Supporting Information

Coordination Polymers from Alkaline-Earth Nodes and Pyrazine Carboxylate Linkers

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Section. S1 X-ray Structure Analysis

Table S1. Crystal Data and Refinement Information for 2,5-H_2pzdc Ligand.

Complexes	**H_2pzdc**
Formula	$C_6H_8N_2O_6$
Formula weight	204.14
Space group	P-1
a (Å)	6.9599 (6)
b (Å)	7.1381 (4)
C (Å)	9.3226 (6)
α (°)	92.721 (7)
β (°)	105.178 (7)
γ (°)	110.866 (8)
Volume (Å^3)	412.56 (6)
Z	2
Dx (g/cm^3)	1.643
μ (cm^{-1})	1.492
Reflections Collected	5008
Reflections Unique	1767
R_1[a] [$I > 2\sigma(I)$]	0.0463
wR_2[b]	0.1674

[a]$R_1 = \Sigma||Fo|-|Fc|| / \Sigma|Fo|$, [b]$wR_2 = \{\Sigma[w(|Fo|^2 - |Fc|^2)^2] / \Sigma[w(|Fo|^4)]\}^{1/2}$

Table S2. Crystal Data and Refinement Information for Complexes.

Complexes	**1**	**2**	**3**	**4**	**5**
Formula	$C_6H_8CaN_2O_7$	$C_6H_{10}CaN_3O_8$	$C_{12}H_{16}Sr_2N_4O_{18}$	$C_6H_{10}BaN_2O_{10}$	$C_6H_2BaN_2O_6$
Formula weight	260.22	278.23	679.51	407.48	335.42
Space group	P-1	C2/c	P1	C2	C2/c
a (Å)	6.5656 (8)	11.640 (2)	6.2281 (2)	11.7030 (6)	19.899 (2)
b (Å)	8.5184 (11)	5.8956 (4)	9.4499 (4)	16.1087 (8)	6.9856 (5)
C (Å)	9.2413 (10)	15.168 (2)	10.6160 (7)	7.3641 (5)	6.3382 (5)
α (°)	105.140 (5)	90	73.814 (5)	90	90
β (°)	95.387 (4)	104.286 (7)	80. 723 (6)	116.030 (8)	96.274 (7)
γ (°)	99.325 (7)	90	75.136 (5)	90	90
Volume (Å^3)	487.26 (11)	1008.7 (2)	577.24 (5)	1247.5 (2)	875.8 (2)
Z	2	4	1	4	4
Dx (g/cm^3)	1.773	1.832	1.955	2.169	2.544
μ (cm^{-1})	6.668	6.575	47.071	32.335	45.444
Reflections Collected	4912	3900	8952	3901	2630
Reflections Unique	2038	1160	4760	2439	996
R_1[a] [$I > 2\sigma(I)$]	0.0449	0.0437	0.0418	0.0246	0.0361
wR_2[b]	0.1215	0.1057	0.1175	0.0810	0.0932

[a]$R_1 = \Sigma||Fo|-|Fc|| / \Sigma|Fo|$, [b]$wR_2 = \{\Sigma[w(|Fo|^2 - |Fc|^2)^2] / \Sigma[w(|Fo|^4)]\}^{1/2}$

Section. S2 Phase Purity and Thermal Stability

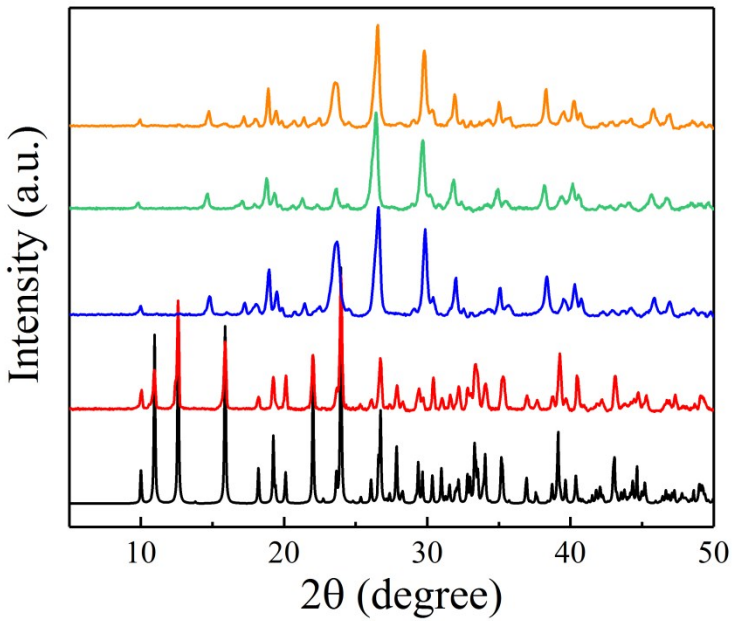

Figure S1. PXRD patterns of the simulated **1** (black), as-synthesized **1** (red), dehydrated **1** at 100 °C (blue), dehydrated **1** at 200 °C (green) and **1** after water adsorption measurement (orange)**,** respectively.

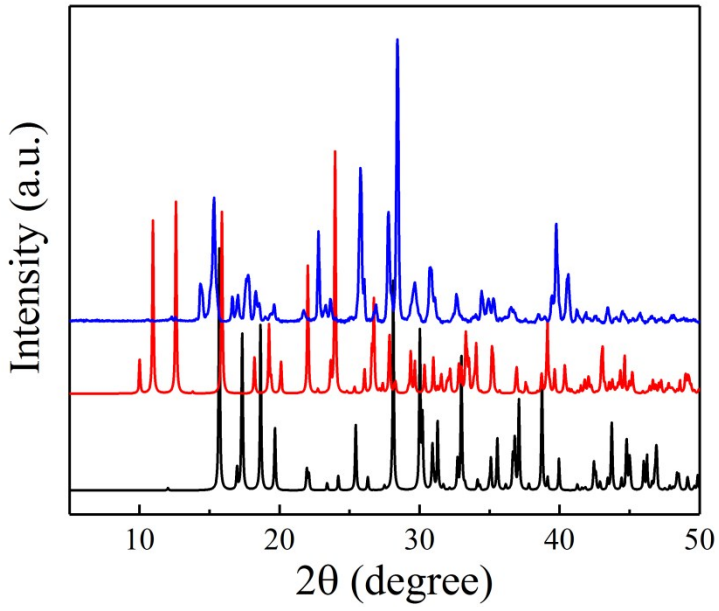

Figure S2. PXRD patterns of the simulated **2** (black), simulated **1** (red) and as-synthesized **2** (blue)**,** respectively. It shows that the as-synthesized compound **2** is a mixture containing the compounds $[Ca(2,5\text{-pzdc})(H_2O)_2]\cdot H_2O$ and $[Ca(2,5\text{-pzdc})(H_2O)_4]$. This is in agreement with our observation during the single-crystal XRD measurement, in which we found two kind of crystals with independent shapes and crystal structure parameters.

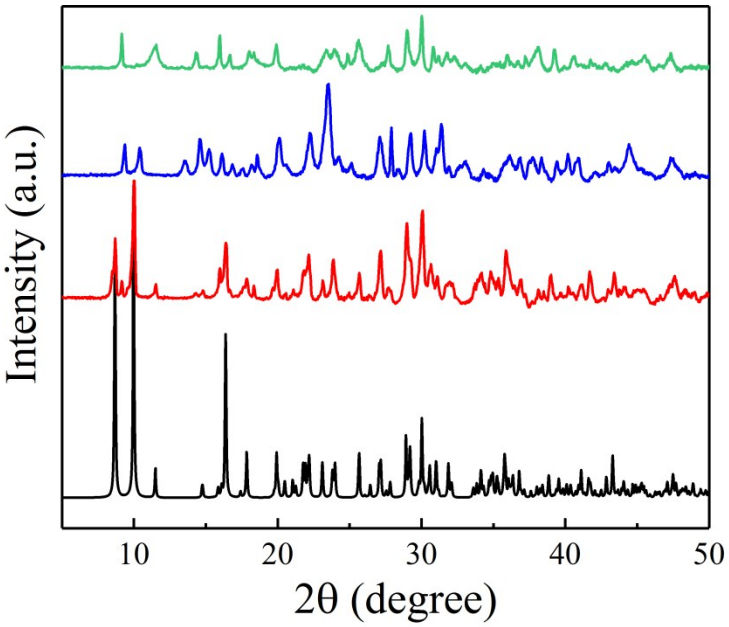

Figure S3. PXRD patterns of the simulated **3** (black), as-synthesized **3** (red), activated **3** at 100 °C (blue) and activated **3** at 200 °C (green)**,** respectively.

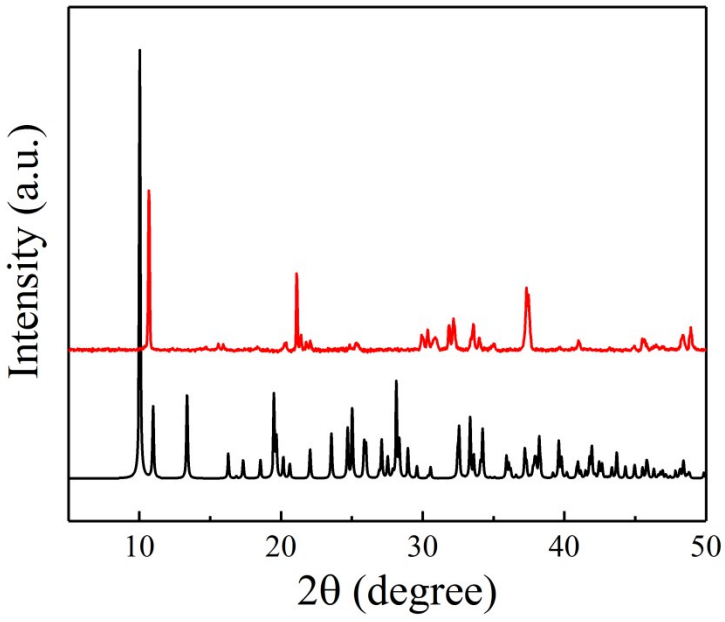

Figure S4. PXRD patterns of the simulated (black) and as-synthesized **4** (red), respectively.

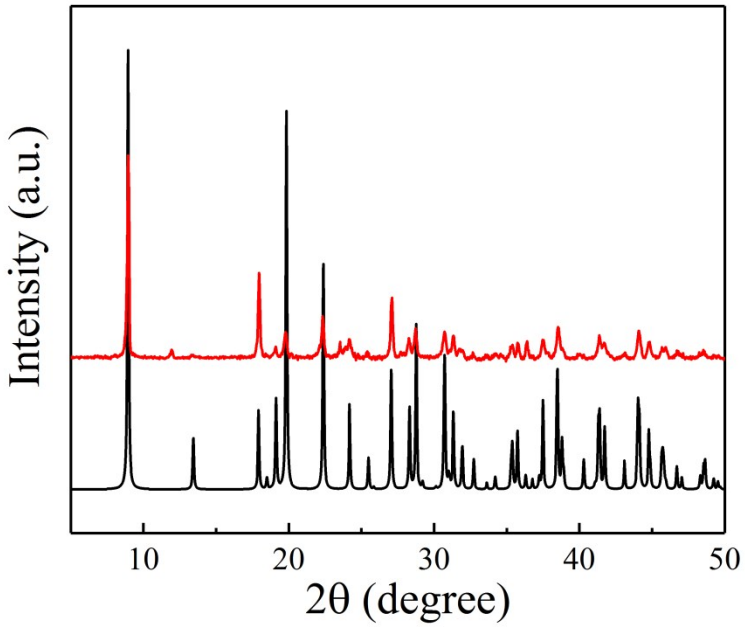

Figure S5. PXRD patterns of the simulated (black) and as-synthesized **5** (red), respectively.

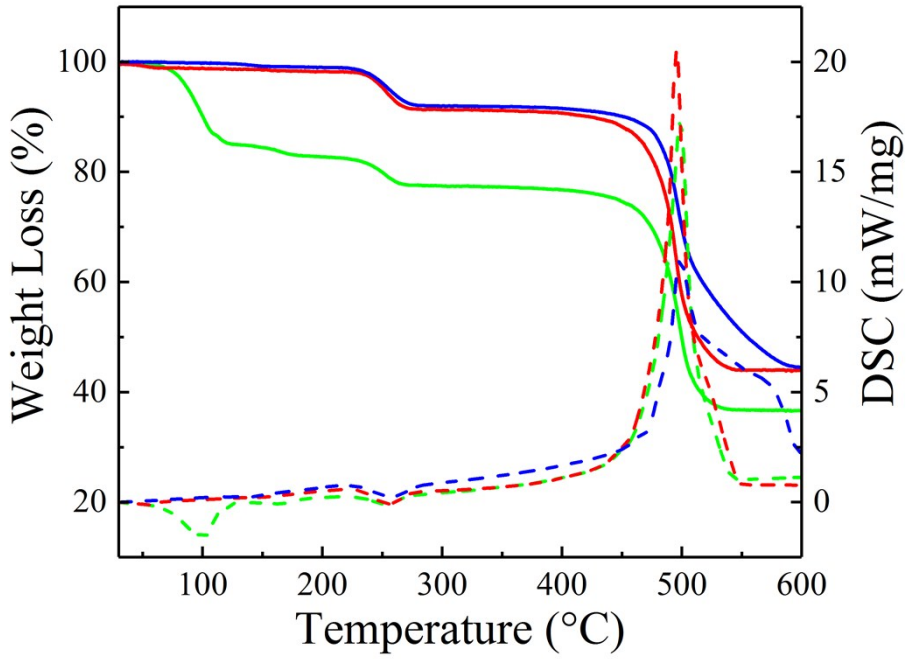

Figure S6. TGA (solid line) and DSC (dash lines) curves of the as-synthesized compound **1** (green), dehydrated **1** at 100 °C (red) and dehydrated **1** at 200 °C (blue).

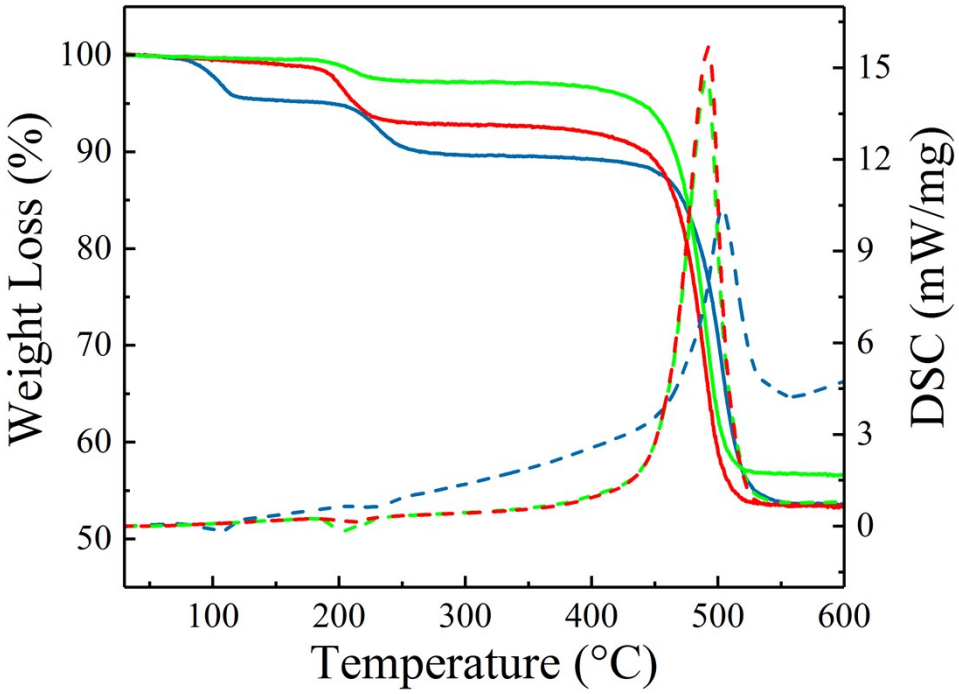

Figure S7. TGA (solid line) and DSC (dash lines) curves of the as-synthesized compound **3** (dark blue), dehydrated **3** at 100 °C (red) and dehydrated **3** at 200 °C (green).

Section. S3 Water Adsorption Study

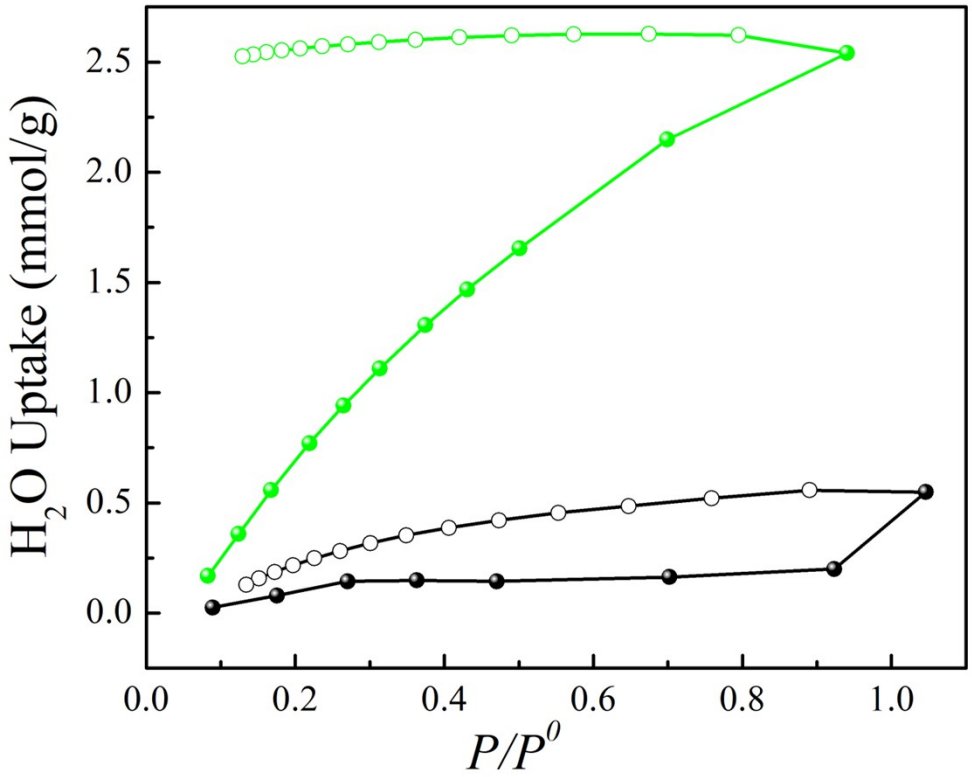

Figure S8. Water uptake of the as-synthesized compound **1** (green) and the dehydrated compound **1** (black) at 30 °C.

Section. S4 Crystal Structure Comparison

Table S3. Structural details and potential applications of some alkaline-earth metal based coordination compounds/MOFs.

Compound[1]	Metal Salts	Ligands[2]	Coordination[3]	Metal Cluster	Application	*Ref.*
Ca-IRMOF-1	_[4]	1,4-H_2BDC	4	$Ca_4O(BDC)_3$	_	1
Ref.2-**3**	$Ca(NO_3)_2{\cdot}4H_2O$	H_3TCM	6,7,7	$Ca(TCM)_{6,}$ $Ca(TCM)_5DMF$, $Ca(TCM)_4(DMF)(H_2O)$	_	2
Ref.3-**2**	_	HDCPP	6	$Ca(DCPP)_4(DMF)_2$	Adsorption	3
Ref.4-**1**	$Ca(NO_3)_2{\cdot}4H_2O$	H_2BDC-F_4	7	$Ca(BDC\text{-}F_4)_5(H_2O)$	Adsorption	4
Ref.5-**1**	$Ca(NO_3)_2{\cdot}4H_2O$	2,3-H_2pzdc	8	$Ca(2,3\text{-}pzdc)_2(NO_3)(H_2O)_3$	Magnetism	5
$Ca_4(pztc)_2(H_2O)_2$	$Ca(OAc)_2{\cdot}4H_2O$	2,3,4,6-H_4PZTC	7,8	$Ca(pztc)_3(H_2O)_4$ $Ca(pztc)_4(H_2O)_3$	_	6
$Ca(pztc)(H_2O)_3$	$Ca(NO_3)_2{\cdot}4H_2O$	2,3,4,6-H_4PZTC	9	$Ca(pztc)_2(H_2O)_3$	_	7
Ca-BTC-H_2O	$Ca(OAc)_2{\cdot}4H_2O$	1,3,5-BTC	8	$Ca(BTC)_5(H_2O)$	Proton Conductivity	8
Ca-BTC-DMF	$Ca(NO_3)_2{\cdot}4H_2O$	1,3,5-BTC	7,8	$Ca(BTC)_5DMF$ $Ca(BTC)_4(DMF)(H_2O)$	Proton Conductivity	8
Ca-BTC-DMSO	$Ca(OAc)_2{\cdot}4H_2O$	1,3,5-BTC	6,8	$Ca(BTC)_2(H_2O)_2(DMSO)_2$ $Ca(BTC)_4(H_2O)(DMSO)$	Proton Conductivity	8
Ca-BTC	$CaCl_2$	1,3,5-BTC	6	$Ca(BTC)_6$	Proton Conductivity	8
Ref.9-**1**	$Sr(NO_3)_2{\cdot}4H_2O$	2,6-H_2pzdc	8,9	$Sr(2,6\text{-}pzdc)_2(H_2O)_4$ $Sr(2,6\text{-}pzdc)_2(H_2O)_5$	_	9
$[Sr_3\{H_2diol)_3(DMF)_5]$	$SrCl_2$	H_4diol/ DABCO	8	$Sr(H_2diol)_3(DMF)_5$	Fluorescence	10
Ref.11-**1**	$Sr(NO_3)_2$	1,3-bdc	7,8	$Sr(1,3bdc)_5(H_2O)$	Interlayer dielectric material	11
Ref.12-**3**	$Ba(OH)_2$	H_4BPTC	7,8,9	$Ba(BPTC)_4(H_2O)$ $Ba(BPTC)_4(H_2O)_2$ $Ba(BPTC)_2(H_2O)_5$	Proton Conductivity	12
Ref.3-**4**	_	HDCPP	8	$Ba(DCPP)_5(H_2O)(DMA)$	Adsorption	3
Ref.5-**3**	$BaCl_2$	2,3-H_2pzdc	9	$Ba(2,3\text{-}pzdc)_4(H_2O)_5$	Magnetism	5
Ba-SBBA	$Ba(NO_3)_2$	SBBA	9,10	$Ba(SBBA)_5DEF$ $Ba(SBBA)_5(DEF)_3$	_	13

Notes: [1] Owing to the length of name of some compounds are too long to be putted in Table S3, thus only their abbreviation name in references are shown in column 1. The exact name are shown below:

Ref.2-**3** : $\{[Ca_{5/2}(TCM)_2(DMF)_2(H_2O)](Me_2NH_2)(DMF)_2(H_2O)\}_n$

Ref.3-**2** : $[Ca(HDCPP)_2(H_2O)_2]_n(DMF)_{1.5n}$

Ref.4-**1 :** $\{[Ca_4(BDC\text{-}F_4)_4(H_2O)_4]{\cdot}4H_2O\}_n$

Ref.5-**1** : $[Ca_2Co(pzdc)_2(NO_3)_2(H_2O)_8]_n{\cdot}2nH_2O$

Ref.9-**1:** $Sr_2(2,6\text{-}pzdc)_2(H_2O)_7{\cdot}1.5H_2O$

Ref.11-**1**: $\{[Sr_2(1,3\text{-}bdc)_2(H_2O)_2]{\cdot}H_2O\}_n$

Ref.12-**3**: $[Ba_6(BPTC)_3(H_2O)_6]{\cdot}11H_2O$

Ref.3-**4**: $[Ba(DCPP)(H_2O)(DMA)]_n$

Ref.5-**3**: $[Ba_2Co(pzdc)_2(H_2O)_{10}]_n{\cdot}2nCl$

Ba-SBBA: $Ba_2(SBBA)_2{\cdot}4DEF$

[2] 1,4-H_2BDC 1,4-benzenedicarboxylic acid;

H_3TCM 4,4',4"-{[(2,4,6-trimethylbenzene-1,3,5-triyl)tris-(methylene)]tris(oxy)]}tribenzoic acid;
HDCPP metal free 5,15-di(4-carboxypheneyl)porphyrin;
H_2BDC-F_4 2,3,5,6-tetrafluorobenzenedicarboxylic acid;
2,3-H_2pzdc Pyrazine-2,3-dicarboxylic acid
2,3,5,6-H_4PZTC Pyrazine-2,3,5,6-tetracarboxylic acid
1,3,5-BTC Bezene-1,3,5-tricarboxylic acid
2,6-H_2pzdc Pyrazine-2,6-dicarboxylic acid
H_4diol 2,2'-dihydroxybiphenyl-4,4'-dicarboxylic acid
H_4BPTC 2,2',6,6'-tetracarboxybiphenyl acid
SBBA 4,4'-sulfobisbenzoic acid

[3] It indicates that there are at least two independent coordinated metal ions in compound when the number in column 3 is above two.

[4] Sign _ indicates that the reference didn't mention the starting metal salt or potential application.

Section. S5 Proton Conductivity Comparison

Table S4. Performance indicators for alkaline-earth based MOFs in proton conductivity.

Compound	Conductivity (S cm^{-1})	Activation energy (eV)	Measurement Condition	Reference
Ca-SBBA	8.58×10^{-6}	0.23	298K; 98% RH	13
Sr-SBBA	4.4×10^{-5}	0.56	298K; 98% RH	13
Ca-BTC-DMF	4.8×10^{-5}	0.32	298K; 98% RH	8
Ca-BTC-DMA	1.46×10^{-5}	0.40	298K; 98% RH	8
Mg-BPTC	6.9×10^{-7}	0.47	296K; 98% RH	12
Sr-BPTC	1.6×10^{-6}	0.77	296K; 98% RH	12
MIL-53 (Al)	3.6×10^{-7}	0.47	353K; 95% RH	14
MIL-53 (Al)-NH_2	4.1×10^{-8}	0.45	353K; 95% RH	14
MIL-53 (Al)-OH	1.9×10^{-6}	0.27	353K; 95% RH	14

Section. S6 Proton Conductivity Mechanism

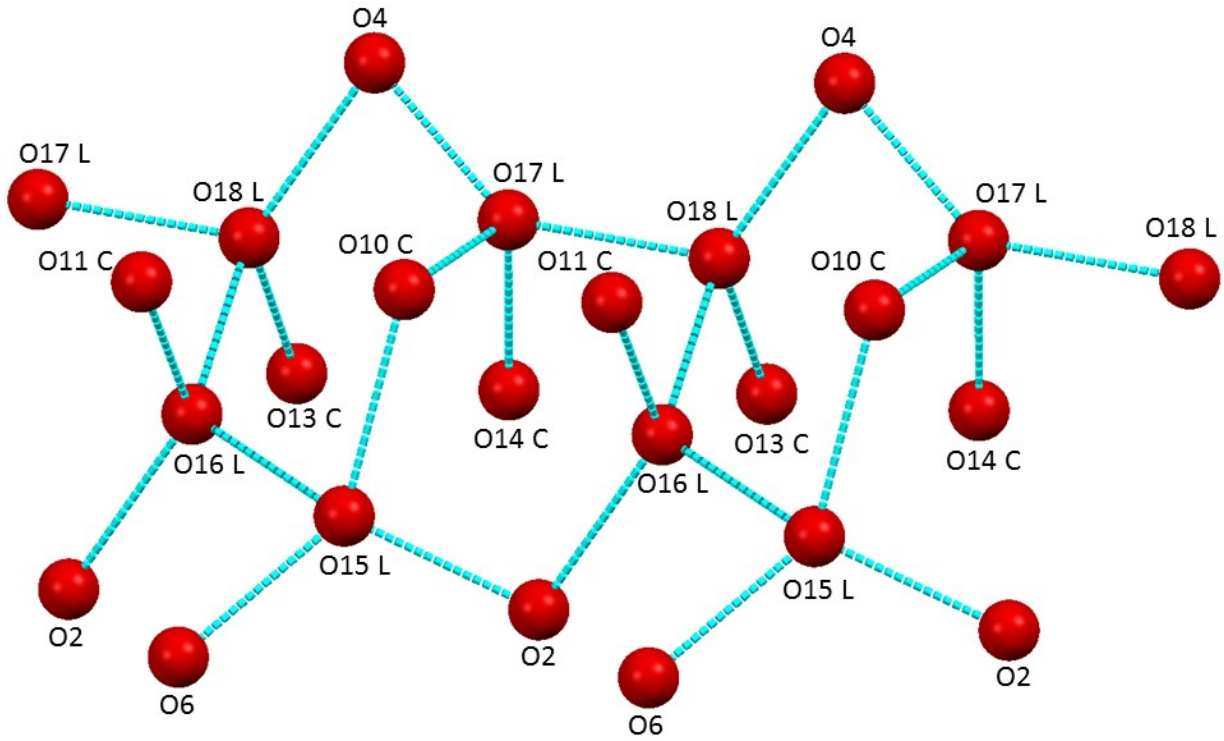

Figure S9. The proposed possible pathway of proton migration by Grotthuss mechanism in compound **3**. O15L, O16L, O17L and O18L are assigned to the lattice water molecules; O10C, O11C, O13C and O14C are assigned to the coordinated water molecules; O2, O4 and O6 are assigned to the uncoordinated oxygen atoms of carboxylate groups of 2,5-pzdc^{2-} linkers. All the hydrogen atoms are removed for clarify.

Section. S7 ORTEP representations, including thermal ellipsoids

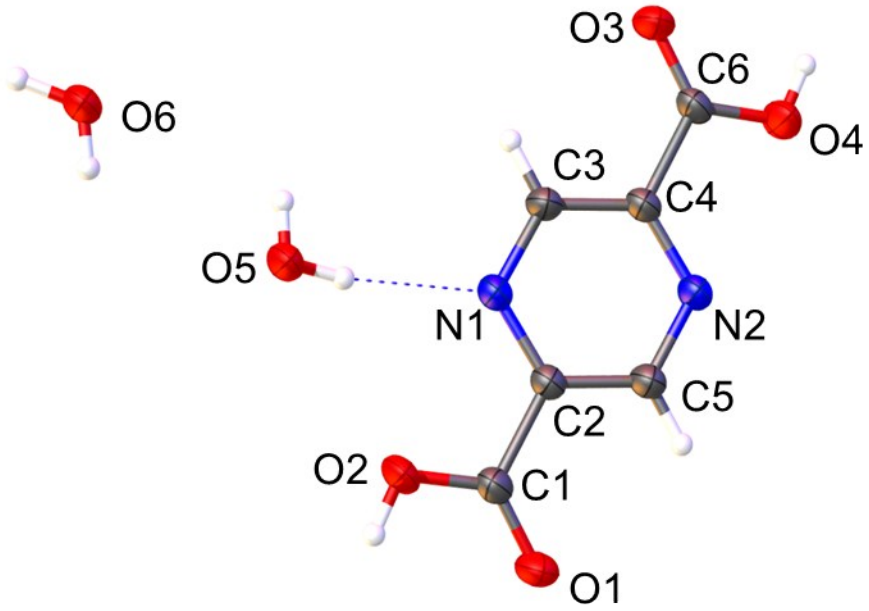

Figure S10. Molecular structure of the ligand 2,5-H_2pzdc.

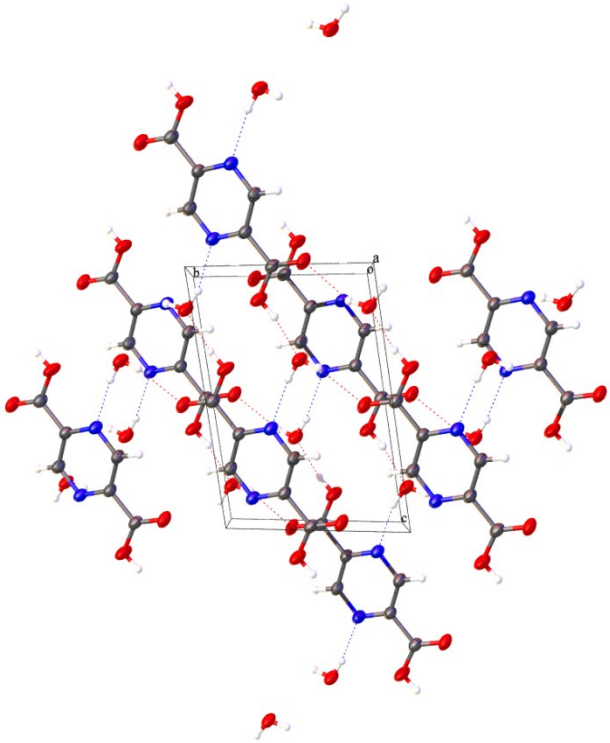

Figure S11. Molecular packing of the ligand 2,5-H_2pzdc along the *a* crystallographic axis.

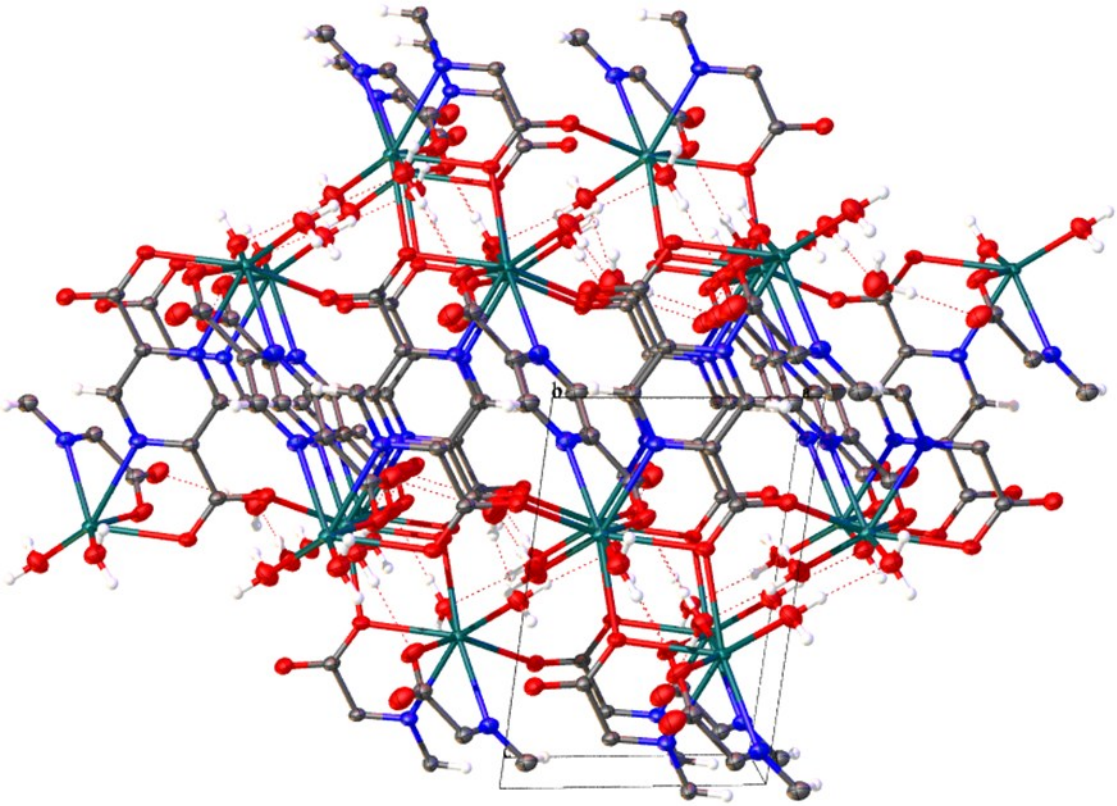

Figure S12. Molecular packing of **1** along the *b* crystallographic axis.

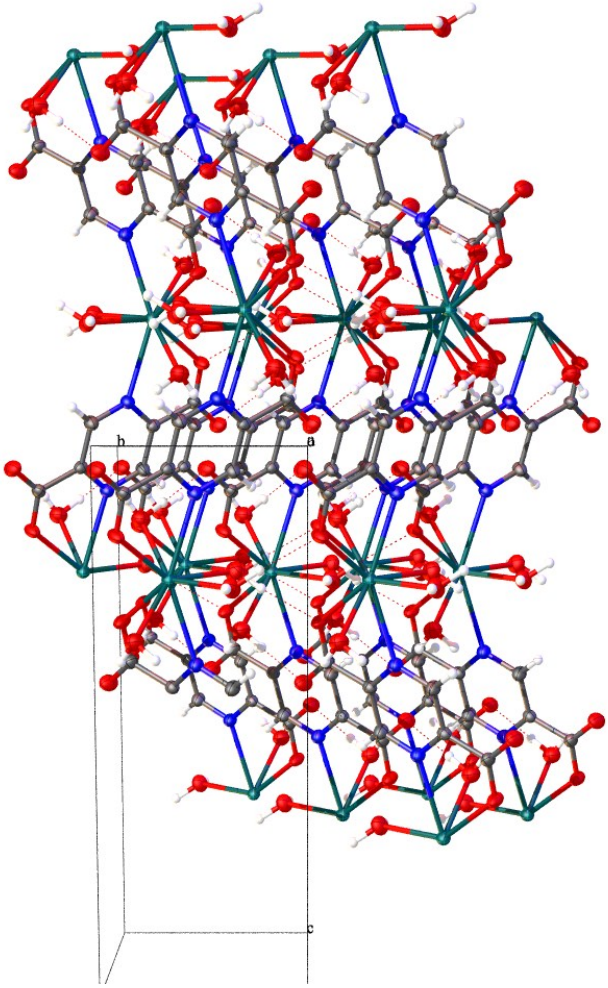

Figure S13. Molecular packing of **2** along the *a* crystallographic axis.

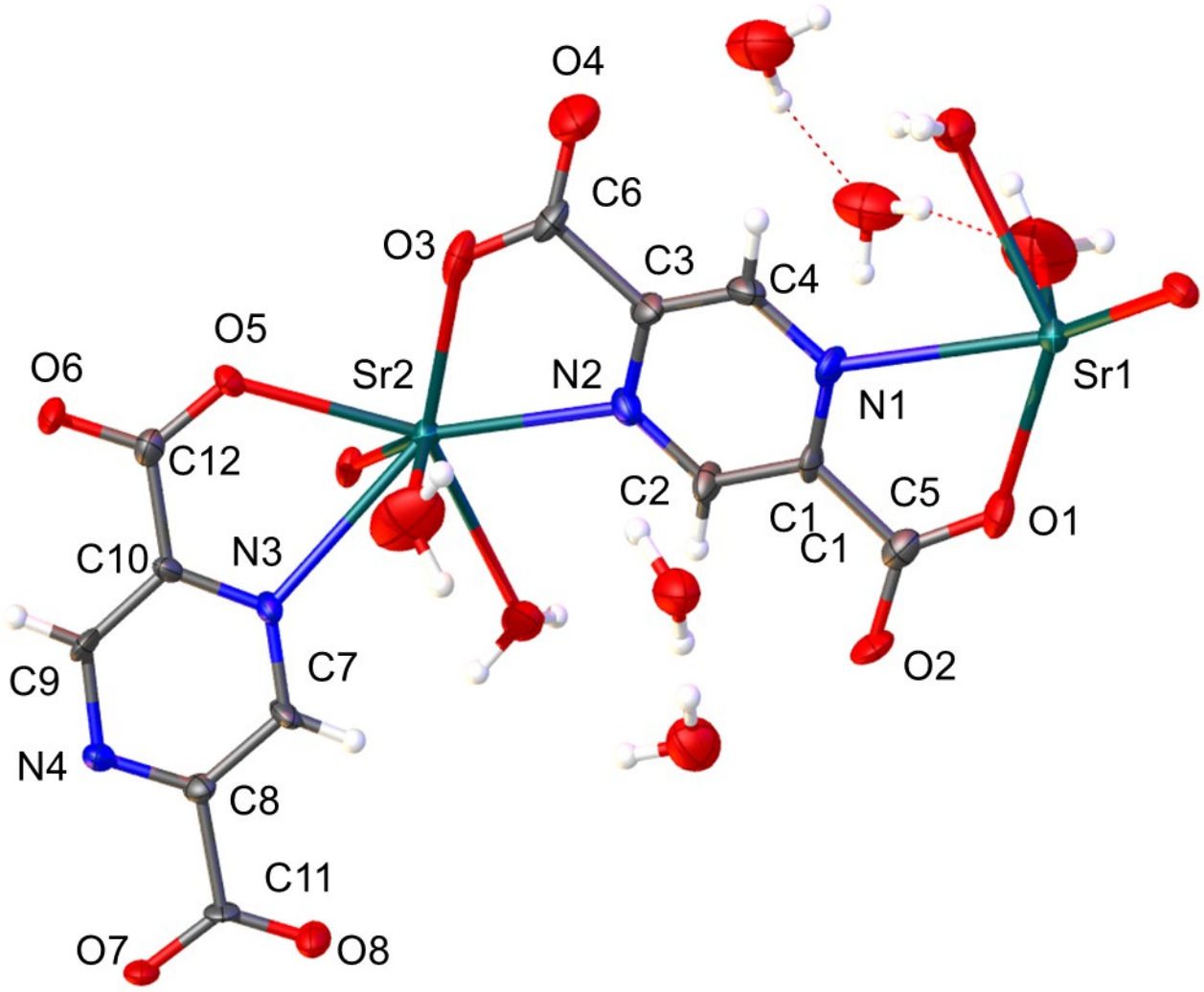

Figure S14. Molecular structure of the dimeric unit of **3**.

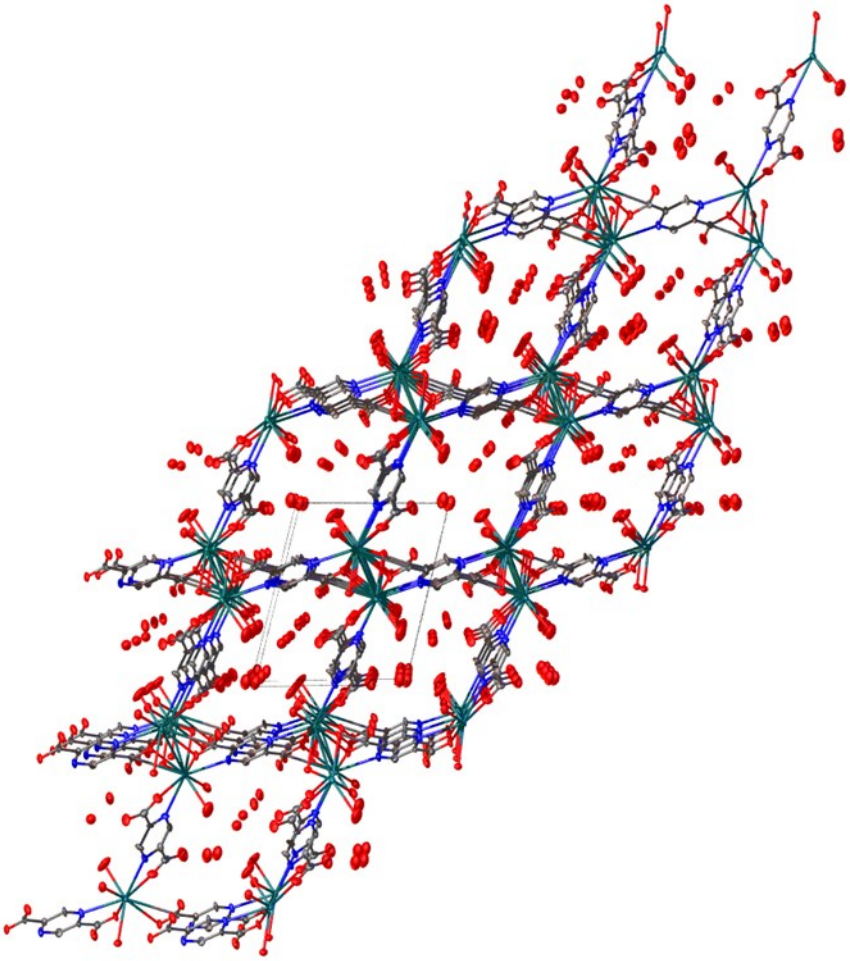

Figure S15. Molecular packing of **3** along the *a* crystallographic axis.

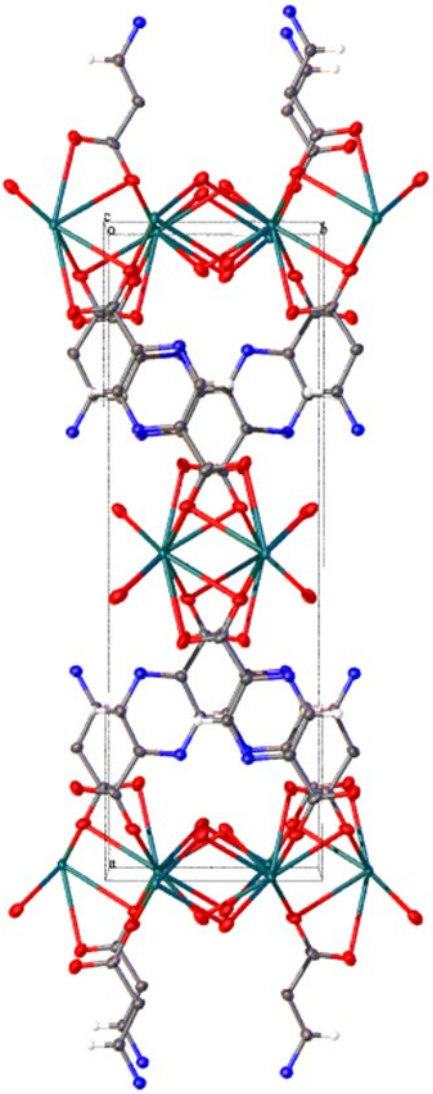

Figure S16. Molecular packing of **5** along the *c* crystallographic axis.

References

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