Electronic supplementary information (ESI)

Reversible Solid-State Structural Conversion between Three-dimensional Network and One-dimensional Chain of Cu(II) Triazole Coordination Polymers in Acidic/Basic-Suspensions or Vapors

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Here, we present supplementary figures S1~S6, which were mentioned in the main text. Then we also describe TG-DTA results and X-ray crystallographic data for $[Cu_3(trz)_3(\mu_3\text{-}OH)]Cl_2 \cdot 6H_2O$ (**1**) and $[Cu_3(trz)_3(\mu_3\text{-}OH)]Br_2 \cdot 6H_2O$ (**2**).

Supplementary figures mentioned in main text.

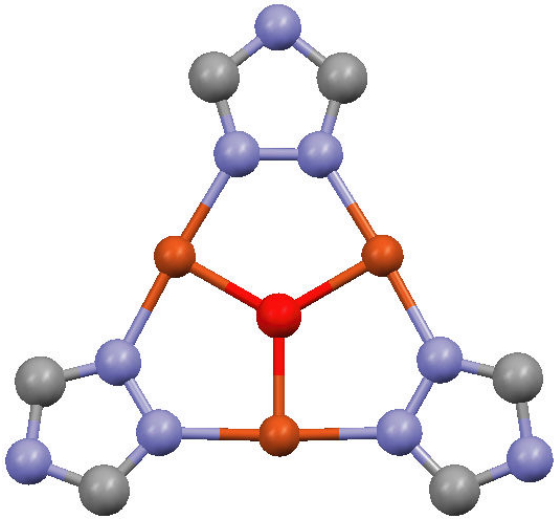

Fig. S1 $[Cu_3(trz)_3(\mu_3\text{-}OH)]$ as a building block of three dimensional network of **1** and **2**. H atoms were omitted. Color code: red, O; orange, Cu; purple, N; gray, C.

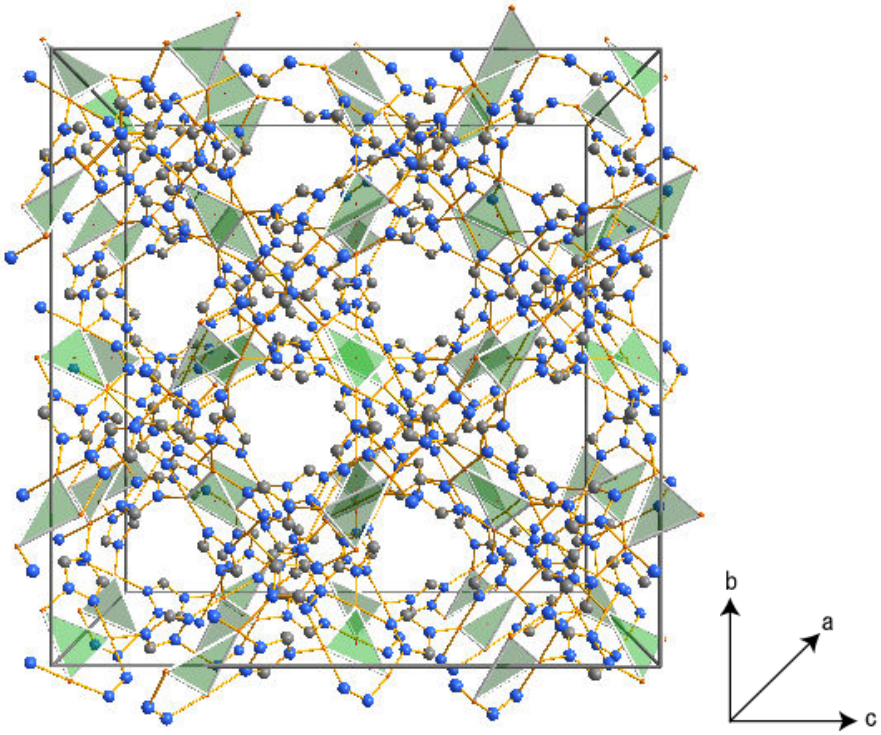

Fig. S2 $[Cu_3(trz)_3(\mu_3\text{-}OH)]$ building block in three dimensional network in a Unit cell. Colored triangles indicate equilateral triangles made of copper trimer.

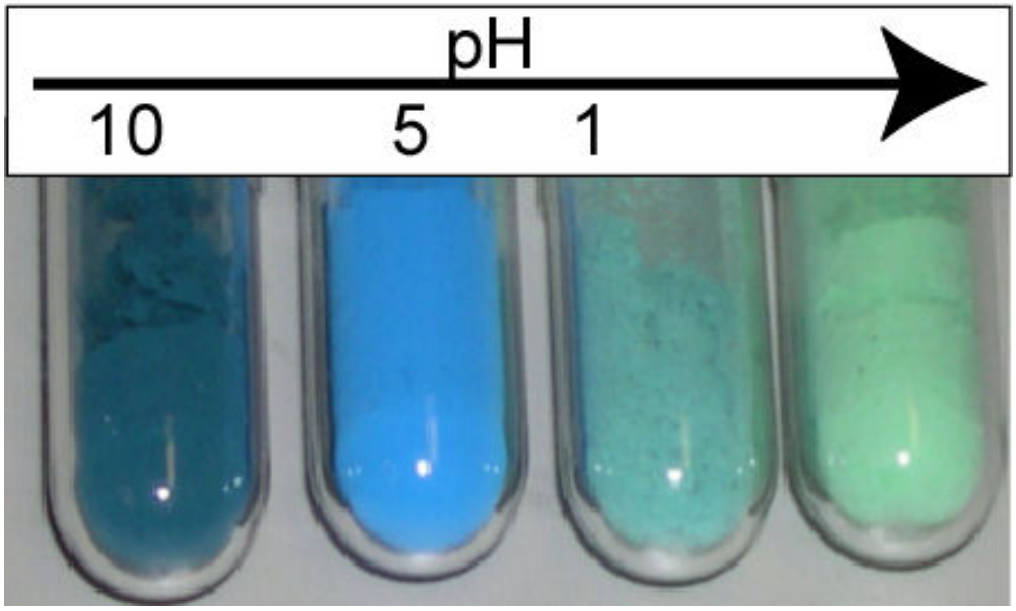

Fig. S3(a) Color change depending on pH condition of suspension for a series of **1**.

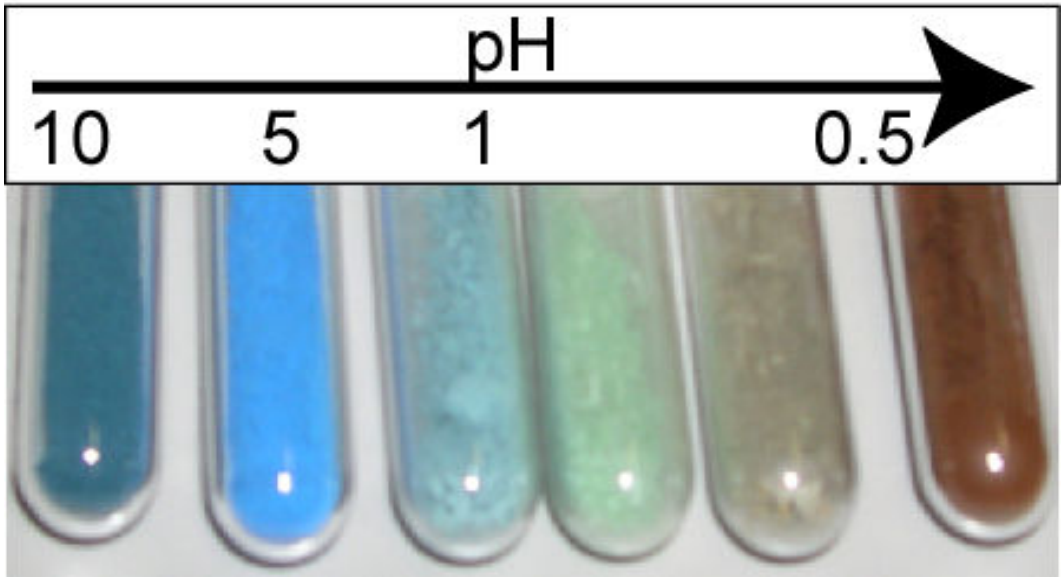

Fig. S3(b) Color change depending on pH condition of suspension for a series of **2**.

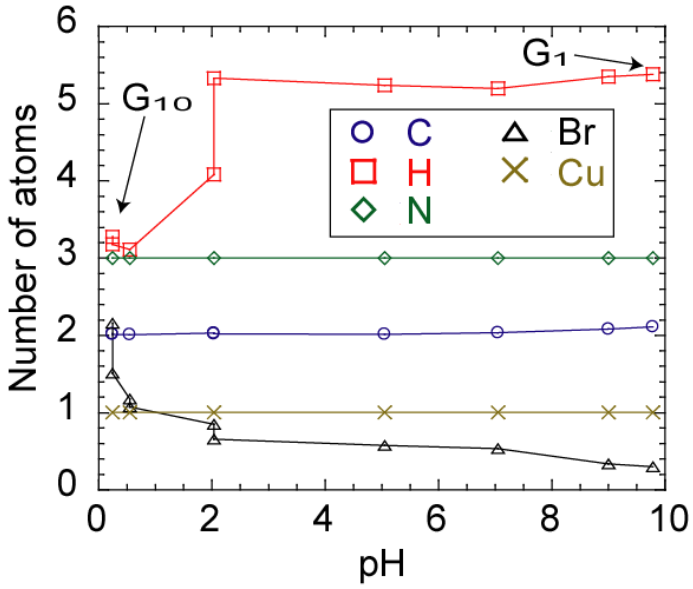

Fig. S4 Relative composition of each element to 3N of trz calculated from of elemental analysis for successively converted powder specimens from **2**.

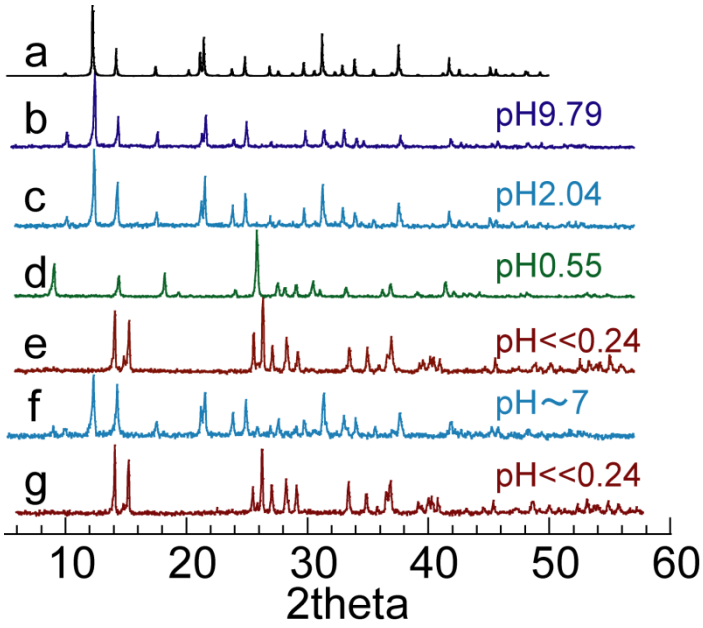

Fig. S5 Powder X-ray diffraction pattern of specimens after successive conversions. a was calculated for **2** from single crystal data. b, c, d and e correspond to G1, G5, G6 and G7 stemmed from **2** in the 1st series of successive conversions with decreasing pH as shown in Fig. S4, f was observed for 2nd series of conversion with increasing pH after 1st series, and g was observed for 3rd series of conversion with decreasing pH after 1st and 2nd series. Color of diffraction pattern corresponds to the sample color. Cu-Kα irradiation (λ=1.5444Å) was used at 25°C.

No Rietveld analysis was performed for powder specimens stemmed from **1** and **2**. Structural identification of **4** and **5** were not performed since their crystal structure and PXRD profiles have never been reported but only their colors were reported.

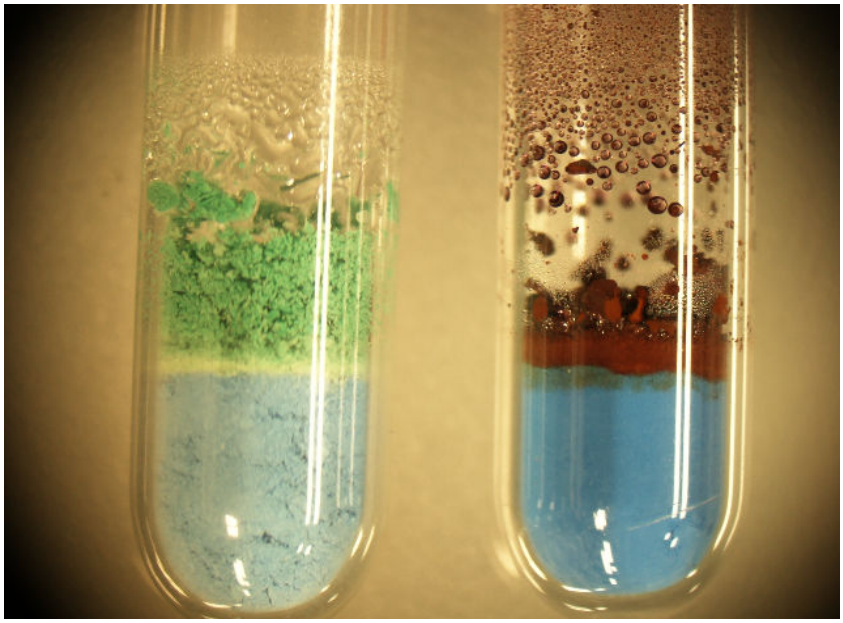

Fig. S6 Color change after **1** and **2** were exposed to acidic gas HCl or HBr, respectively. Left is **1** and right is **2**. Water droplets inside the glass tube were found during the conversion under HCl and HBr gas for **1** and **2**, respectively.

TG-DTA

TG-DTA measurements were performed for **1** and **2** in the temperature region between 25 and 200°C. For both samples, a similar weight loss occurred below ~ 150°C as the temperature was increased. The weight losses of 18% for **1** and 15% for **2** almost correspond to $6H_2O$ molecules of formula $[Cu_3(trz)_3(\mu_3\text{-}OH)]X_2{\cdot}6H_2O$ (X = Cl, Br, trz = triazolate). Below 100°C two crystal water molecules were lost, *i.e.* 6% for **1** and 5% for **2**, and between 100°C and 150°C four water molecules coordinating to copper ions were lost. After loss of two crystal water molecules, both crystals showed almost the same PXRD pattern as the virgin sample, pointing out that the crystal structure without crystal waters is very similar to that of $[Cu_3(trz)_3(\mu_3\text{-}OH)]X_2{\cdot}6H_2O$.

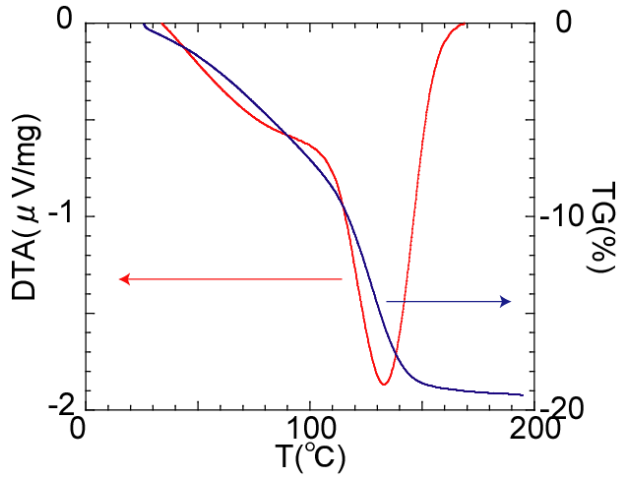

Fig. S7(a) Result of TG-DTA for **1**. Red solid curve shows DTA (μV/mg) and blue solid shows weight loss (%).

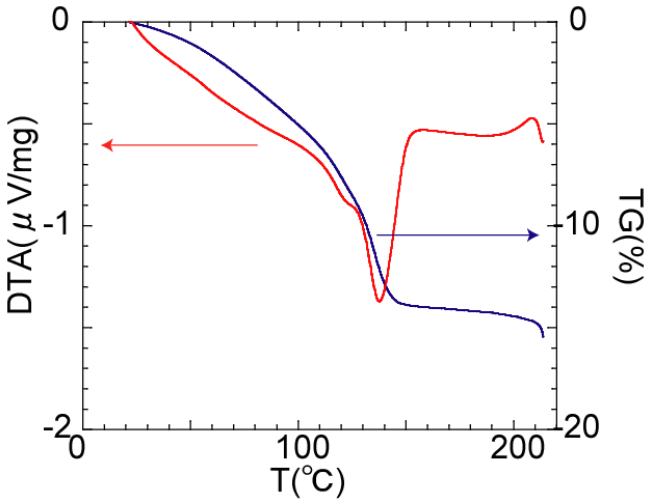

Fig. S7(b) Result of TG-DTA for **2**. Red solid curve shows DTA (μV/mg) and blue solid shows weight loss (%).

X-ray Crystallography

Category-A alerts appeared in Check CIF. This is because of intrinsic random disordering of water molecules and halogen ions coordinating to copper ion.

Table S1 Crystal data and structure refinement summary for **1** and **2**

Compound reference	**1**	**2**
Chemical formula	$C_6H_{19}Cl_2Cu_3N_9O_7$	$C_6H_{19}Br_2Cu_3N_9O_7$
Formula Mass	590.82	679.72
Crystal system	Cubic	Cubic
a/Å	24.743(4)	24.719(8)
b/Å	24.743(4)	24.719(8)
c/Å	24.743(4)	24.719(8)
α/°	90.0000	90.0000
β/°	90.0000	90.0000
γ/°	90.0000	90.0000
Unit cell volume/Å^3	15148(4)	15104(8)
Temperature/K	140	26
Space group	$Fd\bar{3}\ c$	$Fd\bar{3}\ c$
No. of formula units per unit cell, *Z*	32	32
Radiation type	Mo Kα (0.71073 Å)	Sr (0.6884 Å)
Absorption coefficient, *μ*/mm^{-1}	3.68	7.60
No. of reflections measured	31859	21348
No. of independent reflections	31859	19123
R_{int}	0.0354	0.04
Final R_1 values ($I > 2\sigma(I)$)	0.047	0.0841
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.050	0.0993
Final R_1 values (all data)	0.0581	0.0959
Final $wR(F^2)$ values (all data)	0.0688	0.1415
Goodness of fit on F^2	1.066	0.922

$$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo|, \; R_W = [\, \Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2]^{1/2}$$

Table S2(a) Bond lengths (Å) and angles (°) for **1**

Cu(1)-O(1)	1.977	Cu(1)#3-O(1)-Cu(1)#4	120.0
Cu(1)-O(2)	2.452	Cu(1)-N(2)-N(2)#1	120.95
Cu(1)-N(1)	1.977	C(1)-N(2)-N(2)#1	106.51
Cu(1)-N(2)	1.998	C(1)-N(2)-Cu(1)	132.21
Cu(1)-Cl(1)	2.834	C(1)-N(1)-C(1)	103.72
C(1)-N(1)	1.348	N(1)-Cu(1)-N(2)	91.47
C(1)-N(2)	1.321	N(1)-C(1)-N(2)	111.63
N(2)-N(2)#1	1.370	N(2)-Cu(1)-N(2)#1	177.06
O(1)-O(3)#2	9.540	O(1)-Cu(1)-N(2)#1	88.53
O(2)-O(3)	3.027	O(1)-Cu(1)-N(1)	180.0
Cl(1)-O(3)	2.744	O(2)-Cu(1)-O(2)#5	175.42
Cu(1)-Cu(1)#3	3.424	O(2)-Cu(1)-O(1)	87.71
		O(2)-O(3)-O(2)#6	89.97
Cu(1)-O(1)-Cu(1)#3	120.0	Cl(1)-Cu(1)-Cl(1)#7	178.26
Cu(1)-O(1)-Cu(1)#4	120.0	Cl(1)-Cu(1)-O(1)	91.10

Symmetry transformations used to generate equivalent atoms:

#1 1/4+y,-1/4+x,-z #2 1/2+y, 1/4-z, 3/4-x #3 1.25-y,1/2+z,3/4-x

#4 1.5-x, 1/2-z, 1/2-y #5 3/4+z, 1-y, -3/4+x #6 1/2+y, 1/2+z, -1+x

#7 3/4+z, 1-y, -3/4+x

Table S2(b) Bond lengths (Å) and angles (°) for **2**

Cu(1)-O(1)	1.975	Cu(1)#4-O(1)-Cu(1)#5	120.0
Cu(1)-O(2)	2.687	Cu(1)-N(2)-N(2)#1	121.19
Cu(1)-N(1)	1.996	C(1)-N(2)-N(2)#1	106.58
Cu(1)-N(2)	1.976	C(1)-N(2)-Cu(1)	132.04
Cu(1)-Br(1)	3.008	C(1)-N(1)-C(1)	103.39
C(1)-N(1)	1.345	N(1)-Cu(1)-N(2)	91.62
C(1)-N(2)	1.320	N(1)-C(1)-N(2)	111.72
N(2)-N(2)#1	1.357	N(2)-Cu(1)-N(2)#1	176.76
O(1)-O(3)#2	9.933	O(1)-Cu(1)-N(2)#1	88.38
O(2)-O(3)#3	3.089	O(1)-Cu(1)-N(1)	180.0
Br(1)-O(3)#3	2.792	O(2)-Cu(1)-O(2)#6	178.36
Cu(1)-Cu(1)#4	3.421	O(2)-Cu(1)-O(1)	89.18
		O(2)-O(3)#3-O(2)#7	77.04
Cu(1)-O(1)-Cu(1)#4	120.0	Br(1)-Cu(1)-Br(1)#8	178.67
Cu(1)-O(1)-Cu(1)#5	120.0	Br(1)-Cu(1)-O(1)	90.67

Symmetry transformations used to generate equivalent atoms:

#1 1-y, 1-x, 1.5-z #2 1-y, 1/4+x, -1/4+z #3 1/4+y, 1-x, -1/4+z

#4 y, 1.25-z, 1.25-x #5 1.25-z, x, 1.25-y #6 1-x, -1/4+z, 1/4+y

#7 z, x, y #8 1-x, -1/4+z, 1/4+y