thank the Principal and Management of the PSG College of Technology for the facilities. Authors wish to thank Mr. S. S. Subramanian, Asst. Prof. Department of Applied Science, PSGCT, for the contact angle measurements. Authors sincerely thank the SAIF - IIT Madras for single crystal data collection, solving and refining of the structures. Authors further wish to thank the STIC-Cochin for the elemental and the TGA analyses, and the Karunya University, Coimbatore for PXRD measurements.

References

- (a) Luo J, Wang J-W, Zhang J-H, Lai S and Zhong D-C 2018 Hydrogen-bonded organic frame works: Design, structures and potential applications *CrystEngComm* **20** 5884; (b) Lin R-B, He Y, Li P, Wang H, Zhou W and Chen B 2019 Multifunctional porous hydrogen-bonded organic framework materials *Chem. Soc. Rev.* **48** 1362
- (a) Xing G, Yan T, Das S, Ben T and Qiu S 2018 Synthesis of crystalline porous organic salts with high proton conductivity *Angew. Chem. Int. Ed.* **57** 5345; (b) Yoon M, Suh K, Kim H, Kim Y, Selvapalam N and Kim K 2011 High and highly anisotropic proton conductivity in organic molecular porous materials *Angew. Chem. Int. Ed.* **50** 7870; (c) Ma H, Liu B, Li B, Zhang L, Li Y-G, Tan H-Q, Zang H-Y and Zhu G 2016 Cationic covalent organic frameworks: a simple platform of anionic exchange for porosity tuning and proton conduction *J. Am. Chem. Soc.* **138** 5897; (d) Meng Z, Aykanat A and Mirica K A 2019 Proton conduction in 2D Aza-fused covalent organic frameworks *Chem. Mater.* **31** 819; (e) Chandra S, Kundu T, Kandambeth S, BabaRao R, Marathe Y, Kunjir S M and Banerjee R 2014 Phosphoric acid loaded azo ($-N=N-$) based covalent organic framework for proton conduction *J. Am. Chem. Soc.* **136** 6570; (f) Liu M, Chen L, Lewis S, Chong S Y, Little M A, Hasell T, Aldous I M, Brown C M, Smith M W, Morrison C A, Hardwick L J and Cooper A I 2016 Three-dimensional protonic conductivity in porous organic cage solids *Nat. Commun.* **7** 12750; (g) Yang W, Yang F, Hu T-L, King S C, Wang H, Wu H, Zhou W, Li J-R, Arman H D and Chen B 2016 Microporous diaminotriazine-decorated porphyrin-based hydrogen bonded organic framework: Permanent porosity and proton conduction *Cryst. Growth Des.* **16** 5831
- (a) Tayade S B, Bhat S S, Illathvalappil R, Dhavale V M, Kawade V A, Kumbhar A S, Kurungot S and Näther C 2018 Water mediated proton conductance in a hydrogen-bonded Ni(II)bipyridine-glycoluril chloride self-assembled framework *CrystEngComm* **20** 1094; (b) Tayade S B, Dhavale V M, Kumbhar A S, Kurungot S, Lönnecke P, Hey-Hawkins E and Pujari B 2017 Proton conduction in a hydrogen-bonded complex of copper(II)-bipyridine glycoluril nitrate *Dalton Trans.* **46** 6968
- Karmakar A, Illathvalappil R, Anothumakkool B, Sen A, Samanta P, Desai A V, Kurungot S and Ghosh S K 2016 Hydrogen-Bonded Organic Frameworks (HOFs): A new class of porous crystalline proton-conducting materials *Angew. Chem. Int. Ed.* **55** 10667

5. Chand S, Pal S C, Pal A, Ye Y, Lin Q, Zhang Z, Xiang S and Das M C 2019 Metallo-hydrogen bonded organic frameworks (MHOs) as new class of crystalline materials for protonic conduction *Chem. Eur. J.* **25** 1691
6. (a) Desiraju G R 1996 The C-H...O Hydrogen Bond: Structural implications and supramolecular design *Acc. Chem. Res.* **29** 441; (b) Moncol J, Púčeková Z, Lis T and Valigura D 2006 An enriched hydrogen-bond system in trans-diaquabis(N,N-diethylnicotinamide- κ N)-bis(3-methoxysalicylato- κ O)copper(II) dihydrate *Acta Cryst.* **E62** m448; (c) Wang X and Vittal J J 2003 Nature of the reactants and influence of water on the supramolecular assembly *Inorg. Chem.* **42** 5135
7. (a) Meng X, Wang H-N, Song S-Y and Zhang H-J 2017 Proton-conducting crystalline porous materials *Chem. Soc. Rev.* **46** 464; (b) Wang C, Liu X, Demir N K, Chen J P and Li K 2016 Applications of water stable metal-organic frameworks *Chem. Soc. Rev.* **45** 5107; (c) Liu R, Liu Y, Yu S, Yang C, Li Z and Li G 2019 A highly proton-conductive 3D ionic cadmium-organic Framework for ammonia and amines impedence sensing *ACS Appl. Mater. Interfaces* **11** 1713; (d) Wahiduzzaman M, Wang S, Schnee J, Vimont A, Ortiz V, Yot P G, Retoux R, Daturi M, Lee J S, Chang J-S, Serre C, Maurin G and Devautour-Vinot S 2019 A high proton conductive hydrogensulfate decorated titanium carboxylate MOF *ACS Sustain. Chem. Eng.* **7** 5776; (e) Kim S, Joarder B, Hurd J A, Zhang J, Dawson KW, Gelfand B S, Wong N E and Shimizu G K H 2018 Achieving superprotonic conduction in metal - organic frameworks through iterative design advance *J. Am. Chem. Soc.* **140** 1077
8. Asensio J A, Sánchez E M and Gómez-Romero P 2010 Proton-conducting membranes based on benzimidazole polymers for high-temperature PEM fuel cells. A chemical quest *Chem. Soc. Rev.* **39** 3210
9. Alberti G, Casciola M, Costantino U and Vivani R 1996 Layered and pillared metal(IV) phosphates and phosphonates *Adv. Mater.* **8** 291
10. Horike S, Umeyama D and Kitagawa S 2013 Ion conductivity and transport by porous coordination polymers and metal-organic Frameworks *Acc. Chem. Res.* **46** 2376
11. Yoon M, Suh K, Natarajan S and Kim K 2013 Proton conduction in metal-organic frameworks and related modularly built porous solids *Angew. Chem. Int. Ed.* **52** 2688
12. Ramaswamy P, Wong N E and Shimizu G K H 2014 MOFs as proton conductors – challenges and opportunities *Chem. Soc. Rev.* **43** 5913
13. Saravanabharathi D, Obulichetty M, Rameshkumar S and Kumaravel M 2012 Rapid crystallization and proton conductivity of copper (II)-L-tartrate *Synth. Met.* **162** 1519
14. Saravanabharathi D, Obulichetty M, Rameshkumar S and Kumaravel M 2014 Humidity based proton conductivity of calcium-L-tartrate tetrahydrate: An environmentally benign coordination polymer as a solid electrolyte *Synth. Met.* **196** 76
15. Saravanabharathi D, Obulichetty M, Rameshkumar S and Kumaravel M 2015 New 2-methyl benzimidazole based zinc carboxylates: Supramolecular structures, biomimetic proton conductivities and luminescent properties *Inorg. Chim. Acta* **437** 167
16. Wei M-L, Zhuang P-F, Miao Q-X and Wang Y 2011 Two highly proton-conductive molecular hybrids based on ionized water clusters and poly-Keggin-anion chains *J. Solid State Chem.* **184** 1472
17. Wei M-L, Wang J-H and Wang Y-X 2013 Two proton-conductive hybrids based on 2,2' -biimidazole molecules and Keggin-type heteropolyacids *J. Solid State Chem.* **198** 323
18. Dayan N 2017 In *Handbook of Formulating Dermal Applications: A Definitive Practical Guide* (New Jersey: Wiley & Sons) p. 103
19. Zhang S, Chen J, Wang Y and Wei X 2012 Humic acids decrease the photodegradation of the sunscreen UV filter 2-phenylbenzimidazole-5-sulfonic acid in natural waters *Environ. Chem. Lett.* **10** 389
20. Cha M S, Lee J W, Kang S W and Jung O-S 2005 A solid structure of 2-pyridinesulfonic acid *Bull. Korean Chem. Soc.* **26** 334
21. Arora S K and Sundaralingam M 1971 The crystal and molecular structure of 4-Methyl sulfonic acid (p-toluenesulfonic acid) monohydrate, $C_7H_8SO_3^- \cdot H_3O^+$, an oxonium salt *Acta Cryst.* **B27** 1293
22. Smith G, Wermuth U D, Young D J and White J M 2004 Zwitterionic 5-amino-2-naphthalenesulfonic acid *Acta Cryst.* **E60** o2014
23. Zhu Z-B, Gao S and Ng S W 2011 4-Aminopyridinium-3-sulfonate monohydrate *Acta Cryst.* **E67** o456
24. Gao S, Huo L-H and Ng S W 2005 3-Ammonio-4-methoxybenzenesulfonate *Acta Cryst.* **E61** o539
25. Mahmood A, Rashid A, Arshad M N, Sharif H M A and Khan I U 2009 1-Ammonionaphthalene-2-sulfonate *Acta Cryst.* **E65** o2505
26. Burrows A D, Harrington R W and Mahon M F 1999 2, 2'-Bipyridine-5-sulfonic acid *Acta Cryst.* **C55** 1921
27. Dexter D D 1971 The crystal and molecular structure of p-toluene sulfonic acid monohydrate *Z. Kristallog.* **134** 350
28. Sheldrick G M 2015 Crystal structure refinement with SHELXL *Acta Cryst.* **C71** 3
29. Obulichetty M and Saravanabharathi D 2014 Influence of molecular structure on the photoluminescence of 2 - methyl benzimidazolium picrate: A new fluorescent material *Spectrochim. Acta A* **118** 861
30. Cruz-Cabeza A J 2012 Acid-base crystalline complexes and the pKa rule *CrystEngComm* **14** 6362
31. Lemmerer A, Govindraj S, Johnston M, Motloung X and Savig K L 2015 Co-crystals and molecular salts of carboxylic acid/pyridine complexes: can calculated pKa's predict proton transfer? A case study of nine complexes *CrystEngComm* **17** 3591
32. Obodovskaya A E, Starikova Z A, Belous S N and Pokrovskaya I E 1991 Crystal and molecular structure of 2-methylbenzimidazole *J. Struct. Chem.* **32** 421
33. Perpétuo G J, Gonçalves R S and Janczak J 2015 Supramolecular hydrogen-bonding network in 1-(diaminomethylene)thiourea-1-ium 4-hydroxybenzenesulfonate crystal *J. Mol. Struct.* **1096** 74
34. Langner R and Zundel G 1998 FT IR investigation of O—H—O hydrogen bonds with large proton polarizability in sulfonic acid-N-oxide systems in the middle and far-IR *J. Chem. Soc., Faraday Trans.* **94** 1805

35. Luo J, Hu J, Saak W, Beckhaus R, Wittstock G, Vank-
elecom I F J, Agert C and Conrad O 2011 Protic
ionic liquid and ionic melts prepared from methane-
sulfonic acid and 1*H*-1,2,4-triazole as high tem-
perature PEMFC electrolytes *J. Mater. Chem.* **21**
10426
36. Shishlov N M and Khursan S L 2016 Effect of ion inter-
actions on the IR spectrum of benzenesulfonate ion.
Restoration of sulfonate ion symmetry in sodium ben-
zenesulfonate dimer *J. Mol. Struct.* **1123** 360
37. K. Nakamoto 1986 In *Infrared and Raman Spectra of
Inorganic and Coordination Compounds* (Wiley: New
York)
38. (a) Zhai Q-G, Mao C, Zhao X, Lin Q, Bu F, Chen X,
Bu X and Feng P 2015 Cooperative crystallization of
hetero metallic indium–chromium metal–organic poly-
hedra and their fast proton conductivity *Angew. Chem.
Int. Ed.* **54** 7886; (b) Ramaswamy P, Matsuda R, Kosaka
W, Akiyama G, Jeon H J and Kitagawa S 2014 Highly
proton conductive nanoporous coordination polymers
with sulfonic acid groups on the pore surface *Chem.
Commun.* **50** 1144; (c) Manna B, Anothumakkool B,
Desai AV, Samanta P, Kurungot S and Ghosh S K 2015
Coherent fusion of water array and protonated amine in
a metal- sulphate - based coordination polymer for pro-
ton conduction *Inorg. Chem.* **54** 5366; (d) Dybtsev D N,
Ponomareva V G, Aliev S B, Chupakhin A P, Gallyamov
M R, Moroz N K, Kolesov B A, Kovalenko K A, Shutova
E S and Fedin V P 2014 High proton conductivity and
spectroscopic investigations of metal-organic framework
materials impregnated by strong acids *ACS Appl. Mater.
Interfaces* **6** 5161; (e) Ponomareva VG, Kovalenko K
A, Chupakhin A P, Dybtsev D N, Shutova E S and
Fedin V P 2012 Imparting high proton conductivity to
a metal-organic framework material by controlled acid
impregnation *J. Am. Chem. Soc.* **134** 15640
39. Wojdyr M 2010 Fityk: a general-purpose peak fitting
program *J. Appl. Cryst.* **43** 1126
40. Huggins R A 2002 Simple method to determine elec-
tronic and ionic components of the conductivity in Mixed
Conductors A Review *Ionics* **8** 300
41. Stankiewicz J, Tomás M, Dobrinovitch I T, Forcén-
Vázquez E and Falvello L R 2014 Proton conduction
in a nonporous one dimensional coordination Polymer
Chem. Mater. **26** 5282
42. Bazaga-García M, Angeli G K, Papathanasiou K E,
Salcedo I R, Olivera-Pastor P, Losilla E R, Choquesillo-
Lazarte D, Hix G B, Cabeza A and Demadis K D
2016 Luminescent and proton conducting lanthanide
coordination networks based on a zwitterionic tripodal
triphosphonate *Inorg. Chem.* **55** 7414
43. Dong X-Y, Wang R, Wang J-Z, Zang S-Q and Mak T
C W 2015 Highly selective sensing Fe³⁺ and proton
conduction in a water-stable sulfonate-carboxylate Tb-
organic-framework *J. Mater. Chem. A* **3** 641
44. Irvine J T S, Sinclair D C and West A R 1990 Electro-
ceramics: Characterization by Impedance Spectroscopy
Adv. Mater. **2** 132
45. Zhu M, Hao Z-M, Song X-Z, Meng X, Zhao S-N, Song S-
Y and Zhang H-J 2014 A new type of double-chain based
3D lanthanide (III) metal–organic framework demon-
strating proton conduction and tunable emission *Chem.
Commun.* **50** 1912
46. He S, Yu J, Li C, Fang J, Xu J and Guan R 2011 Sul-
fonated poly(bis-A)-sulfones as proton exchange mem-
branes for direct methanol fuel cell application *Polym.
Eng. Sci.* **51** 264
47. Bureekaew S, Horike S, Higuchi M, Mizuno M, Kawa-
mura T, Tanaka D, Yanai N and Kitagawa S 2009 One-
dimensional imidazole aggregate in aluminium porous
coordination polymers with high proton conductivity
Nature Mat. **8** 831
48. Kundu T, Sahoo S C and Banerjee R 2012 Alkali earth
metal (Ca, Sr, Ba) based thermostable metal–organic
frameworks (MOFs) for proton conduction *Chem. Com-
mun.* **48** 4998