# Correlation between Coordinated Water Content and Proton Conductivity in Ca-BTC-based Metal-Organic Frameworks

(Supporting Information: 31 pages)

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#### Section S1. Synthesis of Ca-BTC-MOFs Materials:

All reagents were commercially available and used as received. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PANalytical diffractometer for Cu K<sub> $\alpha$ </sub> radiation ( $\lambda = 1.5406$  Å), with a scan speed of 2° min<sup>-1</sup> and a step size of 0.02° in 20. Fourier transform infrared (FT-IR) spectra were taken on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 6004000 cm<sup>-1</sup> region or using a Diamond ATR (Golden Gate). Thermo-gravimetric' analyses (TGA) were carried out on a TG50 analyzer (Mettler-Toledo) or a SDT Q600 TG-DTA analyzer under N<sub>2</sub> atmosphere at a heating rate of 10 °C min<sup>-1</sup> within a temperature range of 20-800 °C. Leica M-80 optical microscope with hot stage and camera attachment was used for collecting photographs. Proton conductivity data were measured in a quasi-two-probe method, with a Solartron 1286 Electrochemical Interface with frequency response analyzer.

**Ca-BTC-H<sub>2</sub>O:** A mixture of 1,3,5-benzenetricarboxylic acid ( $C_9H_6O_6,H_3$ , BTC, 0.042 g, 0.2 mmol), Ca(OAc)<sub>2</sub> (0.0316 g, 0.2 mmol), H<sub>2</sub>O (3.0 mL), and Ethanol (EtOH, 1.0 mL) was stirred for 20 min at room temperature in a 15 ml vial to form a homogeneous solution. The vial was capped and kept in oven at 90 °C for 24 h. After this time, colourless needle like crystals were obtained, which were filtered off using Whatmann filter paper and washed thoroughly with 99.9 % as received EtOH. The so-obtained MOF [Ca<sub>2</sub>(BTC)(H<sub>2</sub>O)·H<sub>2</sub>O] (41.8 mg, 81% yield) was dried at RT under air atmosphere (60 min). **FT-IR (4000-600 cm<sup>-1</sup>):** 3216 (m, br), 1670 (m), 1616 (m), 1550 (s), 1450 (m), 1381 (s), 1297 (w), 1244 (m), 1170 (w), 1085 (m), 1043 (w), 900 (w), 773 (m), 740 (m), 683 (m); elemental analysis calcd (%) for activated sample (C<sub>9</sub>H<sub>9</sub>O<sub>8</sub>Ca): C, 25.24; H, 3.16; found: C, 24.79; H, 3.29.

**Ca-BTC-DMF:** A mixture of 1,3,5-benzenetricarboxylic acid ( $C_9H_6O_6,H_3$ , BTC, 0.021 g, 0.1 mmol),  $Ca(NO_3)_2 \cdot 4H_2O$  (0.0708 g, 0.3 mmol), DMF (5.0 mL), and water ( $H_2O$ , 1.0 mL) was stirred for 20 min at room temperature in a 15 ml vial to form a homogeneous solution. The vial was capped and kept in oven at 85 °C for 48 h. After this time, colourless plate like crystals were obtained, which were filtered off using filter paper and washed thoroughly with 99.9% as received EtOH. The so-obtained MOF [ $Ca(BTC)_2(DMF)_2(H_2O)_2 \cdot 3H_2O$ ] (67.55mg, 57% yield) was dried at RT under air atmosphere (60 min). **FT-IR (4000-600 cm<sup>-1</sup>):** 3304 (m, br), 2305 (w),1608 (s), 1548 (s), 1421 (s), 1356 (s), 1200 (w), 1100 (m), 932 (w), 758 (m), 711 (s);

elemental analysis calcd (%) for activated sample (C<sub>10</sub>H<sub>4</sub>N<sub>3</sub>O<sub>5</sub>Ca): C, 40.24; H, 1.96; N, 21.82; found: C, 39.20; H, 1.99; N, 22.24.

**Ca-BTC-DMA:** A mixture of 1,3,5-benzenetricarboxylic acid ( $C_9H_6O_6,H_3$ , BTC, 0.063 g, 0.3 mmol), Ca(OAc)<sub>2</sub> (0.0158 g, 0.1 mmol), DMA (2.0 mL), and water (H<sub>2</sub>O, 0.5 mL) was stirred for 10 min at room temperature in a 5 ml vial to form a homogeneous solution. The vial was capped and kept in oven at 90 °C for 24 h. After this time, colourless plate like crystals were obtained, which were filtered off using filter paper and washed thoroughly with 99.9% as received EtOH. The so-obtained MOF [Ca<sub>2</sub>(BTC)(DMA)(H<sub>2</sub>O)] (18.85 mg, 76% yield) was dried at RT under air atmosphere (60 min). **FT-IR (4000-600 cm<sup>-1</sup>):** 3425 (m, br), 1615 (s), 1555 (s), 1434 (s), 1681 (s), 1247 (w), 1106 (m), 1026 (m), 938 (w), 824 (w), 764 (s), 725 (s); elemental analysis calcd (%) for activated sample (C<sub>26</sub> H<sub>28</sub> N<sub>2</sub> O<sub>16</sub>Ca<sub>3</sub>): C, 41.89; H, 3.75; N, 3.76; found: C, 41.91; H, 3.58; N, 3.57.

**Ca-BTC-DMSO:** A mixture of 1,3,5-benzenetricarboxylic acid ( $C_9H_6O_6,H_3$ , BTC, 0.063 g, 0.3 mmol), Ca(OAc)<sub>2</sub> (0.0158 g, 0.1 mmol), DMSO (2.0 mL), and water (H<sub>2</sub>O, 0.5 mL) was stirred for 10 min at room temperature in a 5 ml vial to form a homogeneous solution. The vial was capped and kept in oven at 90 °C for 24 h. After this time, colourless plate like crystals were obtained, which were filtered off using filter paper and washed thoroughly with 99.9% as received EtOH. The so-obtained MOF [Ca<sub>2</sub>(BTC)(H<sub>2</sub>O)(DMSO)·DMSO] (22.07 mg, 75% yield) was dried at RT under air atmosphere (60 min). **FT-IR (4000-600 cm<sup>-1</sup>):** 3424 (m, br), 1615 (s), 1555 (s), 1428 (s), 1368 (s), 1207 (w), 1100 (m), 1006 (s), 946 (s), 772 (s),0, 718 (s), 628 (w); elemental analysis calcd (%) for activated sample (C<sub>10</sub>H<sub>4</sub>N<sub>3</sub>O<sub>5</sub>Ca): C, 35.60; H, 3.82; S, 10.82; found: C, 35.43; H, 3.75; S, 9.53.

**Ca-BTC:** A mixture of 1,3,5-benzenetricarboxylic acid ( $C_9H_6O_6,H_3$ , BTC, 0.063 g, 0.3 mmol), CaCl<sub>2</sub> (0.0111 g, 0.1 mmol), DMF (2.0 mL) was stirred for 10 min at room temperature in a 5 ml vial to form a homogeneous solution. The vial was capped and kept in oven at 90 °C for 24 h. After this time, colourless polyhedral crystals were obtained, which were filtered off using filter paper and washed thoroughly with 99.9% as received EtOH. The so-obtained MOF [Ca(BTC)] (16.15 mg, 70% yield) was dried at RT under air atmosphere (60 min). **FT-IR (4000-600 cm<sup>-1</sup>):** 1616 (s), 1553 (s), 1435 (s), 1680 (s), 1250 (w), 1107 (m), 1016 (m), 941 (w), 820 (w), 764 (s), 725 (s); elemental analysis calcd (%) for activated sample ( $C_6$  H<sub>2</sub> Ca O<sub>4</sub>): C, 40.39; H, 1.25; found: C, 40.04; H, 1.18.

## Section S2. IR Spectroscopy of all the MOFs under different condition.

Fourier transform infrared (FT-IR) spectra confirmed the presence of carboxylate groups in the coordination sphere of the metal and suggest that the carboxylic groups of BTC are deprotonated in the MOFs materials. In this regard, BTC ligand shows the C=O stretching frequency of free aromatic carboxylic acid at ca. 1690 cm<sup>-1</sup>. When the carboxylic acid coordinates to the metal atoms, C=O stretching frequency shifted to lower frequencies (ca. 1550 cm<sup>-1</sup>), which is clearly observed in Ca-BTC-MOFs.



**Figure S1:** FT-IR spectra patterns of BTC ligand (black) Ca-BTC-H<sub>2</sub>O (magenta), Ca-BTC-DMF (red), Ca-BTC-DMA (cyan), Ca-BTC-DMSO (blue) and Ca-BTC (green).

#### Section S3. Single crystal X-ray diffraction data refinement procedures

Data was collected on a Super Nova Dual source X-ray Diffractometer system (Agilent Technologies) equipped with a CCD area detector and operated at 250 W power (50 kV, 0.8 mA) to generate Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å). 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. CrysAlis<sup>Pro</sup> program software was used suite to carry out overlapping  $\varphi$  and  $\omega$  scans at detector ( $2\theta$ ) settings ( $2\theta = 28$ ). Following data collection, reflections were sampled from all regions of the Ewald sphere to redetermine unit cell parameters for data integration. 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 CrysAlis<sup>Pro</sup> software with a narrow frame algorithm. Data were subsequently corrected for absorption by the program SCALE3 ABSPACK<sup>1</sup> scaling algorithm.

These structures were solved by direct method and refined using the SHELXTL  $97^2$  software suite. Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. Final model was refined anisotropically (if the number of data permitted) until full convergence was achieved. Hydrogen atoms were placed in calculated positions (C-H = 0.93 Å) and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U<sub>eq</sub> of the attached C atoms. In some cases modeling of electron density within the voids of the frameworks did not lead to identification of recognizable solvent molecules in these structures, probably due to the highly disordered contents of the large pores in the frameworks. Highly porous crystals that contain solvent-filled pores often yield raw data where observed strong (high intensity) scattering becomes limited to ~1.0 Å at best, with higher resolution data present at low intensity. 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 this case, as the intensity from low angle data saturated the detector and minimal improvement in the high angle data was achieved. Additionally, diffused scattering from the highly disordered solvent within the void spaces of the framework and from the capillary to mount the crystal

contributes to the background and the 'washing out' of the weaker data. The only optimal crystals suitable for analysis were generally small and weakly diffracting. 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 have not yet been fruitful. Data were collected at 190(2) K for the MOF presented in this paper. This lower temperature was considered to be optimal for obtaining the best data. Electron density within void spaces has not been assigned to any guest entity but has been modeled as isolated oxygen and/or carbon atoms. The foremost errors in all the models are thought to lie in the assignment of guest electron density. The structure was examined using the Adsym subroutine of PLATON<sup>3</sup> to assure that no additional symmetry could be applied to the models. The ellipsoids in ORTEP diagrams are displayed at the 50% probability level unless noted otherwise. For all structures we note that elevated R-values are commonly encountered in MOF crystallography for the reasons expressed above by us and by other research groups.<sup>4-13</sup> Crystallographic data (excluding structure factors) for the structures are reported in this paper have been deposited with the CCDC as deposition No. CCDC 885042 - 885046. 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@ccdc.cam.ac.uk].

1. CrysAlisPro, Version 1.171.33.66; Oxford Diffraction Ltd.: Abingdon, U.K., 2010.

2. G. M. Sheldrick, (1997). SHELXS '97 and SHELXL '97. University of Göttingen, Germany.

3. A. L. Spek (2005) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.

4. L. A. Dakin, P. C. Ong, J. S. Panek, R. J. Staples, and P. Stavropoulos, Organometallics, 2000, **19**, 2896.

5. S. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka, and M. Yamashita, J. Am. Chem. Soc. 2002, **124**, 2568.

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6. M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O'Keeffe, and O. M. Yaghi, Proc. Natl. Acad. Sci. USA, 2002, **99**, 4900.

7. R. A. Heintz, H. Zhao, X. Ouyang, G. Grandinetti, J. Cowen, and K. R. Dunbar, Inorg. Chem. 1999, **38**, 144.

8. K. Biradha, Y. Hongo, and M. Fujita, Angew. Chem. Int. Ed. 2000, **39**, 3843.

9. P. Grosshans, A. Jouaiti, M. W. Hosseini, and N. Kyritsakas, New J. Chem, (Nouv. J. Chim,) 2003, **27**, 793.

N. Takeda, K. Umemoto, K. Yamaguchi, and M. Fujita, Nature (London) 1999, **398**,
794.

11. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, and O. M. Yaghi, Science, 2002, **295**, 469.

12. B. Kesanli, Y. Cui, M. R. Smith, E. W. Bittner, B. C. Bockrath, and W. Lin, Angew. Chem. Int. Ed. 2005, 44, 72.

13. F. A. Cotton, C. Lin, and C. A. Murillo, Inorg. Chem. 2001, 40, 478.

## **Ca-BTC-DMA (MONOCLINIC)**

## **Experimental and Refinement Details for Ca-BTC-DMA**

A white block like crystal  $(0.25 \times 0.19 \times 0.15 \text{ mm}^3)$  of **Ca-BTC-DMA** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a Super Nova Dual source X-ray Diffractometer system (Agilent Technologies) equipped with a CCD area detector and operated at 250 W power (50 kV, 0.8 mA) to generate Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å) at 190(2) K in a liquid N<sub>2</sub> cooled stream of nitrogen. A total of 3737 reflections were collected of which 3207 were unique. The range of  $\theta$  was from 1.85 to 28.92. Analysis of the data showed negligible decay during collection. The structure was solved in the monoclinic *C 2/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  $R_1 = 0.0742$  ( $F > 2\sigma F$ ) and  $wR_2 = 0.1651$  (all data) with GOF = 1.597.



**Figure S2:** Ortep Drawing of the assymetric unit of Ca-BTC-DMA. Thermal ellipsoids set to 50% probability level.

# Table S1. Crystal data and structure refinement for Ca-BTC-DMA

Empirical formula	C26 H28 Ca3 N2 O16
Formula weight	744.74
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>C 2/c</i>
	$a = 16.552(7) \text{ Å} \alpha = 90^{\circ}$
Unit cell dimensions	$b = 10.961(5)$ Å $\beta = 111.514(7)^{\circ}$
	$c = 18.691(11) \text{ Å} \gamma = 90^{\circ}$
Volume	3155(3)
Z	4
Density (calculated)	1.568
Absorption coefficient	0.602
F(000)	1544
Crystal size	$0.25 \times 0.19 \times 0.15 \text{ mm}^3$
Theta range for data collection	1.85–28.92
Index ranges	$-21 \le h \le 21$ , $-14 \le k \le 13$ , $-23 \le 1 \le 24$
<b>Reflections collected</b>	3737
Independent reflections	3207
Completeness to theta = 26.02°	98 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3696 / 0 / 216
Goodness-of-fit on F <sup>2</sup>	1.597
Final R indices [I>2sigma(I)]	$R_1 = 0.0742, wR_2 = 0.1613$
R indices (all data)	$R_1 = 0.0869, wR_2 = 0.1651$
Largest diff. peak and hole	0.768 and -0.787 e.Å <sup>-3</sup>

## **Ca-BTC-DMSO (MONOCLINIC)**

## **Experimental and Refinement Details for Ca-BTC-DMSO**

A white block like crystal ( $0.31 \times 0.23 \times 0.14 \text{ mm}^3$ ) of **Ca-BTC-DMSO** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a Super Nova Dual source X-ray Diffractometer system (Agilent Technologies) equipped with a CCD area detector and operated at 250 W power (50 kV, 0.8 mA) to generate Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å) at 190(2) K in a liquid N<sub>2</sub> cooled stream of nitrogen. A total of 5252 reflections were collected of which 3542 were unique. The range of  $\theta$  was from 1.85 to 29.07. Analysis of the data showed negligible decay during collection. The structure was solved in the monoclinic *C 2/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  $R_1 = 0.0809$  ( $F > 2\sigma F$ ) and  $wR_2 = 0.2522$  (all data) with GOF = 1.139.



**Figure S3:** Ortep Drawing of the assymetric unit of Ca-BTC-DMSO. Thermal ellipsoids set to 50% probability level.

# Table S1. Crystal data and structure refinement for Ca-BTC-DMSO

Empirical formula	C24 H28 Ca3 O18 S4
Formula weight	852.98
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>C 2/c</i>
	$a = 15.547(3) \text{ Å} \alpha = 90^{\circ}$
Unit cell dimensions	$b = 13.6128(19) \text{ Å} \beta = 101.88(2)^{\circ}$
	$c = 18.981(4) \text{ Å} \gamma = 90^{\circ}$
Volume	3931.0(12)
Z	4
Density (calculated)	1.441
Absorption coefficient	0.700
F(000)	1760
Crystal size	$0.31 \times 0.23 \times 0.14 \text{ mm}^3$
Theta range for data collection	1.85–29.07
Index ranges	$-20 \le h \le 17, -17 \le k \le 15, -25 \le l \le 25$
<b>Reflections collected</b>	5252
Independent reflections	3542
Completeness to theta = 26.02°	99.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4502 / 0 / 220
Goodness-of-fit on F <sup>2</sup>	1.139
Final R indices [I>2sigma(I)]	$R_1 = 0.0809, wR_2 = 0.2320$
R indices (all data)	$R_1 = 0.0976, wR_2 = 0.2522$
Largest diff. peak and hole	1.929 and -1.866 e.Å <sup>-3</sup>

## **Ca-BTC (TRIGONAL)**

## **Experimental and Refinement Details for Ca-BTC**

A white block like crystal  $(0.21 \times 0.19 \times 0.15 \text{ mm}^3)$  of **Ca-BTC** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a Super Nova Dual source X-ray Diffractometer system (Agilent Technologies) equipped with a CCD area detector and operated at 250 W power (50 kV, 0.8 mA) to generate Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å) at 190(2) K in a liquid N<sub>2</sub> cooled stream of nitrogen. A total of 795 reflections were collected of which 580 were unique. The range of  $\theta$  was from 1.85 to 28.92. Analysis of the data showed negligible decay during collection. The structure was solved in the trigonal *R* -3 space group, with *Z* = 9, 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  $R_1 = 0.0375$  ( $F > 2\sigma F$ ) and  $wR_2 = 0.0874$  (all data) with GOF = 1.139.



**Figure S4:** Ortep Drawing of the assymetric unit of Ca-BTC. Thermal ellipsoids set to 50% probability level.

# Table S1. Crystal data and structure refinement for Ca-BTC

Empirical formula	C6 H2 Ca O4
Formula weight	178.16
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	R -3
	$a = 8.9636(3) \text{ Å} \alpha = 90^{\circ}$
Unit cell dimensions	$b = 8.9636(3) \text{ Å} \beta = 90^{\circ}$
	$c = 19.2832(11) \text{ Å} \gamma = 120^{\circ}$
Volume	1341.76(10)
Z	9
Density (calculated)	1.984
Absorption coefficient	1.000
F(000)	810
Crystal size	$0.21 \times 0.19 \times 0.15 \text{ mm}^3$
Theta range for data collection	1.85–28.92
Index ranges	$-12 \le h \le 7$ , $-10 \le k \le 12$ , $-26 \le l \le 13$
<b>Reflections collected</b>	795
Independent reflections	580
Completeness to theta = 26.02°	99.8 %
Absorption correction	Semi-empirical from equivalents
<b>Refinement method</b>	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	795 / 0 / 51
Goodness-of-fit on F <sup>2</sup>	1.139
Final R indices [I>2sigma(I)]	$R_1 = 0.0375, wR_2 = 0.0874$
R indices (all data)	$R_1 = 0.0468, wR_2 = 0.0953$
Largest diff. peak and hole	0.410 and -0.417 e.Å <sup>-3</sup>

## Ca-BTC-H<sub>2</sub>O-348 K (TRICLINIC)

### Experimental and Refinement Details for Ca-BTC-H<sub>2</sub>O

A white block like crystal  $(0.31 \times 0.25 \times 0.14 \text{ mm}^3)$  of **Ca-BTC-H<sub>2</sub>O** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a Super Nova Dual source X-ray Diffractometer system (Agilent Technologies) equipped with a CCD area detector and operated at 250 W power (50 kV, 0.8 mA) to generate Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å) at 348(2) K in a liquid N<sub>2</sub> cooled stream of nitrogen. A total of 2980 reflections were collected of which 2100 were unique. The range of  $\theta$  was from 1.85 to 29.24. Analysis of the data showed negligible decay during collection. The structure was solved in the triclinic *P* -*I*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  $R_1 = 0.0410$  ( $F \ge 2\sigma F$ ) and  $wR_2 = 0.1072$  (all data) with GOF = 1.079.



**Figure S5:** Ortep Drawing of the assymetric unit of Ca-BTC-H<sub>2</sub>O. Thermal ellipsoids set to 50% probability level.

# Table S1. Crystal data and structure refinement for Ca-BTC-H<sub>2</sub>O (348 K)

Empirical formula	C9 H6 Ca O7
Formula weight	266.22
Temperature	348(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
	$a = 6.8656(11) \text{ Å} \alpha = 101.341(13)^{\circ}$
Unit cell dimensions	$b = 9.1287(16) \text{ Å} \beta = 99.683(12)^{\circ}$
	$c = 9.9209(14) \text{ Å} \gamma = 111.950(16)^{\circ}$
Volume	545.11(18)
Z	2
Density (calculated)	1.622
Absorption coefficient	0.596
F(000)	272
Crystal size	$0.31 \times 0.25 \times 0.14 \text{ mm}^3$
Theta range for data collection	1.85–29.24
Index ranges	$-9 \le h \le 9$ , $-11 \le k \le 12$ , $-13 \le l \le 13$
Reflections collected	2980
Independent reflections	2100
Completeness to theta = 26.02°	100 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2493 / 0 / 156
Goodness-of-fit on F <sup>2</sup>	1.079
Final R indices [I>2sigma(I)]	$R_1 = 0.0410$ , $wR_2 = 0.0983$
R indices (all data)	$R_1 = 0.0502, wR_2 = 0.1072$
Largest diff. peak and hole	0.342 and -0.312 e.Å <sup>-3</sup>

# Ca-BTC-DMF-313 K (MONOCLINIC)

## **Experimental and Refinement Details for Ca-BTC-DMF**

A white block like crystal ( $0.32 \times 0.25 \times 0.18 \text{ mm}^3$ ) of **Ca-BTC-DMF** was placed in 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a Super Nova Dual source X-ray Diffractometer system (Agilent Technologies) equipped with a CCD area detector and operated at 250 W power (50 kV, 0.8 mA) to generate Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å) at 348(2) K in a liquid N<sub>2</sub> cooled stream of nitrogen. A total of 8481 reflections were collected of which 5946 were unique. The range of  $\theta$  was from 1.85 to 8.08. Analysis of the data showed negligible decay during collection. The structure was solved in the triclinic *P* -*I* 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  $R_1 = 0.0610$  ( $F > 2\sigma F$ ) and  $wR_2 = 0.1728$  (all data) with GOF = 1.062.



**Figure S6:** Ortep Drawing of the assymetric unit of Ca-BTC-DMF. Thermal ellipsoids set to 50% probability level.

# Table S1. Crystal data and structure refinement for Ca-BTC-DMF (313 K)

Empirical formula	C54 H30 Ca6 N6 O31
Formula weight	1499.32
Temperature	313(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	С 2
	$a = 16.2817(3)$ Å $\alpha = 90^{\circ}$
Unit cell dimensions	$b = 13.5141(3)$ Å $\beta = 93.2540(18)^{\circ}$
	$c = 15.7591(3) \text{ Å} \gamma = 90^{\circ}$
Volume	3461.92(12)
Z	4
Density (calculated)	1.438
Absorption coefficient	0.549
F(000)	1528
Crystal size	$0.32 \times 0.25 \times 0.18 \text{ mm}^3$
Theta range for data collection	1.85–28.08
Index ranges	$-10 \le h \le 21$ , $-16 \le k \le 17$ , $-20 \le l \le 20$
Reflections collected	8481
Independent reflections	5946
Completeness to theta = 26.02°	96.7 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6352 / 1 / 384
Goodness-of-fit on F <sup>2</sup>	1.062
Final R indices [I>2sigma(I)]	$R_1 = 0.0610$ , $wR_2 = 0.1671$
R indices (all data)	$R_1 = 0.0647, wR_2 = 0.1728$
Largest diff. peak and hole	0.979 and $-0.973 \text{ e.Å}^{-3}$

#### Section S4. Single crystal structure of Ca-BTC-based-MOFs

**Crystal structure of [Ca-BTC-DMA] Ca<sub>2</sub>(BTC)(DMA)(H<sub>2</sub>O):** The asymmetric unit of Ca-BTC-DMA (space group C 2/c) consists of two crystallographycally independent Ca(II) centers, one BTC ligand, one DMA, one coordinated- H<sub>2</sub>O molecule. The first Ca(II) site is coordinated to four BTC carboxylate oxygens and two DMA oxygen atoms. On the other hand the second Ca(II) center is coordinated to six BTC carboxylate oxygen atoms and one coordinated H<sub>2</sub>O molecule. Ca-BTC-DMA contains 1D channel along the crystallographic c axis and the coordinated DMA solvents are facing towards the channel (figure 2c).



**Figure S7:** a) Coordination environment of Ca in the SBU of Ca-BTC-DMA. b) Coordination mode of solvents in asymmetric unit. c) Packing diagram showing the 3D arrangement of the Ca-BTC-DMA along crystallographic *c* axis.

**Crystal Structure of [Ca-BTC-DMSO] Ca<sub>2</sub>(BTC)(H<sub>2</sub>O)(DMSO)·DMSO:** X-ray single crystal diffraction reveals That Ca-BTC-DMSO crystallizes in space group C2/c and it has structural determination by a three dimensional network of Ca(II) linked by 1,3,5-benzenetricarboxylate ligands. The asymmetric unit of Ca-BTC-DMSO consists of only two crystallographycally independent Ca(II) centers, one BTC ligand, one DMSO, one coordinated- H<sub>2</sub>O molecule and one lattice DMSO molecule. The first Ca(II) site is coordinated to four BTC carboxylate oxygen atoms, two DMSO oxygen atoms. Whereas the second Ca(II) center is coordinated to six BTC carboxylate oxygen atoms, one DMSO oxygen atom and one oxygen atom of the coordinated H<sub>2</sub>O molecule. Ca-BTC-DMSO contains 1D channel along the crystallographic c axis.



**Figure S8:** a) Coordination environment of Ca in the SBU of Ca-BTC-DMSO. b) Coordination mode of solvents in asymmetric unit. c) Packing diagram showing the 3D arrangement of the Ca-BTC-DMSO along crystallographic *c* axis.

**Crystal Structure of [Ca-BTC] Ca<sub>2</sub>(BTC)<sub>3</sub>:** The Ca-BTC crystallizes in space group *R-3* and structural determination by x-ray single crystal diffraction reveals a three dimensional network of Ca(II) linked by 1,3,5-benzenetricarboxylate ligands. The asymmetric unit of Ca-BTC consists of only two crystallographycally independent Ca(II) centers and one BTC ligand. The first Ca(II) site is octahedrally coordinated to six BTC carboxylate oxygen atoms in which three  $\mu^2$  type and three  $\mu^1$  type oxygen. The second Ca(II) center is also octahedrally coordinated to six BTC carboxylate oxygen. The Ca-BTC is nonporous and there are no solvent molecules coordinated to the metal centers.



**Figure S9:** a) Coordination of BTC with Ca in the SBU of Ca-BTC. b) Coordination mode of Ca(II) in the asymmetric unit. c) Packing diagram showing the 3D arrangement of the Ca-BTC along crystallographic *a* axis.

**Crystal Structure of Ca-BTC-H<sub>2</sub>O [Ca(BTC)·H<sub>2</sub>O]:** Ca-BTC-H<sub>2</sub>O was first reported by M. J. Platers *et al.* The asymmetric unit of Ca-BTC-H<sub>2</sub>O (space group *P*-1) consist of one crystallographically independent Ca(II) centre, one BTC, one coordinated and one lattice H<sub>2</sub>O molecule. In the framework each Ca(II) is coordinated by eight oxygens of which seven arise from interaction of Ca with five distinct carboxylate anions. Three BTC anions act as monodentate ligands whereas the other two BTC anions coordinate in a bidentate fashion. One lattice H<sub>2</sub>O molecule completes the coordination sphere of Ca(II) metal centre. The Ca-BTC-H<sub>2</sub>O contains 1D channel along crystallographic *a* axis with coordinated H<sub>2</sub>O molecules that facing the channel. The channel contains one dimensional array of lattice H<sub>2</sub>O molecules which are strongly hydrogen bonded with the coordinated H<sub>2</sub>O molecules and oxygen atom of carboxylate group. Here the hydrogen bonding is continuous through the channel.



**Figure S10:** a) Coordination environment of Ca in the SBU of Ca-BTC-H<sub>2</sub>O. b) Coordination mode of solvents in asymmetric unit. c) Packing diagram showing the 3D arrangement of the Ca-BTC-H<sub>2</sub>O along crystallographic *a* axis.

**Crystal Structure of [Ca-BTC-DMF] Ca(BTC)<sub>2</sub>(DMF)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>·3H<sub>2</sub>O:** The crystal structure of Ca-BTC-DMF was reported by P. C. Liang *et al.* Ca-BTC-DMF contains three crystallographically independent Ca(II) centers in the asymmetric unit. The first Ca(II) center [Ca1] is eight coordinated to oxygen atoms from four BTC ligands, one H<sub>2</sub>O and one DMF, whereas second and third Ca(II) centers are seven coordinated to oxygen atoms from BTC, H<sub>2</sub>O and DMF molecules. CaO<sub>8</sub> and CaO<sub>7</sub> edge shared polyhedrons are connected in helical fashion along crystallographic *c* axis to form a chain. These helical chains are further bridged through BTC ligand to form a 3D framework. Ca-BTC-DMF contains 1D channel along crystallographic *c* axis and the DMF molecules pointing towards the channel. There is three lattice H<sub>2</sub>O molecules, first one is hydrogen bonded with the coordinated H<sub>2</sub>O molecules. Second H<sub>2</sub>O molecule is hydrogen bonded with the carboxylate oxygen atom and third H<sub>2</sub>O molecule is hydrogen bonded with the other two lattice H<sub>2</sub>O molecules. Here the hydrogen bonding is not continuous through the channel.



**Figure S11:** a) Coordination environment of Ca in the SBU of Ca-BTC-DMF. b) Coordination mode of solvents in asymmetric unit. c) Packing diagram showing the 3D arrangement of the Ca-BTC-DMF along crystallographic *c* axis.





**Figure S12:** Comparison of PXRD patterns of a) Ca-BTC-H<sub>2</sub>O (red) with the simulated pattern from the single-crystal structure (black) b) Ca-BTC-DMF (blue) with the simulated pattern from the single-crystal structure (red) c) Ca-BTC-DMA (red) with the simulated pattern from the single-crystal structure (black) d) Ca-BTC-H<sub>2</sub>O (black) with the simulated pattern from the single-crystal structure (red). e) Ca-BTC (red) with the simulated pattern from the single-crystal structure (red). e) Ca-BTC (red) with the simulated pattern from the single-crystal structure (black). f) Comparison of PXRD patterns of Ca-BTC-DMSO after water treatment (red) with the simulated pattern from the single-crystal structure (black).



Section S6. Thermal stability of the MOFs and the TGA data

**Figure S13:** TGA traces of Ca-BTC-H<sub>2</sub>O (red), Ca-BTC-DMF (green), Ca-BTC-DMA (cyan) and Ca-BTC-DMSO (blue).

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**Figure S14:** VTSCXRD of Ca-BTC-DMF showing loss of lattice water molecules after 308 K (35 °C).



Section S7. Proton conductivity measurement of all the MOFs.

**Figure S15:** Nyquist plot of Ca-BTC-H<sub>2</sub>O at lower temperatures showing decreasing trend of proton conductivity values.



**Figure S16**: Nyquist plot of Ca-BTC-H<sub>2</sub>O at elevated temperatures showing decreasing trend of proton conductivity values.



**Figure S17:** Nyquist plot of Ca-BTC-DMF at elevated temperatures showing decreasing trend of proton conductivity values.



**Figure S18:** Nyquist plot of Ca-BTC-DMF at elevated temperatures showing decreasing trend of proton conductivity values.



**Figure S19:** Nyquist plot of Ca-BTC-DMA at lower temperatures showing decreasing trend of proton conductivity values.



**Figure S20:** Nyquist plot of Ca-BTC-DMA at elevated temperatures showing decreasing trend of proton conductivity values.