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

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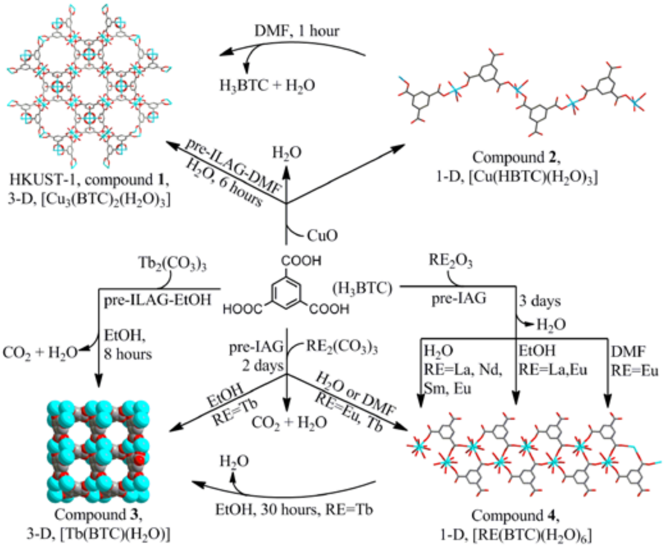
Four functional MOFs including HKUST-1 were prepared quantatively from CuO and rare earth sesquioxides/ carbonates under vapour-assisted aging at room temperature within hours or days. Two 1-D complexes show high reactivity under VAG to be transformed into two 3-D compounds within hours.

The development of novel, environment-friendly and efficient synthetic methodologies has been a research hotspot of modern chemistry. In recent decades, most efforts have concentrated on using water as a solvent, using less organic solvent or employing an energy-efficient method, which is also an important part of green chemistry and sustainable chemistry. Metal-organic frameworks (MOFs) or coordination polymers (CPs), a large family of functional materials, are of great interest due to their potential applications in hydrogen and methane storage, gas separation, catalysis, and sensor technology.[1, 2] And rare-earth MOFs demonstrate a number of impressive properties such as catalysis,[3] magnetic resonance imaging,[4] luminescence,[5] gas storage[6] and sensing.[7] However, the conventional solution-based or recently developed mechanochemical synthesis of MOFs requires either bulk solvent and/or thermo- or mechanical energy intervention.

In contrast, vapor-assisted aging (VAG), [8-11] a milder and greener synthetic method mimics mineral neogenesis, in which the corresponding reaction between starting materials takes place in the presence of moisture or organic solvent vapors at room temperature or mild temperature. Meanwhile, the products obtained through in situ vapor-assisted aging show high crystalline quality. Up to now, by using VAG, some co-crystals,[12, 13] salts,[12, 13] metal oxalates[11] as well as metal-organic minerals[8-10] have been obtained.

BTC-based 3-dimensional (3-D) microporous $[Cu_3(BTC)_2]$ (also called HKUST-1; 1,3,5-benzenetricarboxylic acid abbreviated as H_3BTC) and $[RE(BTC)(H_2O)]$ (RE: rare earth) with potential applications such as hydrogen and methane storage, gas separation and purification,[14-20] catalysis,[21, 22] and surface deposition,[23, 24] have been intensively studied. And 1-dimensional (1-D) $[RE(BTC)(H_2O)_6]$ shows a very interesting white-light emission.[25] Yet, these multi-functional BTC-based MOFs have not been prepared under VAG conditions when CuO and rare earth oxides (RE_2O_3)/carbonates are used as starting materials, which are ideal feedstock in large-scale industrial preparation due to their low price and clean reaction.

Here we demonstrate an updated VAG method to convert copper oxide and rare-earth sesquioxides/carbonates to MOFs within hours. Notably, two 1-D MOFs show high reactivity under VAG conditions at room temperature and transform their structures into 3-D microporous MOFs within several hours; especially for 1-D $[Cu(HBTC)(H_2O)_3]$, an hour is enough for completing such a conversion to HKUST-1.



Scheme 1 VAG reactions between H_3BTC and copper oxide, rare earth oxides or carbonates.

The overall reaction scheme is shown in Scheme 1 and Table 1. Three solvent vapors, DMF, EtOH and water, were selected to assist in situ aging of the mixtures of the crude materials to produce the functional MOFs at room temperature. To allow sufficient contact then reaction between H_3BTC and copper oxide in the aging process, we conducted three pretreatment methods: neat grinding reactants, namely, pre-grinding (pre-G); grinding the starting materials in the presence of small amounts of NH_4Cl, namely, pre-ion assisted ground (pre-IAG); grinding the starting materials in the presence of small amounts of NH_4Cl as well as a small amount of liquid, namely, pre-ion and liquid assisted ground (pre-ILAG-liquid). All these pretreatments were carried out in a mixer mill for only 1 minute instead of manual grinding for 5 minutes in a mortar, in which the former demonstrates that ball milling is more efficient in providing smaller and more uniform particles.[8] As indicated by powder X-ray diffraction (Fig. S1), there was no reaction observed in the pre-ball milled, pre-ion assisted ground and the pre-ILAG reactants unless a cocrystal formation between DMF and H_3BTC (CSD code: XAVPOZ)[26] was formed in the presence of DMF molecules.

Table 1 Overview of VAG reactions between H_3BTC and copper oxide, rear-earth oxides or rare earth carbonates respectively.

		DMF	EtOH	H_2O
CuO	Pre-G, 30d	×	**1***	**2**√
	Pre-IAG	**1**(20d)*	**1**(6d)√	**2**(3h)√
	Pre-ILAG-DMF	**1**(10d)*	**1**(24h)√	**1**(6h)√
	Pre-ILAG-EtOH	**1**(10d)*	**1**(36h)√	**1**(12h)√
	Pre-ILAG-water	**1**(6d)√	**1**(12h)√	**2**(8h)√
RE_2O_3 (pre-IAG, 3d)	La_2O_3	**4***	**4**√	**4**√
	Nd_2O_3	×	**4***	**4**√
	Sm_2O_3	×	×	**4**√
	Eu_2O_3	**4**√	**4**√	**4**√
	Dy_2O_3	×	×	×
	Er_2O_3	×	×	×
$RE_2(CO_3)_3$ (pre-IAG, 2d)	$Sm_2(CO_3)_3$	×	×	**4**√
	$Eu_2(CO_3)_3$	**4**√	**4**√	**4**√
	$Gd_2(CO_3)_3$	NS	NS	**4**√
	$Tb_2(CO_3)_3$	**4**√	**3**√	**4**√

The number **1**, **2**, **3** and **4** denote compounds **1**, **2**, **3** and **4** respectively; The letter 'h' and 'd' in parentheses denote 'hours' and 'days' for VAG time; √ Quantitative reaction to give a crystalline product; × No reaction; NS No matching structure identified; * Partial reaction - some unreacted starting materials observed.

To simplify the vapor-assisted aging procedures, all VAG reactions were conducted at room temperature, *ca*. 20 ℃. Initially, we tried three solvent vapors, DMF, EtOH and water, to assist in situ aging the pre-G reactants including H_3BTC and CuO. For DMF vapor, as shown in Fig. S2d, only the cocrystal between H_3BTC and DMF formed and no reaction between H_3BTC and CuO was observed after 30 days aging. When the pre-G mixture was exposed to EtOH vapor for 30 days, the famous HKUST-1 (**1**) was partially achieved and the color of the mixtures was still black, which shows a certain amount of unreacted H_3BTC and CuO remained (Fig. S2e). For water vapor (the relative humidity=RH: 80%), formation of 1-D complex, $[Cu(HBTC)(H_2O)_3]$ (**2**)[27] (CSD VUXBUL), was examined by PXRD (Fig. S2g) after 30 days aging. Although it took over a month of aging in ethanol vapor to partially yield compound **1**, it is still quite exciting.

Inspired by the work related VAG and mechanchemical synthesis of MOFs[9, 28] reported by Friščić, addition of a catalytic amount of ammonium salts can accelerate the coordination reaction. So to encourage reactivity, we turned to the second pre-treatment method, pre-IAG. NH_4Cl (5 wt.%) was chosen to be pre-ball milled with H_3BTC and CuO for 1 minute. An intermediate phase $[Cu(NH_3)_2Cl_2]$[29] was formed between NH_4Cl and CuO and confirmed by the PXRD (Fig. S3). After a further 3 hours aging in water vapor, the reactant mixtures changed color from black to light green; however, its PXRD revealed that porous HKUST-1 was not obtained, and it gave place to the 1-D compound **2**, $[Cu(HBTC)(H_2O)_3]$ (Fig. 1d and Fig. S4f). Interestingly, the known HKUST-1 could be obtained in quantitative yield on reaction between pre-IAG H_3BTC and CuO under EtOH vapor aging in 6 days (Fig. S4d). HKUST-1 was also obtained partially in DMF vapor within 20 days, and the unreacted reactants remained (Fig. S4e).

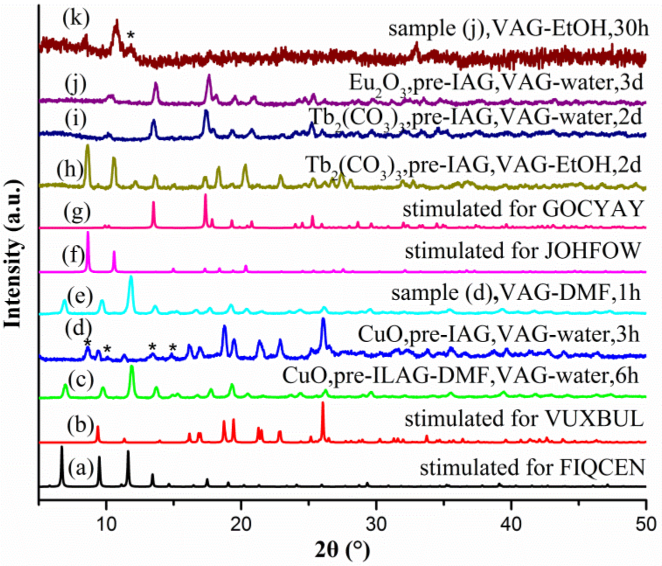


Fig. 1 PXRD patterns of the products from reactions between H_3BTC and copper oxide or rear-earth oxides/carbonates at room temperature: (a) stimulated for HKUST-1(FIQCEN); (b) stimulated for VUXBUL; (c) the pre-ILAG mixtures of H_3BTC and CuO exposed to water vapor for 6 hours; (d) the pre-IAG mixtures of H_3BTC and CuO exposed to water vapor for 3 hours; (e) preparation of **1** by exposing **2** to DMF vapor for 1 hour; (f) stimulated for JOHFOW;[6] (g) stimulated for GOCYAY;[30] (h) the pre-IAG mixtures of H_3BTC and $Tb_2(CO)_3$ exposed to EtOH vapor for 2 days; (I) the pre-IAG mixtures of H_3BTC and $Tb_2(CO)_3$ exposed to EtOH vapor for 2 days; (j) the pre-IAG mixtures of H_3BTC and Eu_2O_3 exposed to water vapor for 3 days; (k) preparation of **3**-Tb by exposing **4**-Tb to EtOH vapor for 30 hours. The asterisk indicates peaks neither present in patterns of products nor in the starting materials.

Pre-IAG reactants took at least 6 days to yield HKUST-1 under ethanol vapor aging, albeit the VAG time was shortened greatly compared to that of the pre-G sample (over 1 month). Is it possible to further shorten the aging time to a few hours? The answer is yes, through using the third pre-treatment method, pre-ionic and liquid assisted grinding (pre-ILAG); that is, adding NH_4Cl (5 wt.%) and a small amount of solvent (100 μL) in pre-grinding stage. We found that no coordination reaction took place in the pre-ball milled mixtures, even though this liquid-assisted grinding in the mixer mill is prolonged to 2 hours (Fig. S5). Adding 100 μL DMF into the pre-IAG reactants dramatically accelerated the formation of HKUST-1 under water vapor accompanied with a color change from black to turquoise (Fig. S6), in which the aging time was shortened to 6 hours (Fig. 1c and Fig. S7d). Also, the pure product HKUST-1 was obtained by exposing the pre-ILAG materials to the air (RH: 65%) for 12 hours (Fig. S7e); however, only a partial conversion was observed (the color of the mixtures is black) when exposing pre-ILAG materials to a dry air (RH: 25%) for even 1 month (Fig. S8d). Similarly, when decreasing the amount of the added NH_4Cl from 5 to 1 wt.%, the pre-ILAG-DMF sample took 24 hours to make HKUST-

1 under water vapor (Fig. S8e). If we replaced the addition of DMF by ethanol in pre-IAG stage, it took 12 hours to yield pure HKUST-1 under water vapor aging (Fig. S7f). When decreasing the volume of the added EtOH from 100 μL to 60 μL, the mixture containing HKUST-1 and compound **2** was obtained after 36 hours water vapor aging, and further aging for 4 days to give a pure compound **2** (Fig. S7g and S7h). Surprisingly, the pre-ILAG-water sample was aged in DMF or EtOH vapor for 12hours or 6 days to yield clean HKUST-1 (Fig. S7i and S7j); and water vapor triggered compound **2** formation (Fig. S7l).

Remarkably, the 1D product **2** was readily converted to HKUST-1 in DMF or ethanol vapor within 1 or 6 hours at room temperature (Fig. S9), which spangles an alternative two-step way to get this well-known compound **1**. Either through the direct preparation or through the two-step synthesis, ten grams of HKUST-1 was obtained easily.

As illustrated above, the added NH_4Cl in the pretreatment stage plays a key role in shortening the aging reaction time in VAG synthesis. Aging the pre-ground H_3BTC and CuO in ethanol vapor (Scheme 2a), H_3BTC was neutralized with CuO to make HKUST-1 with the sole byproduct water in spite of taking over one month because of the high lattice energy of CuO. Whereas for the pre-G sample aged in water vapor, a large amount of water supply gave rise to the compound **2,** in which there are three coordinated water molecules around each Cu^{2+}. After aging in DMF vapor for 30 days, H_3BTC did not react with CuO, instead, a cocrystal formed between H_3BTC and DMF. This may have stabilized the H_3BTC and thus it could not release protons to neutralize CuO. For the pre-IAG sample, the involved NH_4Cl acts as a catalyst to readily react with CuO to get an intermediate (Fig. S3), $[Cu(NH_3)_2Cl_2]$, in the pretreatment stage. The resulting $[Cu(NH_3)_2Cl_2]$ then was reacted with H_3BTC through vapor-assisted aging to obtain HKUST-1 and/or compound **2** along with the recovery of NH_4Cl within a shortened aging time: 3 hours to 6 days (Scheme 2b).

$$\text{(a)}\quad 2H_3BTC + 3CuO \xrightarrow{\text{pre-G, VAG-EtOH}} [Cu_3(BTC)_2(H_2O)_3]\ (\mathbf{1}) + 3H_2O$$

$$H_3BTC + CuO + 2H_2O \xrightarrow{\text{pre-G, VAG-water}} [Cu(HBTC)(H_2O)_3]\ (\mathbf{2})$$

$$\text{(b)}\quad CuO + 2NH_4Cl \xrightarrow[\text{or pre-ILAG-EtOH}]{\text{pre-IAG, pre-ILAG-DMF,}} [Cu(NH_3)_2Cl_2] + H_2O$$

$$2H_3BTC + 3[Cu(NH_3)_2Cl_2] + 3H_2O \xrightarrow{\text{VAG-DMF or -EtOH}} [Cu_3(BTC)_2(H_2O)_3]\ (\mathbf{1}) + 6NH_4Cl$$

$$H_3BTC + [Cu(NH_3)_2Cl_2] + 3H_2O \xrightarrow{\text{VAG-water}} [Cu(HBTC)(H_2O)_3]\ (\mathbf{2}) + 2NH_4Cl$$

$$\text{(c)}\quad H_3BTC + CuO + 2H_2O \xrightarrow{\text{pre-ILAG-water}} [Cu(HBTC)(H_2O)_3]\ (\mathbf{2})$$

$$\text{(d)}\quad 3[Cu(HBTC)(H_2O)_3]\ (\mathbf{2}) \xrightarrow{\text{VAG-DMF or -EtOH}} [Cu_3(BTC)_2(H_2O)_3]\ (\mathbf{1}) + H_3BTC + 6H_2O$$

Scheme 2 The possible and tentative mechanism of VAG synthesis of HKUST-1 (**1**) and compound **2** from (a) pre-G, (b) pre-IAG, pre-ILAG-DMF, pre-ILAG-EtOH, and (c) pre-ILAG-water reactants, (d) the VAG conversion from **2** to **1**.

To the best of our knowledge, solvents added in the pretreatment stage or used to provide vapor in VAG also play important roles in the VAG reactions: (i) inert solvent can accelerate the solid reactants migration; (ii) some solvent with a certain level of chemically activity not only increases the reactants mobility rate but also acts as a reactant to get involved in some reaction. Scheme 1 shows that DMF and EtOH vapor-assisted aging invariably results in the HKUST-1 (**1**), and water vapor aging leads to the 1-D compound **2** except for the pre-ILAG-DMF and -EtOH samples. Further, VAG-DMF and VAG-ethanol can cause the rapid conversion, **2**→**1,** within hours. It is known that, as shown in Scheme 2a and 2b, water molecule displays stronger coordination ability than DMF and ethanol molecule; consequently, additional water involved in pre-ILAG-water or VAG-water gives rise to the formation of **2** with three coordinated water molecules around each Cu^{2+} (Scheme 2c). In contrast, in the case of the "paddle wheel" HKUST-1, each Cu^{2+} completes its pseudooctahedral coordination sphere with an axial water molecule opposite to the Cu-Cu vector. Interestingly, however, water vapor assisted aging of the pre-ILAG-DMF and pre-ILAG-ethanol samples over 6 and 12 hours produced compound **1** rather than **2**. When decreasing the volume of the added ethanol from 100uL to 60uL, 36 hours water vapor aging led to formation of the mixtures containing **1** and **2**; while, the continued aging for 4 days produced a clean **2**. This reveals that the amount of solvent added in the pre-grinding stage has a great influence on the product structure. We found that complex **2** may be an intermediate in the presence of enough DMF or ethanol, with the likely conversion from **2** to **1** taking place rapidly (Scheme 2d), so pre-ILAG-DMF (100 μL) and pre-ILAG-ethanol (100 μL) gave **1**. That is, DMF or ethanol can keep complex **1** from being hydrolyzed in the presence of water, and acts as a protective atmosphere; but, the amount of these protective solvent is required. As for the difference of the aging time between pre-ILAG-DMF and pre-ILAG-ethanol, this may have resulted from different solubility of H_3BTC in DMF (14.8 g) and ethanol (5.52 g) (Table S1); consequently, DMF behaving higher solubility of H_3BTC diffuses H_3BTC more intensively than ethanol in the pretreatment stage.

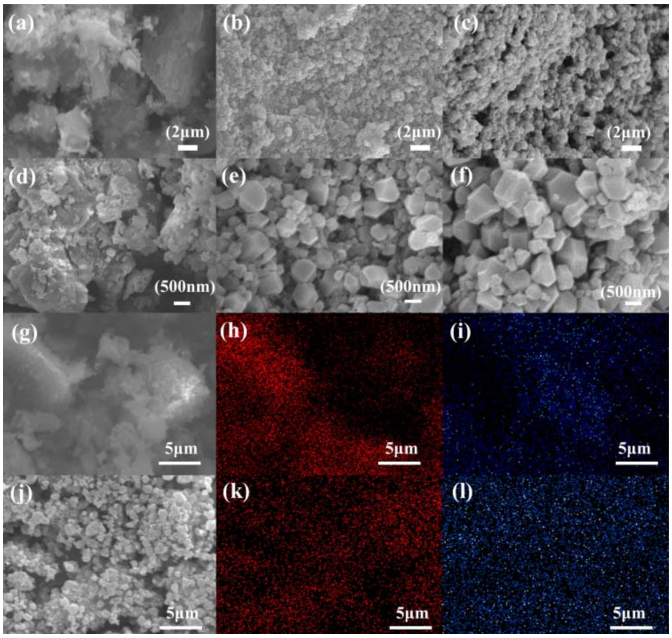


Fig. 2 SEM and the C, Cu element mapping images of the pre-ILAG-DMF reactants in different VAG reaction time, (a), (d), (g), (h) and (i): 0 hour; (b), (e), (j), (k) and (l): 3 hours; (c) and (f): 6 hours. Images (h) and (k) show C element mapping, (i) and (l) shows Cu element mapping.

Moreover, for pre-IAG samples, ethanol vapor assisted aging gave compound **1** quantitatively within 6 days, while for DMF vapor it took 20 days aging and some unreacted starting materials were remaining. This may have been because of the lower solubility of the catalytic NH_4Cl in DMF (0.001 g) compared to that in ethanol (0.013 g) (Table S1), that led to a decrease of the aging reaction rate .

Further, and more importantly, DMF vapor assisted aging of compound **2** for an hour led to the transformation into compound **1**, HKUST-1, in which **2** shows high reactivity under VAG conditions; however, such a conversion takes 6 hours to complete in ethanol vapor. According to the related mechanochemical conversions between coordination compounds,[31] the driving force for the VAGinduced conversions may be dominated by formation of the least soluble product. At the molecular level, the change from **2** to **1** involves the loss of two coordinated water molecules and one third of H_3BTC per Cu^{2+} center, accompanied with two changes: coordination mode of the carboxylate group from monodentate to bridging bidentate as well as the number of coordinated carboxylate group from two to four (Scheme 2c); in the mean time, a μ-4 nod, paddle wheel $Cu_2(CO_2)_4(H_2O)_2$, is formed. The reason of VAG-DMF being faster than VAG-EtOH remains to be established.

Scanning Electron Microscope (SEM) analysis (Fig. 2a-2f) was used to characterize the morphology, particle sizes and shapes of the reactants under DMF vapor-assisted aging at 0, 3 and 6 hours. Compared with the pre-ILAG-DMF sample (Fig. 2a and 2d), namely aging for 0 hour, the sample after 3 hours aging shows that well-shaped crystals with clearly defined faces and edges were obtained (Fig. 2b and 2e); further aging to 6 hours (Fig. 2e and 2f) gave larger crystal particles with an average size of 900 nm than that after 3 hours aging (700 nm).

Moreover, elemental mapping by SEM is very helpful to study the mobility of reactants in aging. As shown in Fig. 2h, 2k, 2l and S10, carbon, copper and chlorine elemental mapping for the pre-ILAG-DMF sample clearly shows an inhomogeneous distribution on the surface of reactants. The pre-ILAG stage exists mainly to reduce the particle size and mix the reactants, allowing them to come together and to be in contact. Along with vapor-assisted aging, at the contacting surface, the two reactants react with each other rapidly until a product layer is formed to separate the two reactants; hopefully, some solvent molecules from solvent vapor adsorbed into the reactant mixture may dissolve and remove the reactants or the products. Thus, a stirrer role played for vapor in aging, which is similar to the role of milling in mechanochemical reactions.[32] And 3 and 6 hours aging show the distribution of elements in the VAG system is in a more uniform distribution than the very beginning.

To know the crystal quality, we determined the Brunauer-Emmett-Teller (BET) surface area of the product obtained by aging the pre-ILAG-DMF reactants in water vapor for 6 hours, it is 1147 m^2/g after activation by heating at 120 ℃ for 3 hours (Fig. S11), which is comparable to the product from solution-based synthesis.[33, 34]

The above results show clearly that CuO can be used as a starting material to react with H_3BTC to get pure HKUST-1 under water vapor-assisted aging only for 6 hours, despite it is not successful only by mechanochemical reaction. Similarly, as we reported before,[35] ball milling was not able to trigger the mechanochemical reaction between RE_2O_3 and H_3BTC to obtain porous $[RE(BTC)(H_2O)]$ or $[RE(BTC)(H_2O)_6]$. In this context, this reaction may take place under VAG conditions.

Consequently, our positive experimental results support this suppose. As shown in Scheme 1 and Table 1, light rare earth sesquioxides did react with H_3BTC to give rise to a 1-D coordination network, $[RE(BTC)(H_2O)_6]$ (**4**, RE=La, Nd, Sm and Eu) under water vapor-assisted aging the pre-IAG reactants for 3 days. Compound **4** is isostructural to the 1-D ribbon-like coordination polymer,[30] in which the rare earth ion is nine-coordinated by six oxygen atoms from water molecules as well as three oxygen atoms from three carboxylate groups (Scheme 1). Comparison of PXRD patterns with that simulated from single-crystal data for the known compound (CSD code GOCYAY)[30] shows a close correspondence (Fig. 1j and S12). When exposed to ethanol vapor for 3 days, RE_2O_3 (RE= La, Nd, Eu) also reacted with H_3BTC to make compound **4**, except that Nd_2O_3 transformed partially to **4**-Nd. For DMF vapor, only La_2O_3 and Eu_2O_3 showed reaction behavior to form **4**-La and **4**-Eu, although the former reaction was fractional. Yet, two heavy rare earth sesquioxides, Dy_2O_3 and Er_2O_3, did not manifest a certain degree of reactivity with H_3BTC compared with the light rare earth sesquioxides under water, ethanol or DMF vapor exposing. The reaction behavior of rare earth sesquioxides here is very similar to their hydration or carbonation when they are exposed to atmospheric carbon dioxide and water vapor at ambient temperature and pressure.[36, 37]

Similar to RE_2O_3, the transformation from rare earth carbonates is another interesting subject to make rare earth MOFs due to its clean reaction, the byproduct is $H_2CO_3(CO_2+H_2O)$. The pre-IAG samples containing rare earth carbonates $RE_2(CO_3)_3$ (RE=Sm, Eu, Gd, Tb) and H_3BTC also led to compound **4** in 2 days under water vapor exposing (Fig. 1h, 1i and S13). However, interestingly, ethanol vapor triggered $Tb_2(CO_3)_3$ to react with H_3BTC to form a 3-D porous compound **3,** $[Tb(BTC)(H_2O)]$,[38] in 2 days (Fig. S13m). Further, addition of a small amount of ethanol to the above pre-IAG mixtures caused a shortened aging time (8 hours) in EtOH vapor. As shown in Scheme 1, in compound **3**, there are 1-D channels with ca. 6×6Å size and a coordinated water molecule around each Tb^{3+}. Take account of the easy conversion from **2** to **1** under DMF or ethanol vapor along with the loss of water molecules, we also used ethanol vapor to drive the similar conversion, **4**→**3**, in 30 hours accompanied with the loss of coordinated water molecules(Fig. 1k).

In conclusion, vapor-assisted aging (VAG) is demonstrated here to be a green and effective strategy for the transformations from copper oxides and rare-earth oxides/carbonates with high lattice energy to yield MOFs. One of the three pretreatment methods for the reagents, pre-ILAG, greatly shortens the VAG reaction time, which demonstrates the role of small amount of liquid in mechanical pretreatment is to bring reagents in contact, to intensify the diffusion and modify the interface and in this way to affect the VAG processes. It is notable that dozens of grams of four high crystalline compounds including HKUST-1 were produced easily and quantitatively by water, ethanol or DMF vapor-assisted aging at room temperature in 3-72 hours. Furthermore, both 1-D compounds show high reactivity under VAG to be transformed into two 3-D compounds in 1-30 hours. We believe that this updated VAG reaction and using the two-step conversion under VAG conditions are a prototype reaction, which is very promising for large scale manufacturing functional solid materials.

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Graphic Abstract

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

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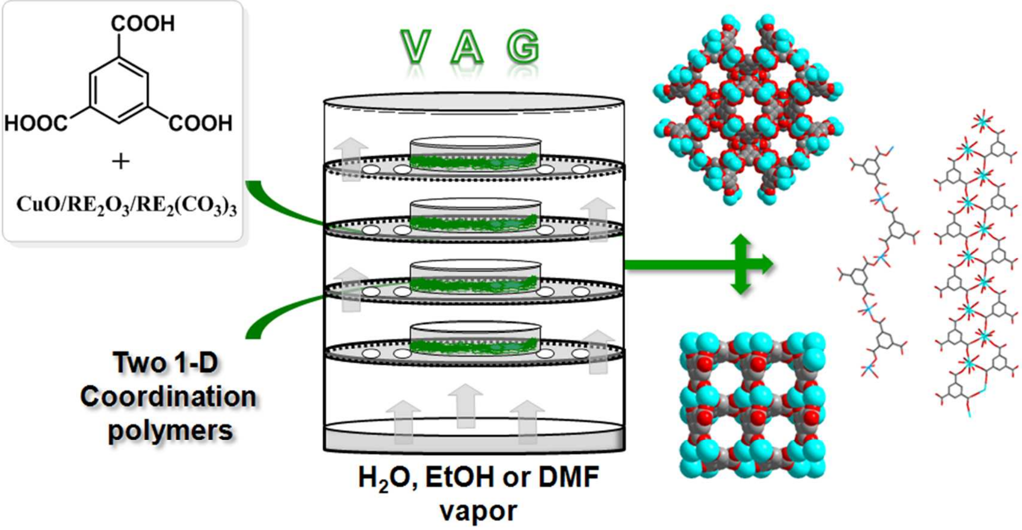

HKUST-1 and rare earth MOFs are synthesized from metal oxides or carbonates under VAG conditions within hours or days at room temperature.