Supporting Information

Self-assembled multicomponent Pd_6 aggregates showing low-humidity proton conduction

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Experimental Section

General: *Cis*-(tmen)Pd$(NO_3)_2$ [tmen = N,N,N',N'-tetramethylethane-1,2-diamine][1], ditopic and tetratopic donors 1,4-di(pyridin-4-yl)benzene (dpb)[2], 1,2,4,5-tetrakis(1-imidazolyl)benzene (timb)[3] were prepared following the literature procedures. 1,2-di(pyridin-4-yl)ethane (dpe) was purchased from Sigma-Aldrich (USA) and used without further purification. The chemical shifts (δ) in the ^1H NMR spectra are accounted in ppm relative to proton resonance resulting from incomplete deuteration of the solvent D_2O at 4.79 ppm and spectra were recorded on a Bruker 400 MHz instrument. Electrospray ionization mass spectrometry (ESI-MS) experiments were carried out in Bruker Daltonics (Esquire 300 Plus ESI model) using standard spectroscopic grade solvents acetonitrile and methanol. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer. TGA analysis of **1** and **2** were performed on a Mettler-Toledo TGA-851^e thermobalance under a stream of nitrogen (flow rate = 50 mL min^{-1}) in the temperature range 30−600 °C (heating rate = 5°C min^{-1}) on alumina crucible of 70 μL volume and DSC was performed using a Mettler Toledo instrument at a heating rate of 10°C min^{-1} under dry N_2 atmosphere. Water adsorption isotherms of the assemblies **1** and **2** are recorded volumetrically using BELSORP-max apparatus (BEL Japan) after elimination of guest water molecules by evacuation at 120^{o}C over 12 h.

General procedure for the synthesis of aggregates (1 & 2): An aqueous yellow solution of *cis*-(tmen)Pd$(NO_3)_2$ was added into the solid mixture of 1,2,4,5-tetrakis(1-imidazolyl)benzene (timb) and linear dipyridyl donors (dpe or dpb) and the suspension was allowed to stir at room temperature. After 24 h the colourless solution was filtered, concentrated under reduced pressure and the product (**1** or **2**) was isolated in pure form after triturating with acetone.

Synthesis of 1: The aqueous solution of *cis*-(tmen)Pd$(NO_3)_2$ (150 mg, 0.433 mmol) was added into the solid mixture of 1,2,4,5-tetraimidazole benzene (timb) (49.4 mg, 0.144 mmol) and 1,2-di(pyridin-4-yl)ethane (26.6 mg, 0.144 mmol) to obtain molecular aggregate **1**. Isolated yield: 93 %. IR: υ (cm^{-1}) = 3415, 3120, 1618, 1533, 1470, 1323, 1123, 1071, 1039. ^{1}H NMR (400 MHz, D_2O): δ = 9.07 (s, 4H, $H_{imidazole}$-timb), 8.85 (s, 4H, $H_{imidazole}$-timb), 8.73 (s, 4H, $H_{imidazole}$-timb), 8.70 (s, 4H, $H_{imidazole}$-timb), 8.11 (s, 2H, H_{phenyl}-timb), 7.89 (s, 4H, $H_{imidazole}$-timb), 7.71 (s, 2H, H_{phenyl}-timb), 7.63 (s, 4H, $H_{imidazole}$-timb), 7.50 (s, 4H, H_α-dpe), 7.47 (s, 4H, H_α-dpe), 7.03 (s, 8H, H_β-dpe), 7.00 (s, 4H, H_β-dpe), 4.25 (s, 8H, H_{CH2}-dpe), 3.30-2.21 (m, 96H, $H_{CH3\ \&\ CH2}$-tmen). ESI-MS (m/z) = 719.8 $[\mathbf{1} - 4NO_3^-]^{4+}$, 460.2 $[\mathbf{1} - 6NO_3^-]^{6+}$, 386.1 $[\mathbf{1} - 7NO_3^-]^{7+}$.

Synthesis of 2: The aqueous solution of *cis*-(tmen)Pd$(NO_3)_2$ (150 mg, 0.433 mmol) was slowly added into a solid mixture of 1,4-di(pyridin-4-yl)benzene (dpb) (33.5 mg, 0.144 mmol) and 1,2,4,5-tetraimidazole benzene (49.4 mg, 0.144 mmol) to obtain aggregate **2**. Isolated yield: 85 %. IR: υ (cm^{-1}) = 3409, 3117, 1613, 1530, 1469, 1323, 1123, 1074, 1039. ^{1}H NMR (400 MHz, D_2O): δ = 9.20 (d, 4H, $H_{imidazole}$-timb), 9.01 (d, 4H, $H_{imidazole}$-timb), 8.82 (s, 4H, $H_{imidazole}$-timb), 8.66 (s, 4H, $H_{imidazole}$-timb), 8.20 (d, 4H, H-dpb), 8.14 (s, 2H, H_{phenyl}-timb), 8.10 (d, 4H, H-dpb), 7.95 (s, 8H, H-dpb), 7.61 (s, 2H, H_{phenyl}-timb), 7.52 (s, 4H, $H_{imidazole}$-timb), 6.89 (s, 4H, $H_{imidazole}$-

timb), 6.09 (s, 4H, H-dpb), 5.07 (s, 4H, H-dpb), 3.20-2.08 (m, 96H, $H_{CH3\ \&\ CH2}$-tmen). ESI-MS (m/z) = 585.1 [**2** - $5NO_3$)]$^{5+}$, 399.5 [**2** - $7NO_3$)]$^{7+}$.

X-Ray data collection and structure refinements. The diffraction data of **1** and **2** were collected on a Bruker SMART APEX CCD diffractometer using the SMART/SAINT software.[4] Intensity data were collected using graphite-monochromatic Mo-Kα radiation (0.7107 Å) at 100 K on a crystal as obtained after several attempts. The structures were solved by direct methods using the SHELX-2013[5] incorporated in WinGX.[6-8] Empirical absorption corrections were applied with SADABS.[9] All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients, $U(H) = 1.2U(C)$ or $1.5U$ (C-methyl), and their coordinates were allowed to ride on their respective carbons. The quality of the obtained X-ray data was poor due to the presence of large number of disordered solvent molecules and counter anions. For both the complexes (**1** and **2**), refinements were carried out constraining a few bond distances fixed using DFIX command and final refinements were performed with the modification of the structure factors for the electron densities of the solvent molecules and counter anions using SQUEEZE option of PLATON[10].

Table S1. Crystallographic data and refinement parameters of **1** and **2**

Complex	**1**	**2**
Formula	$C_{96}\ H_{233}\ N_{44}\ O_{78.5}\ Pd_6$	$C_{104}\ H_{230}\ N_{44}\ O_{77}\ Pd_6$
Formula weight	3898.54	3967.61
Crystal system	triclinic	monoclinic

Space group	$P\bar{1}$	$C2/c$
T, K	100	100
λ (Mo Kα), Å	0.71073	0.71073
a, Å	17.4691(17)	50.0277(19)
b, Å	21.0821(22)	11.5534(5)
c, Å	21.4283(22)	35.1453(14)
α, °	95.022(5)	90
β, °	91.544(4)	127.435(2)
γ, °	98.679(5)	90
V, Å^3	7764.9(14)	16129.9(12)
Z	2	4
$\rho_{calcd,}$ g cm^{-3}	1.667	1.634
μ, mm^{-1}	0.794	0.765
F(000)	4041.0	8205.0
GOF[a]	0.973	0.924
R1[b] [I > 2σ(I)]	0.0445 (19419)	0.594 (8341)
wR2[c] [I > 2σ(I)]	0.1151 (26909)	0.1536 (14208)

[a]GOF = $\{\Sigma\ [\ w(F_0^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n and p denotes the number of data points and the number of parameters, respectively. [b]R1 = (Σ IIF_0I - IF_c II)/Σ IF_0I; [c]wR2 = $\{\ \Sigma\ [\ w(F_0^2 - F_c^2)^2]/\Sigma[\ w(F_0^2)^2]\}^{1/2}$, where $w = 1/\ [\ \sigma^2(F_0^2) + (aP)^2 + (bP)]$ and $P = [\ \max\ (0,F_0^2) + 2F_c^2]/3$.

Table S2: Selected bonds distances (Å) and angles (deg) for **1** and **2**

1			
Pd(1)-N(1)	2.0564(32)	Pd(1)-N(2)	2.0601(35)
Pd(2)-N(3)	2.0284(58)	Pd(2)-N(4)	2.0559(41)
Pd(3)-N(5)	2.0601(38)	Pd(3)-N(6)	2.0599(36)
Pd(4)-N(7)	2.0436(39)	Pd(4)-N(8)	2.0426(36)
Pd(5)-N(9)	2.0454(38)	Pd(5-N(10)	2.0043(40)
Pd(6)-N(11)	2.0550(34)	Pd(6)-N(12)	2.0506(36)
Pd(1)-N(13)	2.0192(30)	Pd(2)-N(15)	2.0126(41)
Pd(6)-N(17)	2.0189(31)	Pd(5)-N(19)	2.0213(34)
Pd(3)-N(21)	2.0231(34)	Pd(4)-N(23)	2.0073(30)
Pd(5)-N(25)	2.0228(32)	Pd(6)-N(27)	2.0204(30)
Pd(4)-N(29)	2.0194(35)	Pd(1)-N(30)	2.0069(33)
Pd(2)-N(31)	2.0202(41)	Pd(3)-N(32)	2.0120(37)
N(1)-Pd(1)-N(2)	86.72(15)	N(1)-Pd(1)-N(13)	178.27(14)
N(1)-Pd(1)-N(30)	92.55(14)	N(2)-Pd(1)-N(13)	94.30(13)
N(2)-Pd(1)-N(30)	177.88(13)	N(13)-Pd(1)-N(30)	86.39(13)
N(3)-Pd(2)-N(4)	85.80(20)	N(3)-Pd(2)-N(15)	177.41(19)
N(3)-Pd(2)-N(31)	94.24(20)	N(4)-Pd(2)-N(15)	93.63(16)
N(4)-Pd(2)-N(31)	179.14(16)	N(15)-Pd(2)-N(31)	86.29(16)
N(5)-Pd(3)-N(6)	85.74(15)	N(5)-Pd(3)-N(21)	179.47(14)

N(5)-Pd(3)-N(32)	94.38(14)	N(6)-Pd(3)-N(21)	93.74(14)
N(6)-Pd(3)-N(32)	179.71(14)	N(21)-Pd(3)-N(32)	86.14(13)
N(7)-Pd(4)-N(8)	86.33(16)	N(7)-Pd(4)-N(23)	93.19(15)
N(7)-Pd(4)-N(29)	179.23(15)	N(8)-Pd(4)-N(23)	177.68(15)
N(8)-Pd(4)-N(29)	94.14(15)	N(23)-Pd(4)-N(29)	86.36(14)
N(9)-Pd(5)-N(10)	86.20(15)	N(9)-Pd(5)-N(19)	178.00(14)
N(9)-Pd(5)-N(25)	93.30(13)	N(10)-Pd(5)-N(19)	94.56(14)
N(10)-Pd(5)-N(25)	179.41(14)	N(19)-Pd(5)-N(25)	85.95(12)
N(11)-Pd(6)-N(12)	85.84(14)	N(11)-Pd(6)-N(17)	93.72(14)
N(11)-Pd(6)-N(27)	178.50(14)	N(12)-Pd(6)-N(17)	179.10(14)
N(12)-Pd(6)-N(27)	94.00(14)	N(17)-Pd(6)-N(27)	86.42(13)

2

Pd(1)-N(1)	2.071(5)	Pd(1)-N(2)	2.062(5)	Pd(2)-N(3)	2.069(5)
Pd(2)-N(4)	2.080(6)	Pd(3)-N(5)	2.039(5)	Pd(6)-N(6)	2.061(5)
Pd(1)-N(7)$^{\#}$	2.019(5)	Pd(2)-N(8)	2.033(5)	Pd(1)-N(9)	2.037(5)
N(11)-Pd(2)	2.037(5)	Pd(3)-N(13)	2.036(4)	Pd(3)-N(15)$^{\#}$	2.021(4)

N(7)$^{\#}$-Pd(1)-N(9)	84.9(2)	N(7)$^{\#}$-Pd(1)-N(2)	179.3(3)
N(9)-Pd(1)-N(2)	94.6(2)	N(7)$^{\#}$-Pd(1)-N(1)	94.5(2)
N(9)-Pd(1)-N(1)	178.1(2)	N(2)-Pd(1)-N(1)	85.9(2)
N(8)-Pd(2)-N(11)	85.96(19)	N(8)-Pd(2)-N(3)	178.4(2)
N(11)-Pd(2)-N(3)	95.3(2)	N(8)-Pd(2)-N(4)	92.7(2)
N(11)-Pd(2)-N(4)	178.4(2)	N(3)-Pd(2)-N(4)	86.0(2)

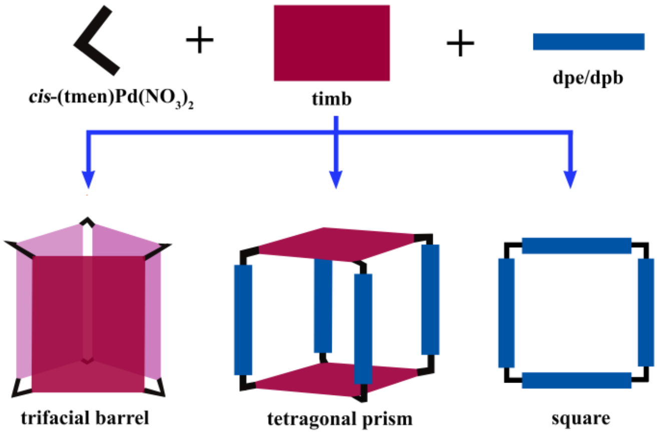
N(15)$^{\#}$-Pd(3)-N(13)	88.08(17)	N(15)$^{\#}$-Pd(3)-N(5)	93.0(2)
N(13)-Pd(3)-N(5)	178.76(19)	N(15)$^{\#}$-Pd(3)-N(6)	177.83(19)
N(13)-Pd(3)-N(6)	93.1(2)	N(5)-Pd(3)-N(6)	85.8(2)

$^{\#}$ Symmetry transformations used to generate equivalent atoms: -x+2, y, -z+5/2.

Impedance analysis. Ac impedance measurements were performed using Solartron SI 1287 Electrochemical Interface and 1255B Frequency Responce Analyser. Compacted pellets were made from powder samples by pressing at 5000 kg for 3 min using a standard 10 mm die. Then a pellet was humidified for 20 h and subjected to analysis for proton conduction over the frequency range of 1 MHz to 0.01 Hz. The resistance was calculated from Nyquist plot and conductivity σ (Scm^{-1}) was estimated as:

$$\sigma = L/(AR)$$

where L is the thickness of the pellet, area in contact with the electrodes is A and R is the real impedance.



Scheme S1. Possible molecular architectures from three-component self-assembly of *cis*-blocked 90^{o} Pd(II) acceptor, timb and linear donors.

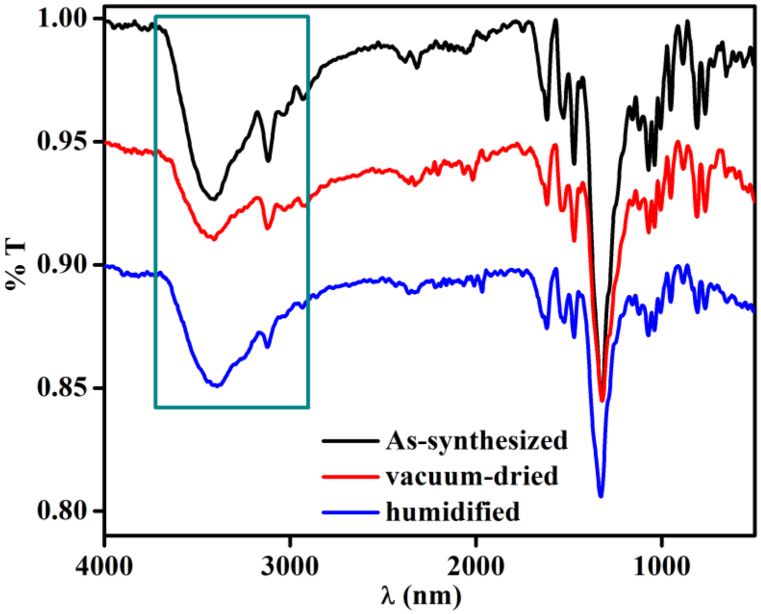


Fig.S1. IR spectra of complex **1** exhibiting hydration/dehydration character.

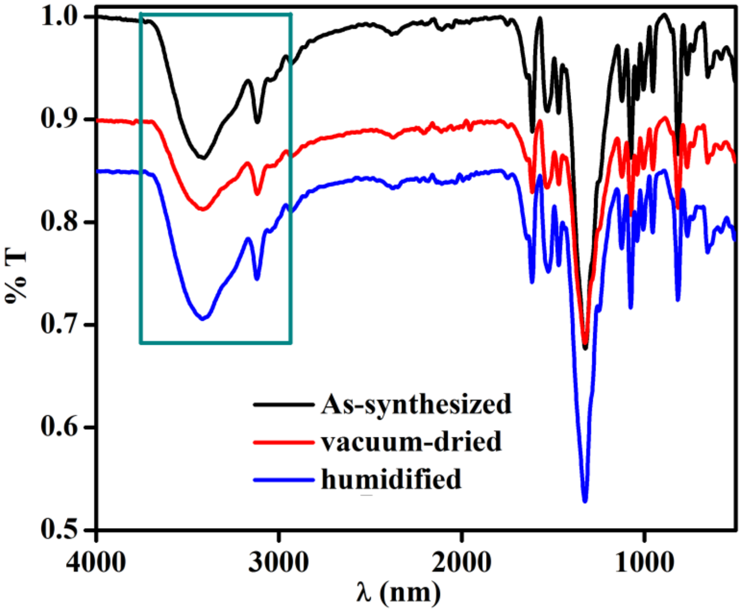
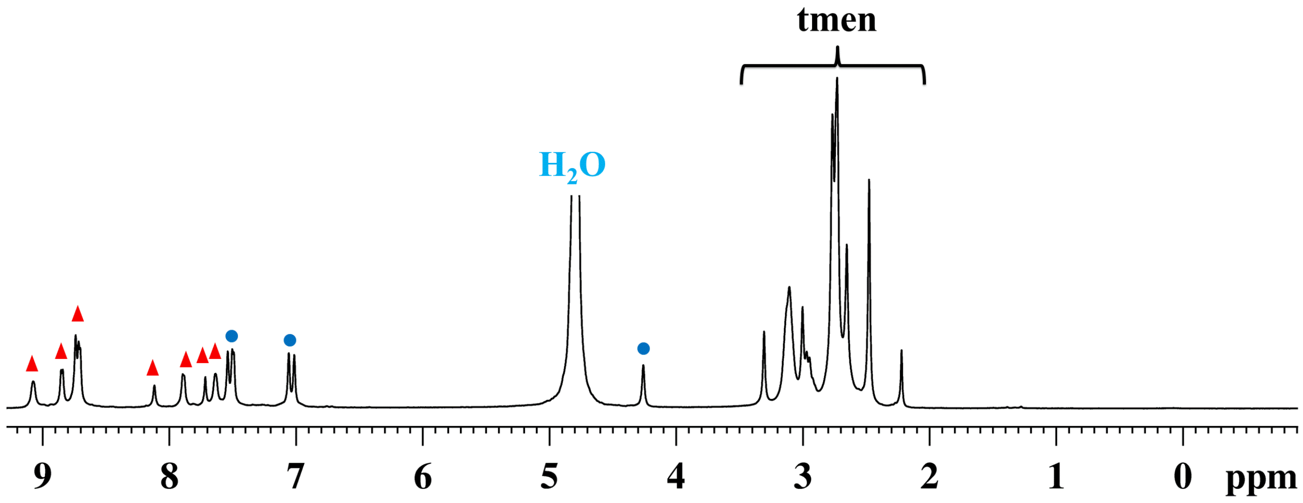


Fig.S2. IR spectra of the as-synthesized **2,** vacuum dried **2** and humidified sample**.**



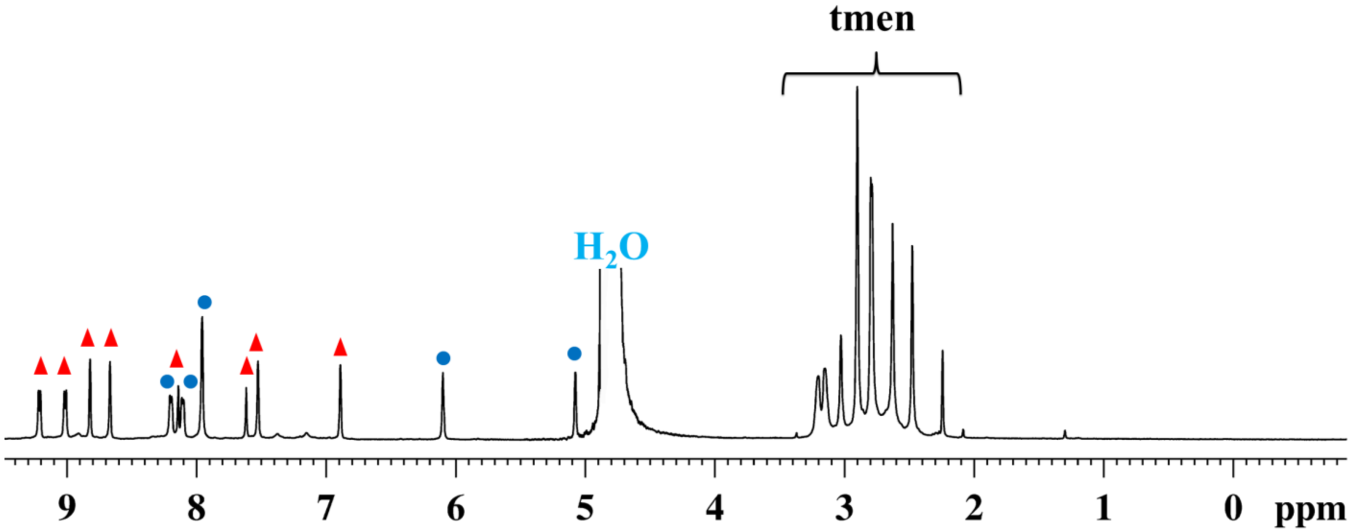


Fig.S3. ^{1}H NMR spectra of **1** (top) and **2** (bottom) recorded in D_2O. (Colour codes: red triangle = timb and, blue circle = dpe/dpb).

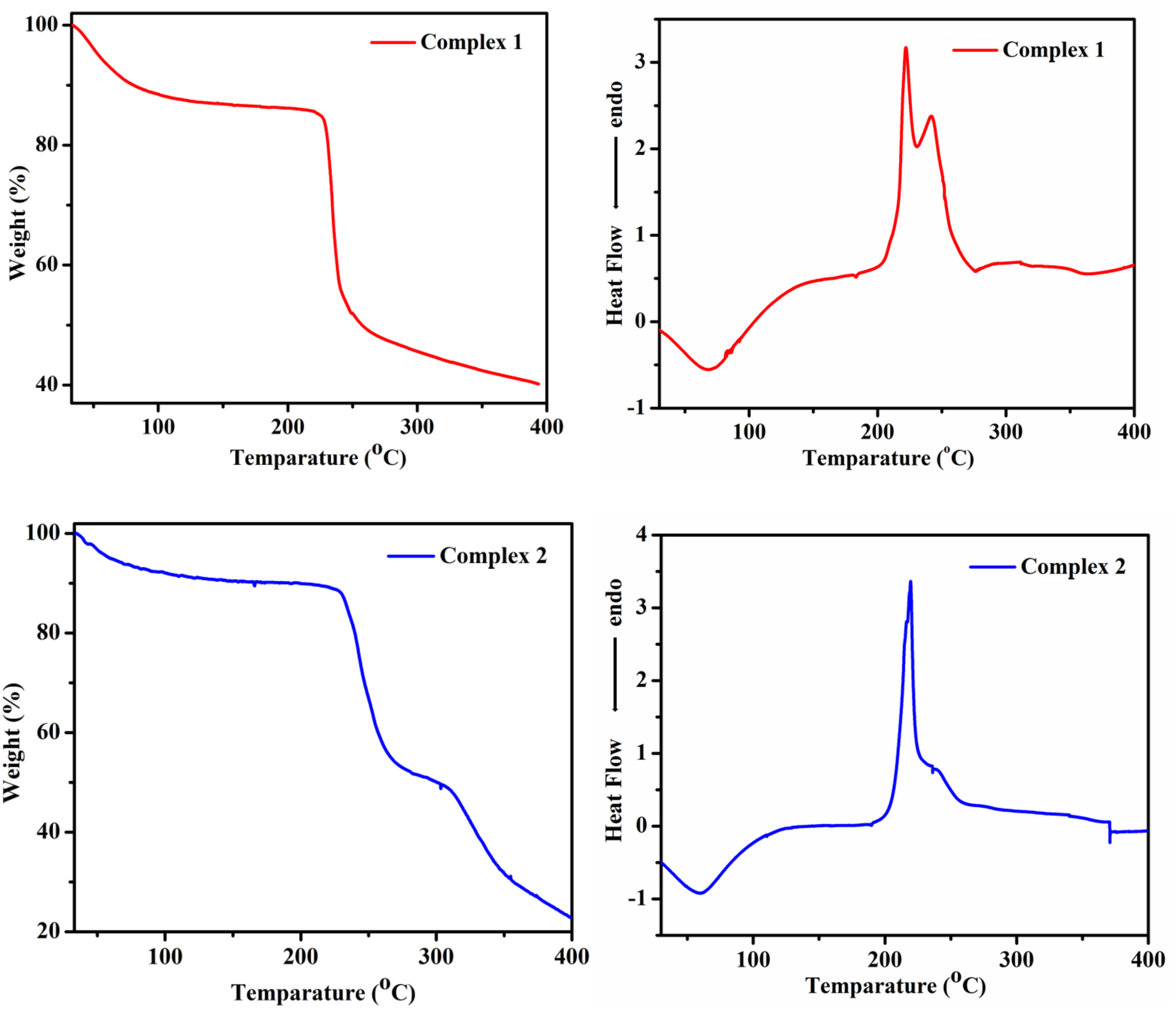


Fig.S4. TGA (left) and DSC (right) plots of **1** (top) and **2** (bottom) showing gradual weight loss up to ~130 ^{o}C due to loss of water from the complexes.

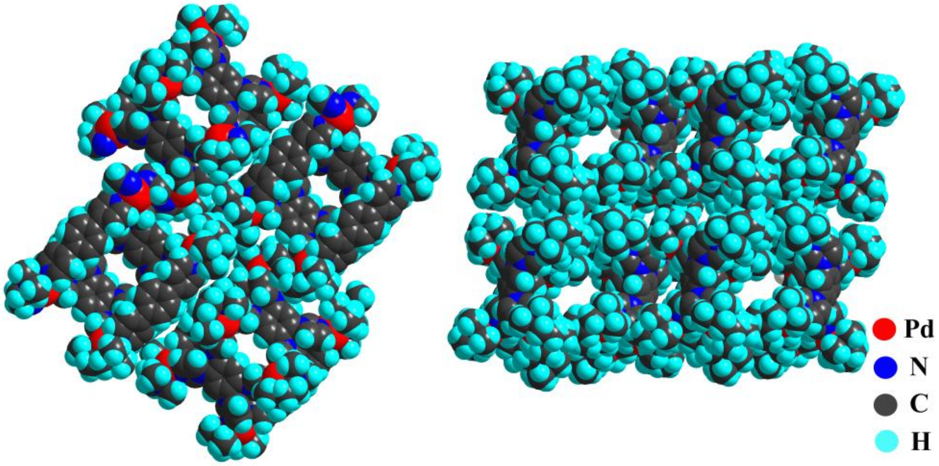


Fig.S5. Space-filling diagrams of the complexes **2** (left) and **1** (right) showing molecular channels.

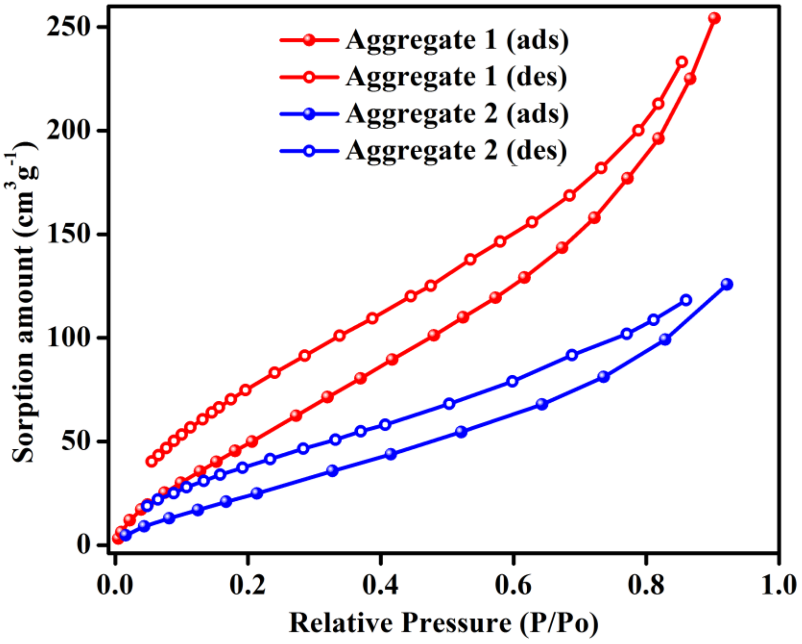


Fig.S6. Water adsorption and desorption isotherms of **1** and **2** at 298 K.

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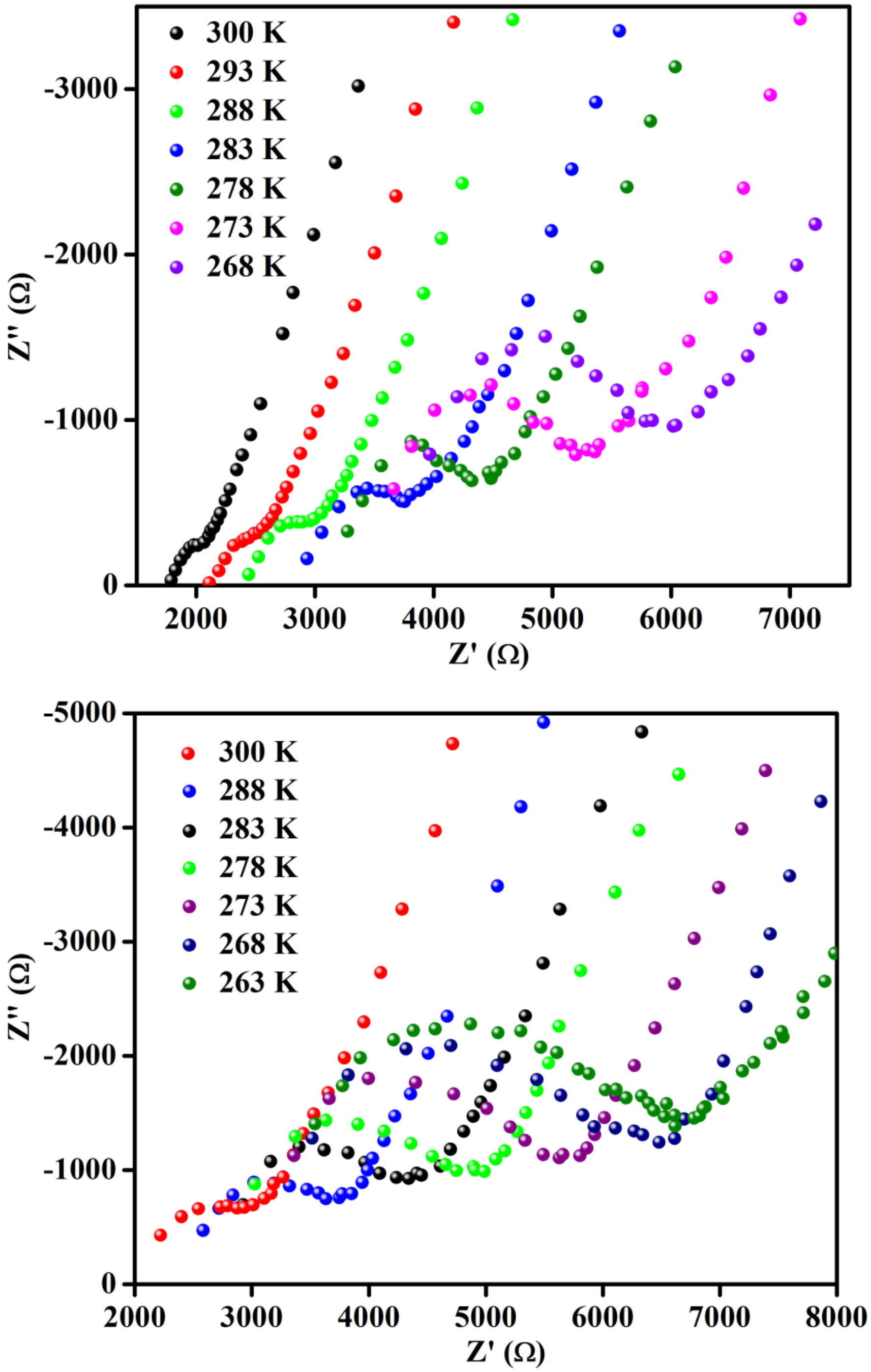

Fig.S7. Nyquist plots for the assembly **1** (top) and **2** (bottom) at different temperature under relative humidity ~46%.

Table S3. Proton conductivities of **1** and **2** at different temperature under relative humidity ~46%.

	Complex 1		**Complex 2**	
Serial No	**Temperature**	**Proton Conductivity at 46% RH (Scm^{-1})**	**Temperature**	**Proton Conductivity at 46% RH (Scm^{-1})**
1	**268 K**	**1.58×10^{-4}**	**263K**	**6.24×10^{-5}**
2	**273K**	**1.97×10^{-4}**	**268 K**	**6.96×10^{-5}**
3	**278 K**	**2.80×10^{-4}**	**273 K**	**7.88×10^{-5}**
4	**283 K**	**3.31×10^{-4}**	**278 K**	**9.12×10^{-5}**
5	**288 K**	**4.68×10^{-4}**	**283 K**	**1.09×10^{-4}**
6	**293 K**	**0.65×10^{-3}**	**288 K**	**0.14×10^{-3}**
7	**300 K**	**0.78×10^{-3}**	**293 K**	**0.19×10^{-3}**
8			**300 K**	**0.22×10^{-3}**

Table S4. Proton conductivities of **1**, **2** and other MOFs under low humidity and ambient temperature.

Compounds	**Conductivity (Scm^{-1})**	**Temperature**	**RH (%)**	**Reference**
Complex 1	**0.70×10^{-3}**	**296 K**	**46**	*This work*
Complex 1	**1.2×10^{-3}**	**296 K**	**75**	*This work*
Complex 2	**0.21×10^{-3}**	**296 K**	**46**	*This work*
Complex 2	**2.3×10^{-3}**	**296 K**	**75**	*This work*
Me-Fe-Cr	**0.8×10^{-4}**	**298 K**	**65**	*J. Am. Chem. Soc.* 2012, **134**, 5472.
$(NH_4)_4[MnCr_2(ox)_6].4H_2O$	**3.0×10^{-5}**	**295 K**	**69**	*J. Am. Chem. Soc.* 2011, **133**, 15328.
$Co[Cr(CN)_6]_{2/3}.zH_2O$	**2.9×10^{-5}**	**293 K**	**69**	*J. Am. Chem. Soc.* 2010, **132**, 6620.
$(NH_4)_2(adp)[Zn_2(ox)_3].2H_2O$[1]	**6.0×10^{-6}**	**298 K**	**70**	*J. Am. Chem. Soc.* 2009**, 131**, 9906
$\{NH(prol)_3\}[MnCr(ox)_3].2H_2O$[2]	**2.0×10^{-6}**	**298 K**	**65**	*J. Am. Chem. Soc***.** 2009**, 131**, 13516

$Zn_3(L)(H_2O)_2.2H_2O$[3]	**1.4×10^{-6}**	**298 K**	**75**	*J. Am. Chem. Soc.* 2010, **132**, 14055
$(HOC_2H_4)_2$dtoaCu[4]	**5.9×10^{-8}**	**300 K**	**70**	*Mol. Cryst. Liq. Cryst.* 2002, **379**, 89
Mn(dhbq)$(H_2O)_2$[5]	**3.5×10^{-9}**	**298 K**	**60**	*Bull. Chem. Soc. Jpn.* 2010, **83**, 42

[1]adp = adipic acid, [2]prol = -C_3H_7OH, [3]L = 1,3,5-benzenetriphosphonate, [4]dtoa = dithiooxamide, [5]H_2dhbq = 2,5-dihydroxy-1,4-benzoquinon.

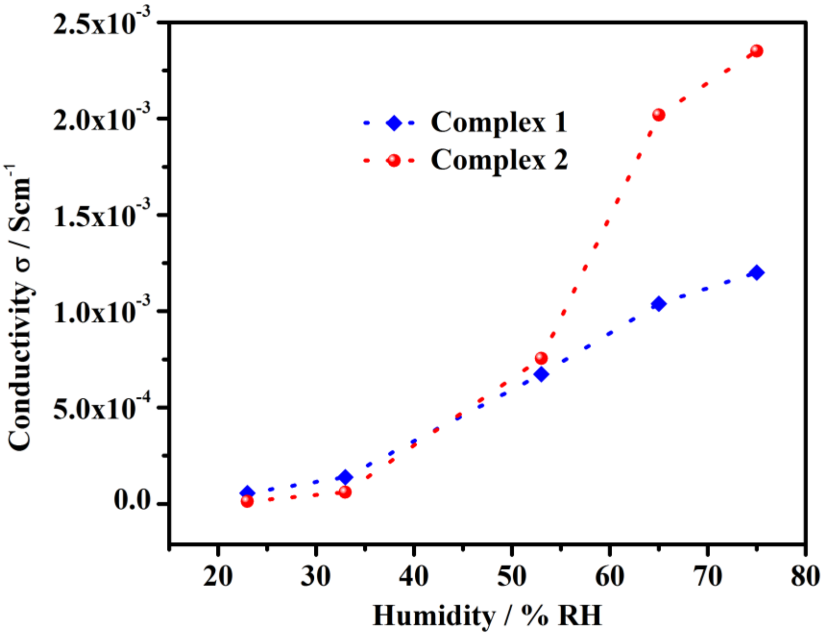

Fig.S8. Humidity versus proton conductivity of **1** and **2** at 296 K.

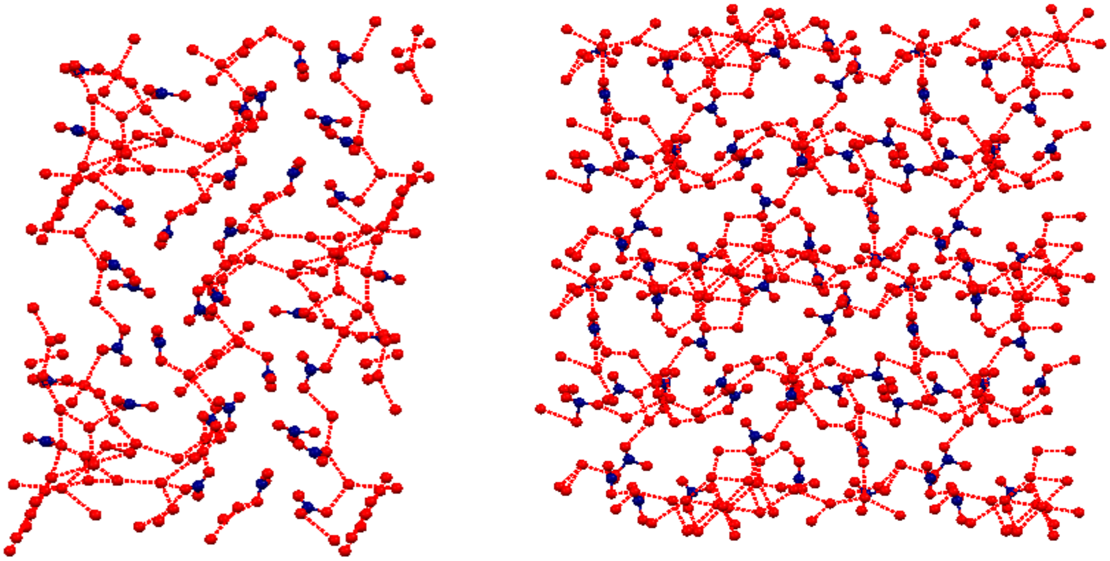

Fig.S9. Crystal structure (ball and stick model) of **1** showing H-bonded interactions between water and counter anions as well as between water molecules along a axis (left) and b axis (right) present in the channels before squeezing solvents and counter anions. Color code: O = red, N = blue. Cationic aggregates have been removed for clarity.

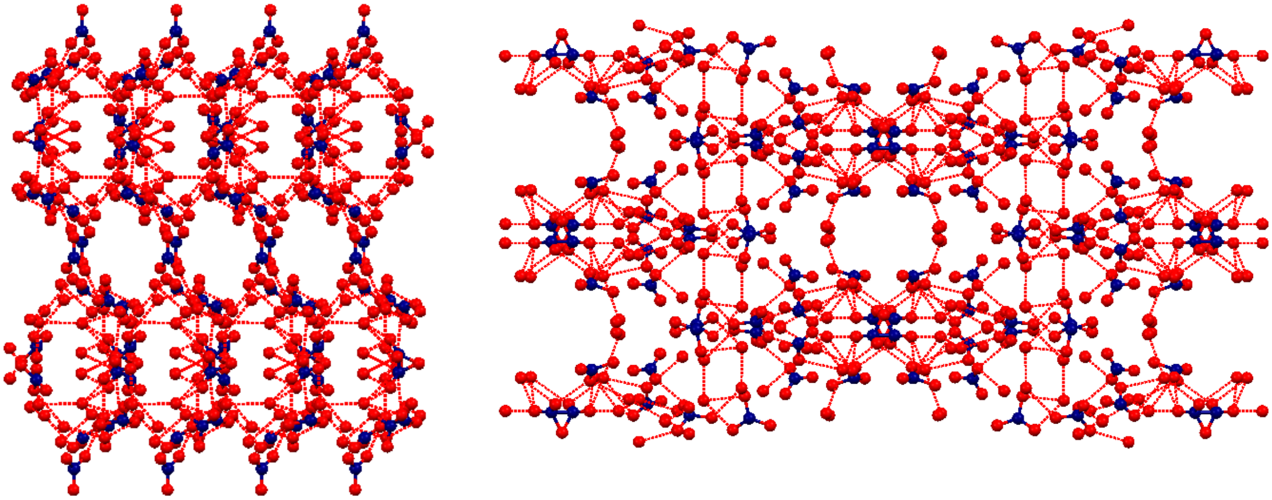

Fig.S10. Ball and stick model of crystal structure of **2** along a axis (left) and c axis (right) exhibiting H-bonding interactions between water and counter anions as well as between water molecules present in molecular pockets before squeezing water and counter anions. Color code: O = red, N = blue. Cationic aggregates have been omitted for clarity.

References

1. A. K. Bar, R. Chakrabarty, P. S. Mukherjee, *Inorg. Chem*. 2009, **48**, 10880.
2. J. C. Barnes, M. Juricek, N. L. Strutt, M. Frasconi, S. Sampath, M. A. Giesener, P. L. McGrier, C. J. Bruns, C. L. Stern, A. A. Sarjeant, J. F. Stoddart, *J. Am. Chem. Soc*. 2013, **135**, 183.
3. A. Rit, T. Pape, A. Hepp, F. E. Hahn, *Organometallics* 2011, **30**, 334.
4. SMART/SAINT; Bruker AXS, Inc.: Madison, WI, 2004.
5. G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr*., 2007, **64**, 112.
6. L. J. Farrugia, WinGX: An Integrated System of Windows Programs for the Solution, Refinement and Analysis for Single Crystal X-ray Diffraction Data, version 1.65.04; Department of Chemistry: University of Glasgow, 2003. (L. J. Farrugia, *J. Appl. Crystallogr*. 1999, **32**, 837).
7. G. M. Sheldrick, SADABS, Bruker Nonius Area Detector Scaling and Absorption Correction, version 2.05; University of Gottingen: Gottingen, Germany, 1999.
8. L. J. Farrugia, ORTEP-3 for Windows, version 1.08. *J. Appl. Crystallogr*. 1997, **30**, 565.
9. A. L. Spek, *Acta Crystallogr*. 1990, **A46**, C34.
10. A. L. Spek, *Acta Cryst*. 2009, **D65**, 148.