

A Proton Conductor Showing an Indication of Single-ion Magnet Based on a Mononuclear Dy(III) Complex

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Table 1. X-ray Diffraction Crystallographic Data for **1**.

Complex 1			
Formula	C ₁₂ H ₁₆ DyN ₁₁ O ₁₁	ρ (mm ⁻¹)	3.747
Fw	652.86	F (000)	1276
Temp (K)	296(2)	Reflns collected	12586
Crystal system	Monoclinic	Independent reflns	1756
Space group	C2/c	R_{int}	0.0170
a , Å	14.3641(2)	Theta range, $^{\circ}$	2.01-25.00
b , Å	15.5489(2)	Params/restraints/data	1756 / 3 / 168
c , Å	9.79550(10)	$R_1 [I > 2\sigma(I)]$	0.0206
β , (deg)	111.0960(10)	wR_2 (all data)	0.0498
V , Å ³	2041.16(4)	GOF on F^2	0.995
Z	4	ρ_{max}/ρ_{min} , e Å ⁻³	0.975/ -0.339
D_c , g/cm ³	2.124		

Table S2. Selected Bond Lengths (Å) and Bond Angles ($^{\circ}$) for **1**

Bond Lengths (Å)		Bond Lengths (Å)	
Dy(1)-O(1W)#1	2.392(3)	Dy(1)-N(1)#1	2.558(3)
Dy(1)-O(1W)	2.392(3)	Dy(1)-N(3)#1	2.558(3)
Dy(1)-O(1)#1	2.456(3)	Dy(1)-N(3)	2.557(3)
Dy(1)-O(1)	2.456(3)	Dy(1)-O(2)#1	2.699(3)
Dy(1)-N(1)	2.558(3)	Dy(1)-O(2)	2.699(3)
N(6)-O(5)	1.230(5)	C(5)-C(6)	1.355(5)
Bond Angles ($^{\circ}$)		Bond Angles ($^{\circ}$)	
O(1W)#1-Dy(1)-O(1W)	146.52(13)	O(1W)#1-Dy(1)-O(1)#1	114.69(9)
O(1W)-Dy(1)-O(1)#1	76.12(9)	O(1W)-Dy(1)-N(1)#1	137.78(9)
O(1W)#1-Dy(1)-N(3)#1	81.12(10)	O(1)#1-Dy(1)-N(3)	139.98(9)

Symmetry Codes for **1**, #1:-x, y, 0.5-z.

Table S3. Summary of SHAPE analysis for **1**.

label	shape	symmetry	Distortion(τ)
DP-10	Decagon	D _{10h}	29.422
EPY-10	Enneagonal pyramid	C _{9v}	20.278
OBPY-10	Octagonal bipyramid	D _{8h}	22.029
PPR-10	Pentagonal prism	D _{5h}	15.868
PAPR-10	Pentagonal antiprism	D _{5d}	16.180
JBCCU-10	Bicapped cube J15	D _{4h}	10.206
JBCSAPR-10	Bicapped square antiprism J17	D _{4d}	7.351
JMBIC-10	Metabidiminshed icosahedron J62	C _{2v}	11.827
JATDI-10	Augmented tridiminshed icosahedron J64	C _{3v}	17.005
JSPC-10	Sphenocorona J87	C _{2v}	4.359
SDD-10	Staggered Dodecahedron (2:6:2)	D ₂	7.726
TD-10	Tetradecahedron (2:6:2)	C _{2v}	7.919
HD-10	Hexadecahedron (2:6:2) or (1:4:4:1)	D _{4h}	13.262

Table S4. H-bonding length and angle table for **1**.

D-H...A	d(H...A)(Å)	d(D...A)(Å)	<DHA(Å)
O1W-H1WA ...O4	1.93(2)	2.727(4)	160(3)
O1W-H1WA...O5	2.557(18)	3.276(3)	145(3)
N2-H2...O4	2.36	3.136(4)	150
N2-H2...O4	2.50	3.219(4)	142
O1W-H1WB...O2	2.10(2)	2.889(4)	157(3)
N4-H4...O5	2.07	2.880(4)	156
O1W-H1WB...O2	2.39(2)	2.776(9)	108

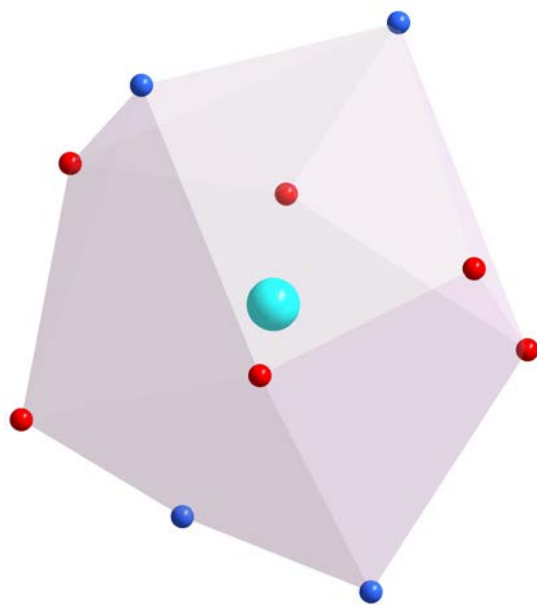


Figure S1. Sphenocorona coordination polyhedron around the Dy^{III} ion in **1**.

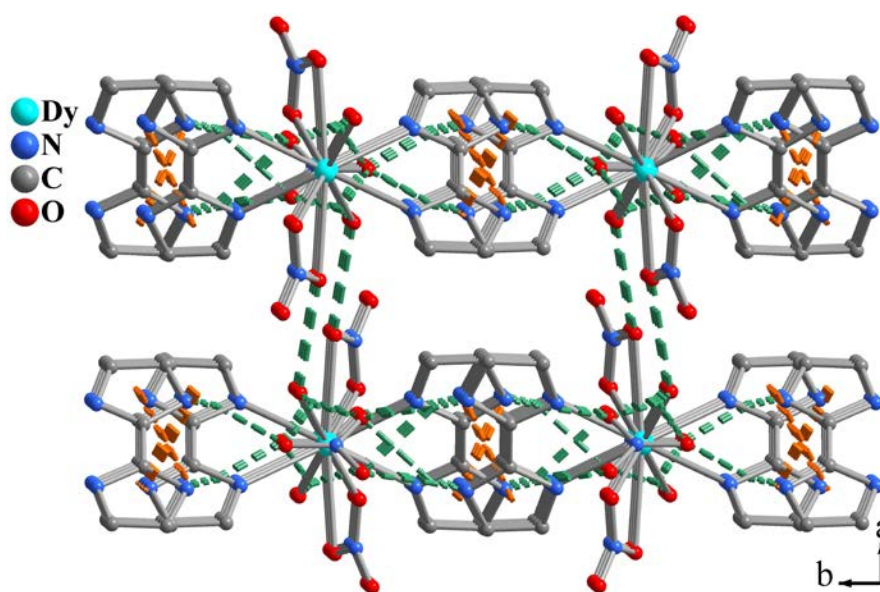


Figure S2. 3-D supramolecular network of **1** formed by H-bond along the *c*-axis (green dashed lines).

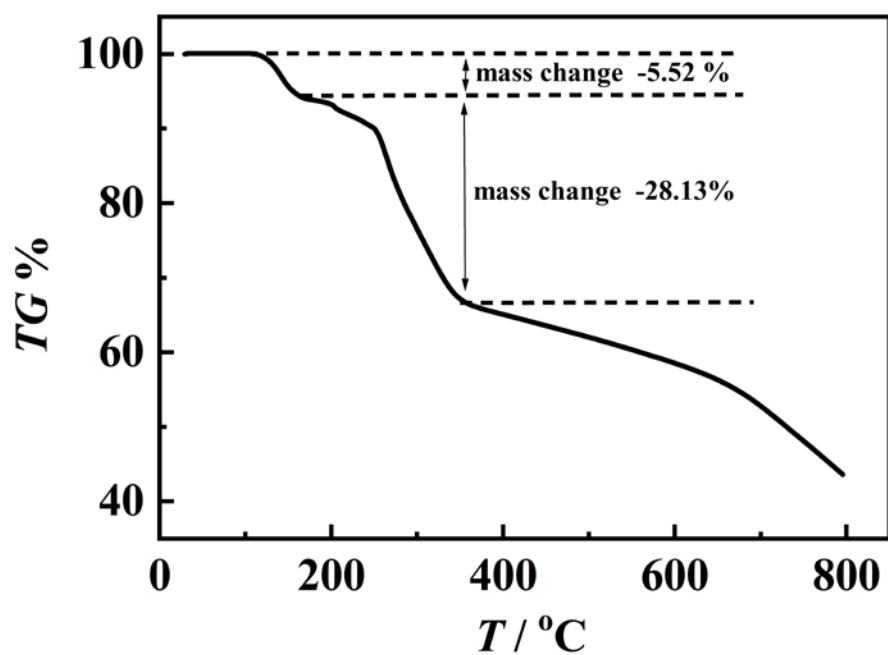


Figure S3. TGA plot of 1.

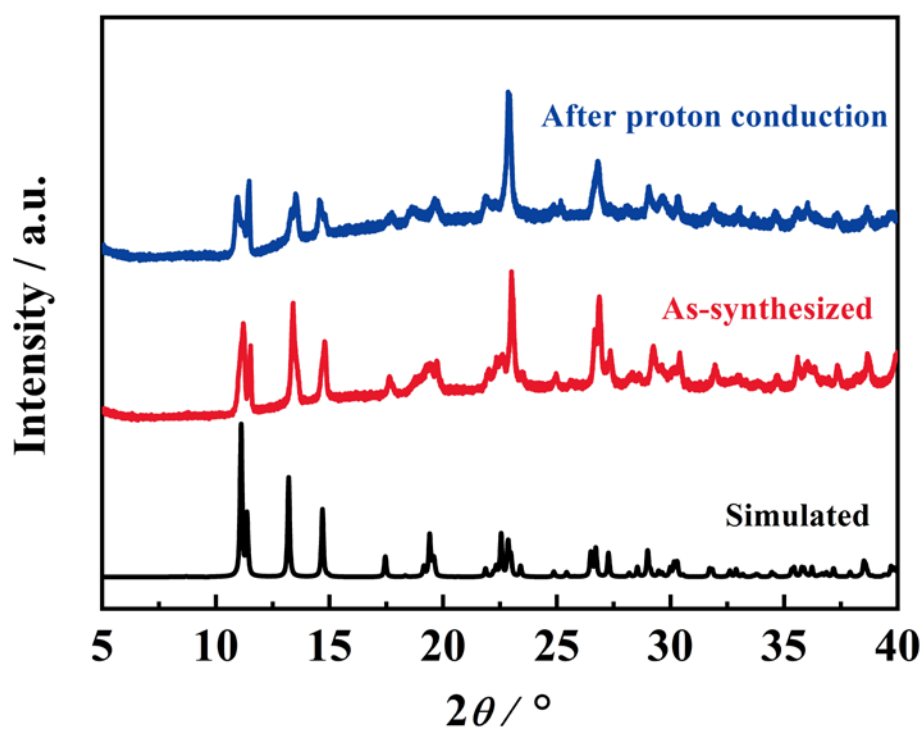


Figure S4. Powder X-ray diffraction patterns of simulated one, as-synthesized sample, the sample after proton conduction of 1.

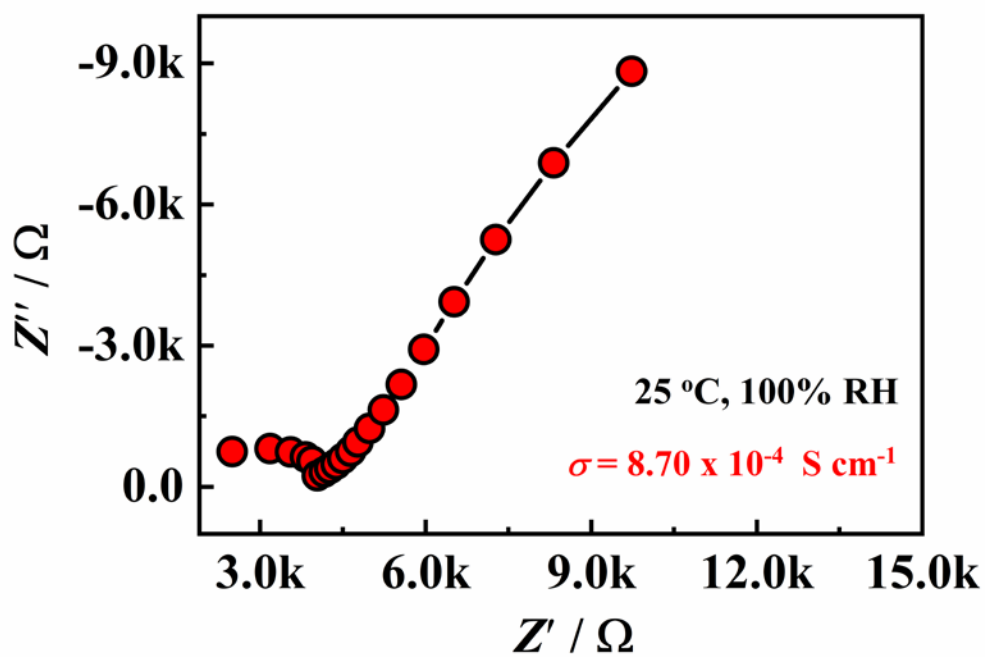


Figure S5. Nyquist plot for **1** at 25 °C under 100% RH.

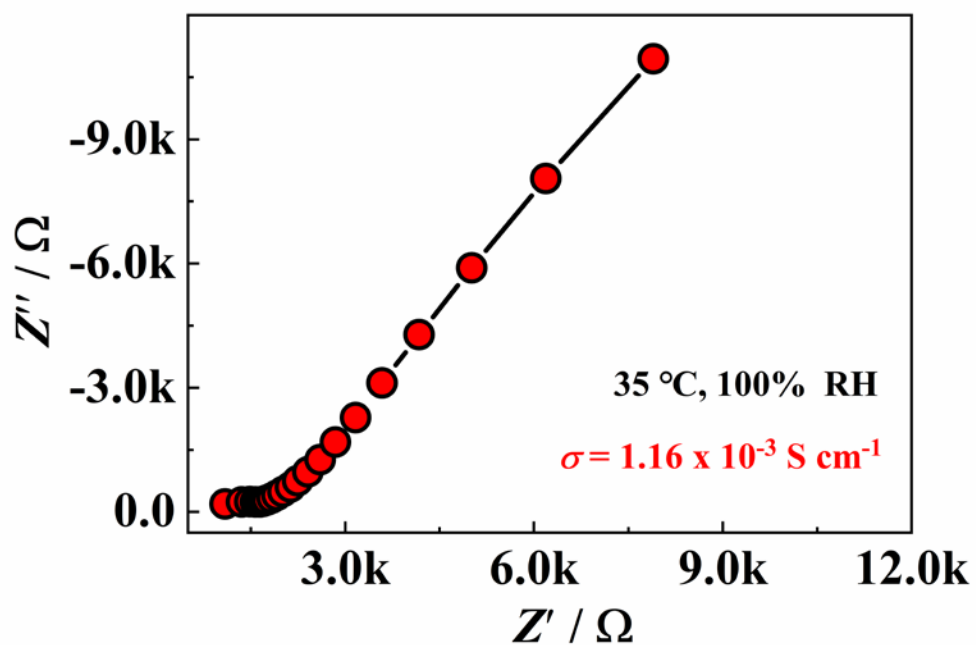


Figure S6. Nyquist plot for **1** at 35 °C under 100% RH.

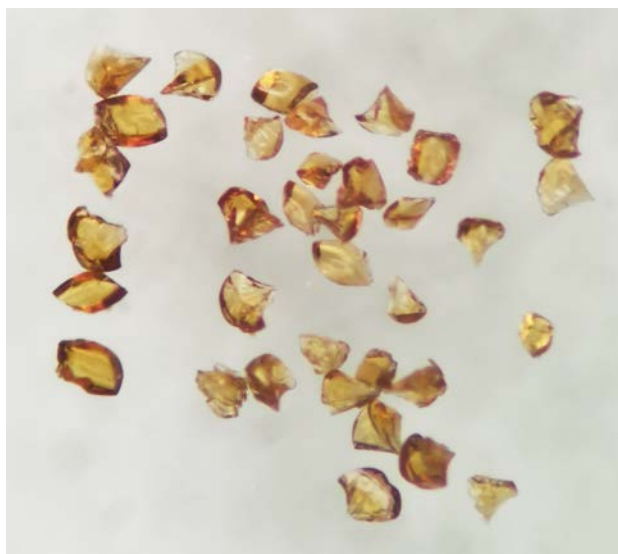


Figure S7. The photograph of crystals of complex **1** after exposed to 25-35 °C and 60-100% RH conditions during the whole proton conductivity measurements.

Table S5. Proton conductivity of **1** at 25 °C under variable relative humidity (RH).

RH / %	σ / S cm ⁻¹
20	5.12×10^{-10}
30	2.47×10^{-9}
40	2.49×10^{-8}
50	1.23×10^{-7}
60	1.16×10^{-6}
70	5.73×10^{-6}
80	4.36×10^{-5}
90	2.80×10^{-4}
100	8.70×10^{-4}

Table S6. Comparison of the proton conductivity of **1** with that of imidazole/imidazole derivatives-based conducting materials by using compacted pellets at relatively low temperature. σ represents proton conductivity and RH stands for relative humidity.

Compounds	Conductivity (S cm ⁻¹)	Conditions (°C, RH)	References

1	[Dy(H ₂ bim) ₂ (NO ₃) ₂ (H ₂ O) ₂]·(NO ₃)	8.70×10 ⁻⁴ 1.16×10 ⁻³	25°C, 100% 35°C, 100%	This work
2	[Cr ₄ In ₄ (Himdc) ₁₂]·H ₂ O [Cr _{7.28} In _{0.72} (Himdc) ₁₂]·H ₂ O (L= 4,5-imidazole-dicarboxylate)	2.3×10 ⁻³ 2.1×10 ⁻³	22.5 °C, 98% 22.5 °C, 98%	<i>Angew. Chem. Int. Edit.</i> , 2015 , 54, 7886–7890
3	{Na[Cd(MIDC)]} _n (H ₃ MIDC=2-methyl-1H-imidazole-4,5-dicarboxylic acid)	1.04×10 ⁻³	100°C, 98%	<i>ACS Appl. Mater. Interfaces.</i> 2019 , 11, 1713–1722
4	{[Co ₃ (p-CPhHIDC) ₂ (4,4'-bipy)(H ₂ O) ₂ H ₂ O]} _n {[Co ₃ (p-CPhHIDC) ₂ (bpe)(H ₂ O) ₃ H ₂ O]} _n (p-CPhH ₄ IDC=2-(4-carboxylphenyl)-1H-imidazole-4,5-dicarboxylic acid; 4,4'-bipy=4,4'-bipyridine, bpe=trans-1,2-bis(4-pyridyl)ethylene)	1.04×10 ⁻³ 7.02×10 ⁻⁴	100°C, 98% 100°C, 98%	<i>Chem. Eur. J.</i> , 2019 , 25, 14108–14116
5	[M ₂ (o-CPhH ₂ IDC) ₂ (H ₂ O) ₆].4H ₂ O (M = Co (1) and Zn (2)) (o-CPhH ₄ IDC = 2-(2-carboxylphenyl)-1H-imidazole-4,5-dicarboxylic acid) and [Mn(o-CPhH ₂ IDC)(2,2'-bipy)(H ₂ O) ₂] (2,2'-bipy = 2,2'-bipyridine)	1.78×10 ⁻⁴ 1.68×10 ⁻⁴ 5.4×10 ⁻⁵	100°C, 98% 100°C, 98% 100°C, 98%	<i>Appl. Supf. Sci.</i> , 2020 , 504, 144484
6	[M(FPhH ₂ IDC) ₂ (H ₂ O) ₂].4H ₂ O (M = Cd (1); Co (2)) Ni(FPhH ₂ IDC) ₂ (2,2'-bipy)·H ₂ O (FPhH ₃ IDC = 2-(fluoro)phenyl-4,5-imidazole dicarboxylic acid, 2,2'-bipy = 2,2'-bipyridine)	2.77×10 ⁻⁴ 3.42×10 ⁻⁵ 4.61×10 ⁻⁵	100°C, 98% 100°C, 98% 100°C, 98%	<i>J. Solid State Chem.</i> , 2019 , 282, 121129
7	M(m ₃ -HPhIDC)(m-C ₂ O ₄) _{0.5} (H ₂ O)·2 H ₂ O (M = Tb; Eu) (H ₃ PhIDC=2-phenyl-1H-imidazole-4,5-dicarboxylic acid)	8.95×10 ⁻⁴ 4.63×10 ⁻⁴	100°C, 98% 100°C, 98%	<i>Chem. Asian. J.</i> , 2019 , 15, 182-190
8	{[Cd(p-TIPhH ₂ IDC) ₂]·H ₂ O} _n [p-TIPhH ₃ IDC = 2-p-(1H-1,2,4-triazoly)phenyl-1H-4,5-imidazoledicarboxylic acid] [Sr(DMPH ₂ IDC) ₂](n) [DMPH ₃ IDC = 2-(3,4-dimethylphenyl)-1H-imidazole-4,5-dicarboxylic acid]	1.24×10 ⁻⁴ 9.2×10 ⁻⁴	100°C, 98%	<i>Inorg. Chem.</i> , 2019 , 58, 5173–5182
9	{[Mn(o-CPhH ₂ IDC)(4,4'-bipy)(0.5)(H ₂ O) ₂]·3H ₂ O}(n) (1)	5.74×10 ⁻⁵ 5.00×10 ⁻⁵	100°C, 98% 100°C, 98%	<i>New J. Chem.</i> , 2019 , 43,

	{[Zn ₅ (<i>o</i> -CPhH ₂ IDC) ₂ (<i>o</i> -CPhHIDC) ₂ (2,2-bipy) ₅]·5H ₂ O} _n (2) (<i>o</i> -CPhH ₄ IDC = 2-phenyl(2-carboxyl)-1-H-imidazole-4,5-dicarboxylic acid; 4,4-bipy = 4,4-bipyridine, 2,2-bipy = 2,2-bipyridine)			4859-4866
10	[Cd(HDMPhIDC)(H ₂ O)] _n (H ₃ DMPHIDC=2-phenyl(3,4-dimethyl)-1-H-imidazole-4,5-dicarboxylic acid)	1.30×10 ⁻⁴	100°C, 98%	<i>New J. Chem.</i> , 2019 , 42, 20197–20204
11	{[CoL ₂ (H ₂ O)(2)](ClO ₄) ₂ ·3DMA·0.4H ₂ O} _n (L=bis(4-imidazol-1-ylphenyl)diazene)	3.96×10 ⁻⁴	80°C, 95%	<i>Cryst. Growth Des.</i> , 2018 , 18, 6211–6220
12	[Ni(Imdz) ₆] _{0.5} (1,5-NDS) _{0.5} ·H ₂ O [Ni(Imdz) ₆] _{0.5} (2,6-NDS) _{0.5} [Ni(Imdz) ₆] _{0.5} (4,4'-BPDC) _{0.5} ·H ₂ O (Imdz = imidazole, 1,5-NDS = 1,5-naphthalenedisulfonic acid, 2,6-NDS = 2,6-naphthalene disulfonate, 4,4'-BPDC = 4,4'-biphenyl dicarboxylic acid)	7.5×10 ⁻⁴ 3.5×10 ⁻⁴ 9.7×10 ⁻⁴	80°C, 98% 80°C, 98% 80°C, 98%	<i>Chem. Eur. J.</i> , 2019 , 25, 1691–1695
13	{[Sr(<i>o</i> -CPhH ₂ IDC)(H ₂ O) ₂]·2H ₂ O} _n	6.08×10 ⁻⁵	100°C, 98%	<i>Polyhedron.</i> , 2019 , 169, 1–7
14	[Cu ₄ (HDMPhIDC) ₄ (H ₂ O) ₄] _n (H ₃ DMPHIDC=2-(3,4-dimethyl)phenyl-4,5-imidazole dicarboxylic acid)	2.58×10 ⁻⁵	100°C, 98%	<i>Polyhedron.</i> , 2019 , 158, 377–385
15	[Sr(H ₂ PhIDC) ₂ (H ₂ O) ₄]·2H ₂ O (H ₃ PhIDC = 2-phenyl-4,5-imidazole dicarboxylic acid)	1.91×10 ⁻⁶	90°C, 98%	<i>J. Alloys Compd.</i> , 2018 , 750, 895–901
16	[Zn(2-MeBIM) ₂ (OAc) ₂]·3H ₂ O [Zn(2-MeBIM)(Pht)(H ₂ O)]·2H ₂ O (2-MeBIM = 2-methyl benzimidazole, OAc = acetate anion and Pht = dianion of phthalate)	4.5×10 ⁻⁶ 1.0×10 ⁻⁵	25°C, 100% 25°C, 100%	<i>Inorg. Chim. Acta.</i> , 2015 , 437, 167–176
17	[Sr(H ₂ PhIDC) ₂ (H ₂ O) ₄]·2H ₂ O (H ₃ PhIDC = 2-phenyl-4,5-imidazole dicarboxylic acid)	1.91×10 ⁻⁶	90°C, 98%	<i>J. Alloys Compd.</i> , 2018 , 750, 895–901
18	Zn ₃ (IBT) ₂ (H ₂ O) ₂ (IBT = 4,5-bis(tetrazol-5-yl)imidazole)	1.98×10 ⁻⁵	30°C, 97%	<i>CrystEenComm.</i> , 2018 , 20, 3158–3161
19	{[Mn(<i>o</i> -CPhH ₂ IDC)(4,4-bipy) _{0.5} (H ₂ O) ₂]·3H ₂ O} _n {[Zn ₅ (<i>o</i> -CPhH ₂ IDC) ₂ (<i>o</i> -CPhHIDC) ₂ (2,2-bipy) ₅]·5H ₂ O} _n (<i>o</i> -CPhH ₄ IDC = 2-phenyl	5.74×10 ⁻⁵ 5.00×10 ⁻⁵	100°C, 98% 100°C, 98%	<i>New J. Chem.</i> , 2019 , 43, 4859–4866

	(2-carboxyl)-1- <i>H</i> -imidazole-4,5-dicarboxylic acid, 4,4-bipy = 4,4-bipyridine, 2,2-bipy = 2,2-bipyridine)			
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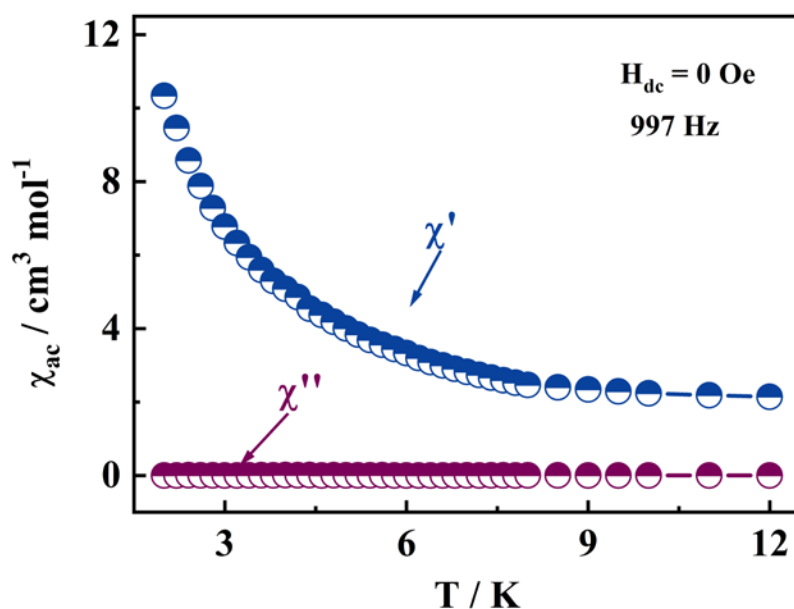


Figure S8. AC susceptibility measurements at frequency with 977 Hz for **1** at $H_{dc} = 0$ Oe, $H_{ac} = 2.5$ Oe

Table S7. Linear combination of two modified debye model fitting parameters from 2 to 7 K at $H_{dc} = 2000$ Oe

T /K	χ^2 /cm ³ mol ⁻¹	χ^1 /cm ³ mol ⁻¹	χ^0 /cm ³ mol ⁻¹	τ_1 /s	α_1	τ_2 /s	α_2
2.0	8.17013(3)	30.88637(3)	0.05932(2)	0.15681(3)	0.61197(3)	0.07813(4)	0.53235(3)
2.5	6.26158(2)	30.05776(3)	0.12518(3)	0.07798(3)	0.57477(2)	0.05504(11)	0.50642(5)
3.0	4.45468(10)	9.362200(4)	0.18504(3)	0.03917(4)	0.59412(8)	0.03087(9)	0.38119(6)
3.5	3.41827(4)	12.06544(2)	0.26272(2)	0.01892(5)	0.52011(6)	0.02244(3)	0.41470(3)

4.0	2.81495(4)	10.13028(4)	0.33112(4)	0.01100(5)	0.48396(5)	0.01581(5)	0.39021(3)
4.5	2.41554(3)	19.61455(5)	0.37435(7)	0.00800(3)	0.44415(6)	0.00963(2)	0.41420(4)
5.0	2.14388(2)	25.28558(3)	0.42505(6)	0.00517(2)	0.41641(6)	0.00590(2)	0.40128(2)
5.5	1.93974(6)	29.67630(8)	0.44859(9)	0.00310(5)	0.39878(4)	0.00342(3)	0.39020(4)
6.0	1.77070(7)	33.17694(2)	0.47873(3)	0.00139(3)	0.36814(3)	0.00149(5)	0.36404(2)
6.5	1.63772(8)	46.78638(7)	0.49054(4)	0.00051(5)	0.34091(3)	0.00053(3)	0.33988(3)
7.0	1.53205(3)	102.80047(6)	0.51386(4)	0.00020(8)	0.31607(2)	0.00020(7)	0.31584(6)

Table S8. The comparisons of the proton conductivity and the U_{eff}/k values of **1** with the previously reported proton-conductive nanomagnet. RH represents for relative humidity.

	Compounds	Proton Conductivity	U_{eff}/k	References
1	[Dy(H ₂ bim) ₂ (NO ₃) ₂ (H ₂ O) ₂](NO ₃) ₃)	8.70×10 ⁻⁴ S·cm ⁻¹ under 25°C and 100% RH 1.16×10 ⁻³ S·cm ⁻¹ under 35°C and 100% RH	71.6 K for the FR phase and 74.4 K for the SR phase at H _{dc} = 2000 Oe.	This work
2	[Dy ₇₂ (mda) ₂₄ (mdaH) ₈ (OH) ₁₂₀ (O) ₈ (NO ₃) ₁₆](NO ₃) ₈ ·16CH ₃ OH·168H ₂ O (mdaH ₂ = N-methyldiethanolamine)	1.80×10 ⁻³ S·cm ⁻¹ under 25 °C and 95% RH	19.6 K at H _{dc} = 0 Oe	<i>Adv. Mater.</i> , 2016 , 28, 10772–10779
3	(H ₅ O ₂) ₂ (H)[Yb ^{III} (hmpa) ₄][Co ^{III} (CN) ₆] ₂ ·0.2H ₂ O (HDBM = 1,3-diphenyl-propane-1,3-dione)	1.74×10 ⁻⁴ S·cm ⁻¹ under 25 °C and 97% RH	31.2 K at H _{dc} = 1000 Oe	<i>J. Am. Chem. Soc.</i> , 2020 , 142, 3970–3979

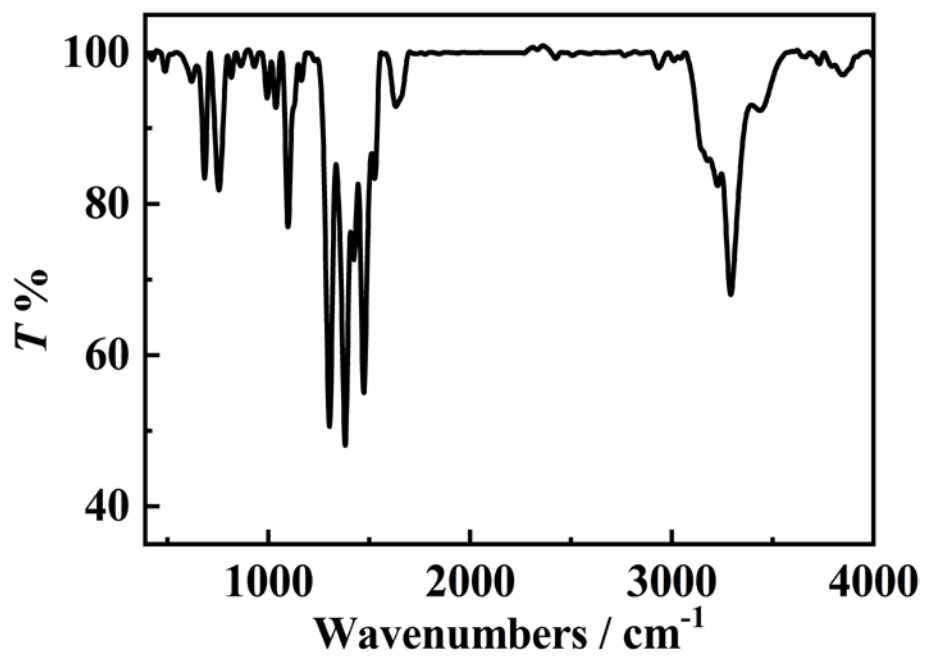


Figure S9. IR spectra for **1**.