

Supporting Information

A robust and multifunctional calcium coordination polymer as selective fluorescent sensor for acetone and iron (+3) and as tunable proton conductor

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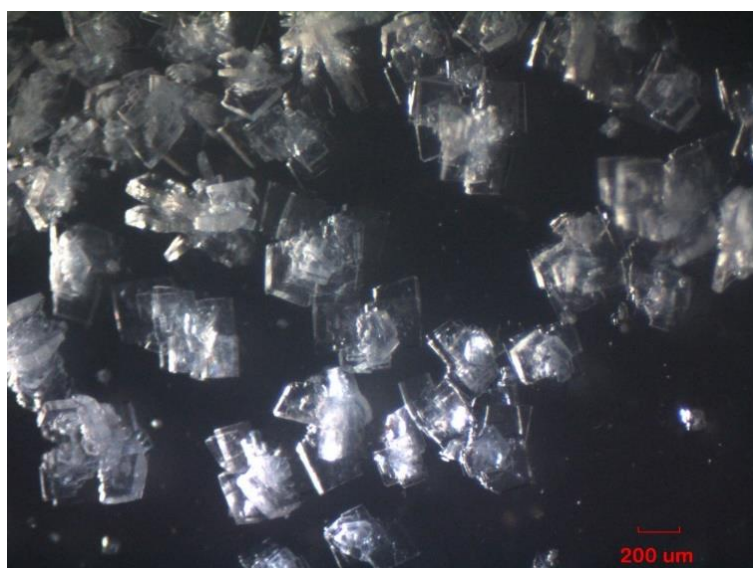


Figure S1. Crystal images of compound **1**.

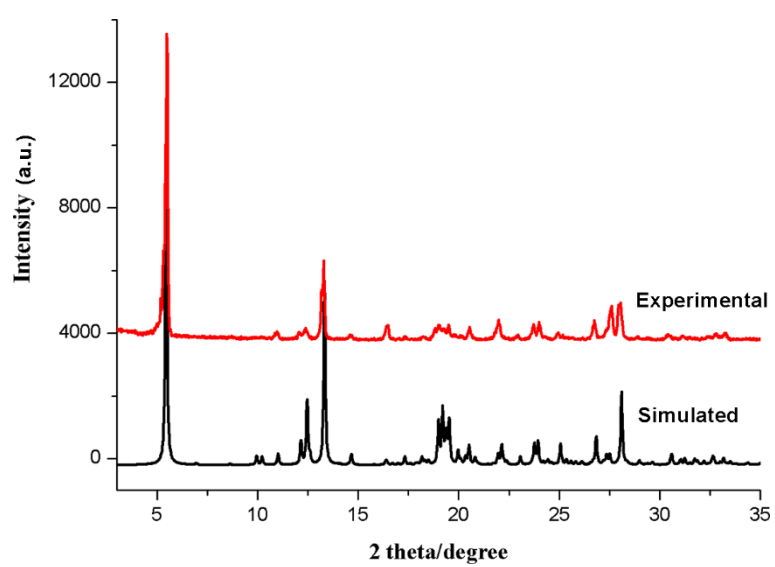


Figure S2. Experimental and simulated PXRD patterns of compound **1**.

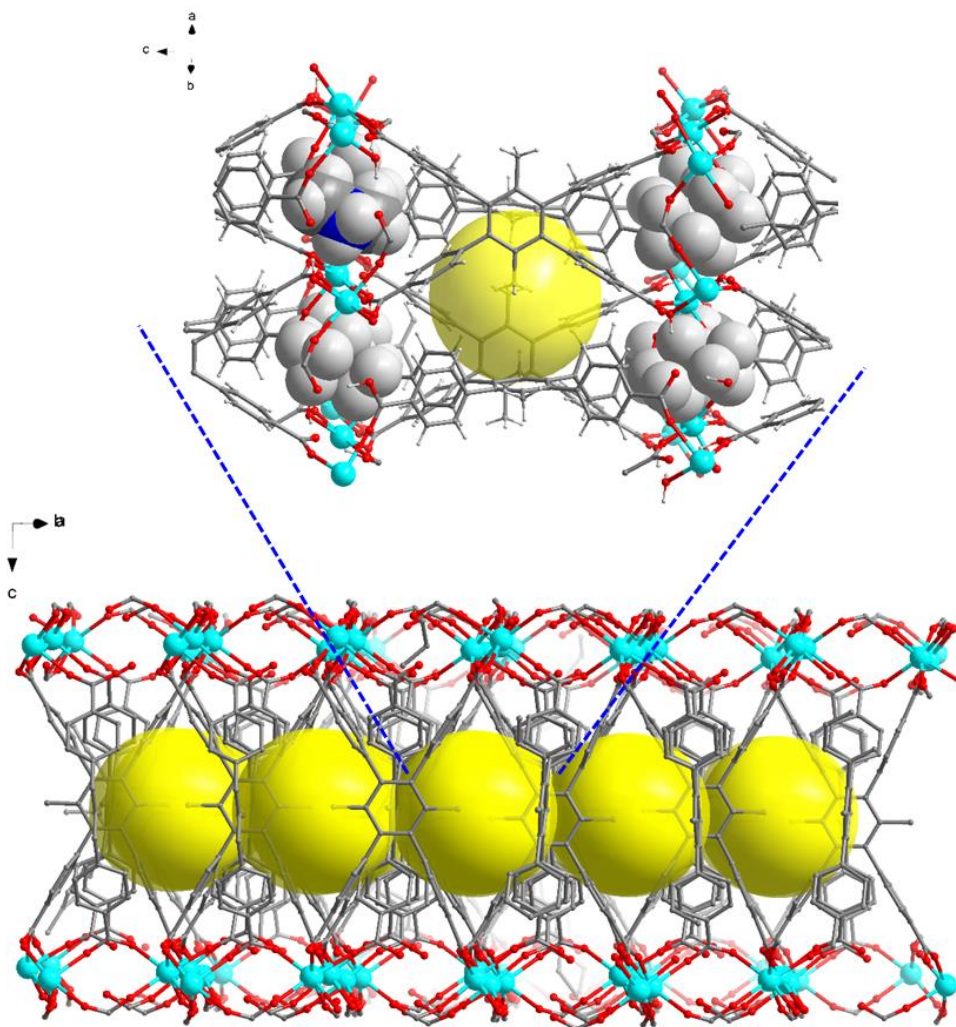


Figure S3. The cage structure in **1**. The $[(\text{CH}_3)_2\text{NH}_2]^+$ cations are shown in space filling mode.

Table S1. Hydrogen bonds in compound **1**.

D-H...A	d(D-H) / Å	d(H...A) / Å	d(D...A)/Å	$\angle(\text{DHA})^\circ$
O(7)-H(7)...O(5)#1	1.00(3)	1.52(3)	2.518(2)	176(3)
O(7)-H(7)...O(6)#1	1.00(3)	2.62(3)	3.216(2)	118(2)
O(9)-H(9A)...O(2)#2	0.84	1.82	2.634(2)	162.7
N(1)-H(1C)...O(3)#3	0.91(3)	2.62(3)	3.230(2)	124(2)
N(1)-H(1C)...O(4)#3	0.91(3)	1.88(3)	2.784(2)	172(2)
N(1)-H(1B)...O(1)	0.95(3)	2.56(3)	3.151(2)	121(2)
N(1)-H(1B)...O(2)	0.95(3)	1.74(3)	2.687(2)	179(3)
C(38)-H(38C)...O(6)#4	0.98	2.56	3.379(3)	140.7

Symmetry transformations used to generate equivalent atoms:

#1 $-x+3/2, -y, z-1/2$; #2 $-x+1, -y+1, -z+1$; #3 $x, -y+3/2, z-1/2$; #4 $x-1/2, y+1, -z+3/2$.

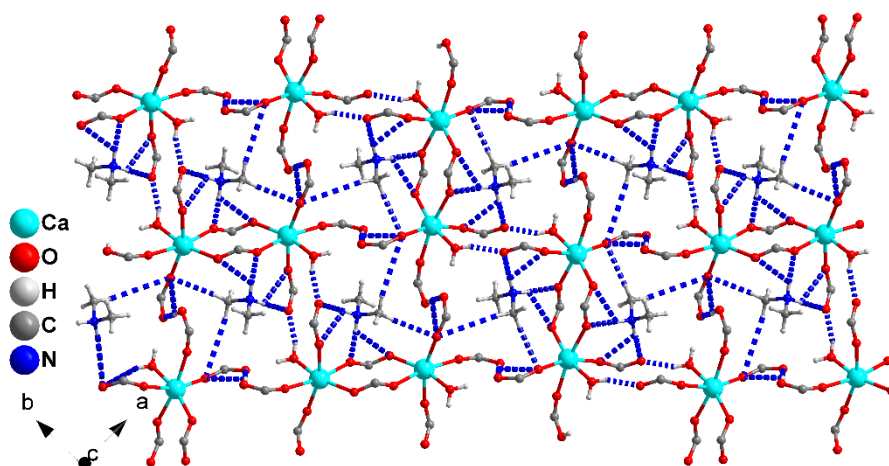


Figure S4. The H-bonding network (highlighted in blue dotted line) in **1** viewed along [100] direction. The H-bonding network was formed between H atoms in terminal water, dimethylamine cation and oxygen atom of carboxylic acid groups.

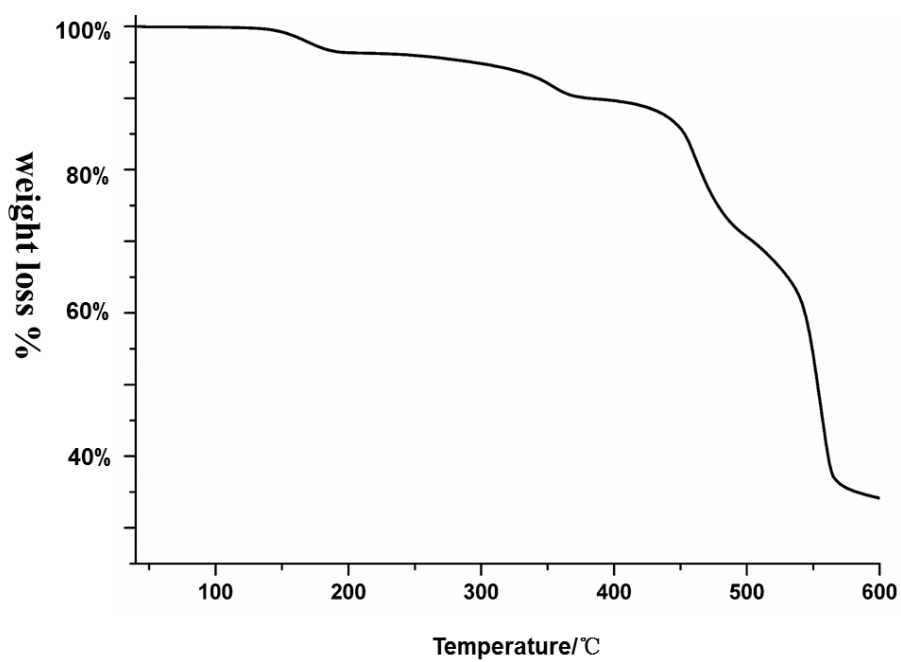


Figure S5. Thermogravimetric curve for compound **1**.

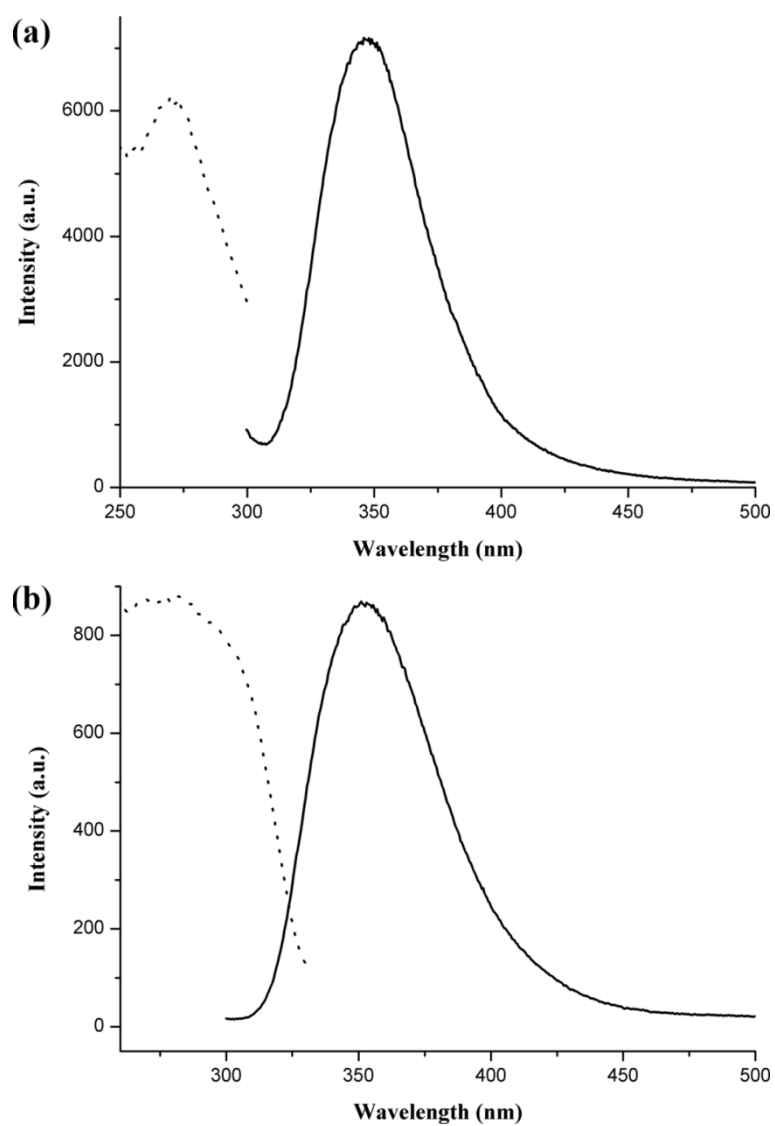


Figure S6. The fluorescence excitation and emission spectra of **1** (a) and the $\text{Me}_2\text{tcpbH}_4$ ligand (b) in the solid state.

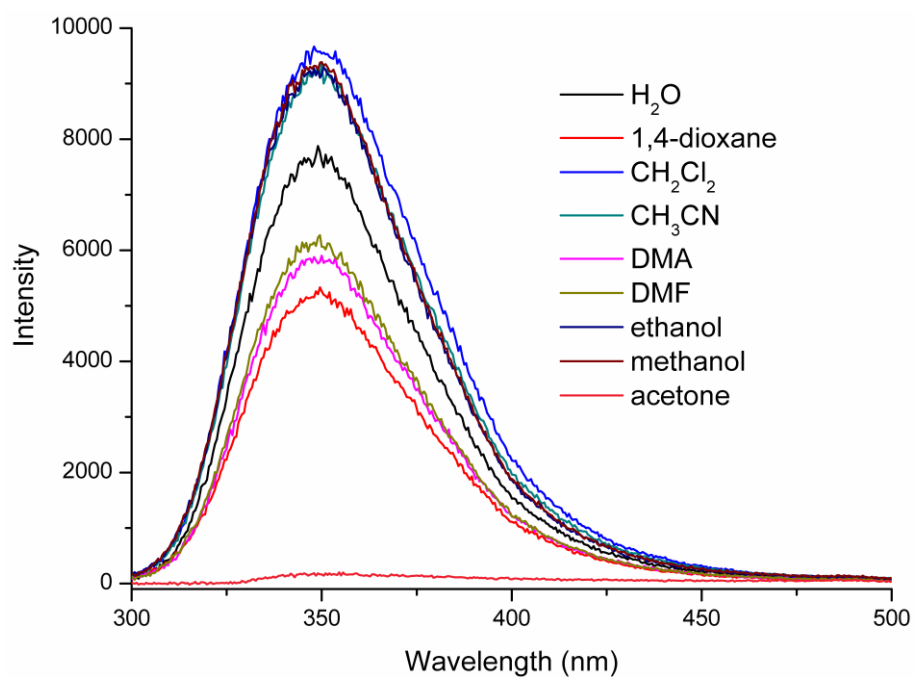


Figure S7. The FL spectra of powdered sample of **1** dispersed in different solvents.

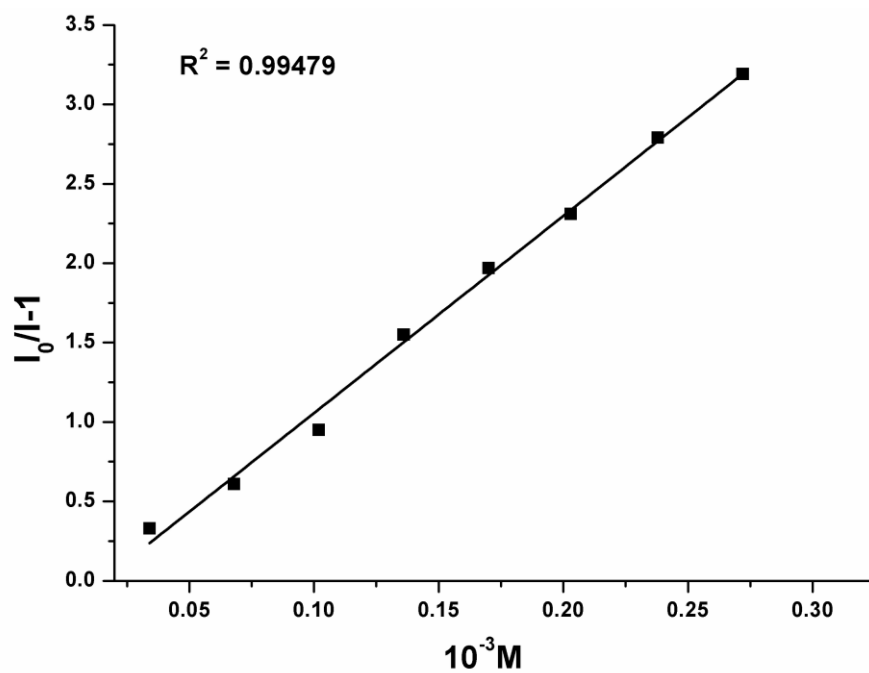


Figure S8. The K_{sv} plot of **1** for acetone.

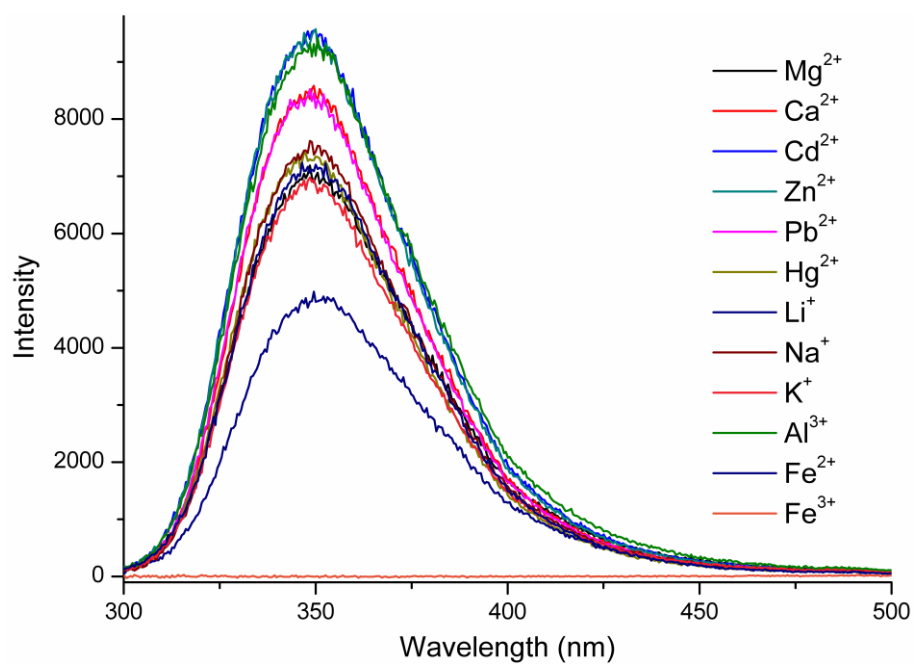


Figure S9. Fluorescence spectra of **1** dispersed in various solutions of 10^{-3} M metal ions.

Table S2. The reported CPs FL sensors for acetone.

compounds	Dispersed solvents	Quenching to almost no FL with vol% of acetone	LOD	Ref.
$[(\text{CH}_3)_2\text{NH}_2][\text{Ca}(\text{Me}_2\text{tcpbH})(\text{H}_2\text{O})]$	H_2O	2.0%	3.12 mM	This work
$\text{Zn}(\text{bpydb})(\text{bimmb})_{0.5}$	DMA	2.4%	0.07 μM	1
$\text{Zn}_2(\text{bpydb})_2(\text{bimb}) \cdot [\text{Zn}(\text{bpydb})(\text{bimb})]$		7.5%	0.18 μM	
$[\text{Eu}_2(\text{BPS})_3(\text{H}_2\text{O})_4] \cdot 18\text{H}_2\text{O}$	H_2O	0.001 M	none	2
$[\text{Eu}_5(\text{DBA})_3]$ (1)	H_2O	none	1.24 μM	3.
$[\text{Cd}(\text{pta})] \cdot \text{H}_2\text{O}$	H_2O	none	825 ppm	4
$\text{Tb}(\text{DBB})(\text{H}_2\text{O})_2$	H_2O	0.007 M	none	5
$[\text{Cd}_{1.5}(\text{DBPT})(\text{DiPyDz})(\text{H}_2\text{O})] \cdot 3.5\text{H}_2\text{O}$	H_2O	4%	0.0013 vol%	6
$[\text{Cd}_4(\text{Ccbp})_3(\text{dpe})_4 \cdot 4\text{H}_2\text{O}] \cdot (\text{ClO}_4)_5 \cdot 4\text{H}_2\text{O}$	H_2O	195.1 μM	none	7
$\text{Eu}(\text{BDC})_{1.5}(\text{H}_2\text{O})_2$	methanol	0.3%	0.075 vol%	8
$\text{Eu}(\text{BTC})(\text{H}_2\text{O}) \cdot 1.5\text{H}_2\text{O}$		0.45%		
$[\text{Me}_2\text{NH}_2]_2[(\text{Ln})_2(\text{ofdp})_2(\text{DMF})(\text{H}_2\text{O})] \cdot 7\text{H}_2\text{O} \cdot \text{DMF}$	i-propane	8%	none	9
$\text{Tb}(\text{HL})(\text{C}_2\text{H}_5\text{OH})_2$	DMF	5%	none	10
$[\text{Cd}_4(\text{L})_4(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot 8\text{DMF} \cdot \text{H}_2\text{O} \cdot \text{NO}_3$	DMF	150 μM	none	11
$[\text{Tb}_4(\mu_6\text{-L})_2(\mu\text{-HCOO})(\mu_3\text{-OH})_3(\mu_3\text{-O})(\text{DMF})_2(\text{H}_2\text{O})_4]$	DMF	100 %	none	12
$[\text{Tb}(\text{L}_1)(\text{L}_2)_{0.5}(\text{NO}_3)(\text{DMF})] \cdot \text{DMF}$	H_2O	18%	none	13
$\text{Eu}(\text{BTB})(\text{H}_2\text{O})_2 \cdot \text{solvent}$	ethanol	6%	none	14
$[\text{Eu}(\text{bpda})_{1.5}] \cdot \text{H}_2\text{O}$	H_2O	0.35%	none	15
$[\text{Ln}_2(\text{BPDC})(\text{BDC})_2(\text{H}_2\text{O})_2]_n$ (Ln = Eu (1), Tb (2), Eu _{0.2} Tb _{1.8} (1a))	H_2O	9.09, 8.26 and 11.11% for 1 , 2 , and 1a ,	none	16
$\text{Yb}_{0.10}\text{Gd}_{0.90}\text{L}$	2-propanol	2.5%	none	17
$[\text{Cd}_3(\text{L})(\text{H}_2\text{O})_2(\text{DMF})_2] \cdot 5\text{DMF}$	1-propanol	1.0%	none	18
$\text{Yb}(\text{BPT})(\text{H}_2\text{O}) \cdot (\text{DMF})_{1.5}$	1-propanol	5%	none	19
$\text{Eu}(\text{BTC})$	1-propanol	3.75%	none	20

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Table S3. The reported CPs FL sensors for Fe³⁺.

Compounds	Dispersed solvents	K_{sv} (M ⁻¹)	LOD	Ref.
[(CH ₃) ₂ NH ₂][Ca(Me ₂ tcphH)(H ₂ O)]	H ₂ O	1.18×10^5	20.85 μM	This work
[Zn ₂ (tpcb)(bpdca) ₂]	H ₂ O	1.326×10^4	0.882 μM	1
Zn(L) ₂	H ₂ O	1.34×10^4	2.24 μM	2
[Tb(μ ₆ -H ₂ cpboda)(μ ₂ -OH ₂) ₂ ·xH ₂ O]	H ₂ O	6.50×10^4	0.84 μM	3
[Zn ₂ (L)(TBIP) _{1.5} (OH) ₂ ·H ₂ O]	DMSO+H ₂ O	3.19×10^4	0.20 μM	4
Zn(L)(DBT)		1.19×10^4	0.65 μM	
Zn(L) _{0.5} (MIP)	EG+H ₂ O	2.25×10^4	0.54 μM	
[Cd(Hcip)(bpea) _{0.5} (H ₂ O)]	DMF	4.10×10^4	3.24 μM	5
[Zn ₂ Na ₂ (TPHC)(4,4'-Bipy)(DMF)]·8H ₂ O	DMF	5.77×10^4	6.4 μM	6
[Cd _{1.5} (DBPT)(DiPyDz)(H ₂ O)]·3.5H ₂ O	H ₂ O	4.78×10^5	78 ppb	7
[Zn(QDA)]·0.3DMF	methanol	1.12×10^6	0.023 μM	8
[Tb(TATAB)(H ₂ O)]·2H ₂ O	H ₂ O	1.25×10^5	0.0221 μM	9
Zn ₂ (NO ₃) ₂ (4,4'-bpy) ₂ (TBA)	H ₂ O	7.48×10^3	7.18 μM	10
[Mg ₂ (APDA) ₂ (H ₂ O) ₃]·5DMA·5H ₂ O	DMF	2.06×10^4	152 ppb	11
Eu(L)(H ₂ O)(DMA)	H ₂ O	2.03×10^4	1.41 μM	12
Tb(L)(H ₂ O)(DMA)		2.11×10^4	1.01 μM	
[Eu ₂ (DMTDC) ₃ (DEF) ₄]·DEF·6H ₂ O	DMF	4.6×10^4	none	13
[Tb ₂ (DMTDC) ₃ (DEF) ₄]·DEF·6H ₂ O		4.3×10^4	none	
[Cd ₂ (L) ₂ (bpe) ₂]·3DMF·2.5H ₂ O	DMF	1.74×10^4	0.61 μM	14
[Cd(L)(bibp)]·2DMF		3.39×10^4	1.24 μM	
Al-MIL-53-N ₃	H ₂ O	6.13×10^3	0.03 μM	15
[Eu(L)(BPDC) _{0.5} (NO ₃) ₃]·H ₃ O	DMF	5.16×10^4	none	16
[Tb(L)(BPDC) _{0.5} (NO ₃) ₃]·H ₃ O		4.3×10^4	none	
[Zr ₆ O ₄ (OH) ₄ (2,7-CDC) ₆]·19H ₂ O·2DMF	H ₂ O	5.5×10^3	0.91 μM	17
[CH ₃ -dpp] ₂ [Mg ₃ (1,4-NDC) ₄ (μ-H ₂ O) ₂ (CH ₃ OH)(H ₂ O)]·1.5H ₂ O	CH ₂ Cl ₂	0.16×10^5	470 μM	18
[Tb ₂ (Ccbp) ₃ ·6H ₂ O]·3Cl·4H ₂ O	ethanol	1.143×10^5	none	19
[Cd(5-asba)(bimb)]	H ₂ O	1.78×10^4	1 ppm	20

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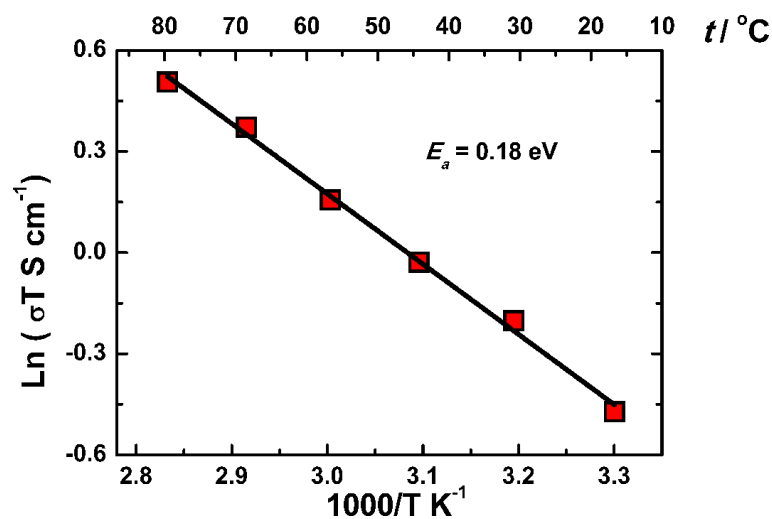


Figure S10. Arrhenius plot of the proton conductivity of **1** at 98% RH; least-squares fitting is shown as a solid line.

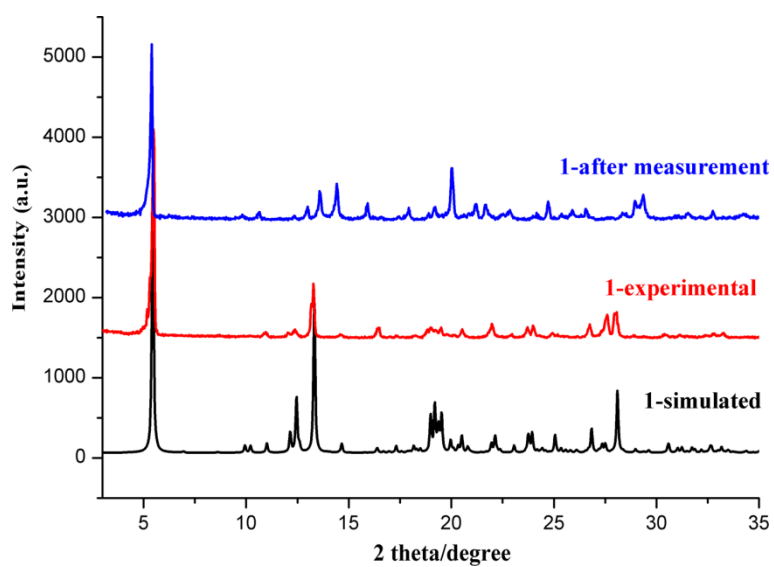


Figure S11. Experimental, simulated PXRD patterns of compound **1** compared with that of the sample after proton conduction measurement.

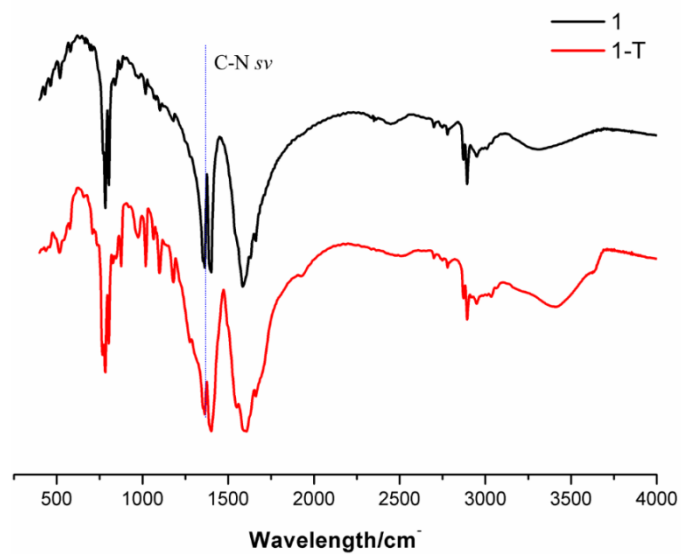


Figure S12. The IR spectra of **1** and **1-T**.

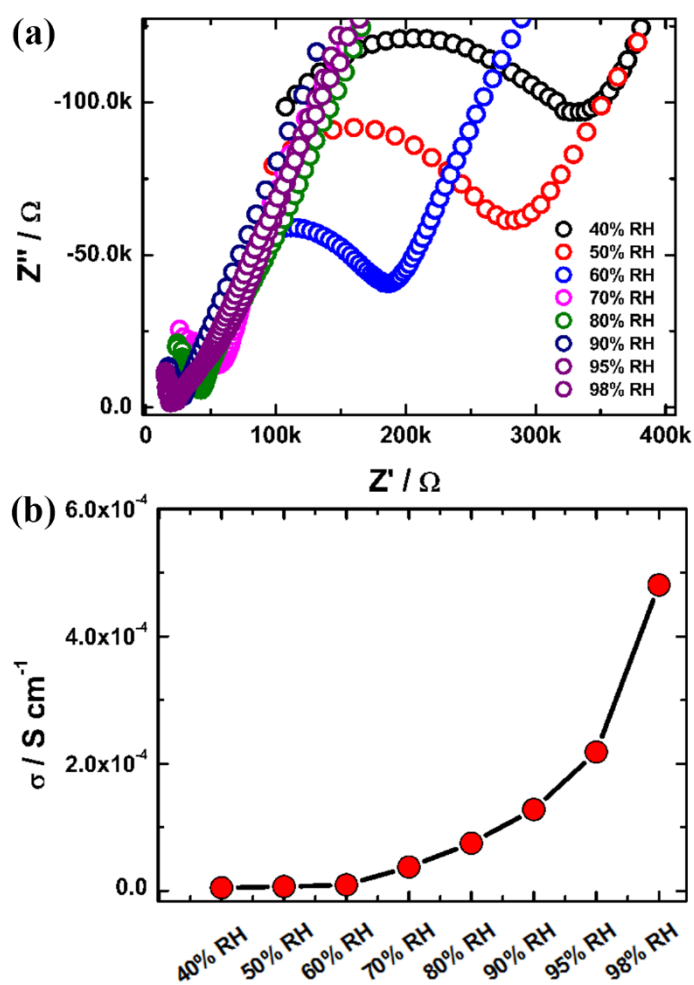


Figure S13. (a) Nyquist plots for **1-T** at 30 °C under 40 to 98% RH. (b) Proton conductivity (σ) values of **1-T** under different humidity conditions.

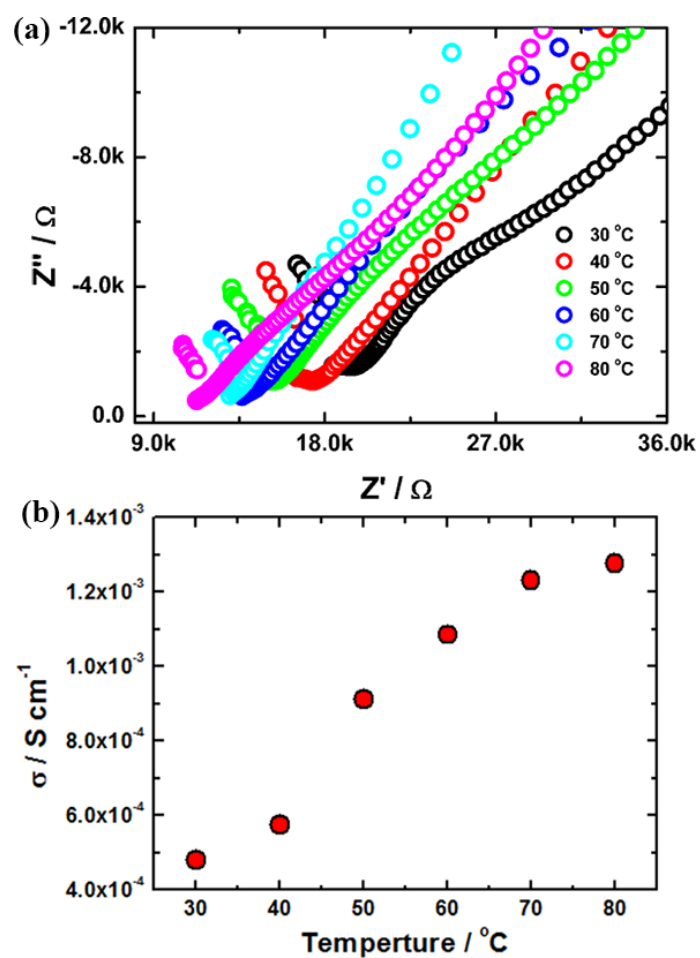


Figure S14 (a) Nyquist plots for **1** at 98% RH varied from 30 to 80 °C. (b) σ values of **1** at different temperatures.

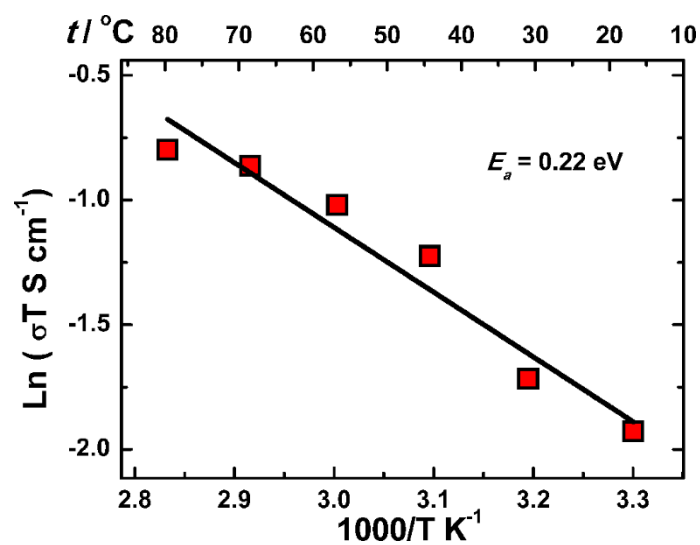


Figure S15. Arrhenius plots of the proton conductivity of **1-T** at 98% RH; least-squares fitting is shown as a solid line.