

Proton-Conducting Metal-Organic Frameworks with Linkers Containing Anthracenyl and Sulfonate Groups

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Experimental Section

General Information. All starting compounds were acquired from chemical suppliers and used directly without further treatment. All solvents were purified by standard drying methods. The dia ligand was synthesized by a reported procedure.¹ Infrared spectra were measured from a Bio-Rad FTS-185 infra-red spectrophotometer. TGA was carried out on a Perkin-Elmer Pyris 6 TG and a Mettler-Toledo 2-HT thermal analyzers under the same conditions of a heating rate of 20 °C min⁻¹ and a N₂ gas flow rate of 20 mL min⁻¹. PXRD analyses were performed on a Shimadzu Lab-X XRD-6000 diffractometer with CuK α radiation ($\lambda = 1.54060 \text{ \AA}$).

Synthesis of Co(dia)_{1.5}(Hsip)(H₂O)·H₂O (1). A mixture of dia (0.10 g, 0.322 mmol), Co(NO₃)₂·6H₂O (0.096 g, 0.322 mmol), and 5-sulfoisophthalic acid monosodium salt (0.086 g, 0.322 mmol) in 10 mL of D.I. H₂O was placed in a 20 mL Teflon container. The vessel was sealed and allowed to heat up to 140 °C in 2 h. This temperature was maintained for 48 h. Afterwards, the vessel was cooled down to 40 °C in 24 h. The red crystals formed were filtered and flushed with D.I. H₂O, CH₃OH, acetone, and DMF. They were then allowed to dry in air. Yield: 89 mg (52%). Anal. Calc. for C₃₈H₂₉N₆O₉SCo: C, 56.72; H, 3.63; N, 10.44%. Found: C, 56.90; H, 3.71; N, 10.62%. IR (KBr disk, cm⁻¹): 3478, 3117, 1695, 1621, 1599, 1564, 1502, 1440, 1413, 1401, 1362, 1327, 1317, 1253, 1228, 1189, 1164, 1158, 1102, 1084, 1040, 999, 939, 913, 867, 851, 839, 814, 799, 764, 741, 680, 655, 641, 610, 577, 550, 525, 490, 437, 416.

Zn₂(μ -OH)(dia)₂(sip)·2H₂O (2). A procedure similar to that of compound of **1** was used. A mixture of dia (0.10 g, 0.322 mmol), Zn(NO₃)₂·6H₂O (0.29 g, 1.220 mmol), and 5-sulfoisophthalic acid monosodium salt (0.0864 g, 0.322 mmol) was used. Orange crystals were obtained. Yield: 66 mg, 39%. Anal. Calc. for C₄₈H₃₅N₈O₁₀SZn₂: C, 55.08; H, 3.37; N, 10.71%. Found: C, 55.10; H, 3.57; N, 10.55%. IR (KBr disk, cm⁻¹): 3472, 3117, 1619, 1572, 1510, 1438, 1415, 1380, 1339, 1322, 1249, 1224, 1199, 1160, 1106, 1082, 1038, 948, 915, 911, 853, 779, 766, 736, 725, 684, 655, 624, 585, 579, 548, 462, 418.

Single-Crystal X-ray Diffraction Analyses. Structural data of **1** was acquired from a Bruker D8 VENTURE with a PHOTON 100 CMOS detector; structure data of **2** was obtained from a Bruker APEX II with a CCD area detector. Data acquisition was carried out at 150(2) K employing MoK α radiation ($\lambda = 0.71073$ Å) from a sealed X-ray tube. Unit cell parameters were refined by least-squares method. Data acquisition and reduction were carried out using the Bruker APEX and SAINT softwares.² Multi-scan method implemented in SADABS was performed for absorption corrections.³ Direct methods were utilized to solve the structures which were then refined by full-matrix least squares methods against F^2 using the SHELXL program.⁴ All non-H atoms were refined in anisotropic manners. All H atoms were fixed at calculated positions and then riding refinements were performed. CCDC file numbers are 2113874 (**1**) and 2113875 (**2**).

Proton Conductivity Measurement. The powder sample was pressed under a pressure of 3,550 kg cm⁻² for 120 sec to form a pellet, the thickness of which was recorded by a micrometer. Copper

wires were glued to both sides of the pellet using silver paste. Then the proton conductivities of the sample were measured with a four-probe setup by the AC impedance spectroscopy. Two sets of experiments were performed. One was tested at 30 °C while humidity levels were varied between 65 and 98% RH. The other was tested at temperatures varying from 40 to 85 °C with humidity levels kept at 98% RH. For acquiring the impedance data at diverse RH and temperatures, the sample were first equilibrated at diverse RH for at least 18 h at 298 K and then were equilibrated at desired temperature for another 5 hours before measurement. The humidity and temperature were controlled by a humidity-controlled oven. The impedance measurements were recorded on a Zahner Zennium-E4 with tuned frequencies of 0.1- 1 MHz and an alternating potential of 500 mV at 308-358 K. Data was collected using THALES USB software. The bulk conductivities (σ , $S\text{ cm}^{-1}$) of the sample were calculated from

the equation: $\sigma = \frac{L}{RA}$ where L (cm) is the sample's thickness, R (Ω) is the resistance estimated from the semicircular arc of the Nyquist plot, and A (cm^2) is the sample's face area ($A = \text{thickness} \times \text{width}$).

The Arrhenius plots of $\log(\sigma T)$ vs $1000/T$ are linear and feasibly be fitted to the equation

$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$, where σ_0 is a pre-exponential factor; E_a is the apparent activation energy for conduction; k is the Boltzmann's constant; and T is the absolute temperature.

Table S1. Crystallographic Data

	1	2
empirical formula	C ₃₈ H ₂₇ CoN ₆ O ₈ S· H ₂ O	C ₄₈ H ₃₂ N ₈ O ₈ SZn ₂ · 2H ₂ O
formula weight	804.66	1047.65
crystal system	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	9.1899(7)	10.9944(9)
<i>b</i> , Å	11.1150(8)	22.1650(18)
<i>c</i> , Å	19.4654(15)	18.7012(14)
α , deg	100.329(3)	90
β , deg	94.053(3)	90.251(6)
γ , deg	113.601(3)	90
<i>V</i> , Å ³	1769.9(2)	4557.3(6)
<i>T</i> , K	150(2)	150(2)
<i>Z</i>	2	4
F(000)	828	2144
no. of unique data	7698	8391
no. of params refined	497	623
<i>R</i> ₁ ^a [<i>I</i> > 2σ <i>I</i>]	0.0310	0.0649
<i>wR</i> ₂ ^b (all data)	0.0793	0.1693

$$^a R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|. \quad ^b wR_2 = [\sum(|F_o|^2 - |F_c|^2)^2 / \sum (F_o^2)]^{1/2}$$

Table S2. Selected Bond length (Å) and Angles (°) in **1**

Co1—O2	2.1288(11)	Co1—N1	2.1355(13)
Co1—O7#1	2.0832(11)	Co1—N3	2.1059(13)
Co1—O8	2.1192(11)	Co1—N5	2.1279(13)
N1—Co1—N5	89.37(5)	N5—Co1—O7#1	93.49(5)
N1—Co1—O7#1	93.49(5)	O7#1—Co1—O8	92.12(5)
N1—Co1—O8	84.13(5)	O8—Co1—O2	90.26(4)
N1—Co1—O2	90.85(5)	O2—Co1—N5	84.38(5)
N3—Co1—N5	91.49(5)	N1—Co1—N3	178.51(5)
N3—Co1—O7#1	87.32(5)	N5—Co1—O8	171.52(5)
N3—Co1—O2	90.45(5)	O2—Co1—O7#1	176.87(4)
N3—Co1—O8	95.13(5)		

#1 x+1, y+1, z

Table S3. Selected Bond length (Å) and Angles (°) in **2**

Zn1—O1	1.904(4)	Zn1—O2	1.948(4)
Zn1—N1	1.989(5)	Zn1—N4	2.007(5)
Zn2—O1	1.919(4)	Zn2—O4	1.950(4)
Zn2—N5	1.973(5)	Zn2—N8	1.985(5)
O2—Zn1—N1	107.9(2)	O1—Zn1—N1	109.79(19)
O2—Zn1—N4	109.96(19)	O2—Zn1—O1	103.02(18)
O1—Zn1—N4	109.96(19)	N1—Zn1—N4	117.1(2)
Zn1—O1—Zn2	124.2(2)		
N8—Zn2—O4	113.12(19)	N8—Zn2—O1	112.14(19)
N8—Zn2—N5	115.3(2)	N5—Zn2—O1	107.73(19)
N5—Zn2—O4	112.20(19)	O1—Zn2—O4	94.39(17)

Table S4. Hydrogen Bonds in **1**

D—H	d(D-H)	d(H···A)	<DHA	d(D···A)	A
O10—H10B	0.87	2.53	139.1	3.2376(16)	O7 [x+1, y+1, z]
O10—H10B	0.87	2.30	146.1	3.0608(16)	O1 [x, y+1, z]
O8—H8B	0.87	2.09	148.0	2.8624(17)	O5 [x+1, y, z]
O8—H8A	0.87	1.93	136.1	2.6280(17)	O6 [x+1, y+1, z]
O4—H4A	0.84	1.83	165.9	2.6545(16)	O3 [x-1, y, z]

Table S5. Hydrogen Bonds in **2**

D—H	d(D-H)	d(H···A)	<DHA	d(D···A)	A
O(10)—H(10B)	0.85	2.11	171.6	2.951(8)	O(2) [x-1/2, -y+1/2, z+1/2]
O(10)—H(10A)	0.85	2.17	145.9	2.912(8)	O(9) [x-1, y, z]
O(9)—H(9B)	0.85	2.06	158.5	2.864(6)	O(7) [x+1, y, z]
O(9)—H(9A)	0.85	2.23	123.8	2.797(7)	O(5) [x+1/2, -y+1/2, z+1/2]
O(1)—H(1)	0.95	2.06	132.6	2.792(6)	O(8) [x+1/2, -y+1/2, z-1/2]

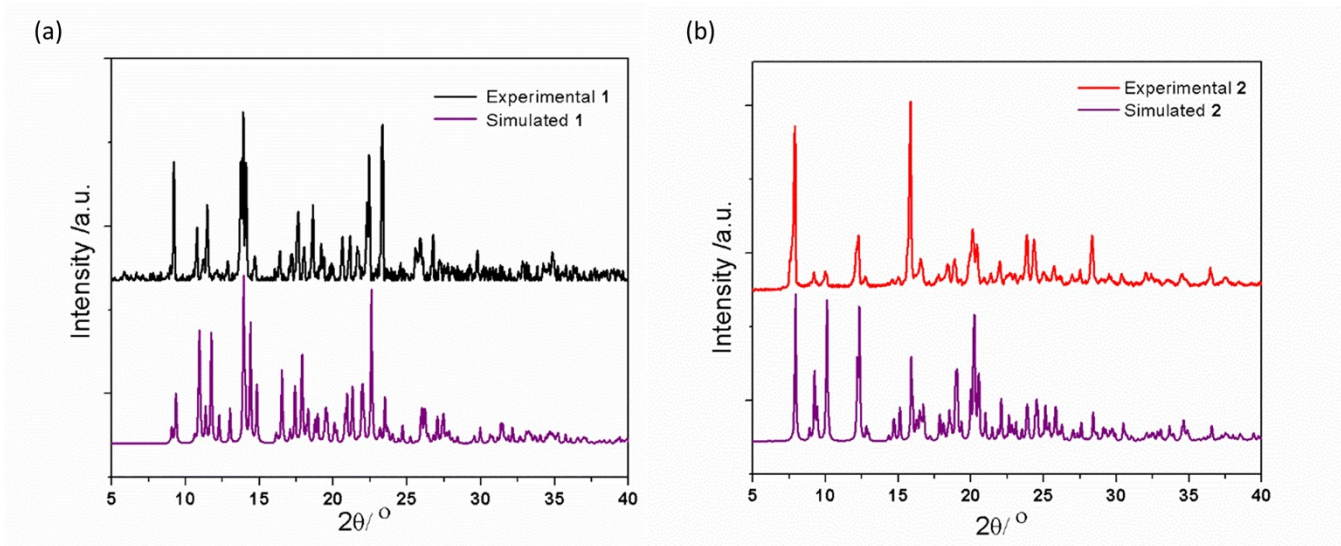


Figure S1. Powder X-ray Diffraction Patterns of **1** and **2**.

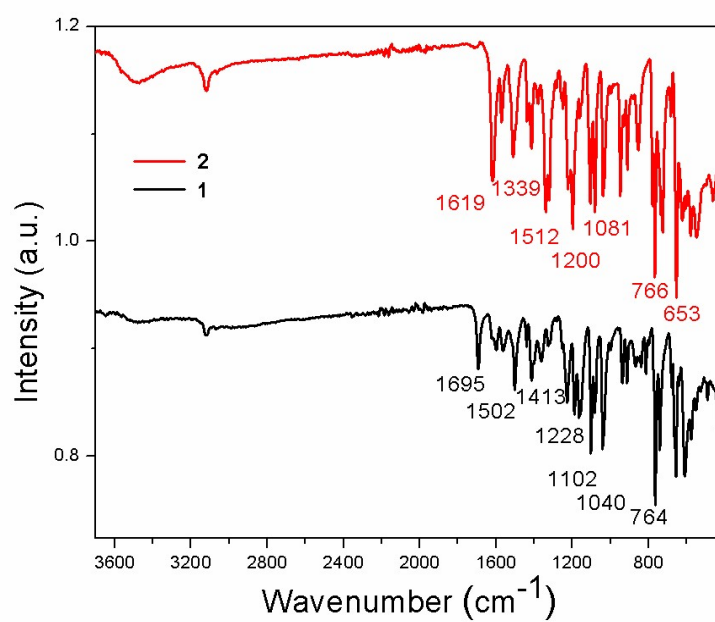


Figure S2. Infrared Spectra of **1** and **2**.

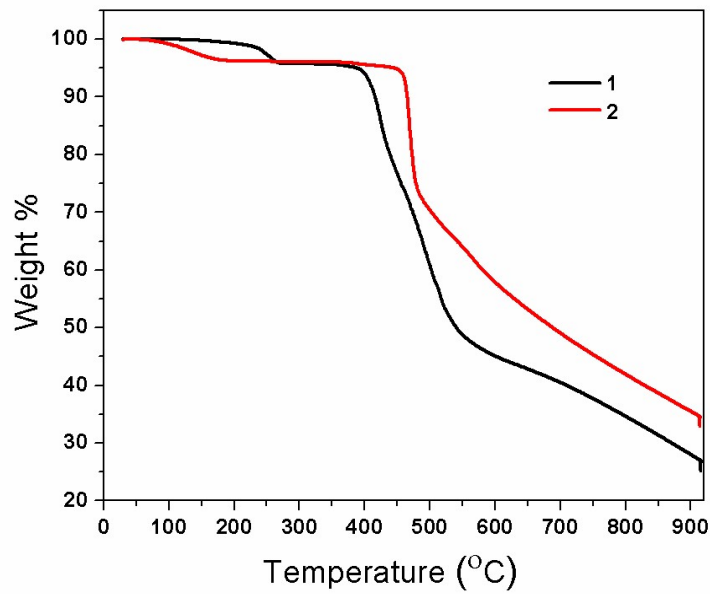


Figure S3A. TGA Curves of 1 and 2 (obtained from a Perkin-Elmer Pyris 6 TG analyzer).

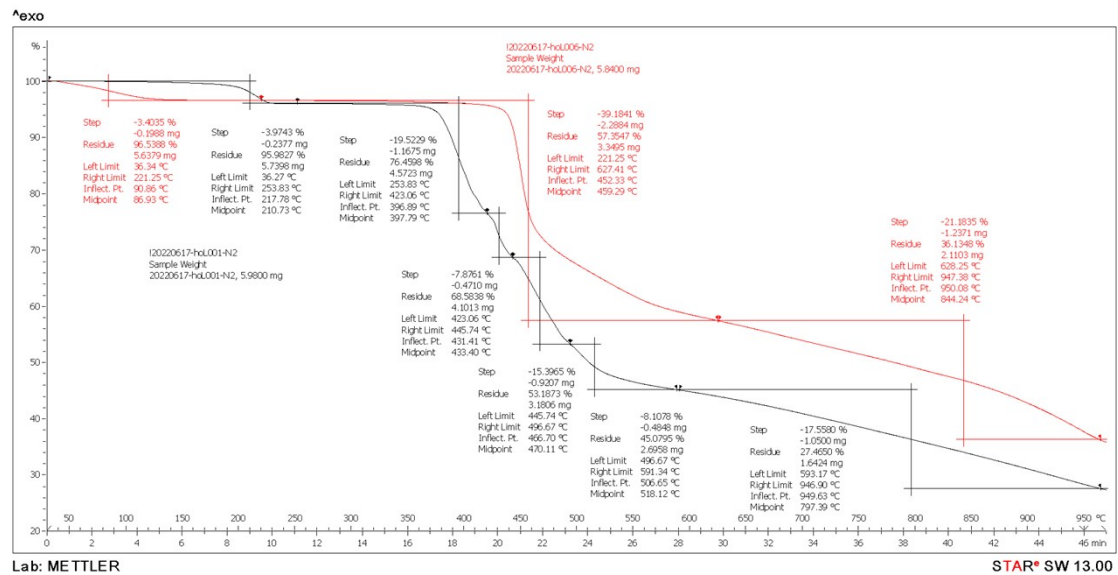


Figure S3B. TGA Curves of 1 (black curve) and 2 (red curve) (obtained from a Mettler-Toledo thermal analyzer).

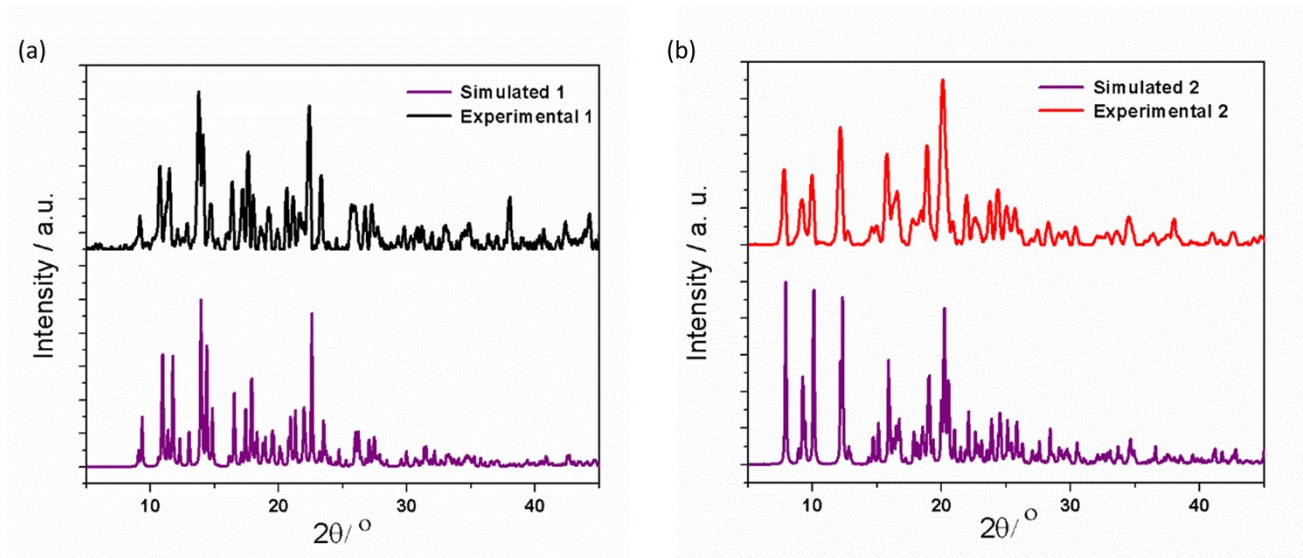


Figure S4. The PXR D patterns after 10-day proton conductivity measurements.

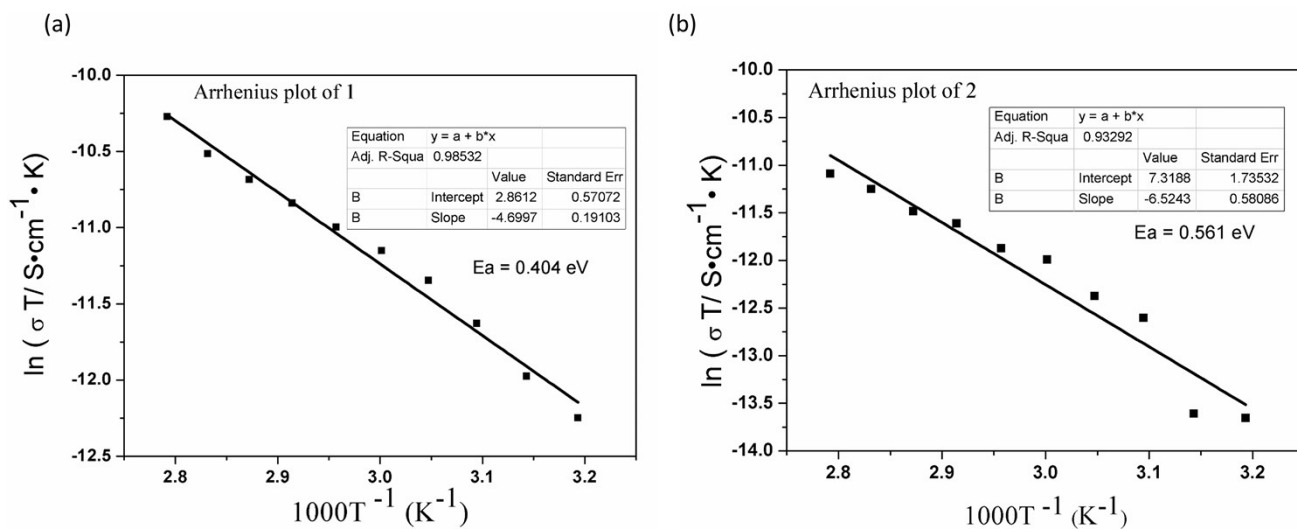


Figure S5. Arrhenius plots of **1** (upper) and **2** (bottom) under 98 % RH.

References

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