Supplementary Information

Efficient vapour-assisted aging and liquid-assisted grinding synthesis of a microporous copper-adeninate framework

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Experimental section

All reagents and solvents were purchased from commercial sources and used without further purification.

PXRD patterns for samples were taken on a flat plate in the 2θ range 4-40°, using a Bruker AXS D8 advance X-ray powder diffractometer, equipped with Cu Kα radiation (γ= 0.15405 nm). IR spectra were recorded on a TENSOR 27 spectrometer by using KBr pellets in the range of 4000-400 cm^{-1}. C, H, N elemental analyses were performed on an Elementar Vario EL analyzer. Thermogravimetric analysis (TGA) was performed under air atmosphere with the heating rate of 10℃/min on a Q600 Thermal analyzer. The microscopic morphology images of the samples were obtained on the S-3000N machine.

Gas sorption experiments were performed with PS2-M091 machine. The samples were synthesized by neat grinding, LAG grinding, neat grinding product followed by washing with DMF and methanol, LAG product followed by washing with DMF and methanol, and VAG product followed by washing with DMF and methanol were degassed at 150℃ for 12 hours on degassing station. VAG product followed by washing with DMF and methanol was also degassed at 170℃ for 5 hours. The temperature of each sample for N_2 adsorption experiments was controlled by a refrigerated bath of liquid nitrogen (77 K).

Preparation of compound 1 under VAG and LAG conditions

In the vapor-assisted aging synthesis of compound **1**, pre-treated starting materials are necessary: A mixture of adenine (0.135g, 1.0 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.199g, 1.0 mmol) was ground in a Retsch MM200 shaking mill at 25Hz for 1 minute, or it was ground manually in a mortar for 5 minutes. For solvent vapor-assisted aging, the pre-ball milled or pre-manually ground mixture was put in a culture dish (60 mm diameter), then this stuff was placed in a capped glass desiccator (180 mm diameter) for aging within a specific time at room temperature (28℃), in which the relative

humidity is 83%. In a neat grinding reaction, a mixture of adenine (0.135g, 1.0 mmol) and $Cu(OAc)_2 \cdot H_2O$ (0.199g, 1.0 mmol) was ground with a Retch MM200 shaking mill for 10 minutes. Based on the above neat grinding, addition of 80 μL (4.4 mmol) of water or acetic acid to the mixture accelerates the mechanochemical reaction to go to complete within 1 or 5 minutes.

Elemental analysis of as-synthesized samples

Synthesis of $[Cu(ade)(OAc)] \cdot 1.40H_2O \cdot 1.25HOAc$ by HOAc vapor-assisted aging the pre-ball milled reactants for 30 minutes. Anal. Calc. (%): C, 31.96; H, 4.18; N, 19.62. Found: C, 31.43; H, 3.095; N, 19.25.

Synthesis of $[Cu(ade)(OAc)] \cdot 0.88H_2O \cdot 0.50HOAc$ by water vapor-assisted aging the pre-ball milled reactants for 12 hours. Anal. Calc. (%): C, 31.76; H, 3.58; N, 23.14. Found: C, 31.79; H, 2.95; N, 23.26.

Synthesis of $[Cu(ade)(OAc)] \cdot 1.35H_2O \cdot 0.18HOAc$ by by water vapor-assisted aging the pre-ball milled reactants for 38 hours. Anal. Calc. (%): C, 30.29; H, 3.60; N, 24.00. Found: C, 29.80; H, 2.991; N, 23.53.

Synthesis of $[Cu(ade)(OAc)] \cdot H_2O$ by heating the pre-ball milled reactants at 200℃ for 12 hours. Calc. (%) :C, 30.6; H, 3.3; N, 25.49. Found: C, 30.24; H, 2.879; N, 25.79.

FT-IR analysis of as-synthesized samples

As shown in Fig. S10, the as-made samples of compound **1** show similar FT-IR spectra. The characteristic strong peaks of adenine are shown at 1673 cm^{-1} for C=N7 and 1604 cm^{-1} for N-H. However, when adenine is coordinated with copper ions, the peak due to N9-H group appears blue shift to 1635 cm^{-1}, whereas C=N7 reveals no shift with weak intensity. The peaks at 1585 and 1288 cm^{-1} are assigned as C=O and C-O stretching bands of coordinated acetate. (KBr, cm^{-1}): 3350(s), 3306(w), 1654(s), 1606(s), 1581(s), 1545(m), 1464(m), 1403(s), 1344(m), 1309(w), 1281(w), 1208(m), 1152(w), 1043(w), 991(w), 939(w), 672(m), 650(m), 624(m), 577(m).

Solubility determination

A known amount of solute, for example 20 mg, was put in a container. Then the weighed solvent was added in batches until, even after vigorous and prolonged stirring, the solute just dissolves. Here, adenine and copper acetate monohydrate are the solutes, water and acetic acid as solvents. These experiments are carried out at 18 (room temperature). The solubilities of adenine in water and acetic acid at room temperature are 0.05 and 11.12 g/100g, and those of copper

acetate monohydrate in water and acetic acid are 6.49 and 0.54 g/100g.

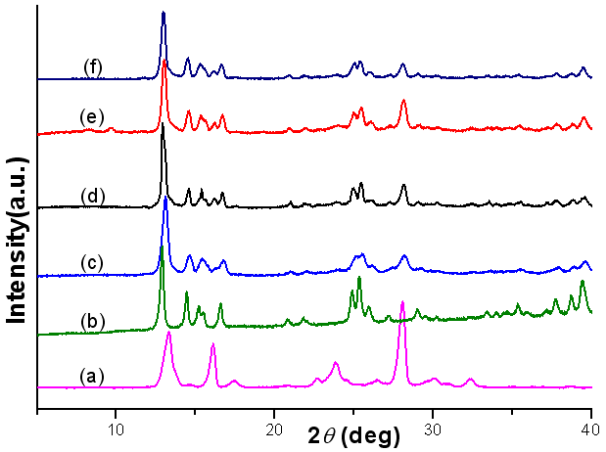

Fig. S1 PXRD patterns for (a) adenine; (b) monohydrate copper acetic; (c) the pre-manually ground reactants; (d) the pre-ball milled reactants; (e) the pre-ball milled mixture of starting materials was left on standing for 5 months at room temperature; (f) the manually ground reactants for 30min.

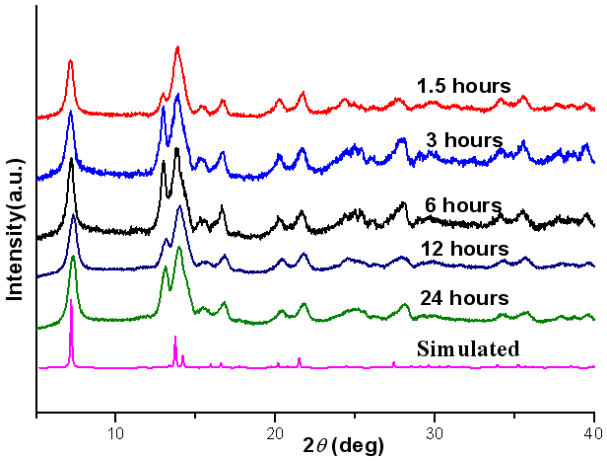

Fig. S2 PXRD patterns for the pre-ball milled mixtures of starting materials exposed to MeOH vapour for 1.5, 3, 6, 12 and 24 hours at room temperature.

(a) (b)

Fig. S3 Visual comparison between (a) the pre-treated reactants and (b) as-made compound **1**.

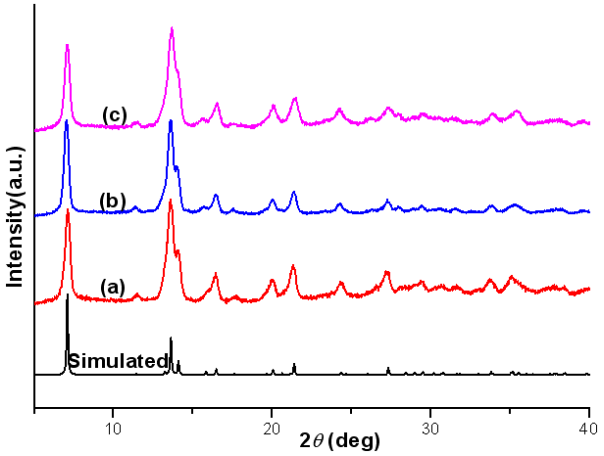

Fig. S4 PXRD patterns for the compound **1** made by water vapor-assisted aging (a) the pre-ball milled reactants for 38 hours; (b) the pre-manually ground reactants for 24 hours; (c) the pre-ball milled reactants for 24 hours at room temperature. The bottom one is the simulated pattern of IZUMUN.

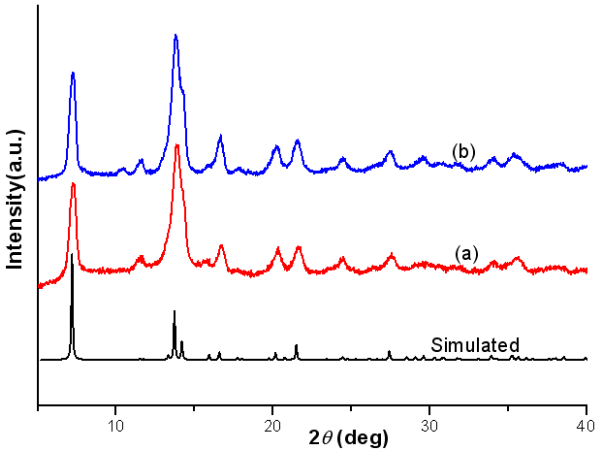

Fig. S5 PXRD patterns for the products made by (a) heating pre-ball milled reactants at 200 ℃ for 12 hours; (b) neat grinding for ten minutes, then heating at 150 ℃ for 12 hours. The bottom one is the simulated pattern of IZUMUN.

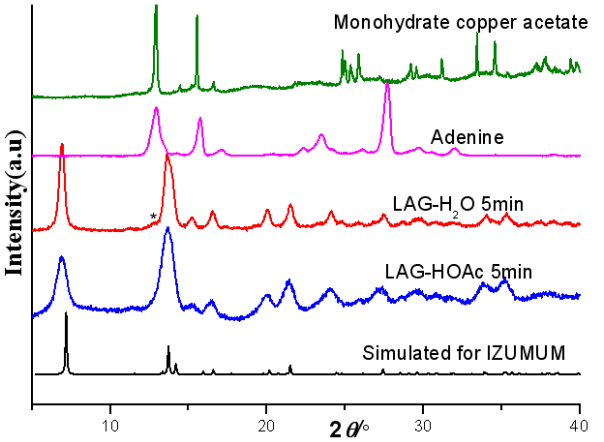

Fig. S6 PXRD patterns for 5 minutes' LAG. The asterisk indicates a weak peak due to unreacted starting materials.

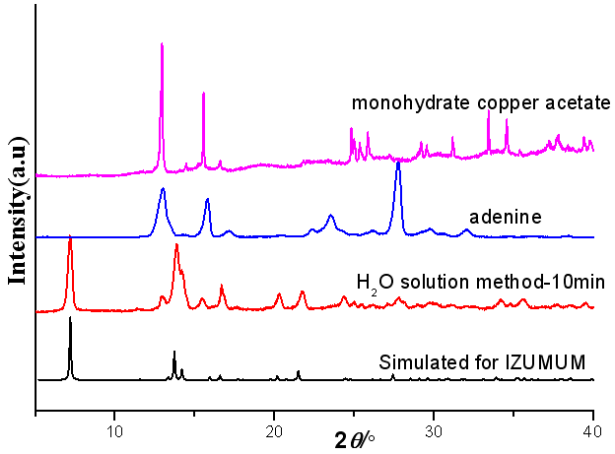

Fig. S7 PXRD patterns for water solution-based reaction.

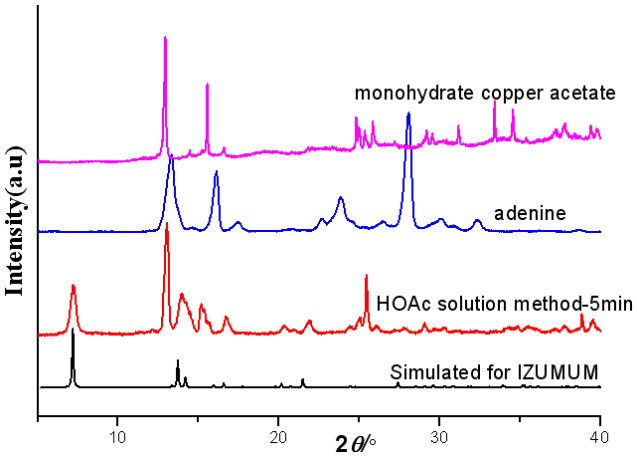

Fig. S8 PXRD patterns for water HOAc-based reaction.

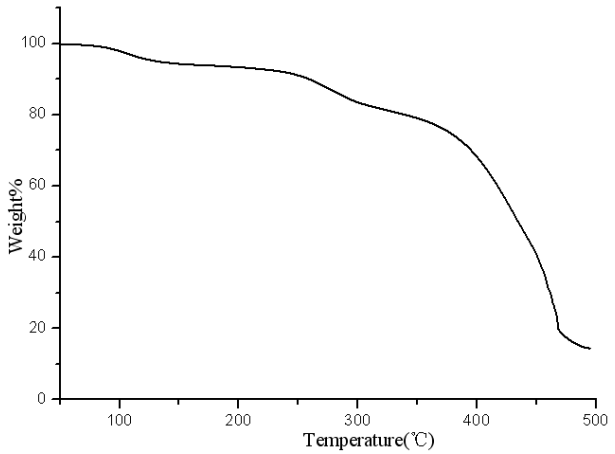

Fig. S9 TGA curves for the product obtained by neat grinding.

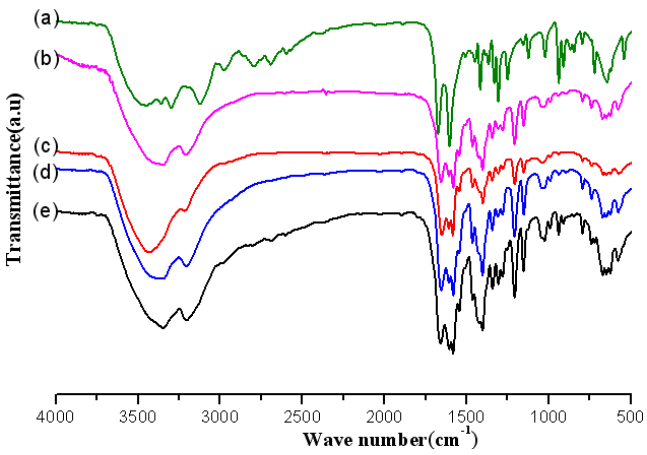

Fig. S10 FT-IR spectra of (a) adenine; as-synthesized samples of compound **1** made by (b) neat grinding; (c) liquid-assisted grinding in the presence of a small amount of water); (d) HOAc vapor-assisted aging; (e) heating the pre-ball milled reactants.