Electronic Supplementary information

Self-assembled single-crystalline hydrogen-bonded frameworks: A potential metal-free molecule towards proton conductivity and electrochemical detection of organic and inorganic pollutants

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Table S1. Crystal data and structure refinement for 231097lt_auto.

Identification code	shelx	
Empirical formula	C42 H36 N10 O19	
Formula weight	984.81	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 3.79460(10) Å	a= 90°.
	b = 23.1642(4) Å	b= 94.7210(10)°.
	c = 22.7365(4) Å	g = 90°.
Volume	1991.73(7) $Å^3$	
Z	2	
Density (calculated)	1.642 Mg/m^3	
Absorption coefficient	1.135 mm^{-1}	
F(000)	1020	
Crystal size	0.180 x 0.060 x 0.050 mm^3	
Theta range for data collection	2.728 to 74.585°.	
Index ranges	-4<=h<=4, -27<=k<=28, -27<=l<=27	
Reflections collected	22566	
Independent reflections	3953 [R(int) = 0.0356]	
Completeness to theta = 67.684°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3953 / 342 / 440	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.1036	
R indices (all data)	R1 = 0.0440, wR2 = 0.1072	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.224 and -0.260 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 231097lt_auto. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1419(4)	6929(1)	5840(1)	23(1)
C(2)	531(4)	7022(1)	6412(1)	26(1)
C(3)	-1227(4)	7533(1)	6516(1)	28(1)
C(4)	-2050(4)	7922(1)	6062(1)	28(1)
C(5)	-1081(4)	7768(1)	5508(1)	26(1)
C(6)	4488(4)	5973(1)	6053(1)	25(1)
C(7)	6168(4)	5602(1)	5714(1)	25(1)
C(8)	4325(4)	6320(1)	5140(1)	23(1)
N(2)	3303(3)	6427(1)	5686(1)	22(1)
N(3)	6043(3)	5827(1)	5149(1)	25(1)
C(9)	-3362(8)	8673(1)	4962(2)	30(1)
C(10)	-3866(7)	8817(1)	4384(2)	32(1)
C(11)	-1677(9)	7943(1)	4419(1)	32(1)
N(4)	-1990(16)	8122(2)	4980(2)	26(1)
N(5)	-2825(7)	8357(1)	4058(1)	32(1)
C(39)	-2520(40)	7993(5)	4512(6)	31(1)
C(30)	-3660(30)	8494(6)	4213(5)	33(1)
C(31)	-2860(30)	8697(5)	5168(5)	31(1)
N(34)	-1960(70)	8126(8)	5100(6)	28(1)
N(35)	-3810(20)	8895(4)	4645(5)	34(1)
C(12)	9687(4)	5140(1)	2408(1)	24(1)
C(13)	9198(4)	5299(1)	2989(1)	24(1)
C(14)	9881(4)	5850(1)	3219(1)	24(1)
C(15)	11242(4)	6270(1)	2851(1)	24(1)
C(16)	11809(4)	6107(1)	2277(1)	24(1)
C(17)	11048(4)	5563(1)	2038(1)	24(1)
C(18)	8561(4)	4519(1)	2256(1)	29(1)
O(1)	8742(4)	4335(1)	1729(1)	46(1)
O(2)	7415(4)	4216(1)	2640(1)	37(1)
C(19)	8900(40)	5923(4)	3831(5)	29(1)
O(3)	8364(13)	6431(1)	4034(1)	49(1)

O(4)	8837(19)	5522(3)	4193(3)	31(1)
C(29)	8810(120)	5995(15)	3883(15)	26(2)
O(23)	8960(70)	5461(10)	4106(11)	29(3)
O(24)	6710(30)	6398(4)	3924(4)	34(2)
C(20)	12260(20)	6886(3)	2975(2)	26(1)
O(5)	11095(8)	7142(1)	3440(1)	32(1)
O(6)	14010(13)	7160(3)	2638(3)	29(1)
C(40)	12240(70)	6893(11)	3117(7)	24(2)
O(45)	12610(30)	6998(4)	3641(4)	38(2)
O(46)	13270(40)	7200(10)	2713(9)	31(2)
C(21)	11830(4)	5514(1)	1390(1)	30(1)
O(7)	11048(4)	5045(1)	1106(1)	51(1)
O(8)	13128(4)	5925(1)	1154(1)	40(1)
N(1)	630(3)	7287(1)	5390(1)	23(1)
O(29)	10990(160)	5105(12)	38(15)	69(5)
O(9)	13309(18)	5081(2)	-60(2)	72(2)
O(10)	-3646(4)	8258(1)	2874(1)	41(1)

Table S3. Bond lengths [Å] and angles [°] for 231097lt_auto.

C(1)-N(1)	1.3328(19)
C(1)-C(2)	1.387(2)
C(1)-N(2)	1.4245(19)
C(2)-C(3)	1.389(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.387(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.387(2)
C(4)-H(4)	0.9500
C(5)-N(34)	1.267(15)
C(5)-N(1)	1.329(2)
C(5)-N(4)	1.470(4)
C(6)-C(7)	1.348(2)
C(6)-N(2)	1.3916(19)
C(6)-H(6)	0.9500
C(7)-N(3)	1.3838(19)
C(7)-H(7)	0.9500
C(8)-N(3)	1.3143(19)
C(8)-N(2)	1.3532(18)
C(8)-H(8)	0.9500
N(3)-H(3A)	0.8800
C(9)-C(10)	1.355(3)
C(9)-N(4)	1.378(4)
C(9)-H(9)	0.9500
C(10)-N(5)	1.374(3)
C(10)-H(10)	0.9500
C(11)-N(5)	1.314(3)
C(11)-N(4)	1.355(4)
C(11)-H(11)	0.9500
N(5)-H(5A)	0.8800
C(39)-N(34)	1.371(13)
C(39)-C(30)	1.396(12)
C(39)-H(39)	0.9500
C(30)-N(35)	1.356(11)

C(30)-H(30)	0.9500
C(31)-N(35)	1.297(10)
C(31)-N(34)	1.378(15)
C(31)-H(31)	0.9500
N(35)-H(35)	0.8800
C(12)-C(13)	1.398(2)
C(12)-C(17)	1.417(2)
C(12)-C(18)	1.531(2)
C(13)-C(14)	1.394(2)
C(13)-H(13)	0.9500
C(14)-C(15)	1.409(2)
C(14)-C(19)	1.480(11)
C(14)-C(29)	1.63(3)
C(15)-C(16)	1.391(2)
C(15)-C(20)	1.501(8)
C(15)-C(40)	1.60(2)
C(16)-C(17)	1.394(2)
C(16)-H(16)	0.9500
C(17)-C(21)	1.531(2)
C(18)-O(2)	1.2286(19)
C(18)-O(1)	1.2788(19)
C(19)-O(4)	1.240(14)
C(19)-O(3)	1.287(10)
C(29)-O(24)	1.24(4)
C(29)-O(23)	1.34(5)
O(24)-H(24)	0.8400
C(20)-O(6)	1.229(9)
C(20)-O(5)	1.320(6)
O(5)-H(5)	0.8400
C(40)-O(45)	1.211(17)
C(40)-O(46)	1.25(3)
C(21)-O(8)	1.217(2)
C(21)-O(7)	1.285(2)
O(7)-H(7A)	0.8400
O(29)-O(29)#1	0.90(10)
O(29)-H(29O)	0.8000

O(29)-H(29P)	0.8000
O(9)-O(9)#2	1.344(13)
O(9)-H(9O)	0.8001
O(9)-H(9P)	0.8000
O(10)-H(10O)	0.8000
O(10)-H(10P)	0.8001

N(1)-C(1)-C(2)	124.58(14)
N(1)-C(1)-N(2)	113.87(13)
C(2)-C(1)-N(2)	121.54(14)
C(1)-C(2)-C(3)	116.69(15)
C(1)-C(2)-H(2)	121.7
C(3)-C(2)-H(2)	121.7
C(4)-C(3)-C(2)	120.60(14)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(5)-C(4)-C(3)	116.65(14)
C(5)-C(4)-H(4)	121.7
C(3)-C(4)-H(4)	121.7
N(34)-C(5)-N(1)	120.3(8)
N(34)-C(5)-C(4)	115.0(8)
N(1)-C(5)-C(4)	124.76(14)
N(1)-C(5)-N(4)	112.8(2)
C(4)-C(5)-N(4)	122.4(2)
C(7)-C(6)-N(2)	106.49(13)
C(7)-C(6)-H(6)	126.8
N(2)-C(6)-H(6)	126.8
C(6)-C(7)-N(3)	107.98(13)
C(6)-C(7)-H(7)	126.0
N(3)-C(7)-H(7)	126.0
N(3)-C(8)-N(2)	108.88(13)
N(3)-C(8)-H(8)	125.6
N(2)-C(8)-H(8)	125.6
C(8)-N(2)-C(6)	107.99(12)
C(8)-N(2)-C(1)	124.21(12)
C(6)-N(2)-C(1)	127.78(12)

C(8)-N(3)-C(7)	108.66(13)
C(8)-N(3)-H(3A)	125.7
C(7)-N(3)-H(3A)	125.7
C(10)-C(9)-N(4)	106.3(2)
C(10)-C(9)-H(9)	126.9
N(4)-C(9)-H(9)	126.9
C(9)-C(10)-N(5)	107.9(2)
C(9)-C(10)-H(10)	126.0
N(5)-C(10)-H(10)	126.0
N(5)-C(11)-N(4)	108.3(3)
N(5)-C(11)-H(11)	125.8
N(4)-C(11)-H(11)	125.8
C(11)-N(4)-C(9)	108.5(3)
C(11)-N(4)-C(5)	124.4(3)
C(9)-N(4)-C(5)	127.1(3)
C(11)-N(5)-C(10)	109.0(2)
C(11)-N(5)-H(5A)	125.5
C(10)-N(5)-H(5A)	125.5
N(34)-C(39)-C(30)	107.9(11)
N(34)-C(39)-H(39)	126.1
C(30)-C(39)-H(39)	126.1
N(35)-C(30)-C(39)	104.2(8)
N(35)-C(30)-H(30)	127.9
C(39)-C(30)-H(30)	127.9
N(35)-C(31)-N(34)	106.8(9)
N(35)-C(31)-H(31)	126.6
N(34)-C(31)-H(31)	126.6
C(5)-N(34)-C(39)	125.3(14)
C(5)-N(34)-C(31)	126.8(12)
C(39)-N(34)-C(31)	107.7(11)
C(31)-N(35)-C(30)	113.4(8)
C(31)-N(35)-H(35)	123.3
C(30)-N(35)-H(35)	123.3
C(13)-C(12)-C(17)	117.51(14)
C(13)-C(12)-C(18)	113.93(13)
C(17)-C(12)-C(18)	128.55(13)

C(14)-C(13)-C(12)	124.13(14)
C(14)-C(13)-H(13)	117.9
C(12)-C(13)-H(13)	117.9
C(13)-C(14)-C(15)	118.30(14)
C(13)-C(14)-C(19)	113.8(4)
C(15)-C(14)-C(19)	127.8(4)
C(13)-C(14)-C(29)	118.9(13)
C(15)-C(14)-C(29)	122.7(12)
C(16)-C(15)-C(14)	117.59(14)
C(16)-C(15)-C(20)	112.1(2)
C(14)-C(15)-C(20)	130.3(2)
C(16)-C(15)-C(40)	123.3(7)
C(14)-C(15)-C(40)	119.0(7)
C(15)-C(16)-C(17)	124.57(14)
C(15)-C(16)-H(16)	117.7
C(17)-C(16)-H(16)	117.7
C(16)-C(17)-C(12)	117.86(14)
C(16)-C(17)-C(21)	113.07(13)
C(12)-C(17)-C(21)	129.07(14)
O(2)-C(18)-O(1)	121.64(15)
O(2)-C(18)-C(12)	118.98(14)
O(1)-C(18)-C(12)	119.36(14)
O(4)-C(19)-O(3)	115.7(10)
O(4)-C(19)-C(14)	123.9(9)
O(3)-C(19)-C(14)	120.1(8)
O(24)-C(29)-O(23)	133(4)
O(24)-C(29)-C(14)	116(3)
O(23)-C(29)-C(14)	99(3)
C(29)-O(24)-H(24)	109.5
O(6)-C(20)-O(5)	120.1(6)
O(6)-C(20)-C(15)	121.2(5)
O(5)-C(20)-C(15)	118.7(5)
C(20)-O(5)-H(5)	109.5
O(45)-C(40)-O(46)	126(2)
O(45)-C(40)-C(15)	123.9(18)
O(46)-C(40)-C(15)	108.2(14)

O(8)-C(21)-O(7)	121.60(15)
O(8)-C(21)-C(17)	119.01(14)
O(7)-C(21)-C(17)	119.37(14)
C(21)-O(7)-H(7A)	109.5
C(5)-N(1)-C(1)	116.69(13)
O(29)#1-O(29)-H(29O)	21.0
O(29)#1-O(29)-H(29P)	116.5
H(29O)-O(29)-H(29P)	105.1
O(9)#2-O(9)-H(9O)	130.8
O(9)#2-O(9)-H(9P)	115.9
H(9O)-O(9)-H(9P)	105.1
H(10O)-O(10)-H(10P)	105.1

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z #2 -x+3,-y+1,-z

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for 231097lt_auto. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	23(1)	21(1)	24(1)	-2(1)	3(1)	-4(1)
C(2)	26(1)	29(1)	22(1)	-2(1)	2(1)	-4(1)
C(3)	26(1)	34(1)	25(1)	-8(1)	5(1)	-6(1)
C(4)	27(1)	25(1)	33(1)	-7(1)	5(1)	-1(1)
C(5)	26(1)	21(1)	30(1)	1(1)	4(1)	-3(1)
C(6)	29(1)	24(1)	23(1)	4(1)	4(1)	-3(1)
C(7)	28(1)	21(1)	27(1)	4(1)	3(1)	-2(1)
C(8)	25(1)	23(1)	19(1)	-1(1)	2(1)	-2(1)
N(2)	25(1)	21(1)	20(1)	0(1)	3(1)	-2(1)
N(3)	28(1)	25(1)	22(1)	-3(1)	4(1)	-1(1)
C(9)	43(1)	25(1)	22(2)	2(1)	5(1)	5(1)
C(10)	46(1)	29(1)	22(2)	3(1)	6(1)	6(1)
C(11)	42(2)	32(1)	22(1)	0(1)	8(1)	8(1)
N(4)	34(1)	24(1)	21(2)	4(1)	5(1)	2(1)
N(5)	47(1)	30(1)	21(1)	2(1)	8(1)	8(1)
C(39)	42(2)	29(2)	24(2)	0(2)	7(2)	7(2)
C(30)	47(2)	32(2)	22(2)	1(2)	6(2)	9(2)
C(31)	43(2)	27(2)	22(3)	4(2)	5(2)	6(2)
N(34)	38(2)	27(2)	20(3)	-2(2)	8(3)	4(2)
N(35)	49(2)	31(2)	22(2)	2(2)	5(2)	8(2)
C(12)	27(1)	22(1)	21(1)	0(1)	2(1)	1(1)
C(13)	30(1)	22(1)	21(1)	2(1)	2(1)	0(1)
C(14)	29(1)	23(1)	19(1)	1(1)	0(1)	2(1)
C(15)	26(1)	21(1)	24(1)	1(1)	1(1)	2(1)
C(16)	28(1)	23(1)	24(1)	3(1)	5(1)	0(1)
C(17)	28(1)	24(1)	21(1)	1(1)	4(1)	1(1)
C(18)	39(1)	24(1)	24(1)	-2(1)	6(1)	-3(1)
O(1)	81(1)	34(1)	26(1)	-10(1)	18(1)	-20(1)
O(2)	62(1)	26(1)	26(1)	-2(1)	14(1)	-9(1)
C(19)	46(2)	23(3)	18(2)	-6(2)	4(2)	-8(2)
O(3)	98(2)	25(1)	27(1)	-4(1)	24(2)	-1(2)

O(4)	47(1)	29(2)	20(2)	4(2)	12(1)	11(1)
C(29)	52(3)	22(4)	7(3)	-3(4)	12(3)	-4(4)
O(23)	57(5)	22(4)	11(4)	-8(3)	14(3)	-12(4)
O(24)	68(4)	22(3)	13(3)	-1(2)	7(3)	7(3)
C(20)	33(1)	23(1)	22(2)	-4(2)	4(2)	2(1)
O(5)	50(1)	22(1)	26(1)	-4(1)	11(1)	0(1)
O(6)	39(2)	23(1)	26(2)	0(1)	10(1)	-5(1)
C(40)	30(3)	21(3)	24(4)	-5(4)	11(4)	-4(3)
O(45)	45(4)	37(3)	33(3)	-9(3)	6(3)	-6(3)
O(46)	41(5)	26(4)	26(4)	-1(3)	10(4)	-9(4)
C(21)	38(1)	26(1)	25(1)	0(1)	8(1)	-1(1)
O(7)	91(1)	37(1)	28(1)	-7(1)	25(1)	-23(1)
O(8)	61(1)	33(1)	30(1)	1(1)	19(1)	-9(1)
N(1)	26(1)	22(1)	23(1)	0(1)	3(1)	-2(1)
O(29)	146(12)	37(9)	28(8)	0(8)	37(10)	2(10)
O(9)	144(6)	40(2)	38(2)	-5(2)	37(3)	-25(3)
O(10)	61(1)	23(1)	39(1)	1(1)	5(1)	2(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 231097lt_auto.

	x	y	z	U(eq)
H(2)	1097	6749	6718	31
H(3)	-1872	7617	6902	34
H(4)	-3219	8277	6127	34
H(6)	4173	5933	6461	30
H(7)	7249	5249	5842	30
H(8)	3873	6562	4805	27
H(3A)	6962	5666	4846	30
H(9)	-3856	8905	5290	36
H(10)	-4778	9173	4231	38
H(11)	-782	7580	4307	38
H(5A)	-2913	8343	3671	39
H(39)	-2199	7625	4340	38
H(30)	-4194	8543	3800	40
H(31)	-2797	8906	5528	37
H(35)	-4486	9254	4577	40
H(13)	8347	5015	3243	29
H(16)	12782	6387	2031	29
H(24)	5933	6506	3585	51
H(5)	10105	6898	3644	49
H(7A)	10208	4805	1334	77
H(29O)	9051	4983	74	103
H(29P)	12062	5055	352	103
H(9O)	12003	5254	136	108
H(9P)	12072	4858	-250	108
H(10O)	-4855	7974	2847	61
H(10P)	-4876	8512	2735	61

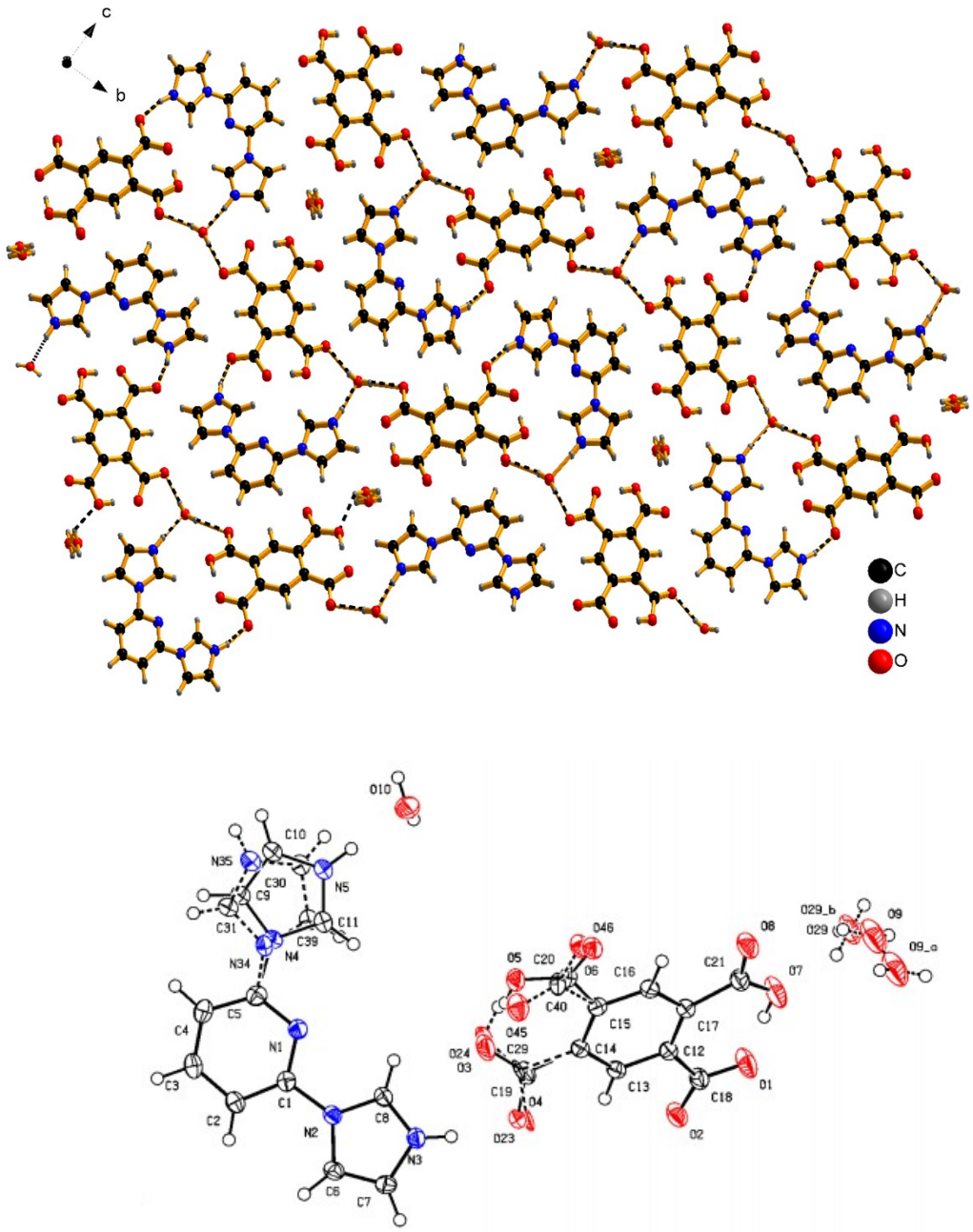

Figure S1. Stacked structure of BTC-bimPy@HOF Here, disordered water fills a narrow infinite pore approximately along the a-axis' (b) ORTEP diagram of BTC-bimpy@HOF

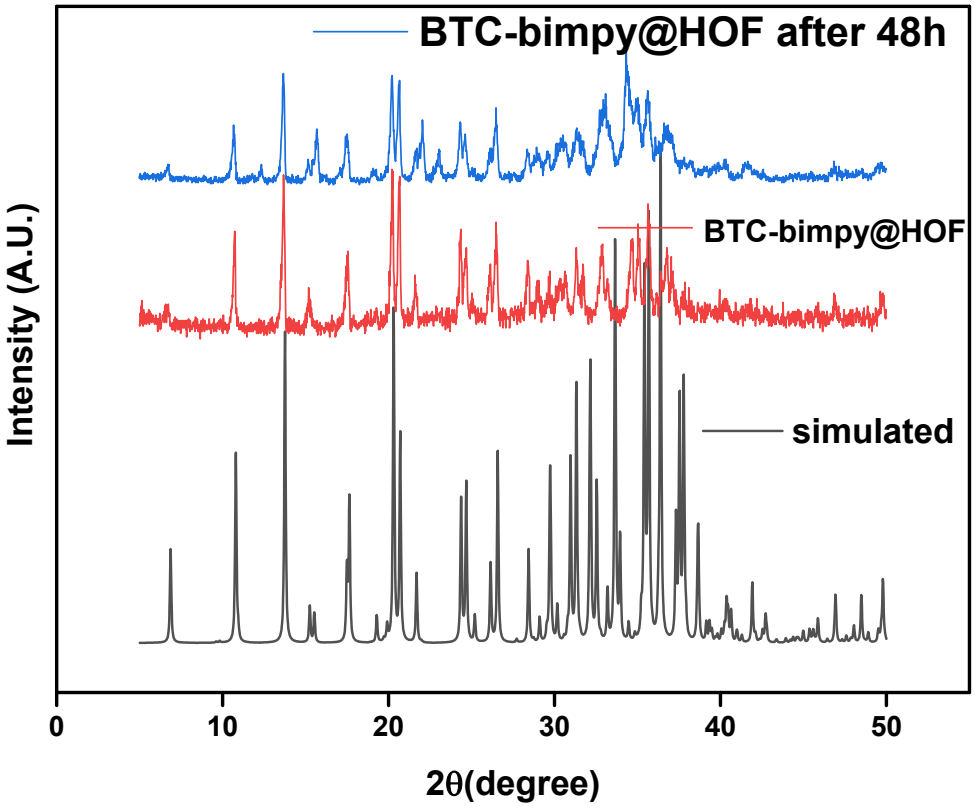

Figure S2: PXRD pattern for BTC-bimpy@HOF before and after recorded at 55 ºC at constant relative humidity of 98 % for 48 h.

Table S6. Proton Conductivity of HOF-1 at different temperature condition

Condition	Conductivity($S.cm^{-1}$)
40°C, 98%RH	$4.4x10^{-4}$
45°C, 98%RH	$5.9x10^{-4}$
50°C, 98%RH	$7.5x10^{-4}$
55°C, 98%RH	**$9.6x10^{-4}$ ($0.96x10^{-3}$)**
60°C, 98%RH	$5.1x10^{-4}$
65°C, 98%RH	$4.1x10^{-4}$
70°C, 98%RH	$3.3x10^{-4}$
75°C, 98%RH	$1.9x10^{-4}$