Alkali Earth Metal (Ca, Sr, Ba) Based Thermostable Metal Organic Frameworks (MOFs) for Proton Conduction

(Supporting Information: 63 pages)

Tanay Kundu, Subash Chandra Sahoo and Rahul Banerjee*[†]

Physical/Materials Chemistry Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India E-mail: <u>r.banerjee@ncl.res.in</u> Fax: + 91-20-25902636; Tel: + 91-20-25902535

Section S1. Synthesis of Alkali Earth Metal based MOFs (Ca-SBBA, Sr-SBI Ba-SBBA)	BA and S-2
Section S2. IR Spectroscopy of all the MOFs under different condition	S-4
Section S3. Single crystal X-ray diffraction data collection, structure solution and refinement procedures	S-10
Section S4. PXRD patterns of all three MOFs under different condition	S-22
Section S5. Thermal stability of the MOFs and the Thermal Gravimetric Ar (TGA) and Differential Scanning Calorimetry (DSC) data	nalysis S-33
Section S6. Proton conductivity measurement of all the MOFs	S-41

Section S1. Synthesis of Alkali Earth Metal based MOFs (Ca-SBBA, Sr-SBBA and Ba-SBBA)

All reagents and solvents for synthesis and analysis were commercially available and used as received. The Fourier transform (FT) IR spectra (KBr pellet) were taken on a *PERKIN ELMER FT-IR SPECTRUM* (Nicolet) spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PNAlytical diffractometer for Cu K α radiation ($\lambda = 1.5406$ Å), with a scan speed of 2° min⁻¹ and a step size of 0.02° in 2 θ . Thermo-gravimetric experiments (TGA) were carried out in the temperature range of 25–700 °C on a SDT Q600 TG-DTA analyzer under N₂ atmosphere at a heating rate of 10 °C min⁻¹.

Synthesis of Ca-SBBA: 1mL 0.2M DMF stock solution of Ca(NO₃)₂.4H₂O was mixed with 1mL 0.2M DMF stock solution of SBBA in a 5 mL screw capped vial and sonicated for 10 minutes. The vial was then heated at 100 0 C for 48h. The block shaped colorless crystals were washed with DMF and collected by filtration. *FT-IR* : (KBr 4000-600cm⁻¹): 3369(br), 3051(w), 1656(s), 1591(s), 1545(s), 1384(s), 1158(s), 1095(s), 744(s), 660(s), Elemental Analysis: C₂₃ N₃ O₉ H₂₉ S₁ Ca₁ = [Ca(SBBA).(DMF)₂].DMF:

Calcd. C, 49.02; H, 5.15; N, 7.46. Found C, 49.41; H, 5.72; N, 7.23.

Synthesis of Sr-SBBA: 1mL 0.2M DMF stock solution of $Sr(NO_3)_2$ was mixed with 1mL 0.2M DMF stock solution of SBBA in a 5 mL screw capped vial and sonicated for 30 minutes. The vial was then heated at 100 0 C for 96h. The needle shaped colorless crystals were washed with DMF and collected by filtration. *FT-IR:* (KBr 4000-600cm⁻¹): 3463(br), 3051(w), 1659(s), 1598(s), 1560(s), 1383(s), 1098(w), 1290(s), 1161(s), 1098(s), 783(s), 730(s), **Elemental Analysis:** C₈₂ H₈₈ N₈ O₃₆ S₄ Sr₅ = [Sr₅(SBBA)₄.(HCOO)₂.(DMF)₈].2DMF : Calcd. C, 42.72; H, 4.16; N, 5.66. Found C, 42.41; H, 4.09; N, 5.47.

Elemental analysis (activated) = C_{82} H₈₈ N₈ O₃₆ S₄ Sr₅ = Sr₅(SBBA)₄.(HCOO)₂.8DMF: Calcd. C, 42.30; H, 3.81; N, 4.81; Found C, 42.39; H, 3. 91; N, 4.93.

Synthesis of Ba-SBBA: 1mL 0.2M DEF stock solution of $Ba(NO_3)_2$ was mixed with 1mL 0.2M DEF stock solution of SBBA in a 5 mL screw capped vial and sonicated for 20 minutes. The vial was then heated at 100 ^oC for 72h. The colorless rod shaped crystals were washed with DEF and collected by filtration. *FT-IR* : (KBr 4000-600cm⁻¹): 2880(br), 1596(s), 1538(s), 1367(s), 1288(s), 1098(w), 1037(m), 783(s), 722(s), Elemental Analysis: C₄₈ H₅₆ Ba₂ N₄ O₁₆ S₂ = Ba₂(SBBA)₂.4DEF: Calcd. C, 44.86; H, 4.44; N, 4.36. Found C, 44.39; H, 4.46; N, 4.39.

Section S2. IR Spectroscopy of all the MOFs

IR Spectra of Ca-SBBA:



Figure S1: IR Spectroscopy of as-synthesized Ca-SBBA.



Figure S2: IR Spectroscopy of Ca-SBBA after humidification for 24h.



Figure S3: Comparison of IR Spectroscopy of as-synthesized Ca-SBBA with humidified one showing structural retention with inclusion of water molecule.



Figure S4: Comparison of IR Spectroscopy of as-synthesized Ca-SBBA with the phase transformed material at 500 0 C, which shows same structural and metal-ligand connectivity retention upon removal of solvent molecules. Characteristic peaks of DMF (1260, 1504, 1660 etc.) are absent in phase transformed sample.

IR Spectra of Sr-SBBA:



Figure S5: IR Spectroscopy of as-synthesized Sr-SBBA.



Figure S6: IR Spectroscopy of Sr-SBBA after humidification for 24h.



Figure S7: Comparison of IR Spectroscopy of as-synthesized Sr-SBBA with humidified one showing structural retention with inclusion of water molecule.



Figure S8: Comparison of IR Spectroscopy of as-synthesized Sr-SBBA with the phase transformed material at 500 0 C, which shows same structural and metal-ligand connectivity retention upon removal of solvent molecules.

IR Spectra of Ba-SBBA:



Figure S9: IR Spectroscopy of as-synthesized Ba-SBBA.



Figure S10: IR Spectroscopy of Ba-SBBA after humidification for 24h.



Figure S11: Comparison of IR Spectroscopy of as-synthesized Ba-SBBA with humidified one showing structural change with inclusion of water molecule.



Figure S12: Comparison of IR Spectroscopy of as-synthesized Ba-SBBA with the phase transformed material at 500 0 C, which shows same structural and metal-ligand connectivity retention upon removal of solvent molecules.

Section S3. Single crystal X-ray diffraction data collection, structure solution and refinement procedures.

General Data Collection and Refinement Procedures:

Data was collected on a Bruker SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo K α radiation ($\lambda = 0.71073$ Å) or Cu K α radiation ($\lambda = 1.54184$ Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. The crystal reported in this paper was mounted on nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research).

Initial scans of each specimen were performed to obtain preliminary unit cell parameters and to assess the mosaicity (breadth of spots between frames) of the crystal to select the required frame width for data collection. *Bruker SMART*¹ software was used suite to carry out overlapping φ and ω scans at detector (2 θ) settings (2 θ = 28). Following data collection, reflections were sampled from all regions of the Ewald sphere to redetermine unit cell parameters for data integration and to check for rotational twinning using *CELL_NOW*². In no data collection was evidence for crystal decay encountered. Following exhaustive review of collected frames the resolution of the dataset was judged. Data were integrated using Bruker SAINT³ software with a narrow frame algorithm and a 0.400 fractional lower limit of average intensity. Data were subsequently corrected for absorption by the program SADABS⁴. The space group determination and tests for merohedral twinning were carried out using *XPREP*³.

10

The structure was solved by direct methods and refined using the *SHELXTL* 97⁵ software suite. Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. Final models were refined anisotropically (if the number of data permitted) until full convergence was achieved. The structure was examined using the *Adsym* subroutine of PLATON⁶ to assure that no additional symmetry could be applied to the models. All ellipsoids in ORTEP diagrams are displayed at the 50% probability level unless noted otherwise. Crystallographic data (excluding structure factors) for the structures are reported in this paper have been deposited with the CCDC as deposition No. CCDC 850219 - CCDC 850221. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 IEZ, U.K. [fax: b 44 (1223) 336 033; e-mail: deposit@ccde.cam.ac.uk].

- Bruker (2005). APEX2. Version 5.053. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2004). CELL_NOW. University of Göttingen, Germany. Steiner, Th. (1998). Acta Cryst. B54, 456–463.
- Bruker (2004). SAINT-Plus (Version 7.03). Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2002). SADABS (Version 2.03) and TWINABS (Version 1.02). University of Göttingen, Germany.
- 5. Sheldrick, G. M. (1997). *SHELXS '97* and *SHELXL '97*. University of Göttingen, Germany.
- 6. A. L. Spek (2005) PLATON, *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands.

Ca-SBBA (MONOCLINIC)

Experimental and Refinement Details for Ca-SBBA

A Colorless block like crystal ($0.3 \times 0.2 \times 0.1 \text{ mm}^3$) of **Ca-SBBA** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Cu K α radiation ($\lambda = 1.54184$ Å) at 296(2) K. A total of 4407 reflections were collected of which 3315 were unique. The range of θ was from 1.71 to 24.99. Analysis of the data showed negligible decay during collection. The structure was solved in the monoclinic $P2_1/c$ space group, with Z = 4, using direct methods. All non-hydrogen atoms were refined anisotropically with hydrogen atoms generated as spheres riding the coordinates of their parent atoms. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0386$ ($F > 2\sigma F$) and $wR_2 = 0.1045$ (all data) with GOF = 1.028.

Sr-SBBA (TRICLINIC)

• •

Experimental and Refinement Details for Sr-SBBA

A colorless needle like crystal ($0.28 \times 0.16 \times 0.08 \text{ mm}^3$) of **Sr-SBBA** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Cu K α radiation ($\lambda = 1.54184$ Å) at 293(2). A total of 11542 reflections were collected of which 8511 were unique. The range of θ was from 3.26 to 73.36. Analysis of the data showed negligible decay during collection. The structure was solved in the

monoclinic *P*-1 space group, with Z = 1, using direct methods. All non-hydrogen atoms were refined anisotropically with hydrogen atoms generated as spheres riding the coordinates of their parent atoms. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0825$ ($F > 2\sigma F$) and $wR_2 = 0.2534$ (all data) with GOF = 1.116.

Modeling of electron density within the voids of the frameworks did not lead to identification of guest entities in Sr-SBBA structure due to the disordered contents of the pores in the frameworks. As is a common strategy for improving x-ray data, increasing the exposure time of the crystal to x-rays did not improve the quality of the high angle data in these cases, as the intensity from low angle data saturated the detector and minimal improvement in the high angle data was achieved. The only optimal crystals suitable for analysis were generally small and weakly diffracting, and unfortunately, larger crystals, which would usually improve the quality of the data, presented a lowered degree of crystallinity and attempts to optimize the crystal growing conditions for large high-quality specimens has not yet been fruitful. Electron density within void spaces, which could not be assigned to any definite guest entity, was modeled as highly disordered DMF molecules and isolated oxygen and carbon atoms, and the foremost errors in all the models lies with assignment of guest electron density. To prove the correctness of the atomic positions in the framework the application of the SQUEEZE routine of A. Spek had been performed. The SQUEEZE structure is devoid of any solvent entity, and matches well with the elemental analysis value of the evacuated Sr-SBBA sample. We have provided the squeezed structure of Sr-SBBA. The formate anion (O8,C44,O7), symmetry generated DMF (O12,C18,C19), disordered DMF (O13,C41,

C42, C43,N5) and (C20,C21,C39) were kept isotropic. Except these all atoms were made anisotropic and the Ortep diagram is provided with 50% probability.

Ba-SBBA (TRICLINIC)

• •

Experimental and Refinement Details for Ba-SBBA

A colorless rod shaped crystal ($0.3 \times 0.2 \times 0.2 \text{ mm}^3$) of **Ba-SBBA** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo K α radiation ($\lambda = 0.71073$ Å) at 296(2) K. A total of 12609 reflections were collected of which 8752 were unique. The range of θ was from 1.71 to 24.99. Analysis of the data showed negligible decay during collection. The structure was solved in the triclinic *P*-1 space group, with Z = 2, using direct methods. All non-hydrogen atoms were refined anisotropically with hydrogen atoms generated as spheres riding the coordinates of their parent atoms. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0557$ ($F > 2\sigma F$) and $wR_2 = 0.1413$ (all data) with GOF = 1.074.

Parameters	Ca-SBBA [1]	Ba-SBBA [2]	Sr-SBBA [3]
Empirical formula	C ₂₃ H ₂₉ Ca N ₃ O ₉ S	C ₄₈ H ₅₆ Ba ₂ N ₄ O ₁₆ S ₂	C80 H76 Sr5N8 O36 S4
Formula weight	563.633	1283.77	2291.87
Temperature	296(2)K	296(2)K	293(2)K
Wavelength	1.54184Å	0.71073Å	1.54184Å
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P 2_1/c$	P 1	P 1
Unit cell dimensions	$a = 8.7220(3)\text{\AA}$ $b = 27.5302(8)\text{\AA}$ $c = 11.2194(3) \text{\AA}$	a = 13.985(2) Å b = 14.614(3) Å c = 16.700(3) Å	a = 13.9492(9) Å b = 15.6692(13) Å c = 15.9071(13) Å
Volume	2572.31(13) Å ³	2784.1(9) Å ³	2871.2(5) Å ³
Ζ	4	2	1
Density (calculated)	1.455/m ³	1.531 /m ³	1.326 /m ³
Absorption coefficient	3.361	1.548	4.247
F(000)	1184	1288	1154
Crystal size	$0.30 \times 0.20 \times 0.10 \text{ mm}^3$	$0.30 \times 0.20 \times 0.20 \text{ mm}^3$	$0.28\times0.16\times0.08~mm^3$
Reflections collected	4407	12609	19525
Independent reflections	3315	8752	8511
Completeness (to theta)	95 %(67.70)	98 %(27.56)	94.8 % (73.36)
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Goodness-of-fit on F ²	1.028	1.074	1.116
Final R indices [I>2sigma(I)]	$R_1 = 0.0386, WR_2 = 0.0936$	$R_1 = 0.0557, wR_2 = 0.1273$	$R_1 = 0.0825, WR_2 = 0.2336$
R indices (all data)	$R_1 = 0.0591, WR_2 = 0.1045$	$R_1 = 0.0837, WR_2 = 0.1413$	$R_1 = 0.0990, WR_2 = 0.2534$

Table S1: Crystal data and structure refinement for all the MOFs:

Ortep Figures of all three MOFs:

Ortep Figure of Ca-SBBA:



Figure S13: Ortep Drawing of the assymetric unit of Ca-SBBA. Thermal ellipsoids set to 50% probability level.

Ortep Figure of Ba-SBBA:

• •



Figure S14: Ortep Drawing of the assymetric unit of Ba-SBBA. Thermal ellipsoids set to 50% probability level.

Ortep Figure of Sr-SBBA:

• •



Figure S15: Ortep Drawing of the assymetric unit of Sr-SBBA. Thermal ellipsoids set to 50% probability level.

Packing Diagram of all three MOFs:

Packing Diagram of Ca-SBBA:



Figure S16: a) Coordination sites of SBBA in Ca-SBBA along crystallographic *b* axis.b) Polyhedral representation of the coordinated chain of Ca atoms. c) Formation of sheet like structure of Ca-SBBA through bridging Ca-Chains via SBBA ligands.



Figure S17: Packing diagram of Ca-SBBA along crystallographic *a* axis.



Packing Diagram of Sr-SBBA:

Figure S18: a) Coordination environment of Sr in Sr-SBBA. b) Polyhedral representation of the pentanuclear Sr structure linked through SBBA ligand. c) Ball and stick representation of the Sr-SBBA chains along crystallographic *b* axis.



Packing Diagram of Ba-SBBA:

Figure S19: a) Coordination environment of Ba in Ba-SBBA. b) Polyhedral representation of the Ba chains linked via SBBA ligand to form the spirane like structure. c) Ball and stick representation of the Ba-SBBA spranes arranged along crystallographic *b* axis.

Section S4. PXRD patterns of all three MOFs

PXRD pattern of Ca-SBBA:



Figure S20: Comparison of simulated (bottom) and experimental (top) PXRD pattern of **Ca-SBBA** showing considerable bulk purity of the crystalline phase.

PXRD pattern of Sr-SBBA:



Figure S21: Comparison of simulated (bottom) and experimental (top) PXRD pattern of **Sr-SBBA** showing considerable bulk purity of the crystalline phase.

PXRD pattern of Ba-SBBA:



Figure S22: Comparison of simulated (bottom) and experimental (top) PXRD patterns of Ba-SBBA showing considerable bulk purity of the crystalline phase.

Solvent stability of Ca-SBBA, Sr-SBBA and Ba-SBBA under different solvents

Solvent stability of Ca-SBBA:



Figure S23: Powder XRD patterns of the solvent treated samples of Ca-SBBA with respect to each other and comparison with simulated ones.

Solvent stability of Sr-SBBA:



Figure S24: Powder XRD patterns of the solvent treated samples of Sr-SBBA with respect to each other and comparison with simulated ones.





Figure S25: Powder XRD patterns of the humidified samples of Ca-SBBA at definite time interval (e.g. 24h, 48h) and comparison with simulated and as-synthesized ones.



Figure S26: Powder XRD patterns of the humidified samples of Sr-SBBA at definite time interval (e.g. 24h, 48h) and comparison with simulated and as-synthesized ones.



Figure S27: Powder XRD patterns of the humidified samples of Ba-SBBA after 24h showing amorphous nature due to collapse of the network architecture.



Figure S28: Powder XRD patterns of the Ca-SBBA before and after proton conductivity experiment and comparison with simulated ones reveal that Ca-SBBA maintain its architectural rigidity during proton conductivity experiment.



Figure S29: Powder XRD patterns of the Sr-SBBA before and after proton conductivity experiment and comparison with simulated ones reveal that Ca-SBBA maintain its architectural rigidity during proton conductivity experiment.



Variable temperature Powder XRD (VTPXRD) of Ca-SBBA:

Figure S30: Variable temperature Powder XRD patterns of Ca-SBBA from 25 °C to 500°C showing irreversible phase change at higher temperatures (above 100 °C).



Variable temperature Powder XRD (VTPXRD) of Sr-SBBA:

Figure S31: Variable temperature Powder XRD patterns of Sr-SBBA from 25 °C to 500°C showing irreversible phase change at higher temperatures (above 100 °C).



Variable temperature Powder XRD (VTPXRD) of Ba-SBBA:

Figure S32: Variable temperature Powder XRD patterns of Ba-SBBA from 25 °C to 500°C showing irreversible phase change at higher temperatures (above 100 °C).

Section S5. Thermal stability of Ca-SBBA, Sr-SBBA and Ba-SBBA with Thermo Gravimetric Analysis (TGA) data



TGA data for Ca-SBBA:

Figure S33: Thermal Gravimetric Analysis curve for Ca-SBBA showing the thermal stability of the framework upto 500 °C.

TGA data for Sr-SBBA:



Figure S34: Thermal Gravimetric Analysis curve for Sr-SBBA showing the thermal stability of the framework upto 500 °C.

TGA data for Ba-SBBA:



Figure S35: Thermal Gravimetric Analysis curve for Ba-SBBA showing the thermal stability of the framework upto 500 °C.





Figure S36: Thermal Gravimetric Analysis curve for humidified Ca-SBBA in comparison with as-synthesized one reveals the water content of the Ca-SBBA and lower weight loss in case of humidified sample as high molecular weight DMF molecules are being replaced by low molecular weight water molecules. However, both these frameworks exhibit identical thermal stability of the Ca-SBBA upto 500 °C.



Figure S37: Thermal Gravimetric Analysis curve for humidified Sr-SBBA in comparison with as-synthesized one reveals the water content of the Sr-SBBA and lower weight loss in case of humidified sample as high molecular weight DMF molecules are being replaced by low molecular weight water molecules. However, both these frameworks exhibit identical thermal stability of the Sr-SBBA upto 500 °C.

Differential Scanning Calorimetry (DSC) data:





Figure S38: DSC data for Ca-SBBA showing endothermic peak at ~120 °C correspond to phase change.

DSC of Sr-SBBA:



Figure S39: DSC data for Sr-SBBA showing endothermic peak at ~120 °C correspond to phase change.

DSC of Ba-SBBA:



Figure S40: DSC data for Ba-SBBA showing endothermic peak at ~90 °C correspond to phase change.

Section S6. Proton conductivity measurement of all the MOFs:

Proton Conductivities were measured using Solartron 1287 Electrochemical Interface with 1255B frequency response analyzer via quasi-four-probe method. ~120mg of assynthesized samples were pressed in a pellet maker to obtain uniform pellets of 0.37-0.38 mm, which was subject to humidification for 24h and subsequently measured the proton conductivity. Resistances were measured from the semicircle of the Nyquist plots. Proton conductivity was measured by the following equation; $\sigma = L/(R.A)$ where $\sigma =$ proton conductivity, L = thickness of the pellet, R = resistance of the pellet and A = area of the pellet = $4\pi r^2$ where r = radius of the pellet.

For high-temperature proton conductivity measurements, the pellets were inserted within a humidification chamber, which was encircled with a controlled heating coil attached with an automated temperature controller. The heat flow within the temperature controller was controlled by a dimerstat accordingly. The temperature of the chamber was measured by an infrared temperature sensor attachment, having a sensing accuracy of ± 0.5 °C.

For low-temperature proton conductivity measurements, the pellets were inserted within a humidification chamber, which was encircled with a water circulation coil attached with a chiller integrated with an automated temperature controller. The heat flow within the chamber was controlled by the chiller accordingly. The temperature of the chamber was measured by an infrared temperature sensor attachment, having a sensing accuracy of ± 0.5 °C.

Proton Conductivity of Ca-SBBA at ambient temperature:



Figure S41: Nyquist plot of Ca-SBBA at 298 K (room temperature) showing proton conductivity value of 8.58×10^{-6} S cm⁻¹.



Proton Conductivity of Ca-SBBA at elevated temperatures:

Figure S42: Nyquist plot of Ca-SBBA at 299 K showing proton conductivity value of 8.38×10^{-6} S cm⁻¹.



Figure S43: Nyquist plot of Ca-SBBA at 307 K showing proton conductivity value of 6.85×10^{-6} S cm⁻¹.



Figure S44: Nyquist plot of Ca-SBBA at 309 K showing proton conductivity value of 6.51×10^{-6} S cm⁻¹.



Figure S45: Nyquist plot of Ca-SBBA at 311K showing proton conductivity value of 5.99×10^{-6} S cm⁻¹.



Figure S46: Nyquist plot of Ca-SBBA at 313K showing proton conductivity value of 5.54×10^{-6} S cm⁻¹.



Figure S47: Nyquist plot of Ca-SBBA at 316 K showing proton conductivity value of 5.01×10^{-6} S cm⁻¹.



Figure S48: Nyquist plot of Ca-SBBA at 318 K showing proton conductivity value of 4.73×10^{-6} S cm⁻¹.



Figure S49: Nyquist plot of Ca-SBBA at elevated temperatures showing decreasing trend of proton conductivity values.

Proton Conductivity of Ca-SBBA at lower temperatures:



Figure S50: Nyquist plot of Ca-SBBA at 297 K showing proton conductivity value of 8.27×10^{-6} S cm⁻¹.



Figure S51: Nyquist plot of Ca-SBBA at 293 K showing proton conductivity value of 7.45×10^{-6} S cm⁻¹.



Figure S52: Nyquist plot of Ca-SBBA at 291 K showing proton conductivity value of 7.09×10^{-6} S cm⁻¹.



Figure S53: Nyquist plot of Ca-SBBA at 290 K showing proton conductivity value of 6.89×10^{-6} S cm⁻¹.



Figure S54: Nyquist plot of Ca-SBBA at 289 K showing proton conductivity value of 6.77×10^{-6} S cm⁻¹.



Figure S55: Nyquist plot of Ca-SBBA at 287 K showing proton conductivity value of 6.21×10^{-6} S cm⁻¹.



Figure S56: Nyquist plot of Ca-SBBA at lower temperatures showing decreasing trend of proton conductivity values.



Figure S57: Arrhenius plot of Ca-SBBA showing activation energy value of 0.23 eV. Least square fitting had been applied while calculating the slope.

Graphical representation of Proton Conductivity as a function of temperature in Ca-SBBA:



Figure S58: Proton conductivity as a function of temperature in case of Ca-SBBA which shows that proton conductivity increases upto 25 °C and then decreases and shows zero conductivity above 45 °C.

Proton Conductivity data for Sr-SBBA:



Proton conductivity of Sr-SBBA at ambient temperature:

Figure S59: Nyquist plot of Sr-SBBA at 298 K showing proton conductivity value of 4.4×10^{-5} S cm⁻¹ under 98% relative humidity.

Proton Conductivity at elevated temperatures:



Figure S60: Nyquist plot of Sr-SBBA at 300 K showing proton conductivity value of 3.44×10^{-5} S cm⁻¹ under 98% relative humidity.



Figure S61: Nyquist plot of Sr-SBBA at 303 K showing proton conductivity value of 2.49×10^{-5} S cm⁻¹ under 98% relative humidity.



Figure S62: Nyquist plot of Sr-SBBA at 306 K showing proton conductivity value of 1.98×10^{-5} S cm⁻¹ under 98% relative humidity.



Figure S63: Nyquist plot of Sr-SBBA at 309 K showing proton conductivity value of 1.57×10^{-5} S cm⁻¹ under 98% relative humidity.



Figure S64: Nyquist plot of Sr-SBBA at 311 K showing proton conductivity value of 1.39×10^{-5} S cm⁻¹ under 98% relative humidity.



Figure S65: Nyquist plot of Sr-SBBA at 313 K showing proton conductivity value of 1.20×10^{-5} S cm⁻¹ under 98% relative humidity.



Figure S66: Nyquist plot of Sr-SBBA at elevated temperatures showing decreasing trend of proton conductivity values.



Proton Conductivity of Sr-SBBA at lower temperatures:

Figure S67: Nyquist plot of Sr-SBBA at 296 K showing proton conductivity value of 3.52×10^{-5} S cm⁻¹ under 98% relative humidity.



Figure S68: Nyquist plot of Sr-SBBA at 295 K showing proton conductivity value of 3.19×10^{-5} S cm⁻¹ under 98% relative humidity.



Figure S69: Nyquist plot of Sr-SBBA at 293 K showing proton conductivity value of 2.68×10^{-5} S cm⁻¹ under 98% relative humidity.



Figure S70: Nyquist plot of Sr-SBBA at 291 K showing proton conductivity value of 2.33×10^{-5} S cm⁻¹ under 98% relative humidity.



Figure S71: Nyquist plot of Sr-SBBA at 289 K showing proton conductivity value of 2.11×10^{-5} S cm⁻¹ under 98% relative humidity.



Figure S72: Nyquist plot of Sr-SBBA at 287 K showing proton conductivity value of 1.91×10^{-5} S cm⁻¹ under 98% relative humidity.



Figure S73: Nyquist plot of Sr-SBBA at lower temperatures showing decreasing trend of proton conductivity values.



Figure S74: Arrhenius plot of Sr-SBBA showing activation energy value of 0.56 eV. Least square fitting had been applied while calculating the slope.

Graphical representation of Proton Conductivity as a function of temperature in Sr-SBBA:



Figure S75: Proton conductivity as a function of temperature in case of Sr-SBBA which shows that proton conductivity increases upto 25 $^{\circ}$ C and then decreases and shows zero conductivity above 40 $^{\circ}$ C.

SL.	MOFs and CPs	Proton	Ea value	Conditions	Reference
No.		conductivity	(eV)		
		(S cm ⁻¹)			
1	$(NH_4)_2(adp)[Zn_2(ox)_3]$ ·	8×10^{-3}	0.63	25 °C and	J. Am. Chem. Soc.,
	3H ₂ O			98% RH	2009 , 131, 9906
2	1D Ferrous Oxalate	1.3×10^{-3}	0.37	25 °C and	J. Am. Chem. Soc.,
	Dihydrate			98% RH	2009, 131, 3144.
3	$(NH_4)_4[MnCr_2(ox)_6]_3$	1.1×10^{-3}	0.23	25 °C and	J. Am. Chem. Soc.,
	4H ₂ O.			98% RH	2011, 133, 15328.
4	Cucurbit[6]uril (CB[6])	1.1×10^{-3}	0.39	25 °C and	Angew. Chem. Int. Ed.
				98% RH	2011, 50, 7870.
5	(b-PCMOF2(Tz) _{0.45})	5×10^{-4}	0.51	150°C	Nat. Chem. 2009, 1,
					705.
6	Mg ₂ (dobdc) ₃ .0.35LiOiP	3.1×10^{-4}	0.14	27 °C	J. Am. Chem. Soc.,
	r ₃ . 0.25LiBF ₄ . EC3.				2011, 133, 14522.
	DEC				
7	{NH(prol)3}[MIICrIII(1×10^{-4}		25 °C and	J. Am. Chem. Soc.,
	ox)3] (MII) =MnII,			75% RH	2009, 131, 13516
	FeII, CoII)				
8	$(H_5C_2)_2(dtoa)$ Cu	1×10^{-4}		25 °C and	Bull. Chem. Soc. Jpn.
				80% RH	2010, 83, 42
9	$[Zn(l-L_{Cl})(Cl)](H_2O)_2$	4.45×10^{-5}	0.34	28 °C and	J. Am. Chem. Soc.,
				98% RH	2011, 133, 17950.
10	Sr-SBBA	4.4×10^{-5}	0.56	25 °C and	This Work
				98% RH	
11	PCMOF-3	3.5×10^{-5}	0.17	25 °C and	J. Am. Chem. Soc.
				98% RH	2010, 132, 14055.
12	Ca-SBBA	8.58×10^{-6}	0.23	25 °C and	This Work
				98% RH	
13	[M IL-53(Fe)-	2.0×10^{-6}	0.21	25 °C and	J. Am. Chem. Soc
	(COOH) ₂]			98% RH	2011, <i>133</i> , 2034.

Table S2: Comparison of proton conductivity of Ca-SBBA and Sr-SBBA with other MOFs:

Effect of MOF integrity and particle size on proton conduction:

The MOF integrity plays a vital role in proton conductivity. To study this effect, we have prepared the pellet with same amount of ligand (SBBA) and encountered no conductivity. Hence, we can say that MOF architecture plays a vital role in systematic arrangement of ligands in definite fashion with solvent molecule to aid proton conductivity. Also, while making pellet no distribution of particle size was observed, but conductivity values remain comparable.



Figure S76: Schematic representation of proton conductivity as a function of MOF integrity as the ligand alone fail to show proton conduction.

Table S3: Comparison of proton conductivity as a function withtemperature with reported Proton Conducting MOFs:

Sr.No.	Proton Conducting MOF	Temperature Range	Value at high temperature (Scm ⁻¹)	Reference
1.	Ferrous Oxalate dehydrate	25-45 °C		J. Am. Chem. Soc., 2009, 131, 3144.
2.	(NH ₄) ₂ (adp)[Zn ₂ (ox) ₃] • 3H ₂ O	25-34 °C		J. Am. Chem. Soc., 2009 , 131, 9906
3.	MIL-53	25-80 °C	3.6 x 10 ⁻⁷	J. Am. Chem. Soc, 2011, 133, 2034.
4.	[Zn(l-L _{Cl})(Cl)](H ₂ O) ₂	25-34 °C		J. Am. Chem. Soc., 2011, 133, 17950.
5.	PCMOF-3	25-40 °C		J. Am. Chem. Soc., 2010, 132, 14055.
6.	Ca-SBBA	25-45 °C	4.7 x 10 ⁻⁶	This Work
7.	Sr-SBBA	25-40 °C	1.2 x 10 ⁻⁵	This Work