**Electronic Supplementary Information (ESI)** 

## From Helix to Helical Pores: Solid-state Crystalline Conversions Triggered by Gas-Solid Reactions

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## **Experimental details**

## **General procedure**

Starting materials, reagents, and solvents were purchased from commercial sources and used without further purification. FT-IR spectra were measured using a Nicolet Avatar 360 FT-IR spectrophotometer. Thermogravimetric analysis was carried out in a nitrogen stream using Q50 TGA (TA) thermal analysis equipment with a heating rate of 5 C min<sup>-1</sup>. Powder X-ray diffraction patterns (PXRD) of the bulk samples were measured on a Rigaku RAPID II with variable-temperature and MiniFlex (Cu K $\alpha$ ,  $\lambda = 1.5418$  Å) under room temperature. EDX spectra were measured on a JED2300 (JSM-6360LA) with 20 K eV. Elemental analyses were carried out with an Elementar vario EL Cube equipment.

**Ligand synthesis**. The ligand 1,2-bis((5H-imidazol-4-yl)methylene)hydrazine (BIm) was prepared by the reported method.<sup>S1</sup>

**Complex synthesis.** All the complexes can be synthesized by reacting BIm and copper salts under solvothermal conditions.

**CuBIm-Cl**: A mixture of CuCl<sub>2</sub> (2.70 mg, 0.02mmol), BIm (3.87 mg, 0.02mmol), and DMF/ethanol, 4:1,(2.0 ml) was sealed in a Pyrex glass tube and heated in an oven at 100 °C for 24 hours and cooled to room temperature at a rate of 5 °C/h. Dark green needle-like crystals were obtained (3.21 mg, 60%). IR spectrum (KBr, pellets, cm-1): 3116.79w, 3029.67w, 2924.52w, 2850.15w, 1623.09vs, 1580.08m, 1528.74w, 1508.08w, 1461.52w, 1438.38w, 1387.67w, 1357.94w, 1297.11m, 1212.20w, 1120.46s, 1080.26m, 1252.57m, 1025.50m, 969.98w, 841.45m, 650.80m, 614.63m, 541.46w, 503.75w. To obtain solvent-free sample, **CuBIm-Cl** was solvent-exchanged with methanol for 3 days, followed by direct evacuation under vacuum. Elemental analysis (CHN), CuC<sub>8</sub>H<sub>12</sub>N<sub>6</sub>ClO<sub>2.5</sub> (corresponding to CuBImCl·2.5H<sub>2</sub>O) calculated (%): C 29.01, H 3.65, N 25.37; found (%): C 29.27, H 3.62, N 25.41.

**CuBIm-Br**: A mixture of CuBr<sub>2</sub> (4.49 mg, 0.02mmol), BIm (3.78 mg), and DMF/ethanol, 4:1,(2.0 ml) was sealed in a Pyrex glass tube and heated in an oven at 100 °C for 24 hours and cooled to room temperature at a rate of 5 °C/h. Dark green needle-like crystals were obtained (3.16 mg, 62.3%). IR spectrum (KBr, pellets, cm-1): 3116.35w, 3018.81w, 2925.34w, 2850.54w, 1622.19vs, 1579.74m, 1506.50w, 1460.36w, 1431.44w, 1387.91w, 1358.18w, 1333.92w, 1297.12w, 1260.04w, 1209.41w, 1120..67s, 1077.68m, 1053.01m, 1015.33m, 968.17w, 841.43m, 820.51w, 650.04m, 612.63m, 541.08w, 502.44w. To obtain solvent-free sample, **CuBIm-Br** was solvent-exchanged with methanol for 3 days, followed by direct evacuation under vacuum. Elemental analysis (CHN), CuC8.5H11.8N6BrO1.9 (corresponding to CuBImBr-0.5methanol·1.4H<sub>2</sub>O), calculated (%): C, 27.45; H, 3.20; N, 22.60; found (%): C 27.34, H 3.33, N 22.87.

**Crystallographic studies:** Crystal structures of both CuBIm-Cl and CuBIm-Br were measured at 100 K. Data collection was performed on a XtaLab PRO MM007HF DW Diffractometer System equipped with a MicroMax-007DW MicroFocus X-ray generator and Pilatus 200K silicon diarray detector (Rigaku, Japan, Cu K $\alpha$ ,  $\lambda$  = 1.54178 Å). The data were processed using CrysAlisPro 1.171.39.28b (Rigaku OD, 2015). The structures were solved by direct methods and refined by full-matrix least-squares refinements based on  $F^2$ . Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. The crystallographic calculations were conducted using the SHELXL-2017/1 programs. The treatment for the guest molecules in both CuBIm-Cl and CuBIm-Br involves the use of the SQUEEZE program of PLATON. The residual electron density per void was 210 electrons for CuBIm-Cl, which correspond to 3DMF, and 5 MeOH guest molecules. For CuBIm-Br, the residual electron density per void was 241 electrons, which correspond to 3 DMF, 5 MeOH, and 3H<sub>2</sub>O guest molecules. The linker between two imidazolate groups (-CH=N-N=CH-) is disordered, which locates on two positions. The ratios of occupancy at two positions are 0.552/ 0.448 and 0.525/0.475 for CuBIm-Cl and CuBIm-Br, respectively. The crystal data of CuBIm-Cl and CuBIm-Br have been deposited at the Cambridge Crystallographic Data Centre, deposited numbers are 1565656 and 1565655, respectively. The crystal data and structure refinement parameters for CuBIm-Cl and CuBIm-Br were summarized in the Table S1.

From the squeeze file of CuBIm-Cl, we obtain the following data:

loop\_

\_platon\_squeeze\_void\_nr

\_platon\_squeeze\_void\_average\_x

\_platon\_squeeze\_void\_average\_y

\_platon\_squeeze\_void\_average\_z

\_platon\_squeeze\_void\_volume

\_platon\_squeeze\_void\_count\_electrons

\_platon\_squeeze\_void\_content

1	0.000	0.000 -	0.011	743	210''
2	0.333	0.667	0.113	741	210''
3	0.667	0.333	0.779	740	210''

From the squeeze file of CuBIm-Br, we obtain the following data: loop\_

\_platon\_squeeze\_void\_nr

```
_platon_squeeze_void_average_x
```

\_platon\_squeeze\_void\_average\_y

\_platon\_squeeze\_void\_average\_z

\_platon\_squeeze\_void\_volume

\_platon\_squeeze\_void\_count\_electrons

\_platon\_squeeze\_void\_content

1 0.000 0.000 -0.006 767 242 ''

S4

2	0.333	0.667	0.612	765	241 ' '
3	0.667	0.333	0.279	765	241 '

'Gas-Sorption Measurements. Gas sorption experiments were carried out on a Micromeritics ASAP 2010 surface area and pore size analyzer. Prior to the measurement, the sample was exchange with methanol solvents for 3 days, and then dried under dynamic vacuum (<10<sup>-3</sup> torr) at room temperature overnight. Then, the sample was dried again by using the "outgas" function of the surface area analyzer for an hour at 150°C. Finally, samples of CuBIm-Cl, CuBIm-Br, STU-3, and that transformed from CuBIm-Cl, CuBIm-Br were used for N2 sorption measurement at 77 K with liquid nitrogen, respectively.

	CuBIm-Cl	CuBIm-Br
formula	C <sub>8</sub> H <sub>7</sub> N <sub>6</sub> CuCl	C <sub>8</sub> H <sub>7</sub> N <sub>6</sub> CuBr
Mr	286.19	330.65
crystal system	Trigonal	Trigonal
Temp (K)	100	100
space group	R3	R3
<i>a</i> (Å)	27.9457(7)	28.5210(7)
<i>b</i> (Å)	27.9457(7)	28.5210(7)
<i>c</i> (Å)	9.7132(2)	9.6037(3)
$\alpha$ (deg)	90	90
$\beta$ (deg)	90	90
γ (deg)	120	120
$V(Å^3)$	6569.4(4)	6765.5(4)
Z	18	18
$Dc (g \text{ cm}^{-3})$	1.302	1.461
$\mu$ (mm <sup>-1</sup> )	3.691	5.064
no. of reflns collected	2857	2934
no. of unique reflns	2637	2755
Rint	0.0354	0.0197
$R_1 [I > 2\sigma(I)]^a$	0.0379	0.0350
$wR_2 [I \ge 2\sigma(I)]^b$	0.1077	0.0836
$R_1$ [all data]	0.0401	0.0370
wR <sub>2</sub> [all data]	0.1060	0.0846

 Table S1. Summary of the crystal data and structure refinement parameters for CuBIm-Cl and CuBIm-Br.

<sup>a</sup>  $R_1 = \sum (||F_0| - |F_c||) / \sum |F_0|;$  <sup>b</sup>  $wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$ 



Fig. S1. Powder X-ray diffraction patterns (Cu K $\alpha$ ,  $\lambda$ =1.5418 Å) of CuBIm-Cl (a calculated, b as-synthesized) and CuBIm-Br (c calculated, d as-synthesized).

![](_page_6_Figure_2.jpeg)

Fig. S2. Crystal structure of CuBIm-Cl: the unsymmetrical unit (Cu-N: 1.956(2) - 2.124(6) Å, Cu-Cl = 2.5884(7) Å, a), left-handed and right-handed helical chain (b), and X-H…Cl (X = C and N)  $\pi \dots \pi$  interactions (highlighted by dashed red line) between two adjacent left-handed and right-handed helical chains (c). Color codes: Cu green, Cl cyan, C gray, H gray, and N blue.

![](_page_7_Figure_0.jpeg)

Fig. S3. IR spectra of CuBIm-Cl (a), CuBIm-Br(b), and BIm (c).

![](_page_7_Figure_2.jpeg)

Fig. S4. The pore apertures of CuBIm-Cl (left) and CuBIm-Br(right). Without considering the van der Waals radius, the pore apertures are 9.215 and 10.524Å, respectively. When adding the van der Waals radius, the pore apertures are 6.815 and 8.124 Å, respectively.

![](_page_8_Figure_0.jpeg)

Fig. S5. TGA Plots of CuBIm-Cl and CuBIm-Cl under a  $N_{\rm 2}$  atmosphere.

![](_page_9_Figure_0.jpeg)

Fig. S6. The variable-temperature powder X-ray diffraction (Cu K $\alpha$ ,  $\lambda$ =1.5418 Å) of CuBIm-Br (up) and CuBIm-Cl (bottom) under a air atmosphere.

![](_page_10_Figure_0.jpeg)

Fig. S7. Powder X-ray diffraction (Cu K $\alpha$ ,  $\lambda$ =1.5418 Å) of CuBIm-Cl (up) and CuBIm-Br (bottom) after being treated in boiling organic solvents THF and benzene.

![](_page_11_Figure_0.jpeg)

Fig. S8. Powder X-ray diffraction(Cu K $\alpha$ ,  $\lambda$ =1.5418 Å) of CuBIm-Cl (up) and CuBIm-Br (bottom) after treatment in boiling water.

![](_page_12_Picture_0.jpeg)

CuBIm-Br

![](_page_12_Figure_2.jpeg)

Fig. S9. The color change after treatment in methylamine atmosphere of CuBIm-Cl and CuBIm-Br.

![](_page_13_Figure_0.jpeg)

Fig. S10. Powder X-ray diffraction (Cu K $\alpha$ ,  $\lambda$ =1.5418 Å) of CuBIm-Cl (up) and CuBIm-Br (bottom) after treatment in methylamine and as synthesized CuBIm-Cl and CuBIm-Br, and STU-3, respectively.

![](_page_14_Figure_0.jpeg)

Fig. S11. Pawley refinements of the PXRD patterns of samples CuBIm-Cl (up) and CuBIm-Br (bottom) after treatment in methylamine. Both patterns were collected on a Rigaku Ultimal V with a Cu K $\alpha$  radiation ( $K\alpha_1$ =1.54051,  $K\alpha_2$ =1.54433,  $I_{K\alpha_1}/I_{K\alpha_2}$ =0.497), from 3° to 50° in a step of 0.02° with the remaining time 0.1°/min. The Pawley refinements by using the Reflex module of Materials Studio v. 7.0. A 20 parameters polynomial function was selected for background correction and the Pearson VII function were employed to fit the peaks.

	STU-3 (Initial model)	STU-3 transformed from CuBIm-Cl	STU-3 transformed from CuBIm-Br		
cryst syst	Cubic	Cubic	Cubic		
space group	Ia3d	<i>I</i> a3d	Ia3d		
<i>a</i> (Å)	34.2896(3)	34.2646	34.2523		
<i>b</i> (Å)	34.2896(3)	34.2646	34.2523		
c (Å)	34 2896(3)	34 2646	34 2523		
	51.2090(5)	51.2010	51.2025		
$\alpha$ (deg)	90	90	90		
$\beta$ (deg)	90	90	90		
γ (deg)	90	90	90		

Table S2 Unit cell parameters of the initial STU-3 obtained from single crystal X-ray diffractions and post-synthetic STU-3 obtained from the refinement of their PXRD patterns

![](_page_15_Figure_2.jpeg)

Fig. S12. Time-resolved X-ray powder diffractions monitoring the transformation of crystalline CuBIm-Br to STU-3 in a methylamine atmosphere.

![](_page_16_Picture_0.jpeg)

Fig. S13. Photographs of products obtained by solvothemal synthesis of CuBIm-Cl (left) and CuBIm-Br (right) at 120 °C. The needle-like crystals are CuBIm-Cl (left) or CuBIm-Br (right), and the block crystals are STU-3.

![](_page_16_Figure_2.jpeg)

Fig. S14. IR spectra of CuBIm-Cl and CuBIm-Br after treatment in methylamine, and as synthesized STU-3, respectively.

![](_page_17_Figure_0.jpeg)

Fig. S15. TGA plots of CuBIm-Cl and CuBIm-Br after treatment in methylamine atmosphere, and as synthesized STU-3, respectively.

Table S3 CHN elemental analyses of CuBIm-Cl and CuBIm-Br, and that after treatment in methylamine atmosphere.

Samples	Formula	Experimented		Calculated:			
		C (%)	H (%)	N (%)	C (%)	H(%)	N(%)
CuBIm-Cl	CuC <sub>8</sub> H <sub>12</sub> N <sub>6</sub> ClO <sub>2.5</sub>	29.27	3.62	25.41	29.01	3.65	25.37
	Corresponding to:						
	CuBImCl·2.5H <sub>2</sub> O						
CuBIm-Br	CuC <sub>8.5</sub> H <sub>11.8</sub> N <sub>6</sub> BrO <sub>1.9</sub>	27.34	3.33	22.87	27.45	3.20	22.60
	Corresponding to:						
	CuBImBr·0.5methanol·1.4H <sub>2</sub> O						
Transformed from	$C_{10.8}H_{14.4}CuN_6O_{1.4}$	41.05	4.76	26.97	41.28	4.62	26.75
CuBIm-Cl	Corresponding to:						
	CuBIm·1.4ethanol						
Transformed from	C <sub>9</sub> H <sub>10</sub> CuN <sub>6</sub> O	38.70	3.76	29.54	38.36	3.58	29.83
CuBIm-Br	Corresponding to:						
	CuBIm·methanol						

![](_page_18_Picture_0.jpeg)

Fig. S16. Photographs of the supernatant of the samples of CuBIm-Cl (left) and CuBIm-Br (right) after being soaked in methanol to react with AgNO<sub>3</sub>.

![](_page_18_Figure_2.jpeg)

Fig. S17. EDX results of CuBIm-Cl (a) and that after treatment in methylamine atmosphere (b, sample was exchanged and washed with methanol).

![](_page_19_Figure_0.jpeg)

Fig. S18. EDX results of CuBIm-Br (a) and that after treatment in methylamine atmosphere (b, sample was exchanged and washed with methanol).

![](_page_20_Figure_0.jpeg)

Fig. S19. Powder X-ray diffraction (Cu K $\alpha$ ,  $\lambda$ =1.5418 Å) of as synthesized STU-3, STU-3 after treatment in HCl vapour, and as synthesized CuBIm-Cl, respectively.

![](_page_21_Figure_0.jpeg)

Fig. S20. Powder X-ray diffraction (Cu K $\alpha$ ,  $\lambda$ =1.5418 Å) of as-synthesized and activated samples of CuBIm-Cl (up) and CuBIm-Br (bottom). After activation, the PXRD shown the intensity of strongest peak at 210 become weaker and all peaks are obviously broadened, which indicate the partial structural collapse occurred after activation.

![](_page_22_Figure_0.jpeg)

Fig. S21. Powder X-ray diffraction (Cu K $\alpha$ ,  $\lambda$ =1.5418 Å) of as-synthesized and activated samples of STU-3 transformed from CuBIm-Cl (up) and CuBIm-Br (bottom).

![](_page_23_Figure_0.jpeg)

Fig. S22. Powder X-ray diffraction (Cu K $\alpha$ ,  $\lambda$ =1.5418 Å) of as-synthesized and activated samples of STU-3 from solvothermal synthesis.

![](_page_23_Figure_2.jpeg)

Fig. S23. TGA plots of as-synthesized and activated CuBIm-Cl.

![](_page_24_Figure_0.jpeg)

Fig. S24. TGA plots of as-synthesized and activated CuBIm-Br.

![](_page_24_Figure_2.jpeg)

Fig. S25. TGA plots of as-synthesized and activated STU-3 transformed from CuBIm-Cl.

![](_page_25_Figure_0.jpeg)

Fig. S26. TGA plots of as-synthesized and activated STU-3 transformed from CuBIm-Br.

![](_page_25_Figure_2.jpeg)

Fig. S27. TGA plots of as-synthesized and activated STU-3 from solvothermal synthesis.

![](_page_26_Figure_0.jpeg)

Fig. S28. DFT pore size distributions for CuBIm-Cl, CuBIm-Br, and STU-3 obtained from solvothermal synthesis and transformation from CuBIm-Cl and CuBIm-Br.

Reference:

S1 X.-P. Zhou, M. Li, J. Liu, D. Li, J. Am. Chem. Soc. 2012, 134, 67-70.