Supplementary Information

Efficient vapor-assisted aging synthesis of functional and high crystalline MOFs from CuO and rare earth sesquioxides/carbonates

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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}. 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 3H-2000PS2 machine. VAG product followed by washing with EtOH were degassed at 120 ℃ for 12 hours on degassing station. The temperature of each sample for N_2 adsorption experiments was controlled by a refrigerated bath of liquid nitrogen (77 K).

Preparations of HKUST-1(**1**)

In the vapor-assisted aging synthesis, pre-treated starting materials are necessary: the reactants were neat ground (pre-G) or ion (NH_4Cl, 5wt.%)-assisted ground (pre-IAG) or ion (NH_4Cl, 5wt.%) and liquid (100 μL)-assisted ground (pre-ILAG) in a Retsch MM200 at 25Hz for 1 min.

The pre-treatment was conducted in 2:3 H_3BTC:CuO ratio in a Retsch MM200 shaking ball at 25Hz for 1 minute. CuO (72mg, 0.9 mmol) and H_3BTC (127mg, 0.6 mmol) was added into a 25ml stainless steel milling jar, along with addition of 100μl DMF and one stainless steel ball with a diameter of 10mm. The added catalytic NH_4Cl was at 5wt.% level to the total amount of crude materials. After ball milling the crude materials at 25Hz for 1 minute, we took the pre-treated samples out and put them in a culture dish (60mm diameter), which was then placed in a capped glass desiccator (180mm diameter) along with a beaker containing 20 mL of solvent. The desiccator was sealed with a cap, and the sample placed inside was allowed to stand for aging in vapor within a specific time at room temperature (20℃). After a specific time, the product was washed with ethanol (5 mL) at room temperature for 1 hour, then dried under reduced pressure. Yield: 100%.

In order for scale-up synthesis of the product to at least ten grams by VAG, we pre-ground 3.0g of starting materials in two 25ml stainless steel milling jars for four times, then put these pre-ball milled reactants together in a 15cm culture dish to age in water vapor (RH: 80%) in a capped desiccator for 24 hours at room temperature (please see its PXRD, Fig. S8, page 7 of ESI).

The preparation of compounds **2**, **3** and **4** is similar to that of **1** except that no solvent was added in pre-treatment stage and RE_2O_3 or $RE_2(CO_3)_3 \cdot xH_2O$ (0.5mmol) was used instead of copper oxide.

IR analysis

IR spectroscopic studies of VAG samples exhibited typical peeks corresponding to the coordination polymer (Fig. S14). The characteristic strong peaks of H_3BTC groups are shown at 1721cm^{-1} for C=O and 1276cm^{-1} for C-O. However, for the coordinated C=O group, the characteristic peaks appeared some blue shift to 1548cm^{-1}, though, peaks for C-O have the same position with H_3BTC, but with weak intensities. Furthermore, the appearance of the C=C stretching bands of uncoordinated H_3BTC at 1400, 1450 and 1610 cm^{-1}, coordinated ones at 1370, 1450 and 1610 cm^{-1}.

TG analysis

In order to determine the thermal stability VAG product, thermogravimetric analysis (TGA) of compound 1 was carried out(Fig. S15). The TGA curve suggests a weight loss of 32.35% in the range of 20-100 ℃ corresponding to a gradual removal of water and ethanol molecules, then progressive weight loss of 6.64% from 100 to 300 ℃ due to the loss of uncoordinated DMF molecules. This water capacity is similar to that of hydration [$Cu_3(BTC)_2(H_2O)_3$] reported by Ian D. Williams.[1] The anhydrous residues start to decompose at 300 ℃.

Table S1. Solubilities of NH_4Cl and H_3BTC in DMF, EtOH and H_2O (100g) respectively.

solvent	NH_4Cl	H_3BTC
DMF	0.001g	14.8g
EtOH	0.0129g	5.52g
H_2O	37.2g	0.0441g

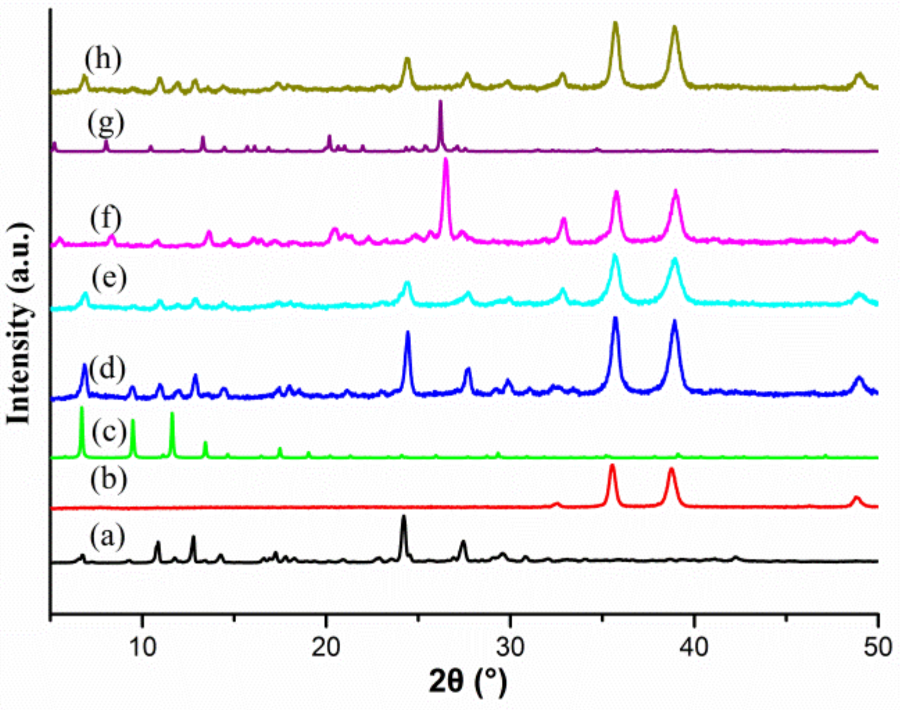

Figure S1. PXRD patterns for the pretreated starting materials: (a) H_3BTC; (b) CuO; (c) the simulated pattern for HKUST-1(CSC code, FIQCEN); (d) the pre-G mixtures of H_3BTC and CuO; (e) the pre-IAG mixtures of H_3BTC, CuO and NH_4Cl; (f) the pre-ILAG-DMF mixtures of H_3BTC, CuO and NH_4Cl; (g) the simulated pattern for XAVPOZ (cocrystal formation between H_3BTC and DMF); (h) the pre-ILAG-EtOH mixtures of H_3BTC, CuO and NH_4Cl.

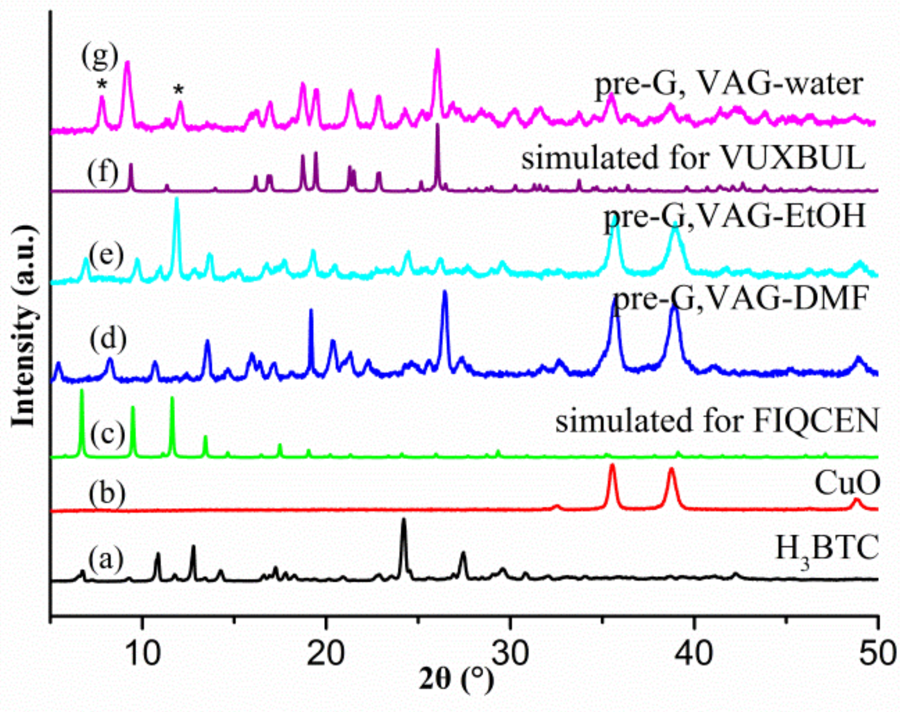

Figure S2. PXRD patterns for the pre-G mixtures of starting materials (H_3BTC and CuO) exposed to DMF, EtOH and H_2O vapors for 30 days at room temperature. The asterisk indicates peaks neither present in patterns of the product nor in starting materials.

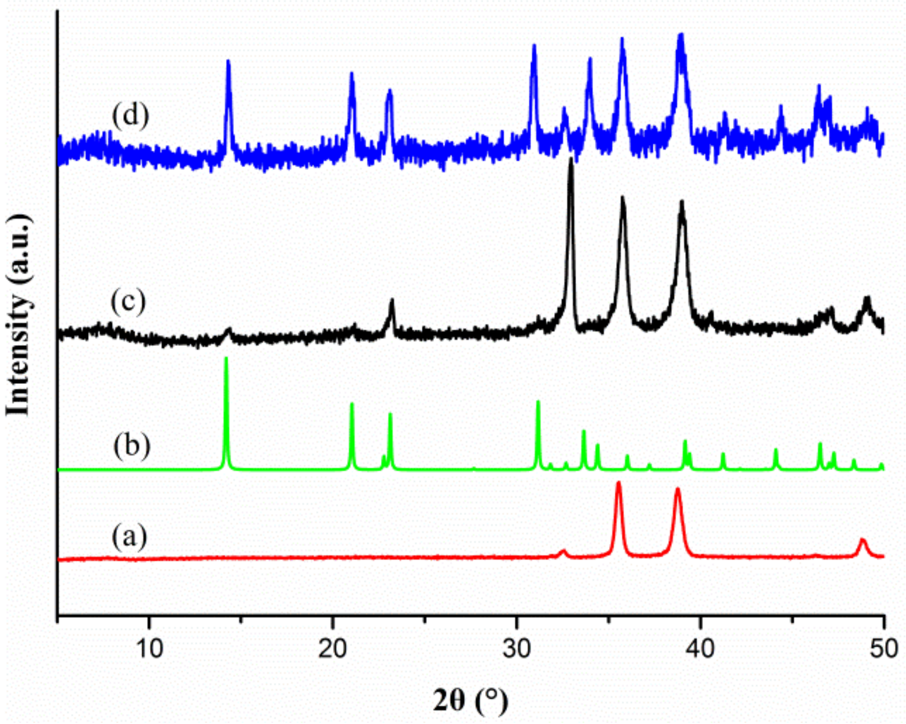

Figure S3. PXRD patterns for $[Cu(NH_3)_2Cl_2]$ synthesized from CuO and NH_4Cl: (a) CuO; (b) the simulated pattern; (c) ball milling for 1 minutes; (4) in H_2O vapor for one day after ball milling.

Result from the above figure: partial reaction was observed with the mixtures of the ball milled mixture of CuO and NH_4Cl for 1 minute. After aging this mixture in H_2O vapor in 1 day, further reaction was observed according to the PXRD.

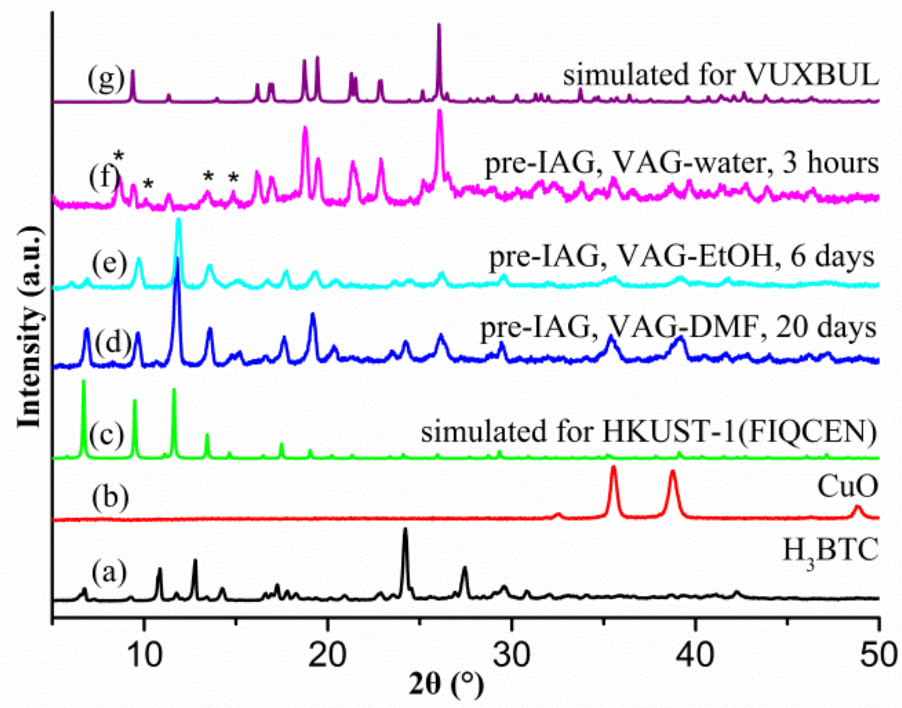

Figure S4. PXRD patterns for the pre-IAG mixtures of starting materials (H_3BTC, NH_4Cl and CuO) exposed to H_2O, EtOH and DMF vapors for 3 hours, 6 and 20 days at room temperature. The asterisk indicates peaks neither present in patterns of the product nor in starting materials.

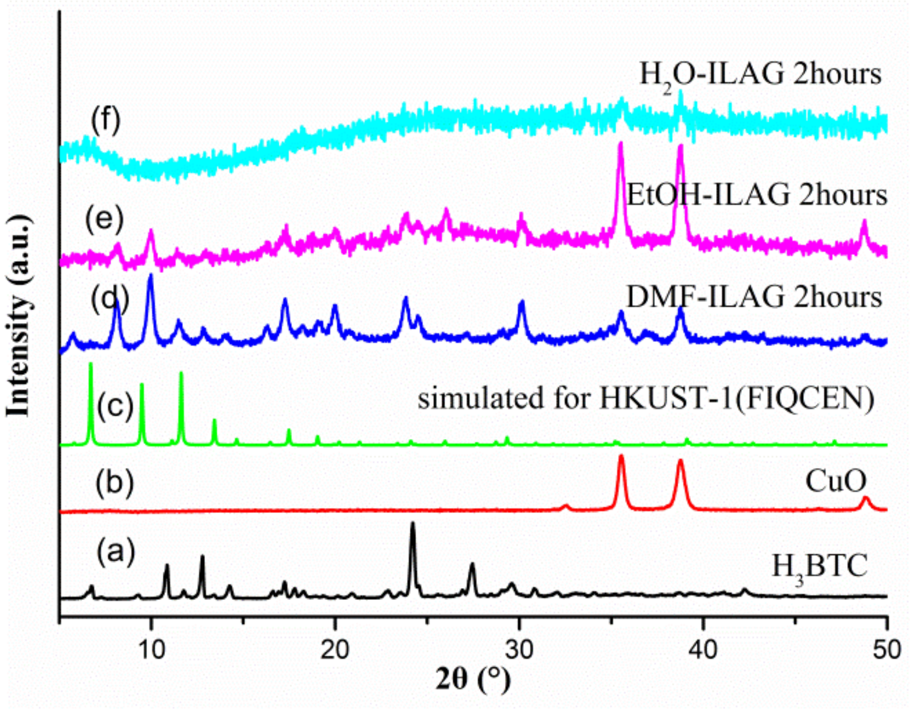

Figure S5. PXRD patterns for (a) H_3BTC; (b) CuO; (c) the simulated pattern for HKUST-1; (d) DMF; (e) water; (f) EtOH liquid assisted ground (pre-ILAG) mixtures of starting materials (H_3BTC, CuO and NH_4Cl) for 2 hours.

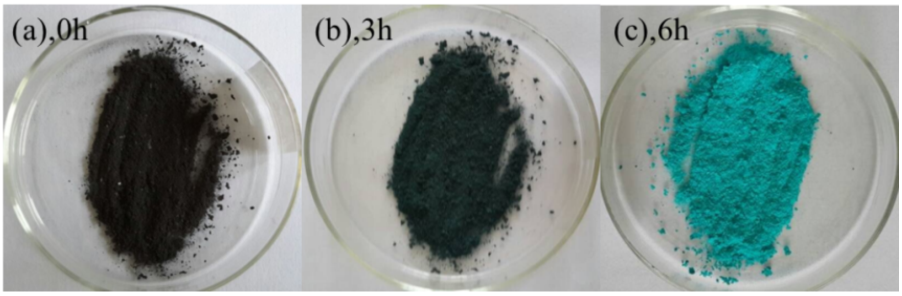

Figure S6. Visual comparison in different reaction stages of the compound **1** obtained by water vapor-assisted aging of the pre-ILAG-DMF reactants.

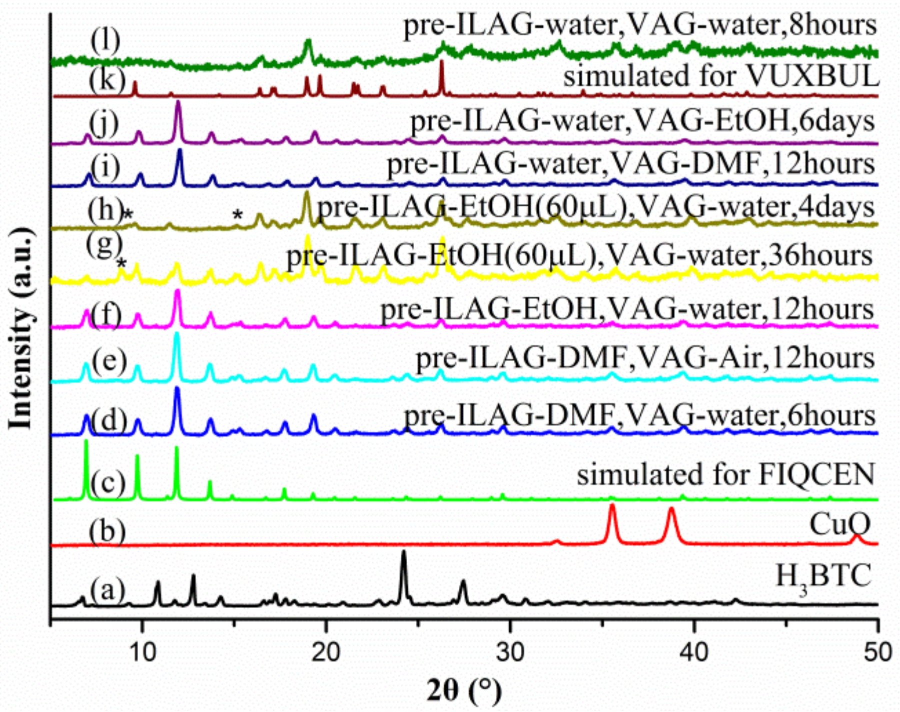

Figure S7. PXRD patterns for the aging of the pre-ILAG mixtures of starting materials. The asterisk indicates peaks neither present in patterns of the product nor in starting materials.

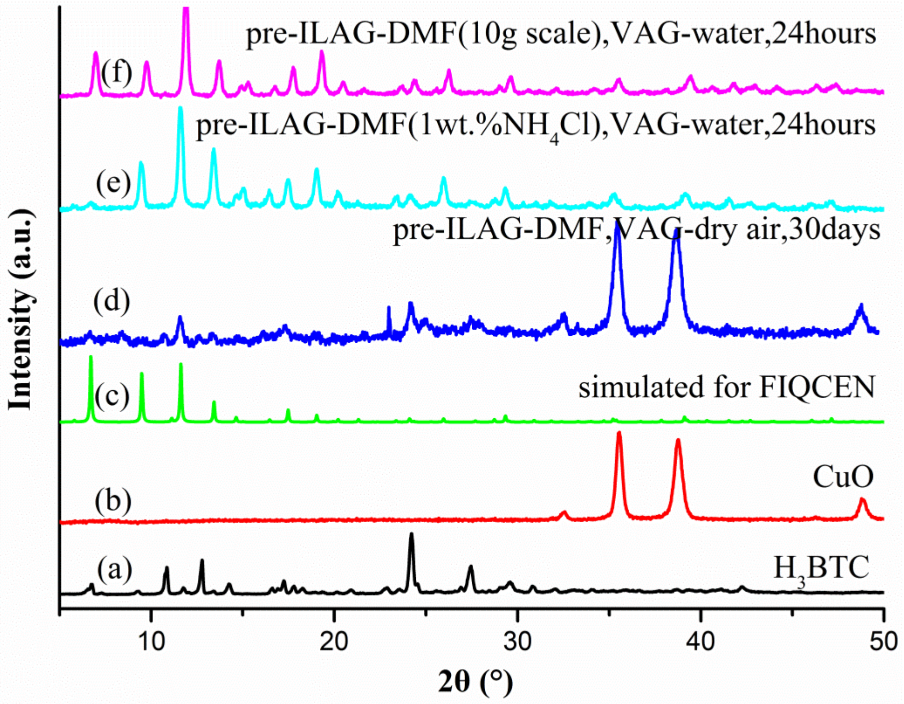

Figure S8. PXRD patterns for (a) H_3BTC; (b) CuO; (c) the simulated pattern for FIQCEN; (d) the pre-ILAG-DMF reactants exposed to dry air for 30 days; (e) the pre-ILAG-DMF (1wt.%NH_4Cl) reactants exposed to water vapor for 24 hours; (f) the pre-ILAG-DMF (10g scale) reactants exposed to water vapor for 24 hours.

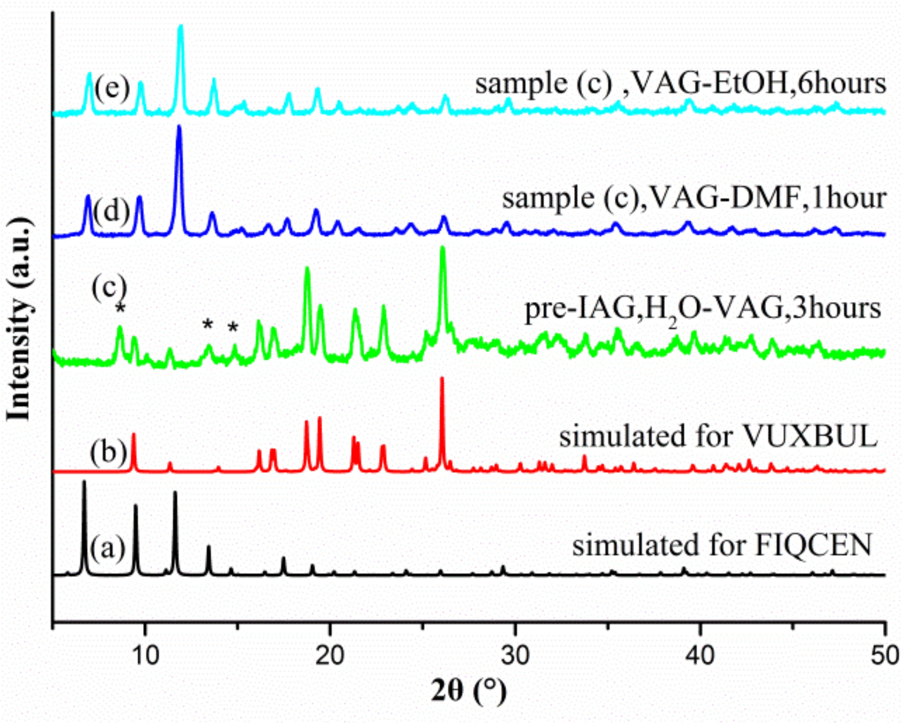

Figure S9. PXRD patterns for transformation from compound **2** to compound **1** in DMF and EtOH vapors at room temperature. The asterisk indicates peaks neither present in patterns of the product nor in starting materials.

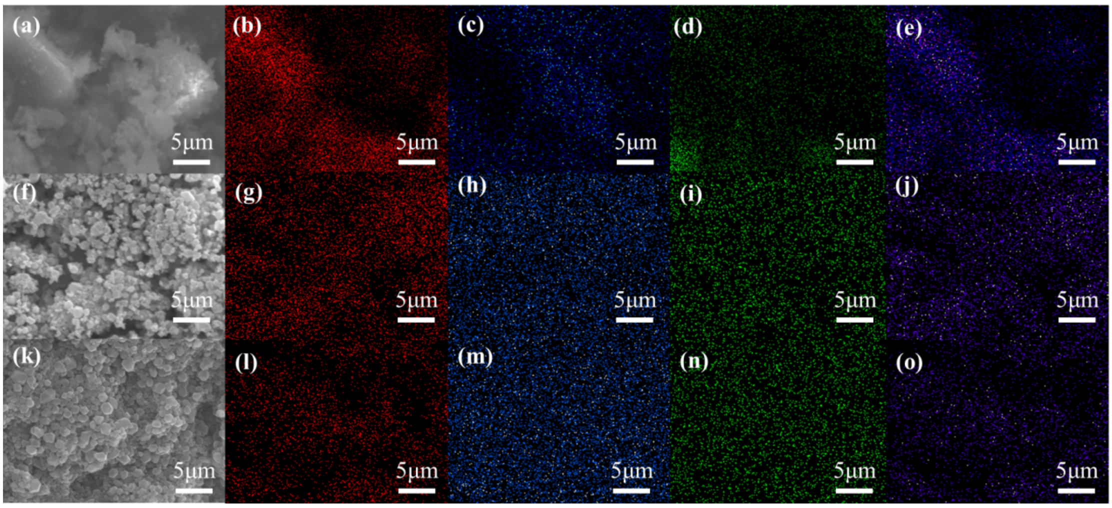

Figure S10. Elemental mapping images by SEM of the aging of the pre-ILAG-DMF reactants and corresponding elemental mapping images of C, Cu, Cl, O in different reaction time: (a), (b), (c), (b) and (e) for 0 hour; (f), (g), (h), (i) and (j) for 3 hours; and (k), (l), (m), (n) and (o) for 6 hours. Red, blue, green and purple dots in above images show C, Cu, Cl and O elemental.

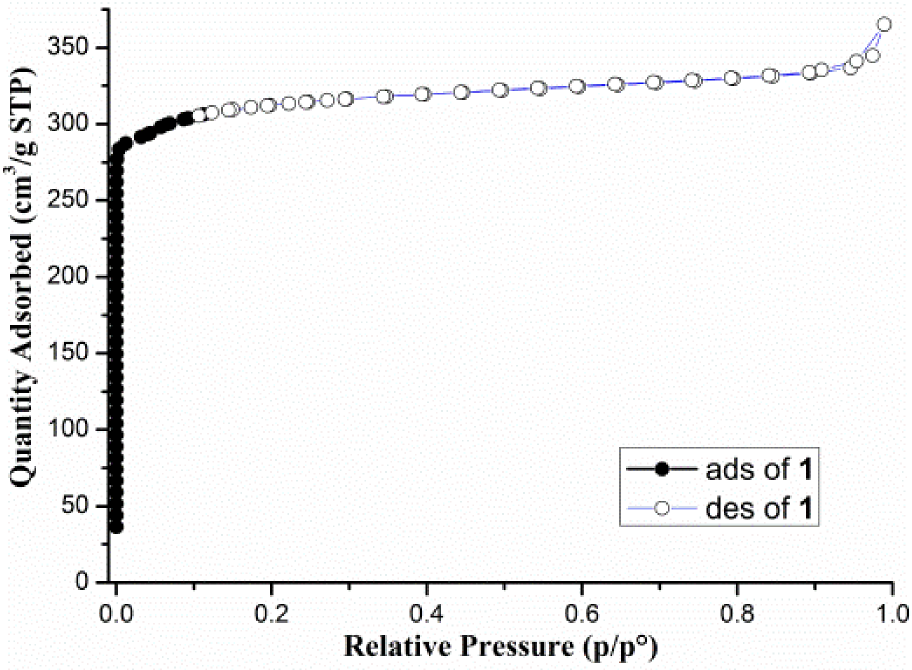

Figure 11. N_2 adsorption and desorption isotherms for **1** prepared by water vapor-assisted aging of the pre-ILAG-DMF followed by washing with EtOH.

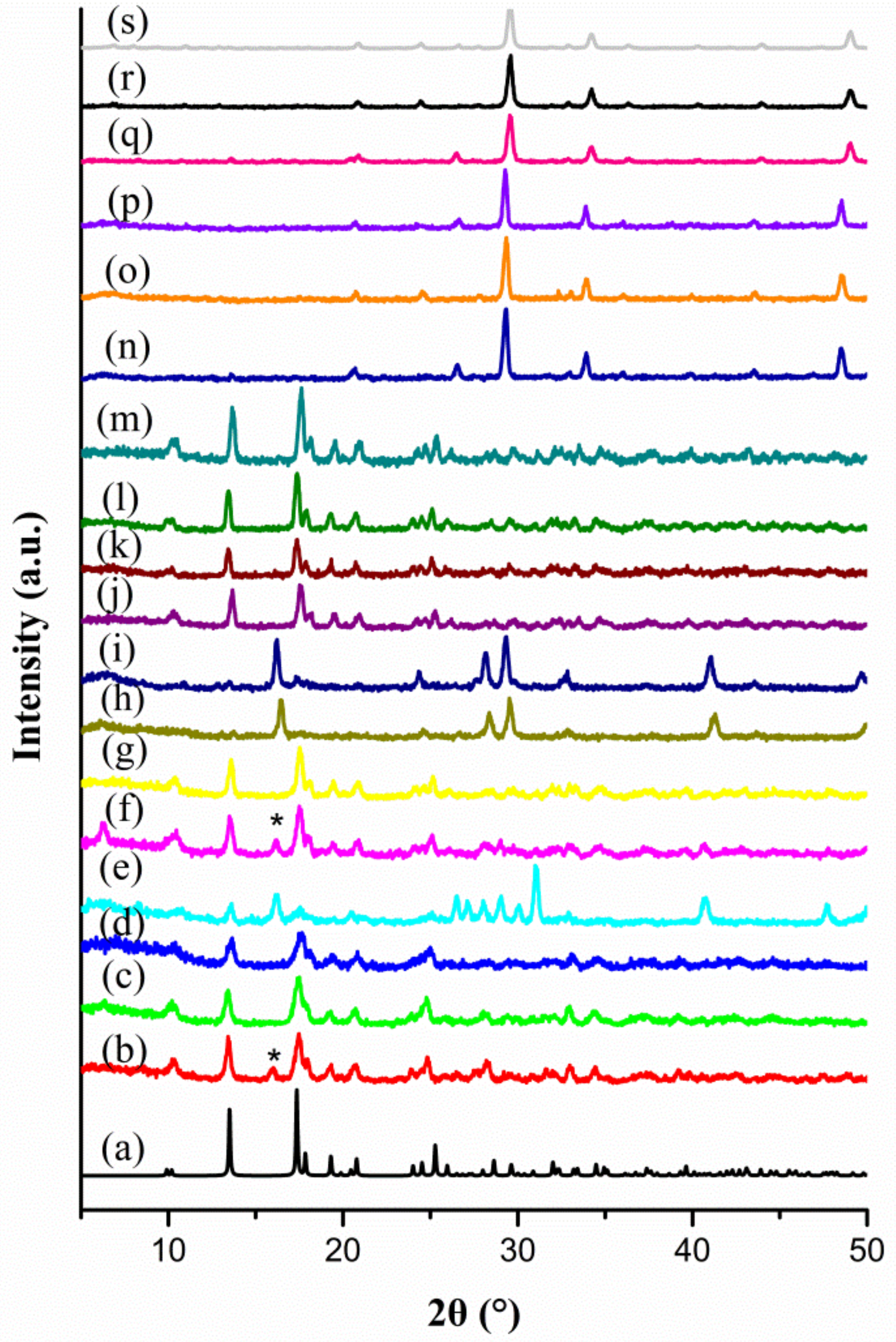

Figure S12. PXRD patterns for products synthesized from RE_2O_3 (RE=La, Nd, Sm, Eu, Dy Er) and H_3BTC under VAG conditions : (a) the simulated pattern for GOCYAY; the pre-IAG mixtures of La_2O_3, NH_4Cl and H_3BTC exposed to (b) DMF; (c) EtOH; (d) H_2O vapor for 3 days at room temperature; the pre-IAG mixtures of Nd_2O_3, NH_4Cl and H_3BTC exposed to (e) DMF; (f) EtOH; (g) H_2O vapor for 3 days at room temperature; the pre-IAG mixtures of Sm_2O_3, NH_4Cl and H_3BTC exposed to (h) DMF; (i) EtOH; (j) H_2O vapor for 3 days at room temperature; the pre-IAG mixtures of Eu_2O_3, NH_4Cl and H_3BTC exposed to (k) DMF; (l) EtOH; (m) H_2O vapor for 3 days at room temperature; the pre-IAG mixtures of Dy_2O_3, NH_4Cl and H_3BTC exposed to (n) DMF; (o) EtOH; (p) H_2O; vapor for 3days at room temperature; the pre-IAG mixtures of Er_2O_3, NH_4Cl and H_3BTC exposed to (q) DMF; (r) EtOH; (s) H_2O vapor for 3 days at room temperature. The asterisks indicate peaks due to remaining reactants.

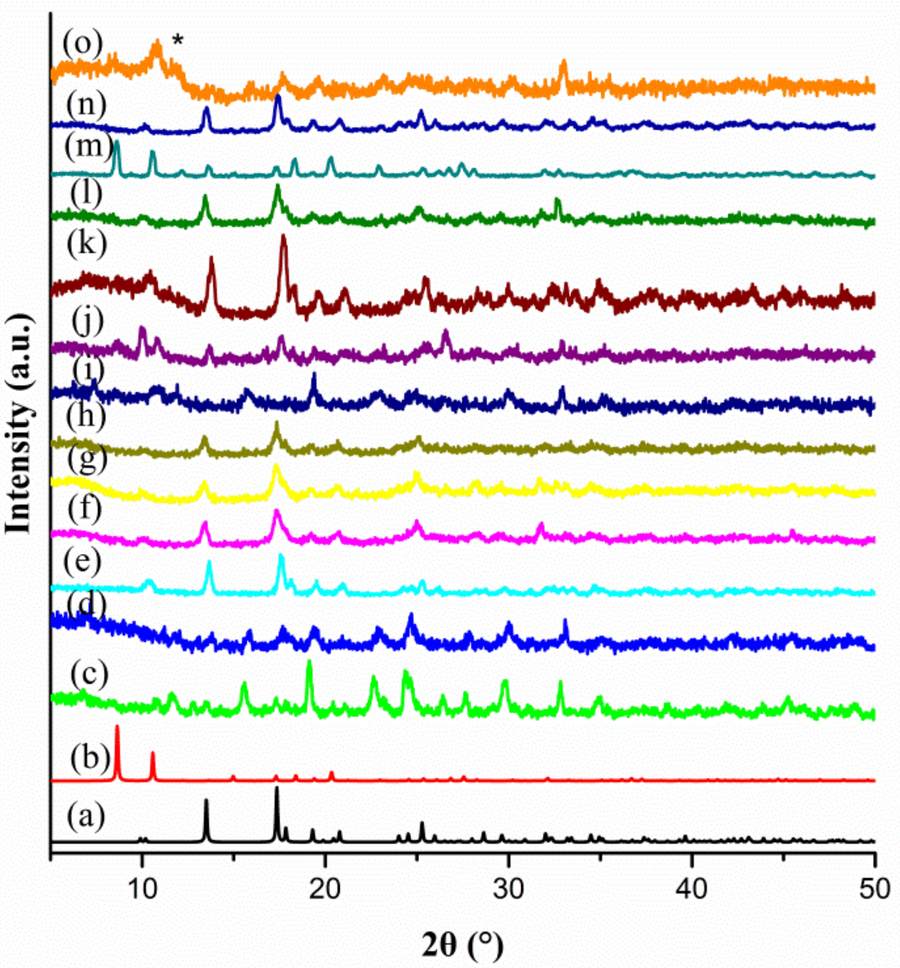

Figure S13. PXRD patterns for products synthesized from $RE_2(CO_3)_3$(RE=Sm, Eu, Gd, Tb) and H_3BTC under VAG conditions: (a) the simulated pattern for GOCYAY; (b) the simulated pattern for JOHFOW; the pre-IAG mixtures of $Sm_2(CO_3)_3$, H_3BTC and NH_4Cl exposed to (c) DMF; (d) EtOH; (e) H_2O vapor for 2 days at room temperature; the pre-IAG mixtures of $Eu_2(CO_3)_3$, H_3BTC and NH_4Cl exposed to (f) DMF; (g) EtOH; (h) H_2O vapor for 2 days at room temperature; the pre-IAG mixtures of $Gd_2(CO_3)_3$, H_3BTC and NH_4Cl exposed to (i) DMF; (j) EtOH; (k) H_2O vapour for 2 days at room temperature; the pre-IAG mixtures of $Tb_2(CO_3)_3$, H_3BTC and NH_4Cl exposed to (l) DMF; (m) EtOH; (n) H_2O vapor for 2 days at room temperature; (o) the pre-ILAG-EtOH mixtures of $Tb_2(CO_3)_3$, H_3BTC and NH_4Cl exposed to EtOH vapor for 8 hours at room temperature. The asterisk indicates peaks neither present in patterns of the product nor in starting materials.

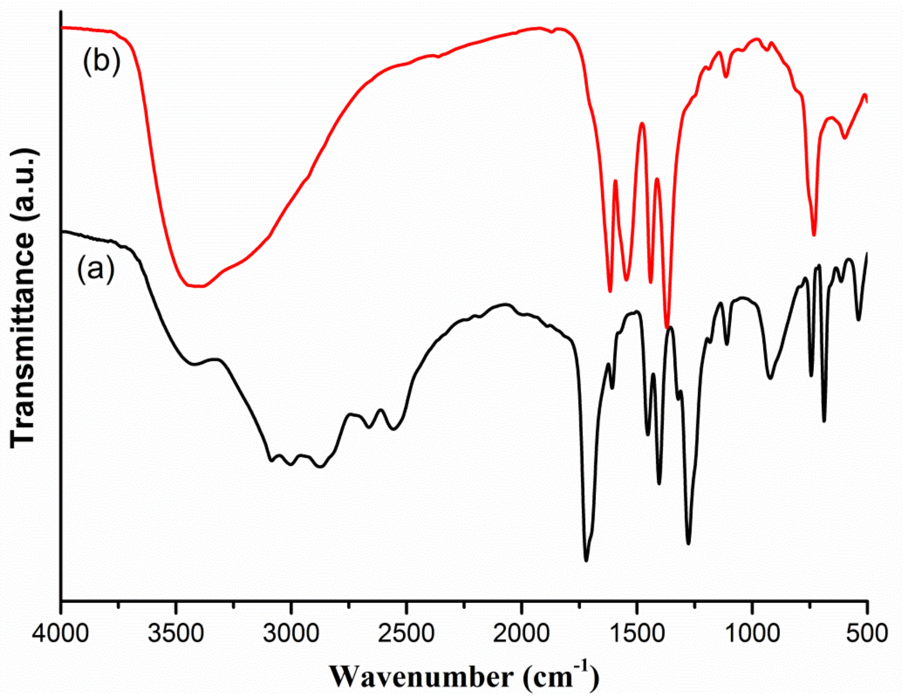

Figure S14. FT-IR spectra of (a) H_3BTC; (b) as-synthesized samples of compound **1** made by water vapor-assisted aging of the pre-ILAG-DMF reactants.

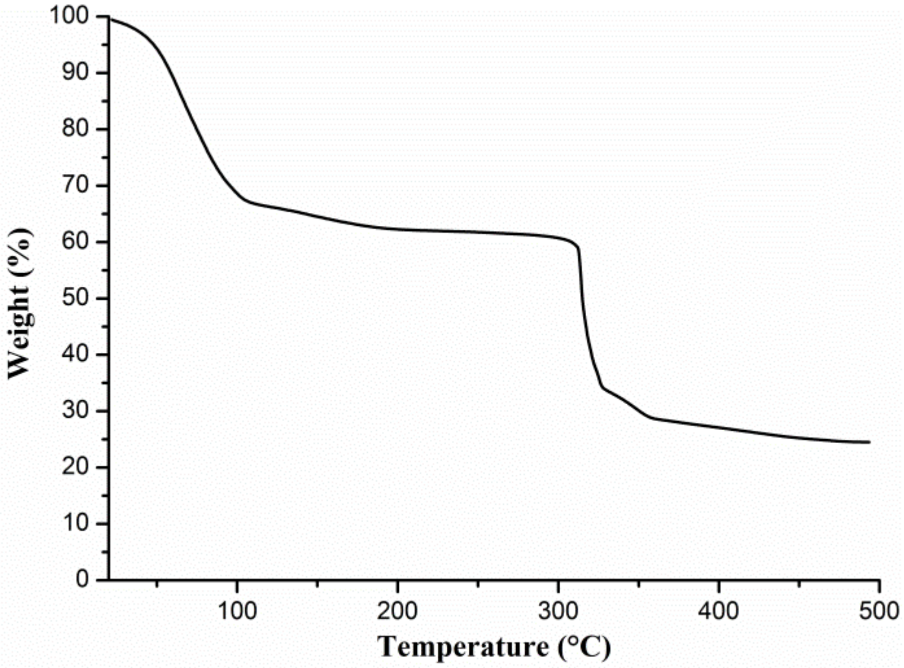

Figure S15. TGA curves for compound **1** obtained by water vapor-assisted aging of the pre-ILAG-DMF reactants.

Reference

1. S. S.-Y. Chui, S. M.-F. Lo, J. P. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148-1150.