Supporting Information

Two-dimensional coordination polymers constructed based on SIE with high proton conductivity and ultrafast highly-efficient molecular sieving

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1. Experiment section

1.1 Measurements and apparatus

All the reagents are commercially obtained and directly used without further purification. The Powder X-ray diffraction (PXRD) was carried out on a Bruker D8 (40kV, 40 mA) advanced diffractometer with Cu-K_α radiation (λ=1.5418 Å). IR spectra were collected on a NEXUS 870 (Nicolet) infrared spectrometer from 400 to 4000 cm^{-1} by a KBr pellet with a resolution of 4 cm^{-1}. Thermogravimetric (TG) analysis data were recorded on a Netzsch STA 409 PC analyzer at a heating rate of 10 °C·min^{-1} under N_2 atmosphere. The *in-situ* various temperature UV-Vis diffuse reflectance spectra were recorded in the range of 200-800 nm with the integrated sphere accessory using $BaSO_4$ as the reference on a UV-Vis diffuse reflectance spectrometer (UV-3700, Shimadzu, Japan). The determination of the proton conductivity was carried out using a Gamry Reference 600+ electrochemical workstation.

1.2 Preparation

The solution of $Cu(NO_3)_2$•$3H_2O$ (0.048 g, 0.20 mmol) in 1 mL deionized water was added to the solution of H_4BTC (0.025 g, 0.10 mmol), TTP (0.044 g, 0.10 mmol) in 4 mL DMF, then 7 drops of 6 mol/L HCl aqueous were added to adjust the pH value to *ca.* 1. The obtained mixture was transferred to a glass tube and sealed in a stainless steel reaction vessel, then heated for about 3 days at 60 ºC. After being cooling back to room temperature, the solution containing blue crystals was filtered, washed with water and alcohol three times respectively, and dried in the air. Finally, the obtained **HNNU-1α** is 0.064 g with a yield of 71.1 % based on H_4BTC. Elemental analysis (EA): Calcd. H: 2.90%; C: 26.59%. Exp.: H: 3.11%; C: 25.47%. **HNNU-1β** and **HNNU-1γ** were prepared under the same conditions with the different inorganic acids (HBr for **HNNU-1β** and HI for **HNNU-1γ**). EA for **HNNU-1β**: Calcd. H: 2.63%; C: 26.13%. Exp.: H: 2.70%; C: 26.01%, EA for **HNNU-1γ**: Calcd. H: 2.39%; C: 23.71%. Exp.: H: 2.18%; C: 23.58%. The FT-IR spectra of **HNNU-1α** to **1β** are almost the same positions and intensities for the observed bands (Figure S18). IR bands (KBr, cm^{-1}) 3404 (w), 1605 (s), 1556 (s), 1495 (s), 1414 (s), 1359 (s), 1317 (s), 1185 (m), 1138 (m), 937 (w), 902

(w), 861 (m), 813 (s), 757 (m), 691 (s), 645 (s), 525 (s), 449 (s).

1.3 Crystallographic Data

Single-crystal X-ray diffraction data of the as-synthesized CPs were collected at 293(2) K on a Bruker SMART APEX Ⅱ diffractometer equipped with a CCD area-detector using graphite-monochromated Mo/Ka radiation (0.71073 Å). The data reduction and absorption correction were executed using the SAINT [1] and SADABS [2] subprograms under APEX3 [3] program package, respectively. The structure was solved using the dual space method using SHELXT-2018 [4] routine and refined by SHELXL-2018 [5] routine with full-matrix least-squares on F^2 under Olex2 [6] software package. During the final refinement circles, all non-hydrogen atoms were refined anisotropically, while all the hydrogen atoms were produced by geometrical calculations and refined isotropically by using the riding model. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre (CCDC No. 1916820, 2132955, 2132956). Summary of structural parameters and crystal data for **HNNU-1α** to **1γ** were given in Table S1 – S6.

1.4 Preparation of the laminates for HNNU-1α

10.1 mg **HNNU-1α** was firstly heated at 170 ºC for 2 h, then soaked in 60 mL ethanol using a 100 mL beaker and placed in the strong ultrasonic environment for about 40 min. 5 mL suspension was transferred to a disposable plastic injector, then passed through the filter nod with a pore size of 0.22 μm and radii of *ca.* 0.8 cm. The laminates were formed and tightened on the filter membrane as support background, then applied to filter the water containing ions or molecules. The sectional area and height of laminate are *ca.* 2.0 cm^2 and *ca.* 216 μm, respectively.

1.5 Proton conductivity measurement

The measurement of proton conductivity was similar to our previous work. Briefly, the as-synthesized sample was finely ground, then compressed into a pellet with a diameter of 6.35 mm. The Gamry Reference 600+ electrochemical workstation and the conventional three-electrode methods were used to measure the AC impedance spectra

at various temperatures and relative humidity (RH), respectively. The RH was adjusted by the saturated salt solutions.

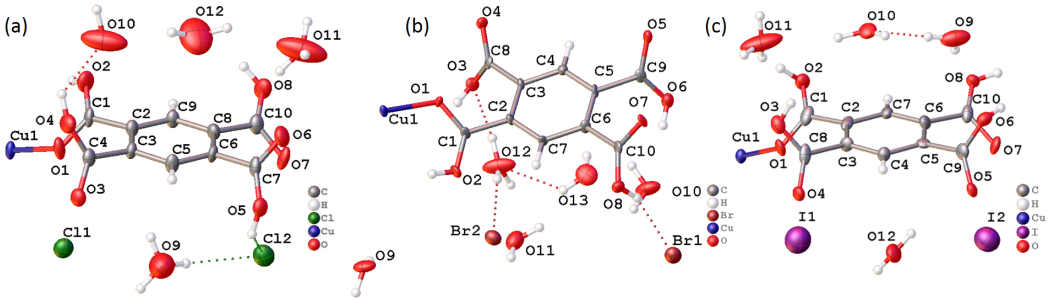

Figure S1. Asymmetric unit with 50 % probability level of HNNU-1α (a), HNNU-1β (b) and HNNU-1γ (c).

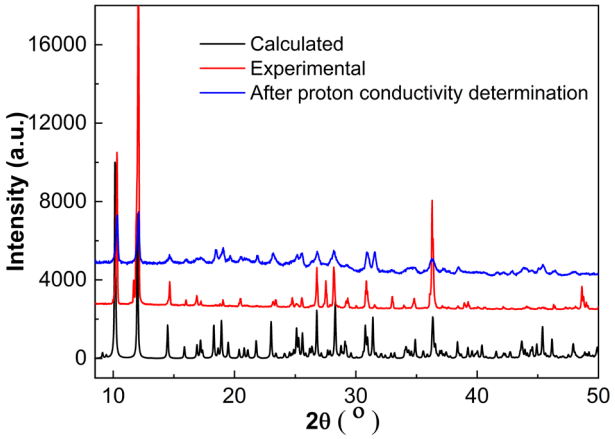

Fig. S2 PXRD of HNNU-1α.

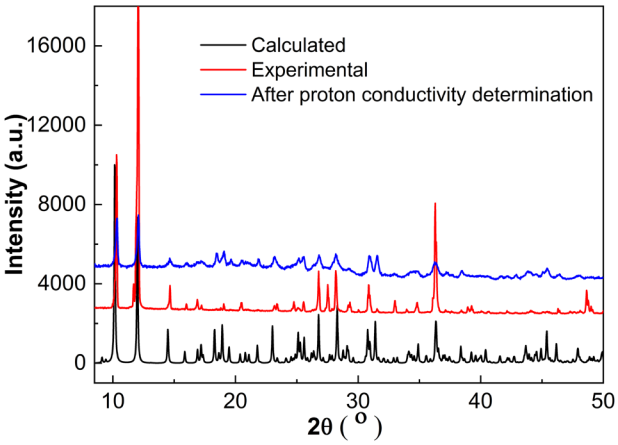

Fig. S3 PXRD of HNNU-1β.

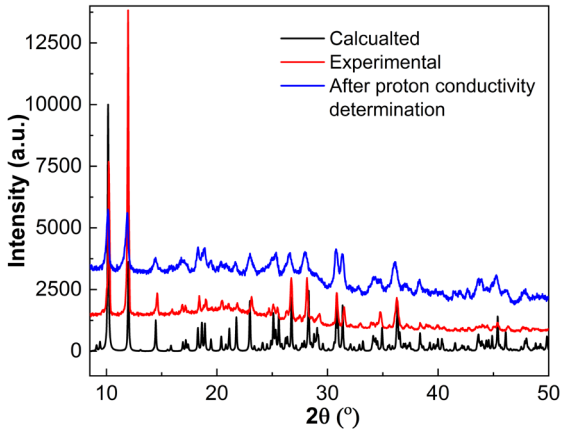

Fig. S4 PXRD of HNNU-1γ.

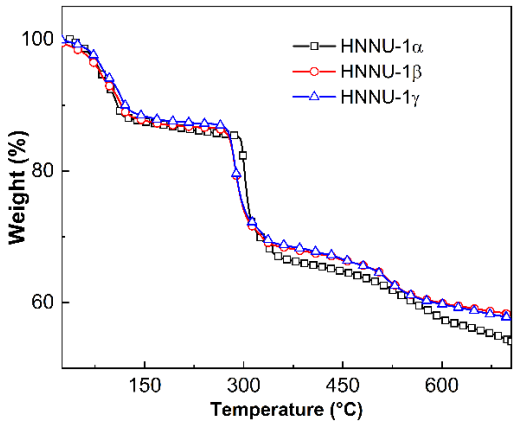

Figure S5. The TG plot of HNNU-1α, 1β, and 1γ.

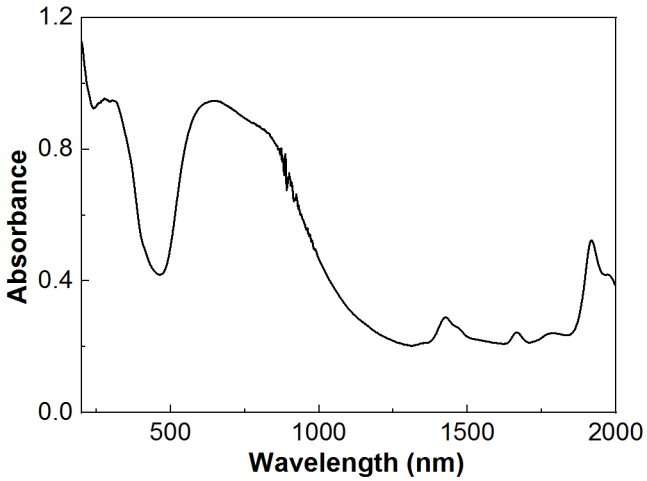

Figure S6. The UV–vis diffuse reflectance spectrum of **HNNU-1α** at room temperature.

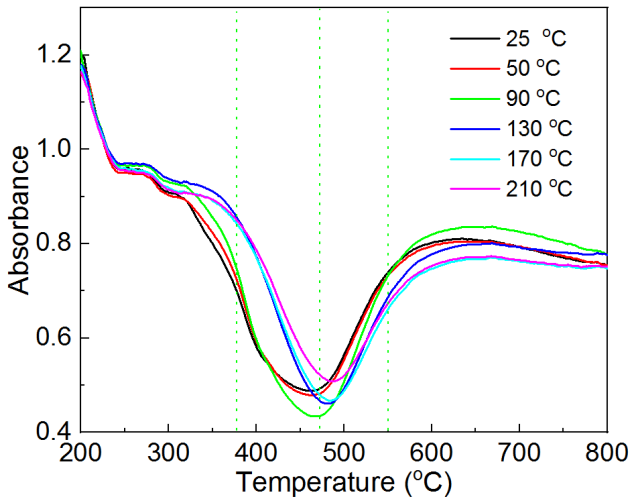

Fig. S7 The *in situ* UV–vis diffuse reflectance spectra of HNNU-1α at different temperatures.

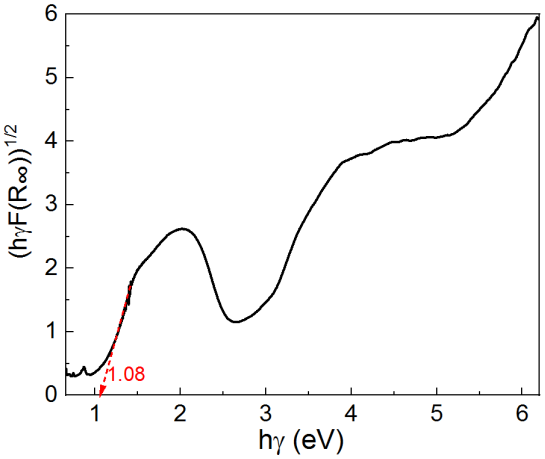

Figure S8. Tauc plots of the transformed Kubelka–Munk function versus the light energy for **HNNU-1α** at room temperature.

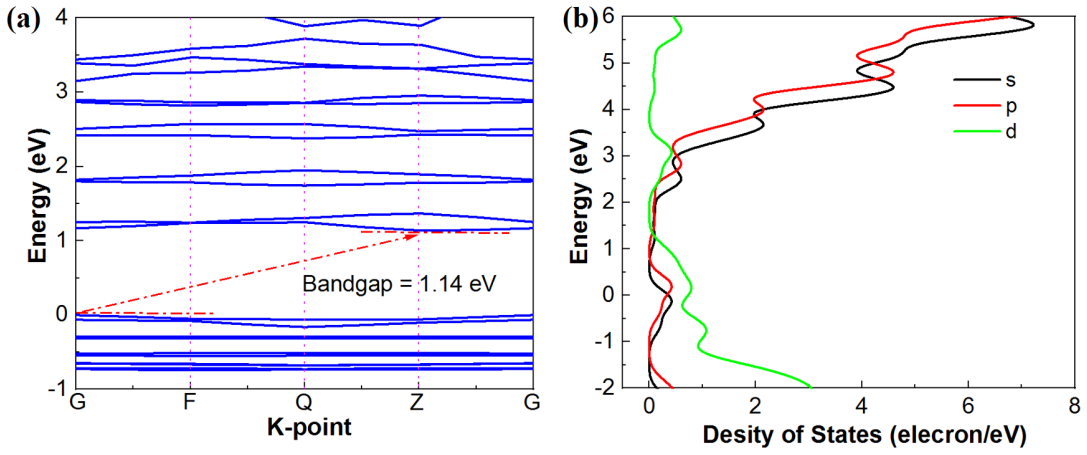

Figure S9. The theoretical calculations on the bandgap (a) and orbital compositions (b) of HNNU-1α.

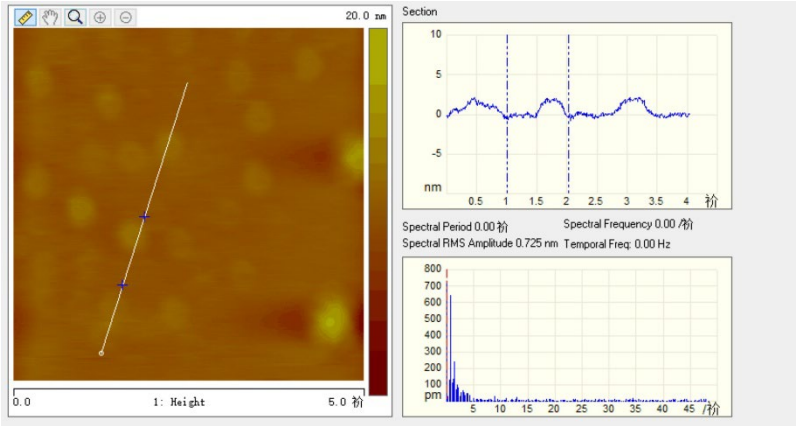

Fig. S10 The lamella thickness of **HNNU-1α** recorded by AFM.

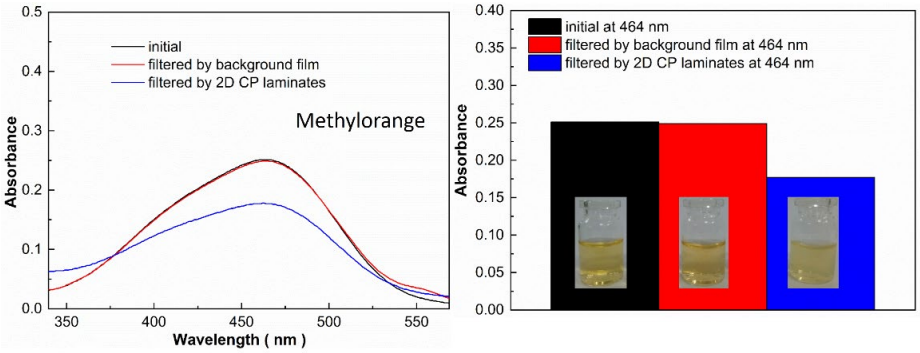

Fig. S11 The UV-Vis absorption spectra of the filtrate by the laminates of **HNNU-1α** for the aqueous solution of methyl orange.

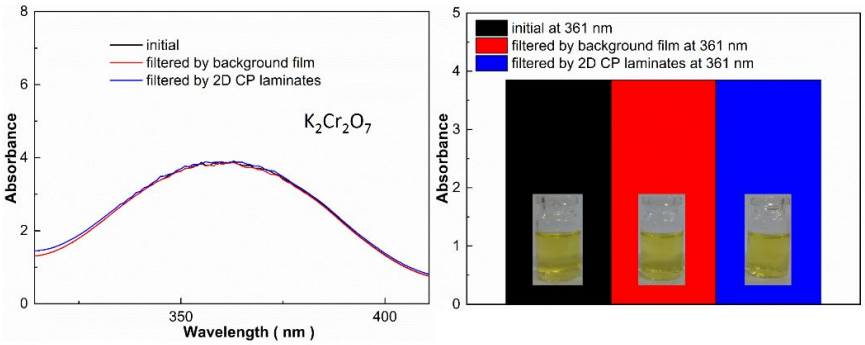

Fig. S12 The UV-Vis absorption spectra of the filtrate by the laminates of **HNNU-1α** for the aqueous solution of $K_2Cr_2O_7$.

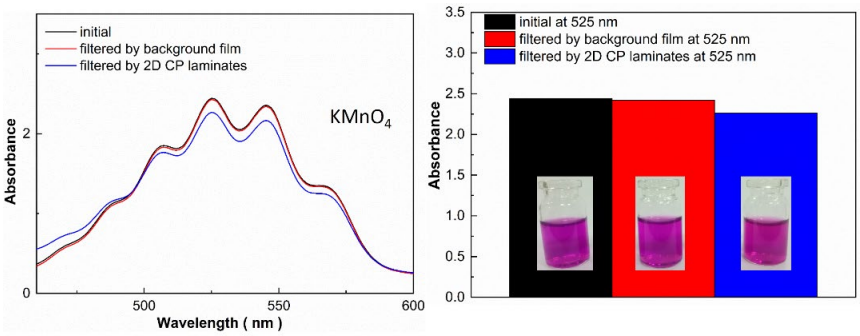

Fig. S13 The UV-Vis absorption spectra of the filtrate by the laminates of **HNNU-1α** for the aqueous solution of $KMnO_4$.

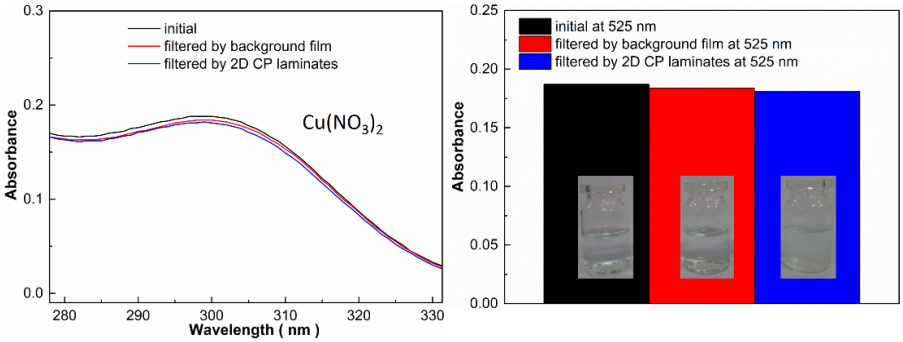

Fig. S14 The UV-Vis absorption spectra of the filtrate by the laminates of **HNNU-1α** for aqueous solution for $Cu(NO_3)_2$.

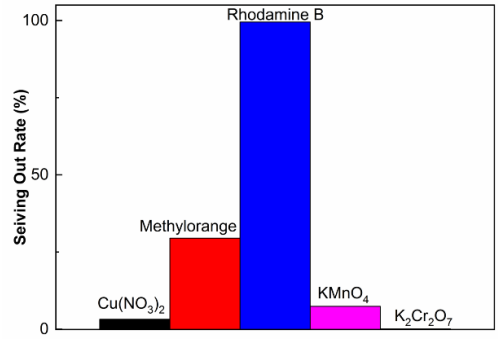

Fig. S15 The sieving out rate by the laminates of **HNNU-1α** for the aqueous solution containing rhodamine B, methyl orange, $KMnO_4$, $K_2Cr_2O_7$, and $Cu(NO_3)_2$.

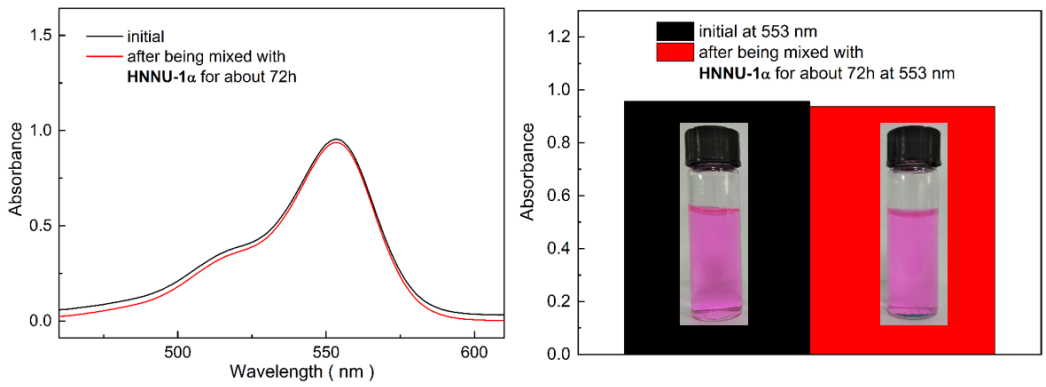

Fig. S16 The UV-Vis absorption spectra of initial and mixed with **HNNU-1α** for rhodamine B.

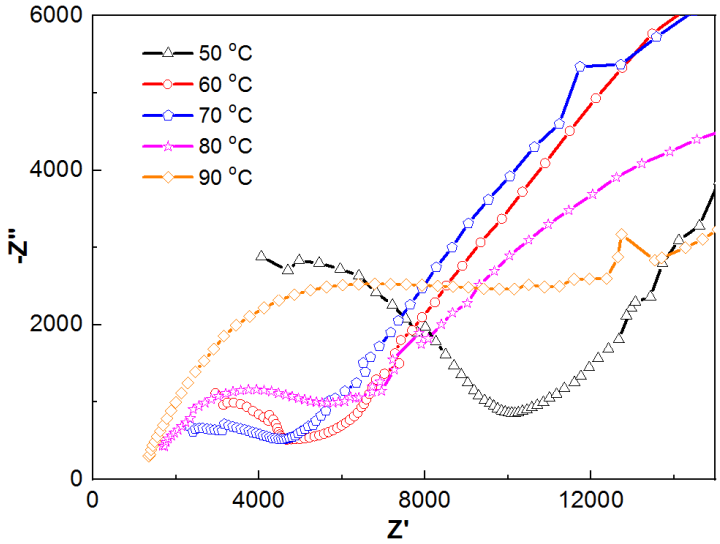

Fig. S17 Nyquist plots of **HNNU-1β.**

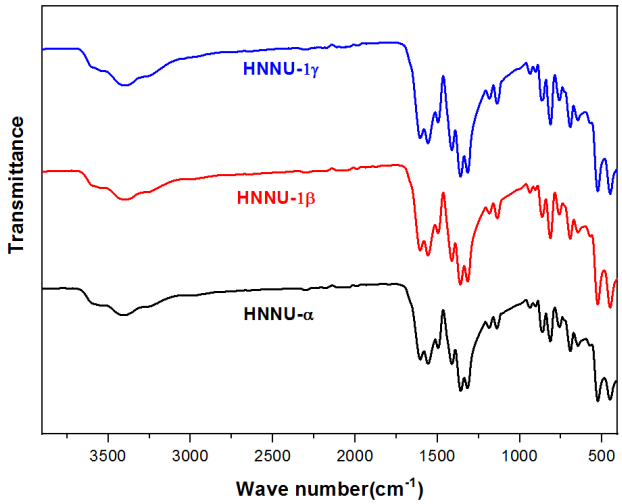

Fig. S18 FT-IR spectra of **HNNU-1α** to **1γ.**

Table S1. Crystal data and structure refinement for **HNNU-1α**.

Empirical formula	C_{20} H_{26} Cl_4 Cu_2 O_{23}	
Formula weight	903.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 7.7389(11) Å	α= 112.829(2)°.
	b = 10.6086(15) Å	β= 90.455(2)°.
	c = 10.6178(15) Å	γ = 104.055(2)°.
Volume	774.27(19) $Å^3$	
Z	1	
Density (calculated)	1.937 g/cm^3	
Absorption coefficient	1.817 mm^{-1}	
F(000)	456	
Crystal size	0.23 x 0.22 x 0.14 mm^3	
Theta range for data collection	2.095 to 27.098°.	
Index ranges	-9<=h<=9, -12<=k<=13, -10<=l<=12	
Reflections collected	6047	
Independent reflections	3068 [R(int) = 0.0312]	
Completeness to theta = 25.242°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.6586	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3068 / 0 / 227	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0574, wR2 = 0.1554	
R indices (all data)	R1 = 0.0762, wR2 = 0.1677	
Largest diff. peak and hole	0.761 and -0.638 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for **HNNU-1β**.

Empirical formula	C_{20} H_{24} Br_2 Cu_2 O_{23}	
Formula weight	919.29	
Temperature	101.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 7.6566(4) Å	α= 67.116(2)°.
	b = 10.5717(5) Å	β= 89.982(2)°.
	c = 10.5825(5) Å	γ = 75.517(2)°.
Volume	759.56(7) $Å^3$	
Z	1	
Density (calculated)	2.010 g/cm^3	
Absorption coefficient	4.128 mm^{-1}	
F(000)	456	
Crystal size	0.18 x 0.12 x 0.12 mm^3	
Theta range for data collection	2.101 to 26.407°.	
Index ranges	-9<=h<=9, -12<=k<=12, -11<=l<=12	
Reflections collected	3109	
Independent reflections	3109 [R(int) = 0.0856]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745 and 0.605	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3109 / 6 / 238	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0807, wR2 = 0.1862	
R indices (all data)	R1 = 0.1087, wR2 = 0.2049	
Largest diff. peak and hole	1.518 and -1.077 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for **HNNU-1γ**.

Empirical formula	$C_{20}H_{24}Cu_2I_2O_{23}$	
Formula weight	1013.27	
Temperature	101.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 7.6629(6) Å	α= 67.176(3)°.
	b = 10.5730(9) Å	β= 89.856(3)°.
	c = 10.5855(9) Å	γ = 75.429(3)°.
Volume	760.70(11) $Å^3$	
Z	1	
Density (calculated)	2.212 g/cm^3	
Absorption coefficient	3.525 mm^{-1}	
F(000)	492	
Crystal size	0.14 x 0.14 x 0.13 mm^3	
Theta range for data collection	2.340 to 25.499°.	
Index ranges	-9<=h<=9, -11<=k<=12, -12<=l<=12	
Reflections collected	5427	
Independent reflections	2611 [R(int) = 0.0318]	
Completeness to theta = 25.242°	92.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0309 and 0.0108	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2611 / 1 / 226	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0967, wR2 = 0.2243	
R indices (all data)	R1 = 0.1361, wR2 = 0.2498	
Largest diff. peak and hole	1.310 and -1.204 $e.Å^{-3}$	

Table S4. Selected Bond lengths [Å] and angles [°] for **HNNU-1α**.

Cu(1)-O(5)#1	1.969(4)
Cu(1)-O(3)#2	1.995(4)
Cu(1)-O(7)#3	1.941(4)
Cu(1)-O(1)	1.941(4)
O(5)#1-Cu(1)-O(3)#2	86.54(17)
O(5)#1-Cu(1)-O(4)#2	91.88(16)
O(5)#1-Cu(1)-O(6)#1	54.93(15)
O(5)#1-Cu(1)-C(7)#1	27.59(17)
O(5)#1-Cu(1)-C(4)#2	86.67(16)
O(3)#2-Cu(1)-O(4)#2	55.71(15)
O(3)#2-Cu(1)-O(6)#1	91.87(15)
O(3)#2-Cu(1)-C(7)#1	87.50(16)
O(3)#2-Cu(1)-C(4)#2	27.99(17)
O(7)#3-Cu(1)-O(5)#1	91.41(17)
O(7)#3-Cu(1)-O(3)#2	177.45(18)
O(7)#3-Cu(1)-O(4)#2	122.93(16)
O(7)#3-Cu(1)-O(1)	90.50(17)
O(7)#3-Cu(1)-O(6)#1	88.17(16)
O(4)#2-Cu(1)-O(6)#1	136.78(14)
O(4)#2-Cu(1)-C(4)#2	27.92(15)
O(1)-Cu(1)-O(5)#1	177.15(18)
O(1)-Cu(1)-O(3)#2	91.61(17)
O(1)-Cu(1)-O(4)#2	88.86(15)
O(1)-Cu(1)-O(6)#1	123.04(16)

Symmetry transformations used to generate equivalent atoms:

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

Table S5. Selected Bond lengths [Å] and angles [°] for **HNNU-1β**.

Cu(1)-O(4)#1	1.980(5)
Cu(1)-O(7)#2	1.944(5)
Cu(1)-O(5)#3	1.973(5)
Cu(1)-O(1)	1.931(5)
O(7)#2-Cu(1)-O(4)#1	177.9(2)
O(7)#2-Cu(1)-O(5)#3	91.2(2)
O(5)#3-Cu(1)-O(4)#1	86.6(2)
O(1)-Cu(1)-O(4)#1	91.4(2)
O(1)-Cu(1)-O(7)#2	90.7(2)
O(1)-Cu(1)-O(5)#3	177.6(3)

Symmetry transformations used to generate equivalent atoms:

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

Table S6. Selected Bond lengths [Å] and angles [°] for **HNNU-1γ**.

Cu(1)-O(7)#1	1.934(9)
Cu(1)-O(5)#2	1.993(8)
Cu(1)-O(1)	1.943(9)
Cu(1)-O(4)#3	1.979(9)
O(7)#1-Cu(1)-O(5)#2	91.2(4)
O(7)#1-Cu(1)-O(1)	91.5(4)
O(7)#1-Cu(1)-O(4)#3	177.6(4)
O(1)-Cu(1)-O(5)#2	177.3(4)
O(1)-Cu(1)-O(4)#3	90.9(4)
O(4)#3-Cu(1)-O(5)#2	86.5(4)

Symmetry transformations used to generate equivalent atoms:

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

Table S7. Hydrogen bonds for **HNNU-1α** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5)...Cl(2)	0.89	2.27	2.850(4)	122.5
O(2)-H(2)...Cl(2)#3	0.90	1.90	2.714(5)	150.5
O(4)-H(4)...O(10)	0.89	2.10	2.729(8)	126.6
O(9)-H(9C)...Cl(2)	0.98	2.40	3.040(7)	122.3
O(11)-H(11A)...O(6)	0.96	2.12	2.674(8)	115.1

Symmetry transformations used to generate equivalent atoms:

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

Table S8. Hydrogen bonds for **HNNU-1β** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(8)-H(8)...Br(1)	0.84	2.38	3.159(6)	155.1
O(3)-H(3)...Br(2)#5	0.81	2.40	2.834(6)	114.5
O(2)-H(2)...Br(1)#6	0.84	2.16	2.689(6)	120.6
O(6)-H(6)...O(9)#4	0.84	2.04	2.628(11)	126.7
O(6)-H(6)...O(10)	0.84	2.32	2.93(3)	130.1
O(11)-H(11A)...Br(2)#6	0.87	2.21	2.935(8)	140.5
O(11)-H(11B)...O(13)#6	0.87	2.10	2.960(17)	172.2
O(12)-H(12A)...Br(2)	0.87	1.97	2.698(7)	139.8
O(12)-H(12B)...O(4)#7	0.87	2.19	2.989(10)	152.7
O(12)-H(12B)...O(6)#8	0.87	2.58	3.090(10)	118.3
O(12)-H(12C)...O(3)	0.90	1.83	2.703(10)	161.5
O(9)-H(9A)...Br(1)#3	0.87	1.95	2.703(9)	143.4
O(9)-H(9A)...O(5)#9	0.87	2.34	2.932(10)	125.7
O(9)-H(9B)...O(3)#5	0.87	2.25	3.065(11)	156.2
O(13)-H(13A)...O(13)#8	0.87	2.37	3.06(3)	136.7
O(13)-H(13B)...O(12)	0.87	2.15	2.756(19)	126.0
O(10)-H(10A)...Br(1)	0.87	2.32	2.82(3)	116.3
O(10)-H(10B)...O(6)	0.87	2.49	2.93(3)	112.2
O(10)-H(10B)...O(13)	0.87	1.83	2.30(4)	111.8

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+2,-z+1 #2 -x+2,-y+1,-z+1 #3 x,y,z+1 #4 x,y,z-1 #5 -x+1,-y+2,-z+1 #6 -x+1,-y+1,-z+1 #7 x-1,y,z #8 -x+1,-y+2,-z #9 x-1,y,z+1

Table S9. Hydrogen bonds for **HNNU-1γ** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(8)-H(8)...O(9)#5	0.83	2.40	3.023(15)	131.7
O(6)-H(6)...O(7)	0.81	2.75	3.148(12)	112.3
O(3)-H(3)...O(9)#6	0.84	2.70	3.093(14)	110.0
O(12)-H(12A)...O(2)#7	0.87	2.05	2.874(13)	156.8
O(9)-H(9B)...O(10)	0.87	1.90	2.75(2)	168.8
O(11)-H(11A)...O(4)#8	0.87	2.05	2.892(13)	161.4
O(11)-H(11C)...O(6)#6	0.87	2.67	3.122(15)	113.4
O(10)-H(10A)...O(10)#6	0.87	2.72	3.13(4)	110.1

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 x,y+1,z #3 -x,-y+1,-z+2 #4 x,y-1,z #5 -x+1,-y,-z+1 #6 -x+1,-y,-z+2 #7 x-1,y,z #8 x+1,y,z

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