Electronic Supplementary Information (ESI)

Stable isomeric layered indium coordination polymers for high proton conduction

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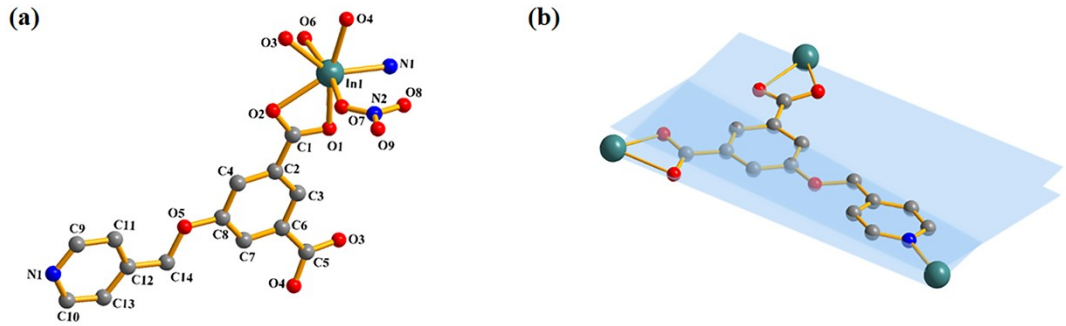

Fig. S1 (a) View of the coordination environment of In^{3+} ion in In-L-NO_3. (b) The coordination mode of the L^{2-} ligands in In-CPs.

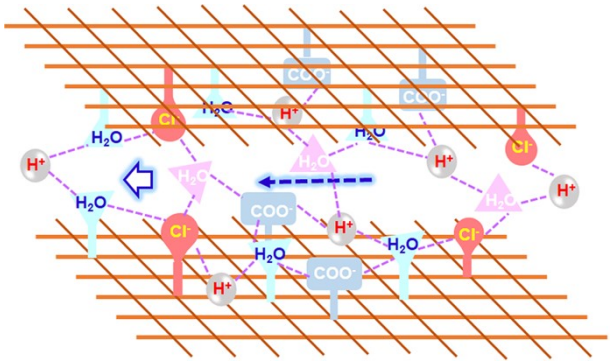

Fig. S2 The schematic diagram of continuous hydrogen bonding network in In-Cl.

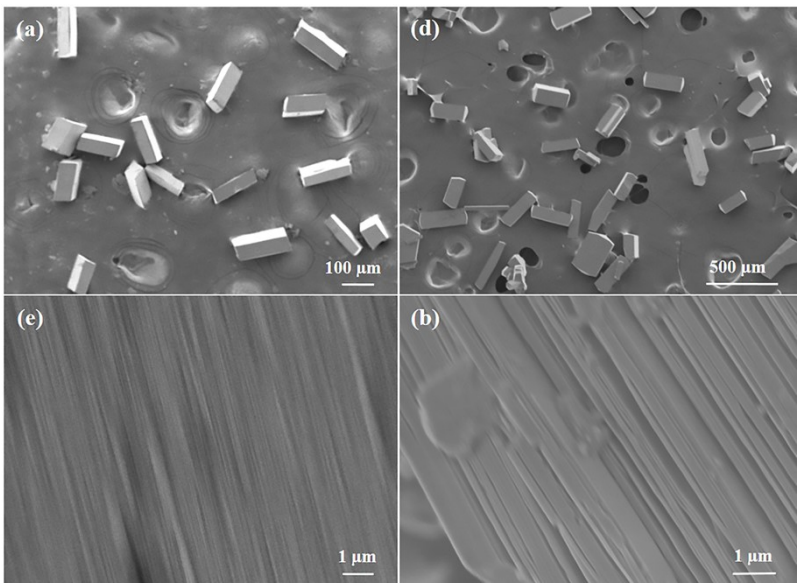

Fig. S3 SEM images of In-L-Cl (a, c) and In-L-NO_3 (b, d) and their corresponding crystal cross-sections.

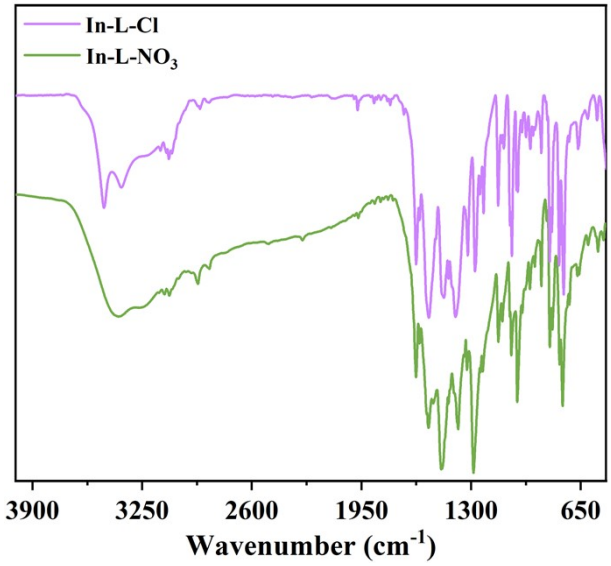

Fig. S4 IR spectra of the prepared In-CPs.

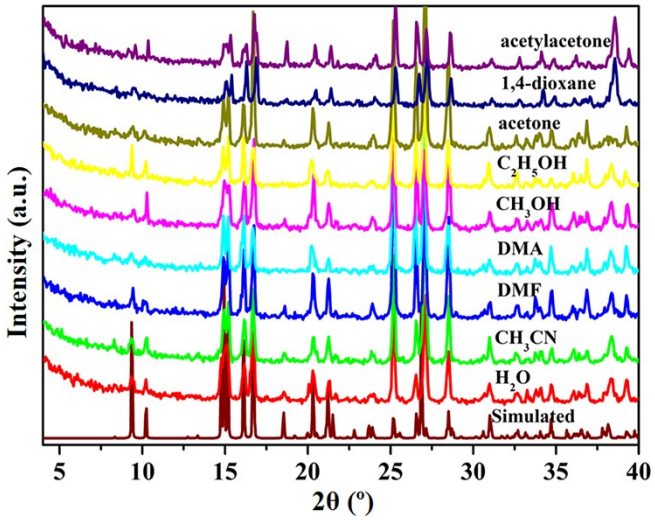

Fig. S5 The PXRD patterns for In-L-Cl after soaking in various solvents for ten days.

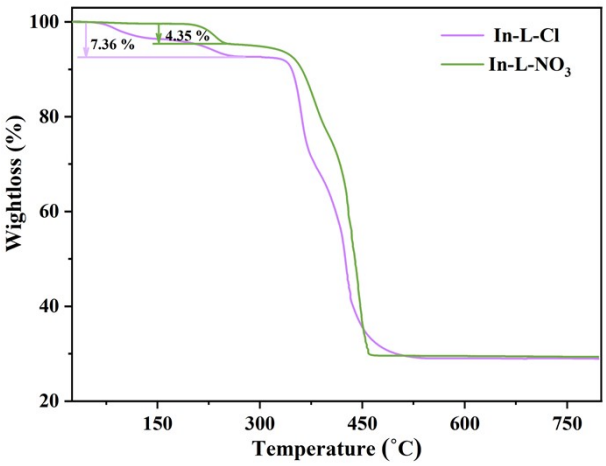

Fig. S6 TGA curves of In-CPs.

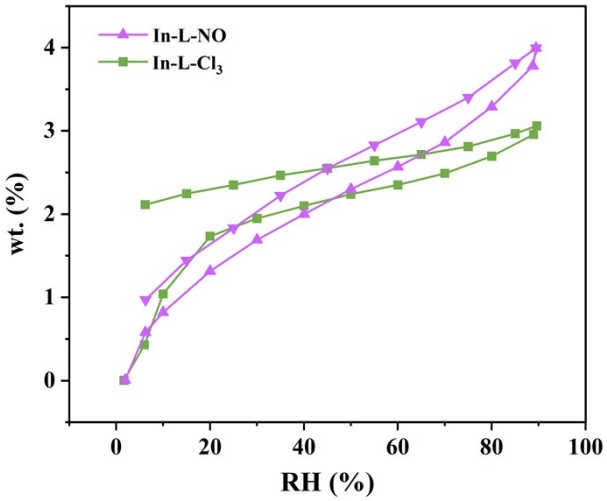

Fig. S7 Water-vapor adsorption/desorption isotherms of In-L-NO_3 and In-L-Cl.

Table S1 Crystallographic data and structure refinement for the prepared In-CPs.

Compounds	**In-L-Cl**	**In-L-NO_3**
Empirical formula	$C_{14}H_{13}ClNO_7In$	$C_{14}H_{11}N_2O_9In$
Formula weight	457.52	466.07
Temperature (K)	199(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C 2/c*	*C 2/c*
a (Å)	19.824(0)	19.849(4)
b (Å)	13.440(4)	13.421(3)
c (Å)	13.623(8)	13.601(3)
β (°)	119.29(1)	119.38(3)
Volume ($Å^3$)	3165.9(2)	3157.2(14)
Z	8	8
Calculated density ($Mg·m^{-3}$)	1.920	1.961
$\mu(mm^{-1})$	1.699	1.553
F(000)	1808	1840
θ range for data collection (°)	4.314 - 28.363	2.355 - 25.190
Limiting indices	-20 ≤ h ≤ 26, -17 ≤ k ≤ 14, -18 ≤ l ≤ 18	-23 ≤ h ≤ 23, -16 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected / unique	10135 / 3781	11578 / 2821
	R_{int} = 0.0136	R_{int} = 0.0553
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3781 / 0 / 269	2826 / 18 / 227
Goodness-of-fit on F^2	1.090	1.192
Final *R* indices [I>2sigma(I)]	R_1 = 0.0205, wR_2 = 0.0485	R_1 = 0.0709 wR_2 = 0.1605
R indices (all data)	R_1 = 0.0208, wR_2 = 0.0487	R_1 = 0.0799, wR_2 = 0.1648
Largest diff. peak and hole (eA^{-3})	0.498 and -0.490	2.072 and -1.374
CCDC No.	2077713	2077712

Table S2 Selected bond lengths [Å] and angles [°] for In-L-Cl.

In-L-Cl			
In(1)-O(5)#1	2.1860(13)	In(1)-O(6)	2.1964(14)
In(1)-O(3)#2	2.2342(13)	In(1)-N(1)	2.2970(15)
In(1)-O(2)#2	2.3339(13)	In(1)-O(4)#1	2.4090(14)
In(1)-Cl(1)	2.4335(5)	O(5)#1-In(1)-O(6)	86.57(6)
O(2)-In(1)#3	2.3339(13)	O(3)-In(1)#3	2.2342(13)
O(4)-In(1)#4	2.4089(13)	O(5)-In(1)#4	2.1859(13)
O(5)#1-In(1)-O(6)	86.59(6)	O(5)#1-In(1)-O(3)#2	164.80(5)
O(6)-In(1)-O(3)#2	92.54(6)	O(5)#1-In(1)-N(1)	82.18(5)
O(6)-In(1)-N(1)	89.65(6)	O(3)#2-In(1)-N(1)	82.64(5)
O(5)#1-In(1)-O(4)#1	56.48(5)	O(6)-In(1)-O(4)#1	81.98(5)
O(3)#2-In(1)-O(4)#1	138.43(5)	N(1)-In(1)-O(4)#1	138.08(5)
O(2)#2-In(1)-O(4)#1	81.27(4)	O(5)#1-In(1)-Cl(1)	90.39(4)
O(4)#1-In(1)-Cl(1)	86.75(4)	O(3)#2-In(1)-Cl(1)	89.62(6)
N(1)-In(1)-Cl(1)	101.36(4)	O(2)#2-In(1)-Cl(1)	93.33(4)
O(6)-In(1)-Cl(1)	168.09(4)		

Symmetry transformations used to generate equivalent atoms:

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

Table S3 Selected bond lengths [Å] and angles [°] for In-L-NO_3.

In-L-NO_3			
In(1)-O(7)	2.171(10)	In(1)-O(5)#1	2.179(7)
In(1)-O(3)#2	2.205(6)	In(1)-O(6)	2.212(8)
In(1)-N(1)	2.254(7)	In(1)-O(2)#2	2.317(6)
In(1)-O(4)#1	2.327(7)	O(3)-In(1)#3	2.318(6)
O(4)-In(1)#3	2.201(6)	O(4)-In(1)#4	2.327(7)
O(6)-In(1)-C(8)#1	87.9(3)	N(1)-In(1)-C(8)#1	110.9(3)
O(5)#1-In(1)-C(8)#1	28.9(3)	O(3)#2-In(1)-C(8)#1	164.2(3)
O(2)#2-In(1)-O(4)#1	78.4(2)	O(7)-In(1)-C(8)#1	88.4(4)
O(6)-In(1)-O(4)#1	83.1(3)	N(1)-In(1)-O(4)#1	138.4(3)
O(5)#1-In(1)-O(4)#1	57.5(2)	O(3)#2-In(1)-O(4)#1	135.8(2)
N(1)-In(1)-O(2)#2	141.1(3)	O(7)-In(1)-O(4)#1	87.9(4)
O(3)#2-In(1)-O(2)#2	57.4(2)	O(6)-In(1)-O(2)#2	84.5(3)
O(7)-In(1)-O(2)#2	84.9(3)	O(5)#1-In(1)-O(2)#2	135.6(2)
O(3)#2-In(1)-N(1)	84.8(3)	O(6)-In(1)-N(1)	88.1(3)
O(7)-In(1)-N(1)	104.7(4)	O(5)#1-In(1)-N(1)	82.8(3)
O(5)#1-In(1)-O(6)	93.5(3)	O(3)#2-In(1)-O(6)	91.8(3)
O(5)#1-In(1)-O(3)#2	166.4(3)	O(7)-In(1)-O(6)	167.2(3)
O(7)-In(1)-O(3)#2	88.5(4)	O(7)-In(1)-O(5)#1	89.2(4)

Symmetry transformations used to generate equivalent atoms:

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

Table S4 Hydrogen bonds for In-L-Cl.

In-L-Cl				
D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
O(6)-H(6B)···O(2)#7	0.87	1.96	2.818(2)	167.6
O(1W)-H(1WB)···O(4)#5	0.87	1.92	2.703(2)	149.7
O(1W)-H(1A)···Cl(1)#5	0.86	2.25	3.104(2)	168.0
O(6)-H(6A)···O(1W)#6	0.87	1.70	2.553(2)	167.0

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+3/2,z+1/2 #2 x,y-1,z #3 x-1/2,-y+3/2,z-1/2 #4 x,y+1,z #5 -x+1,y-1,-z+1/2

#6 x-1/2,-y+1/2,z+1/2 -x,y-1,-z+1/2

Table S5 Hydrogen bonds for In-L-NO_3.

In-L-NO_3				
D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (°)
C(13)-H(13)···O(7)#5	0.93	2.62	3.422(14)	144.2
O(6)-H(6A)···O(2)#7	0.85	1.95	2.796(10)	171.0
O(6)-H(6B)···O(8)#6	0.85	2.13	2.855(18)	142.7

Symmetry transformations used to generate equivalent atoms:

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

#5 x-1/2,y+1/2,z #6 -x,y,-z+1/2 #7 -x, y-1,-z+1/2

Table S6 Proton conductivities (S cm^{-1}) of In-L-Cl and In-L-NO_3 at different RHs under room temperature.

RHs (%)	In-L-Cl	In-L-NO_3
11	4.75×10^{-6}	3.70×10^{-6}
33	1.54×10^{-5}	1.18×10^{-5}
43	1.86×10^{-5}	1.71×10^{-5}
53	4.01×10^{-5}	3.62×10^{-5}
69	6.05×10^{-5}	5.43×10^{-5}
75	1.27×10^{-4}	6.14×10^{-5}
85	2.33×10^{-4}	1.92×10^{-4}
100	3.69×10^{-4}	2.86×10^{-4}

Table S7 Proton conductivities (S cm^{-1}) of In-L-Cl and In-L-NO_3 under H_2O atmosphere.

temp (K)	In-L-Cl	In-L-NO_3
298	4.78×10^{-4}	2.00×10^{-4}
303	6.19×10^{-4}	2.82×10^{-4}
313	8.50×10^{-4}	3.65×10^{-4}
323	1.10×10^{-3}	4.59×10^{-4}
333	1.32×10^{-3}	5.83×10^{-4}
343	1.61×10^{-3}	7.26×10^{-4}
353	1.88×10^{-3}	1.00×10^{-3}

Table S8 The comparison of proton conductivities of the the prepared In-CPs and the reported related crystalline materials

Compounds	Measurement conditions	σ (S cm^{-1})	Ref.
In-L-NO_3	80 °C, 100 % RH	1.0×10^{-3}	This work
In-L-Cl	80 °C, 100% RH	1.88×10^{-3}	This work
[Triethylpropylammonium][PbI_3]	200 °C, 0% RH	4.47×10^{-5}	S1
[H_3O][$(VO_2)_3(SeO_3)_2$]	90 °C, 95% RH	5.95×10^{-5}	S2
{$NBu_3(CH_2COOH)$}[$MnCr(ox)_3$]	25 °C, 90% RH	1.8×10^{-3}	S3
{$NBu_2(CH_2COOH)_2$}[$MnCr(ox)_3$]	25 °C, 90% RH	5.2×10^{-7}	S3
$[CH_3NH_3]_2[H_3O]Ag_5Sn_4Se_{12}\cdot C_2H_5OH$	60 °C, 99% RH	2.62×10^{-4}	S4
$Zn_3(IBT)_2(H_2O)_2$	30 °C, 97% RH	1.98×10^{-5}	S5
$Zn_3(bpdc)_2(pdc)(DMF)\cdot 6DMF$	60 °C , 97% RH	9.5×10^{-3}	S6
$[Me_2NH_2][Eu(ox)_2(H_2O)]\cdot 3H_2O$	55°C, 95%	2.7×10^{-3}	S7
{$[HOOC(CH_2)_2OC]Fcc[CO(CH_2)_2COOH]$}	100 °C, 98% RH	1.14×10^{-2}	S8
[(HOOC)Fcc(COOH)]	100 °C, 98% RH	1.99×10^{-5}	S8
$[Cr(\mu_3\text{-}O)(H_2O)_3(NDC(SO_3H_{5/6})_2)_3]$	80 °C, 100% RH	1.27×10^{-1}	S9
In-BQ	30 °C, 95%	2.10×10^{-4}	S10
In1-H	60 °C, 98% RH	3.45×10^{-4}	S11
{[In(5-Hsip)2(Me2NH2)]·DMF·(H2O)1.4}n	25 °C, 40% RH	1.17×10^{-3}	S12

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