

Supporting Information

Supramolecular hydrogen-bonded organic networks through acid-base pairs as efficient proton-conducting electrolytes

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Experimental section

All chemical reagents employed in the experiments were received from commercial sources without prior purification. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA analyzer at a heating rate of 10 °C/min ranging from 25 to 800 °C under flowing air atmosphere. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR spectra (4000-400 cm⁻¹) were recorded on a Nicolet Magna 560 IR spectrometer using KBr discs. Powder X-ray diffraction (PXRD) patterns were collected in a Siemens D 5005 diffractometer in the range of 5-50 degree. The gas adsorption isotherm was measured with Quantachrome Autosorb-iQ. Contact angle measurements were performed on CA-100D. Scanning electron microscopy (SEM) was carried out with a JEOL JSM 4800F scanning electron microscope. Water vapor adsorption measurement were performed on 3H-200PW instrument at 25°C.

Synthesis of (CH₂SO₃H)(C₃N₆H₆)·H₂O (1) A 25 mL of 7.93 × 10⁻³ M melamine solution was mixed with a 25 mL of 7.93 × 10⁻³ M 1,2-ethanedisulfonic acid dihydrate solution in a 100 mL beaker with constant stirring for 12 h. The solution was filtered, and then white crystals were collected after nearly 20 days at room temperature. The product was washed by acetone and dried at room temperature (Yield: ~58%). Elemental analysis calcd. for C₄N₆O₄SH₁₁(%): C, 20.08; H, 4.63; N, 35.13; found: C, 19.73; H, 4.26; N, 34.79. IR (KBr): ν = 3357 (m), 3172 (w), 1670 (s), 1610 (w), 1560 (w), 1520 (m), 1475 (w), 1398 (m), 1334 (w), 1230 (w), 1194 (w), 1167 (w), 1117 (w), 1034 (s), 980 (w), 783 (s), 640 (w), 578 (w), 546 (m).

Synthesis of (CH₂SO₃H)(C₃N₆H₆)·H₂O (1S) Compound **1S** was the same molecular compound **1**, but it was isolated after grinding melamine (10 mmol) and 1,2-ethanedisulfonic acid dihydrate (10 mmol) by mortar and pestle for 10 minutes. The resulting mixture was washed with water three times and then dried at 60 °C for 48h (Yield: ~81%). Elemental analysis calcd. for C₄N₆O₄SH₁₁(%): C, 20.08; H, 4.63; N, 35.13; found: C, 19.87; H, 4.57; N, 35.04. IR (KBr): ν = 3361 (m), 3178 (w), 2146 (m), 2075 (s), 2019 (s), 1668 (s), 1614 (w), 1558 (w), 1520 (m), 1473 (w), 1396 (m), 1338 (w), 1232 (w), 1194 (w), 1170 (w), 1114 (w), 1036 (s), 982 (w), 785 (s), 636 (w), 578 (w), 548 (m).

Synthesis of (C₅H₃SO₃H)(CH₂CH₂NH) (2) A 25 mL of 7.93 × 10⁻³ M piperazine hexahydrate solution was mixed with a 25 mL of 7.93 × 10⁻³ M 1,5-naphthalenedisulfonic acid tetrahydrate solution in a 100 mL beaker with constant stirring for 12 h. The solution was filtered, then white crystals were collected after nearly 20 days at room temperature, washed by acetone and dried at room temperature (Yield: ~58%). Elemental analysis calcd. for C₇N₃O₃SH₉(%): C, 44.91; H, 4.84; N, 7.48; found: C, 44.36; H, 4.68; N, 7.29. IR (KBr): ν = 3444 (w), 3043 (s), 1583 (s), 1498 (m), 1466 (s), 1417 (m), 1329 (m), 1238 (w), 1197 (s), 1157 (w), 1091 (w), 1041 (s), 999 (w), 951 (s), 874 (m), 791 (m), 767 (m), 663 (m), 609 (s), 577 (m), 524 (m).

Synthesis of (C₅H₃SO₃H)(CH₂CH₂NH) (2S) Compound **2S** has the same molecular structure and was isolated after grinding piperazine hexahydrate (10 mmol) and 1,5-naphthalenedisulfonic acid tetrahydrate (10 mmol) by mortar and pestle for 10 minutes. The resulting mixture was washed with water for three times and then dried at 60 °C for 48h (Yield: ~82%). Elemental analysis calcd. for C₇N₃O₃SH₉(%): C, 44.91; H, 4.84; N, 7.48; found: C, 44.79; H, 4.72; N, 7.35. IR (KBr): ν = 3444 (w), 3045 (s), 2075 (m), 2019 (m), 1583 (s), 1500 (m), 1460 (s), 1417 (m), 1331 (m), 1236 (w), 1186 (s), 1157 (w), 1093 (w), 1047 (s), 1001 (w), 955 (s), 874 (m), 789 (m), 769 (m), 665 (m), 615 (s), 577 (m), 526 (m).

Proton Conductivity measurement

The proton conductivities of materials were prepared by sandwiching pellets of compounds between two Pt foil, and then measured on an IviumStat electrochemical workstation using the two-probe method alternating-current (AC) impedance measurement method in the frequency range 1M-1Hz under an input voltage amplitude of 50 mV. The temperature and relative humidity conditions are controlled using a programmable chamber (BPHS-060A).

Computational Details

The initial structures of compounds **1** and **2** are selected from their crystal structures. The optimization of compounds **1** and **2** is carried out through the combined quantum mechanics and molecular mechanics (QM/MM) approach. During the QM/MM, the central molecules (melamine and 1,2-ethanedisulfonic acid for **1**; piperazine and 1,5-naphthalenedisulfonic acid for **2**) are treated with QM, and the surrounding molecules are calculated with MM. For both **1** and **2**, the optimization of ground state geometry was performed at the B3LYP/6-31+G(d,p) level. All calculations were accomplished with Gaussian 09 program.

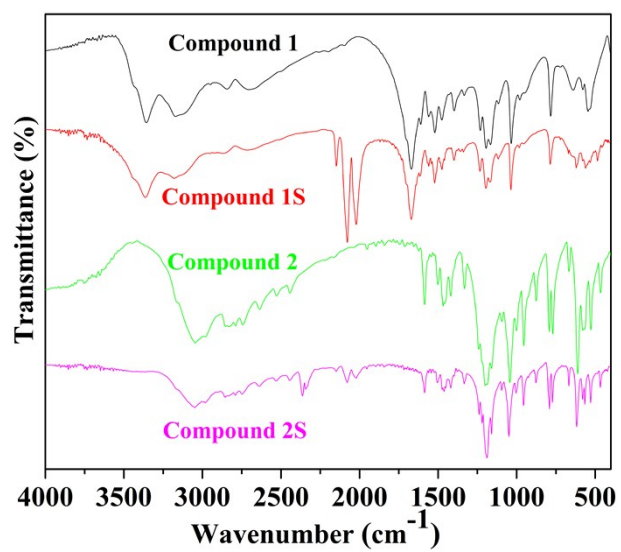


Fig S1. FT-IR spectra of all compounds.

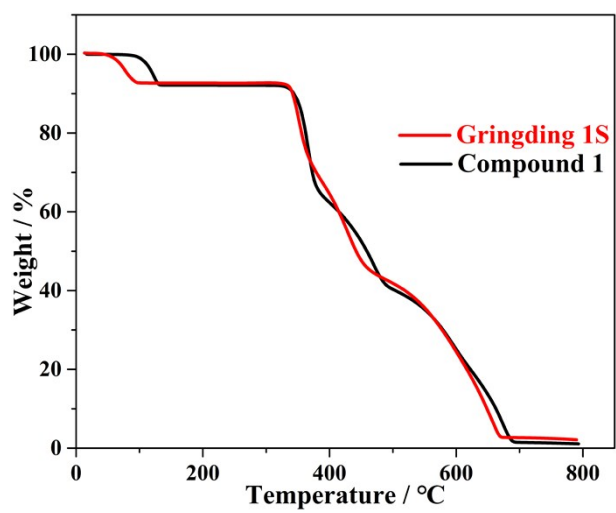


Fig S2. TGA curve of compound 1 and 1S.

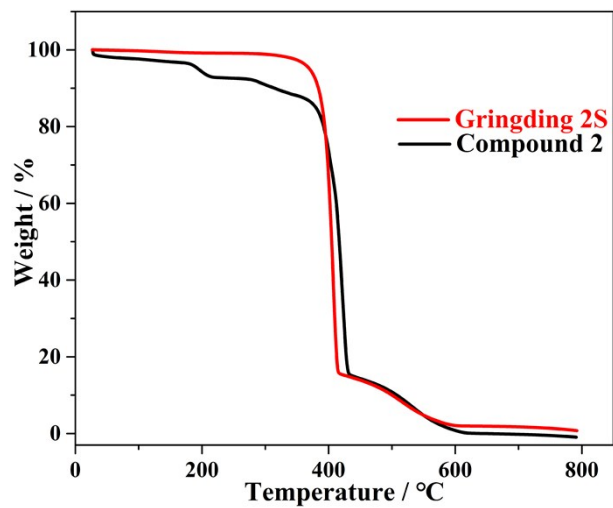


Fig S3. TGA curve of compound 2 and 2S.

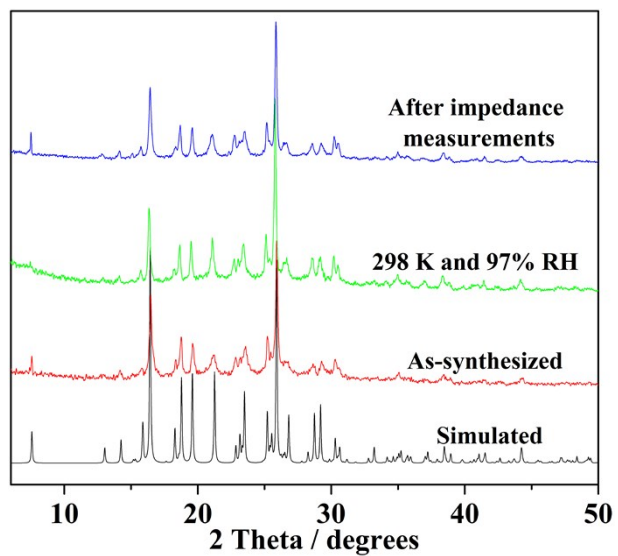


Fig S4. PXRD patterns of compound 1; simulated pattern, as-synthesized pattern, and after impedance measurements pattern.

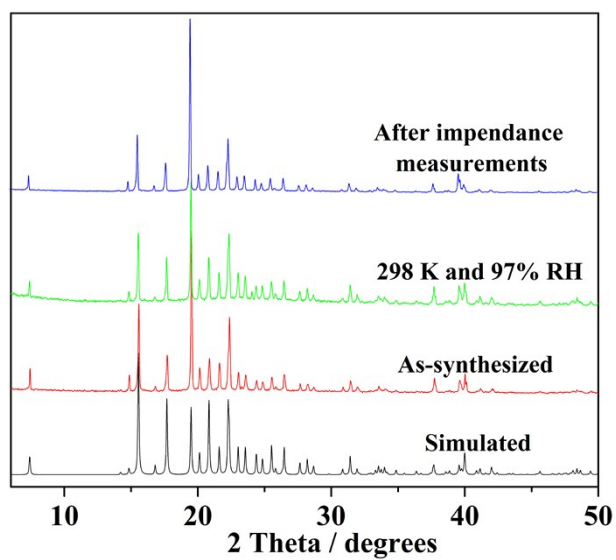


Fig S5. PXRD patterns of compound **2**; simulated pattern, as-synthesized pattern, and after impedance measurements pattern.

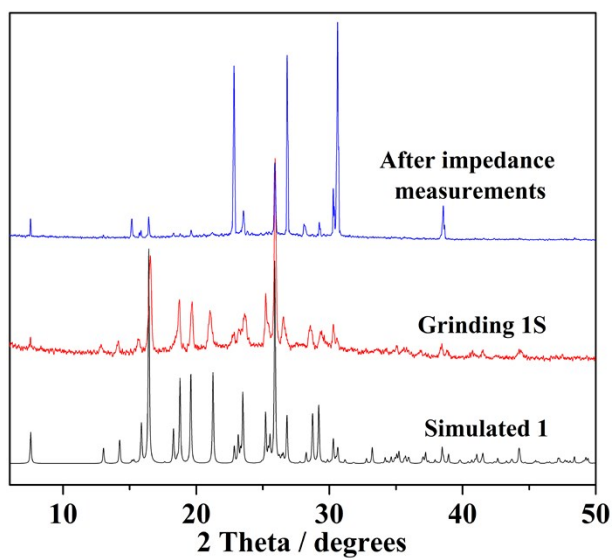


Fig S6. Simulated and grinding and after impedance measurements PXRD patterns of compound **1S**.

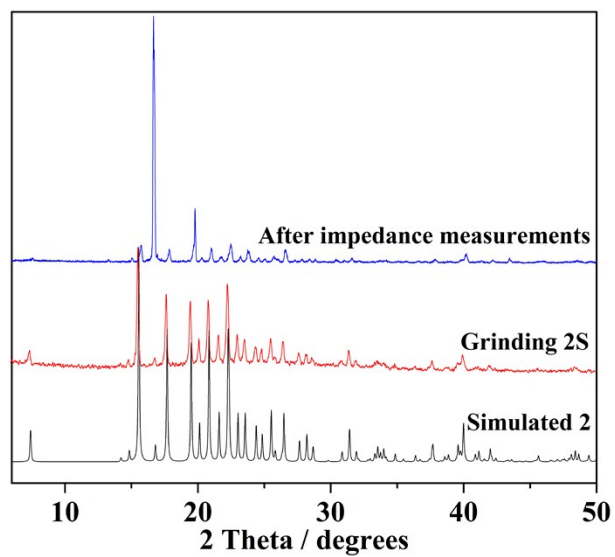


Fig S7. Simulated and grinding and after impedance measurements PXRD patterns of compound 2S.

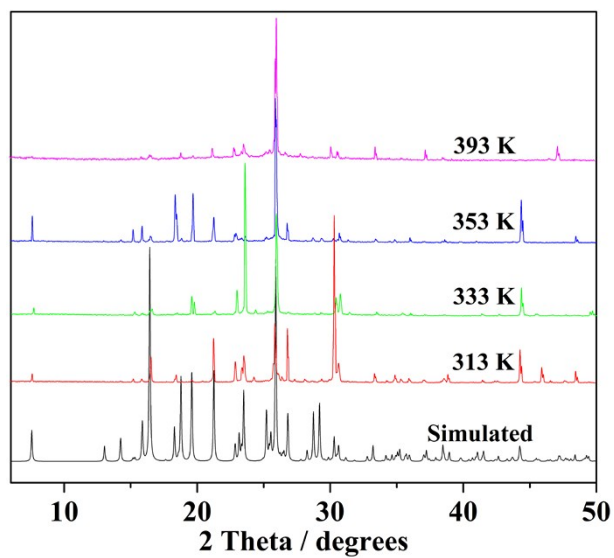


Fig S8. Simulated and variable-temperature PXRD patterns of compound 1.

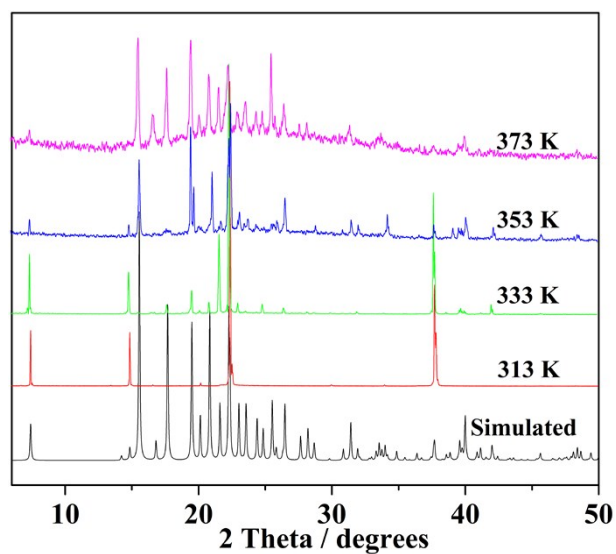


Fig S9. Simulated and variable-temperature PXRD patterns of compound 2.

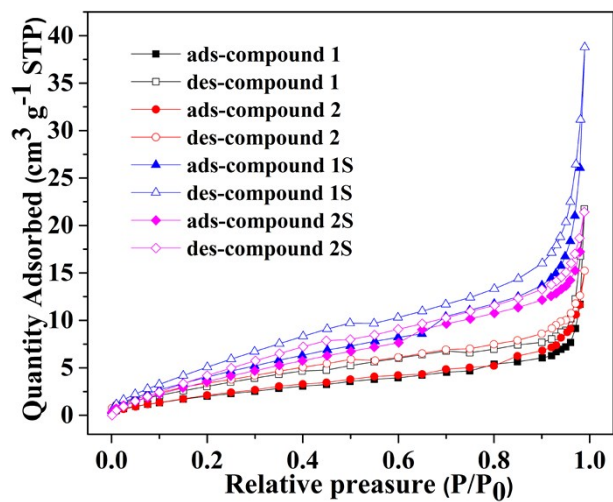


Fig S10. N₂ adsorption isotherms for four compounds at 77 K.

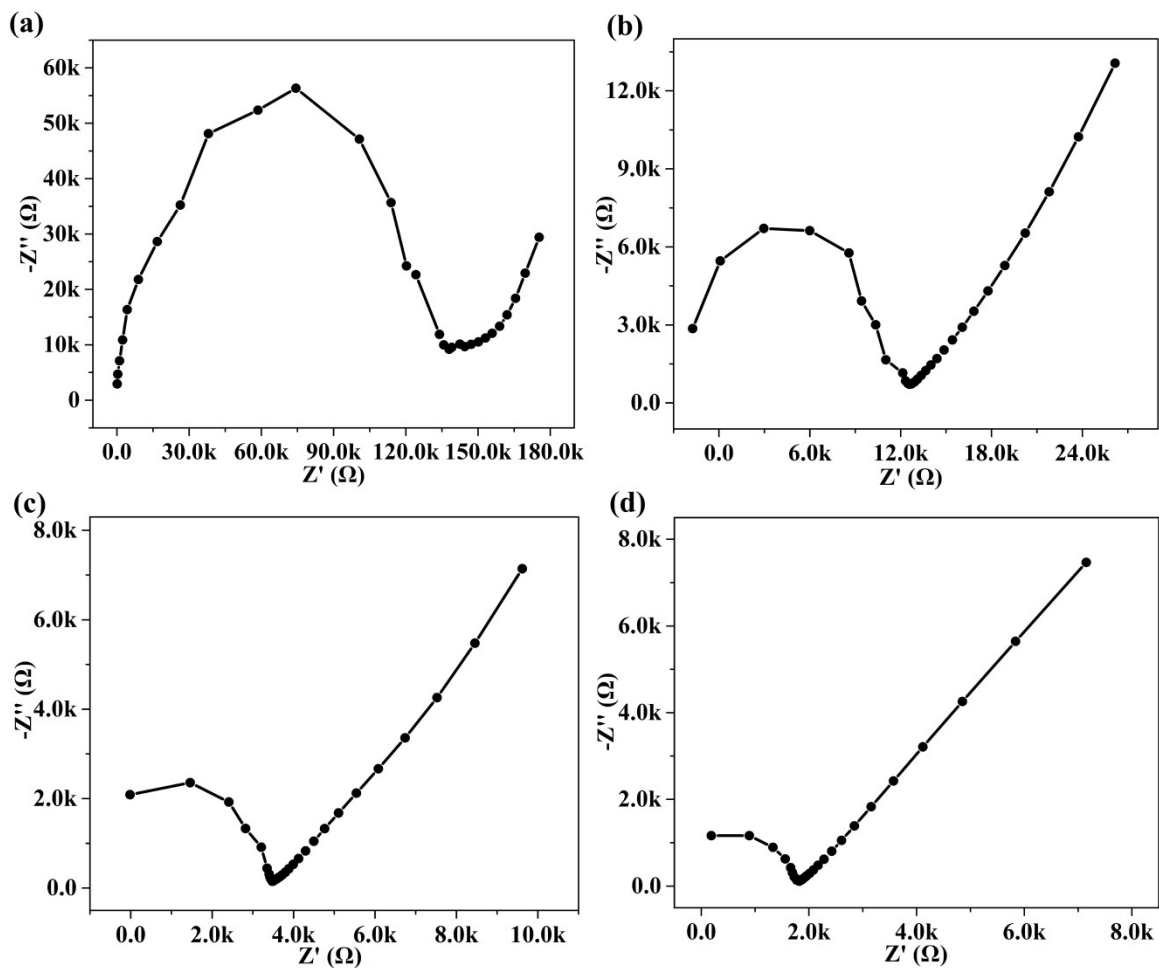


Fig S11. Nyquist plot of compound **1** at 25 °C and 65% RH (a), 75% RH (b), 85% RH (c) and 97% RH (d).

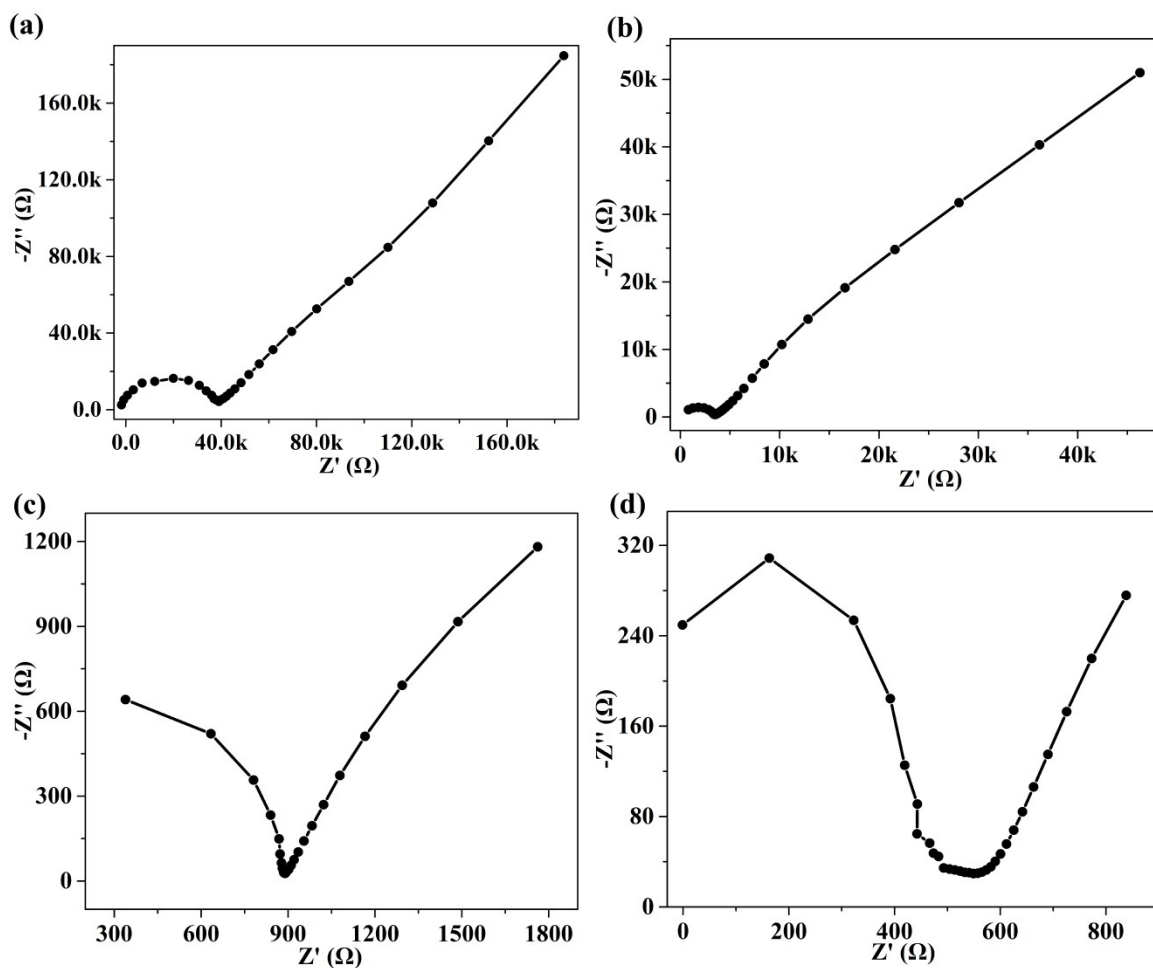


Fig S12. Nyquist plot of compound **2** at 25 °C and 65% RH (a), 75% RH (b), 85% RH (c) and 97% RH (d).

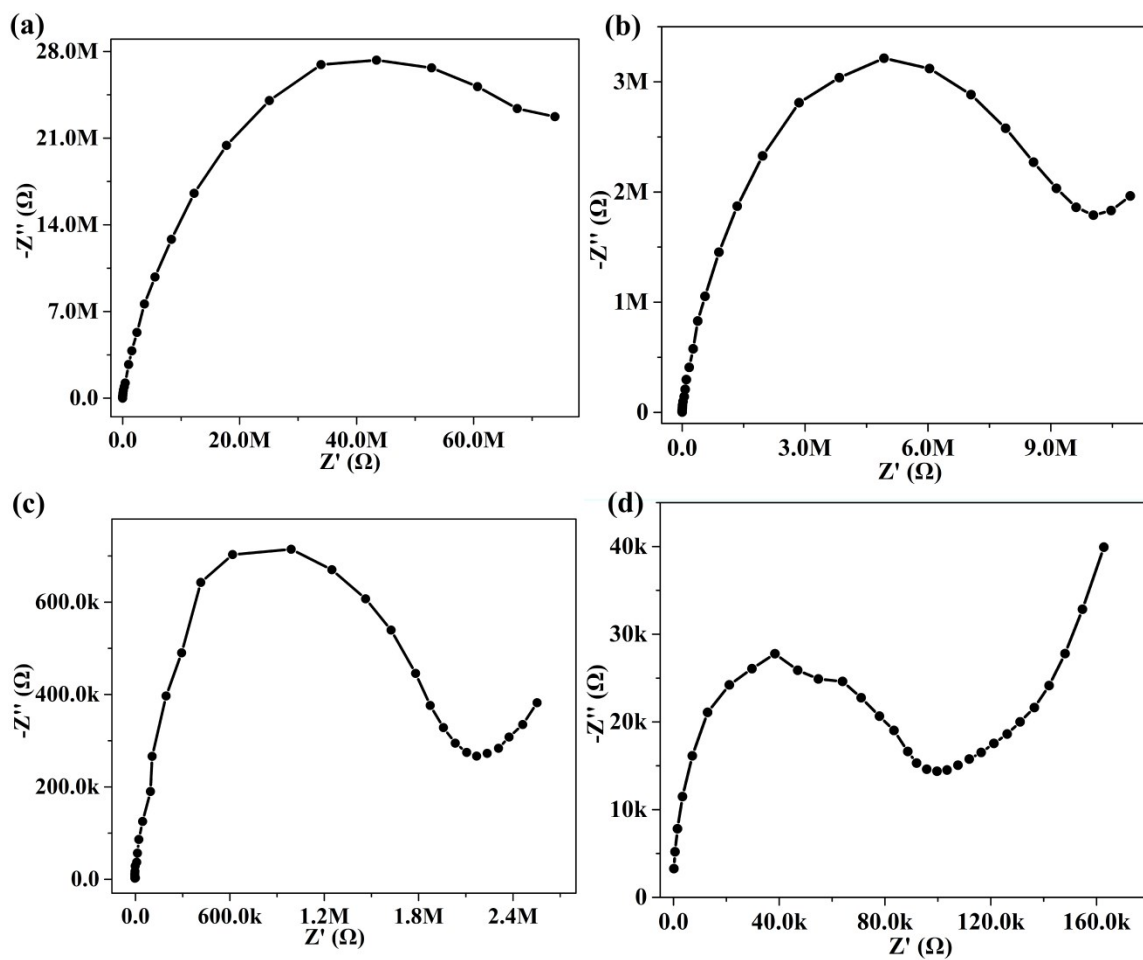


Fig S13. Nyquist plot of compound 1S at 25 °C and 65% RH (a), 75% RH (b), 85% RH (c) and 97% RH (d).

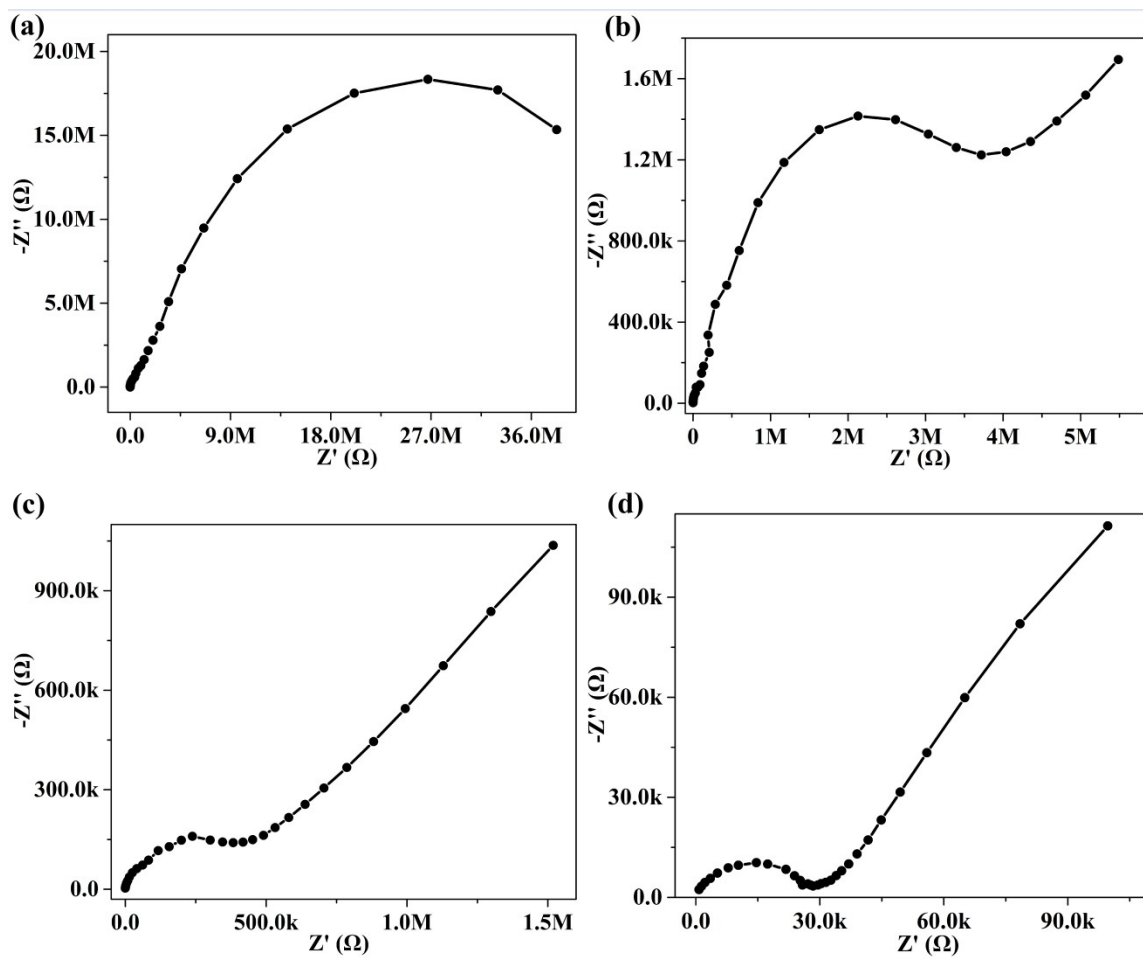


Fig S14. Nyquist plot of compound **2S** at 25 °C and 65% RH (a), 75% RH (b), 85% RH (c) and 97% RH (d).

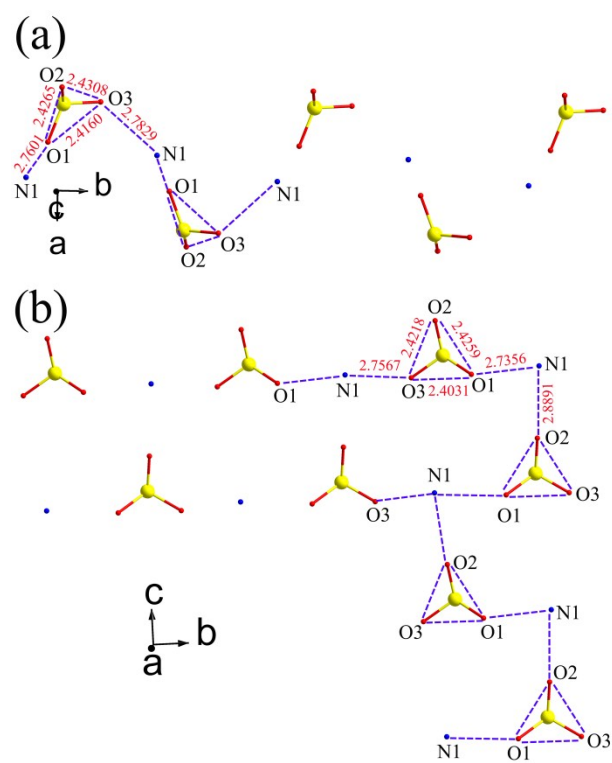


Fig S15. Segment of representation of hydrogen-bond network of compound **1** for (a) and **2** for (b).

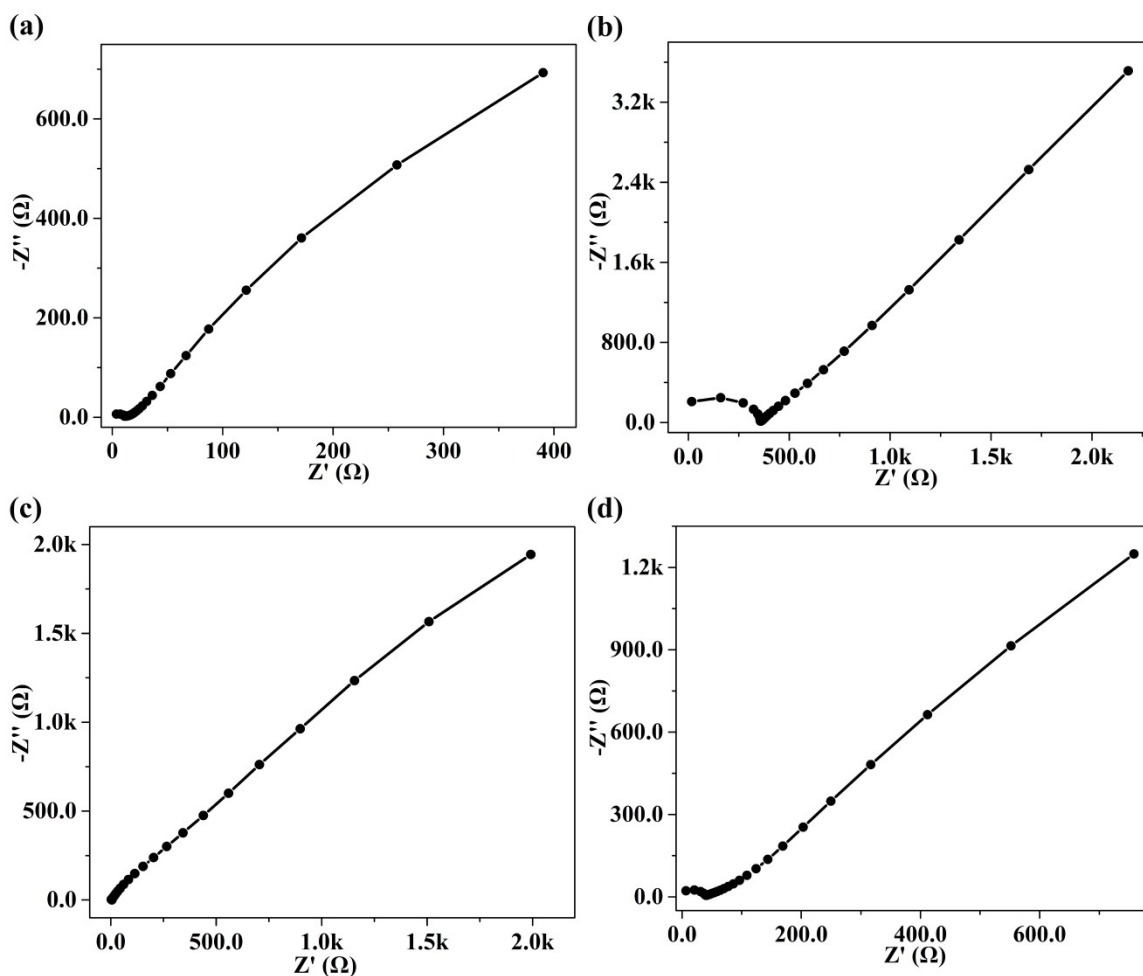


Fig S16. Nyquist plot of compound 1 (a), 1S (b), 2 (c) and 2S (d) at 60 °C and 97% RH.

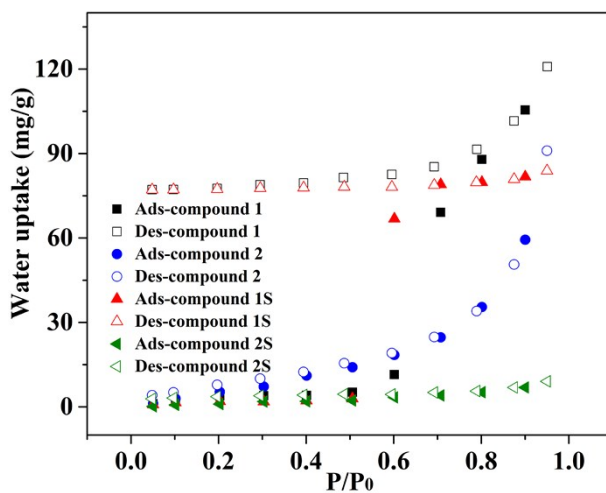


Fig S17. Water vapor adsorption isotherms of compounds 1, 1S, 2 and 2S at 25°C.

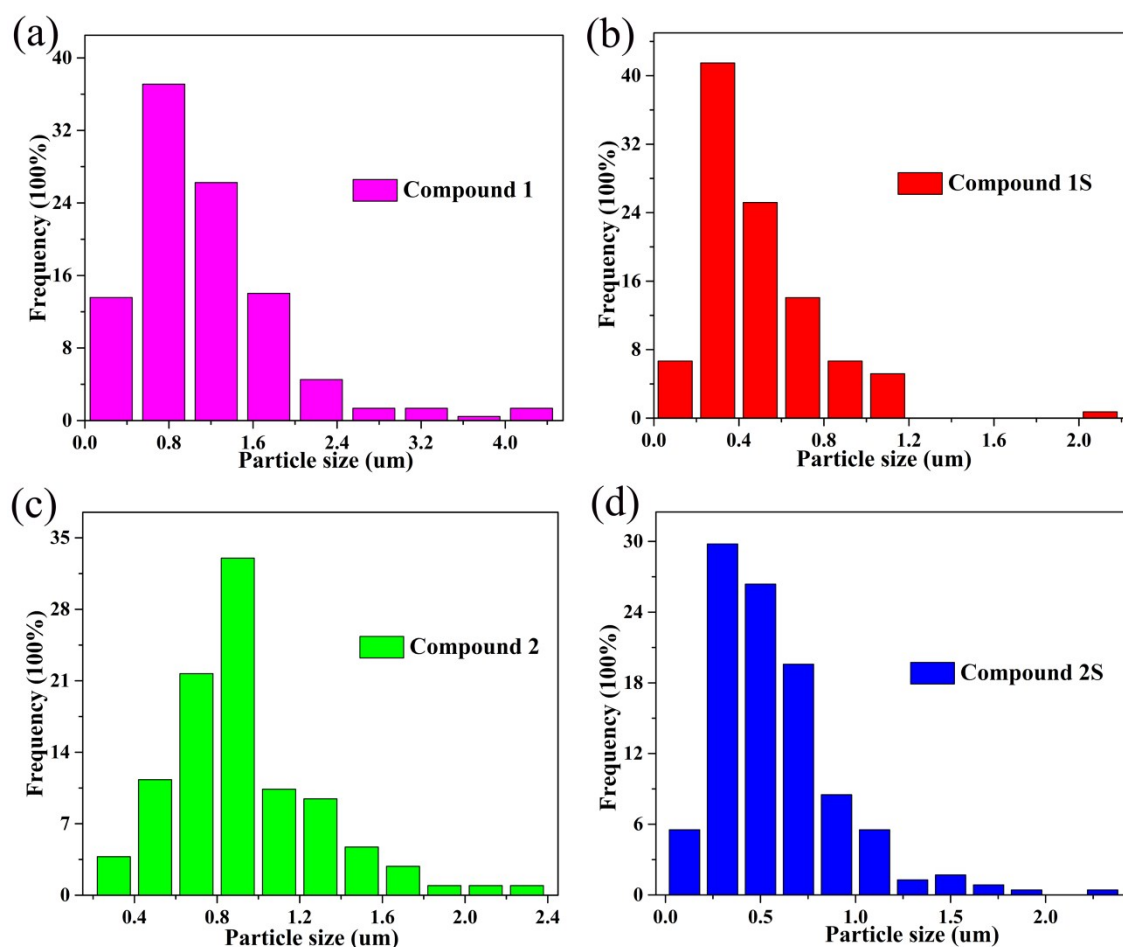


Fig S18. Particle size distributions for compound 1 (a), 2 (b), 1S (c), 2S (d) from ImageJ measurement of SEM images.

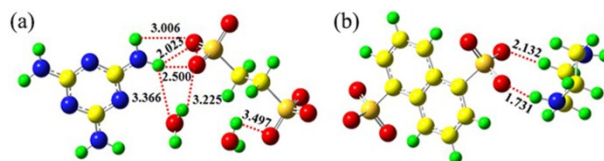


Figure S19. Optimized structures of compounds 1 and 2 and selected distance between adjacent hydrogen and oxygen.

Table S1. Crystal data and structure refinements for compound **1** and compound **2**.

Compound reference	1	2
Chemical formula	C ₈ N ₁₂ S ₂ O ₈ H ₂₂	C ₁₄ N ₂ S ₂ O ₆ H ₁₈
Formula Mass	478.49	374.42
Crystal system	triclinic	monoclinic
<i>a</i> /(Å)	6.206(5)	11.989(5)
<i>b</i> /(Å)	7.228(5)	7.293(5)
<i>c</i> /(Å)	11.882(5)	9.150(5)
α /°	93.919(5)	90
β /°	98.389(5)	96.005(5)
γ /°	108.883(5)	90
Unit cell volume/(Å) ³	495.1(6)	795.6(8)
Temperature/K	293	293
Space group	P -1	P 21/c
No. of formula units per unit cell, <i>Z</i>	1	2
No. of reflections measured	2488	1423
No. of independent reflections	2046	966
<i>R</i> _{int}	0.0278	0.0899
Final <i>R</i> _{<i>I</i>} values (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0471	0.0426
Final <i>wR</i> (<i>F</i> ₂) values (<i>I</i> > 2σ(<i>I</i>)) ^b	0.1399	0.0873
Final <i>R</i> _{<i>I</i>} values (all data)	0.0578	0.0703
Final <i>wR</i> (<i>F</i> ₂) values (all data)	0.1483	0.0965
Goodness of fit on <i>F</i> ₂	1.068	0.923

$$^a R_I = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \sqrt{\sum w(|F_o|^2 - |F_c|^2)^2} / \sum w(F_o^2)^{1/2}$$

Table S2. Comparison of proton conductivity among some reported MOFs and HOFs.

Compounds	T (°C)	RH (%)	Proton conductivity (S cm ⁻¹)	Reference
BUT-8(Cr)A	80	100	1.27 × 10 ⁻¹	<i>Nat. Energy.</i> , 2017, 2 , 877-883.
UiO-66(SO ₃ H) ₂	80	90	8.4 × 10 ⁻²	<i>Angew. Chem. Int. Ed.</i> , 2015, 54 , 5142-5146.
Fe-CAT-5	25	98	5 × 10 ⁻²	<i>J. Am. Chem. Soc.</i> 2015., 137 , 15394-15397.
(Me ₂ NH ₂) ₃ (SO ₄) ₂ [M ₂ (ox) ₃]	25	98	4.2 × 10 ⁻²	<i>Angew. Chem. Int. Ed.</i> , 2014, 53 , 2638-2642.
PCMOF-10	60	95	3.55 × 10 ⁻²	<i>J. Am. Chem. Soc.</i> , 2015, 137 , 7640-7643.

H ⁺ @Ni ₂ (dobdc)(H ₂ O) ₂ (pH = 1.8)	80	98	2.2×10^{-2}	<i>Angew.Chem. Int. Ed.</i> , 2014, 53 , 8383-8387.
PCMOF2 ^{1/2}	85	90	2.1×10^{-2}	<i>J. Am. Chem. Soc.</i> , 2013, 135 , 963-966.
HOF-GS-11	30	95	1.8×10^{-2}	<i>Angew. Chem. Int. Ed.</i> , 2016, 55 , 10667-10671.
CuH(Hsfpip)Cl(H ₂ O)	95	97	1.50×10^{-2}	<i>J. Mater. Chem. A.</i> , 2017, 5 , 1085-1093.
Im-Fe-MOF	60	98	1.21×10^{-2}	<i>J. Am. Chem. Soc.</i> , 2017, 139 , 6183-6189.
(C ₅ H ₃ SO ₃ H)(CH ₂ CH ₂ NH)	60	97	1.18×10^{-2}	<i>This work.</i>
Cu(H ₂ spip)Cl ₂ ·H ₂ O	95	97	1.09×10^{-2}	<i>CrystEngComm.</i> , 2017, 19 , 7050-7056.
(CH ₂ SO ₃ H)(C ₃ N ₆ H ₆)·H ₂ O	60	97	1.03×10^{-2}	<i>This work.</i>
HOF-GS-10	30	95	0.75×10^{-2}	<i>Angew. Chem. Int. Ed.</i> , 2016, 55 , 10667-10671.
(NH ₄) ₂ (H ₂ adp)[Zn ₂ (ox) ₃]·3H ₂ O	25	98	8×10^{-3}	<i>J. Am. Chem. Soc.</i> , 2014, 136 , 7701-7707.
(CH ₂ SO ₃ H)(CH ₂ CH ₂ NH)	60	97	6.91×10^{-3}	<i>This work.</i>
Cu ₂ H ₂ (Hspip) ₂ Cl ₄ ·H ₂ O	95	97	6.47×10^{-3}	<i>CrystEngComm.</i> , 2017, 19 , 7050-7056.
PCMOF-5	62	98	4×10^{-3}	<i>J. Am. Chem. Soc.</i> , 2013, 135 , 1193-1196.
(Me ₂ NH ₂)[Eu(L)]	100	98	3.76×10^{-3}	<i>J. Am. Chem. Soc.</i> , 2017, 139 , 3505-3512.
[Me ₂ NH ₂][Eu(ox) ₂ (H ₂ O)]·3H ₂ O	55	95	2.73×10^{-3}	<i>J. Mater. Chem. A.</i> , 2016, 4 , 16484-16489.
CuH ₂ (Hsfpip) ₂ (H ₂ O)	95	97	2.58×10^{-3}	<i>J. Mater. Chem. A.</i> , 2017, 5 , 1085-1093.
Cu(Hsfpip)(H ₂ O) ₂ ·H ₂ O	95	97	1.43×10^{-3}	<i>J. Mater. Chem. A.</i> , 2017, 5 , 1085-1093.
Fe(ox)·2H ₂ O	25	98	1.3×10^{-3}	<i>J. Am. Chem. Soc.</i> , 2009, 131 , 3144-3145.
CB[6]·1.2H ₂ SO ₄ ·6.4H ₂ O	25	98	1.3×10^{-3}	<i>Angew.Chem. Int. Ed.</i> , 2011, 50 , 7870-7873.
CB[6]·1.1HCl·11.3H ₂ O	25	98	1.1×10^{-3}	<i>Angew.Chem. Int. Ed.</i> , 2011, 50 , 7870-7873.
(H ₁₂ RCC1) ¹²⁺ ·12Cl ⁻ ·4(H ₂ O)	30	95	1.1×10^{-3}	<i>Nat. commun.</i> , 2016, 7 : 12750.
CoCa·nH ₂ O	25	95	1×10^{-3}	<i>Chem. Mater.</i> , 2015, 27 , 8116-8125.
{[Ca(D-Hpmpc)(H ₂ O) ₂]·2HO _{0.5} } _n	60	97	8.9×10^{-4}	<i>Chem. Sci.</i> , 2013, 4 , 983-992.
Ca ^{II} Cu ^{II} ₆ [(S,S)-alamox] ₃ (OH) ₂ (H ₂ O)	80	95	8.6×10^{-4}	<i>Chem. Mater.</i> , 2016, 28 , 4608-4615.
CuH(Hspip)(HPO ₄)·H ₂ O	95	97	6.90×10^{-4}	<i>CrystEngComm.</i> , 2017, 19 , 7050-7056.
MFM-500(Ni)	25	98	4.5×10^{-4}	<i>J. Am. Chem. Soc.</i> , 2016, 138 , 6352-6355.
In-IA-2D-2	27	98	4.2×10^{-4}	<i>Chem. Commun.</i> , 2013, 49 , 6197-6199.
CB[8]·6.8HCO ₂ H·13H ₂ O	25	98	1.3×10^{-4}	<i>Angew.Chem. Int. Ed.</i> , 2011, 50 , 7870-7873.
K ₂ (H ₂ adp)[Zn ₂ (ox) ₃]·3H ₂ O	25	98	1.2×10^{-4}	<i>J. Am. Chem. Soc.</i> , 2014, 136 , 13166-13169.
{NH(prol) ₃ }[MCr(ox) ₃]	25	75	1.0×10^{-4}	<i>J. Am. Chem. Soc.</i> , 2009, 131 , 13516-13522.
[NMe ₃ (CH ₂ CO ₂ H)][FeCr(ox) ₃]·nH ₂ O	25	65	8.0×10^{-5}	<i>J. Am. Chem. Soc.</i> , 2012, 134 , 5472-5475.
In-5TIA	28	98	5.35×10^{-5}	<i>Chem. Commun.</i> , 2012, 48 , 5464-5466.
(Me ₂ NH ₂) ₂ [Li ₂ Zr(C ₂ O ₄) ₄]	17	67	3.9×10^{-5}	<i>J. Am. Chem. Soc.</i> , 2015, 137 , 6428-6431.
(H ₁₂ RCC1) ¹²⁺ ·6(SO ₄) ₂ ·27.25(H ₂ O)	30	95	6.1×10^{-5}	<i>Nat. commun.</i> , 2016, 7 : 12750.
CB[6]·H ₂ O	25	98	6.6×10^{-6}	<i>Angew.Chem. Int. Ed.</i> , 2011, 50 , 7870-7873.
CC3	30	95	6.4×10^{-6}	<i>Nat. commun.</i> , 2016, 7 : 12750.
H ₂ TDPP·(DMF) ₆ ·(THF) ₅	27	97	3.4×10^{-6}	<i>Cryst. Growth Des.</i> , 2016, 16 , 5831-5835