# ELECTRONIC SUPPORTING INFORMATION (ESI)

# Robust synthesis routes and porosity of Al-based metal-organic frameworks Al-fumarate, CAU-10-H and MIL-160<sup>+</sup>

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Metal-Organic Frameworks, Synthesis Optimization, Dry-Gel Conversion, Al-MOFs, [Al(OH)(Linker)], Aluminum fumarate (Alfum), CAU-10-H, MIL-160, Solvent Re-use

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# **S1. Materials and equipment**

All chemicals were used as received by the supplier (*cf.* Table 1).

Chemical	Supplier	Purity
AICl <sub>3</sub> * 6 H <sub>2</sub> O	Janssen Chimica	99%
AI(SO) <sub>4</sub> *18H <sub>2</sub> O	AppliChem	not specified
Al(OH)(acetate)₂	AlfaAesar	not specified
Basolite™ A520	Sigma Aldrich	not specified
Dimethylformamide	Fischer Chemicals	99.99
Ethanol	Sigma Aldrich	> 99.8%
Fumaric acid	Alfa Aesar	99%
2,5-furandicarboxylic acid	OxChem	95%
Isopththalic acid	AlfaAesar	99%
NaOH (microgranulate)	Chem Solute	not specified

Table 1: Used chemicals, supplier and purities.

Dry-gel conversion, DGC inlays were self-built. The full equipment was made of Teflon. The holes in DGC sieves had a diameter of 0.5 mm. The ring inlays, shown in Figure S1, can have various heights for height adjustment. We thank the mechanics workshop of Heinrich-Heine-University Düsseldorf for the manufacturing of the DGC container set.





**Figure S1** Top left: Full Teflon autoclave set for DGC with container, three inlay rings for height adjustment, DGC sieve and cap (from left to right). Top right: Close-up view of a DGC sieve. Bottom: Schematic illustration of the working principle of dry-gel conversion.

# S2. Additional information on Alfum, CAU-10-H and MIL-160

## Aluminum fumarate (Alfum)

Aluminum fumarate was first described in the patent literature in 2013.<sup>1,2</sup> It was the first MOF synthesized on a ton scale and it is marketed by BASF under the name *Basolite*<sup>™</sup> *A520*. Figure S2 shows the structural features of Alfum.



**Figure S2**  $AI^{3+}$ , hydroxide and fumarate building blocks of Alfum, from which in analogy to the structure of MIL-53 a chain of trans- $\mu$ -OH-connected vertex-bridged { $AIO_6$ } octahedra is formed. These chains run along the crystallographic a direction and are connected through the fumarate linkers along the bc diagonal. Graphic produced by software Diamond<sup>3</sup> from cif-file for Basolite A520 (CSD-Refcode DOYBEA).<sup>4</sup>

Aluminum fumarate resembles the MIL-53 topology with its infinite Al-OH-Al chains, bridged by fumarate linkers. It presents the chemical formula  $[Al(OH)(O_2C-CH=CH-CO_2) \cdot n H_2O]_m$  and displays microporous, rhombohedral channels with *ca*. 5.7 x 6.0 Å<sup>2</sup> free dimensions.<sup>4,5</sup> The BET surface area (*Brunauer-Emmett-Teller*) ranges from 925 to 1212 m<sup>2</sup> g<sup>-1</sup>.<sup>6,7</sup> The material exhibits high hydrothermal stability, which is attributed to its aqueous synthesis route and the good hydrolytic stability of the Alcarboxylate bond.

Besides the patented solution-based route, it can as well be prepared in continuous flow reactors,<sup>8</sup> or *via* mechanochemical procedures such as extrusion.<sup>9</sup> Thereby, 27 000 kg m<sup>-3</sup> day<sup>-1</sup> space-time-yields (STY) were calculated to be feasible.<sup>10</sup> Continuous flow methods achieved even STYs up to 97 159 kg m<sup>-3</sup> day<sup>-1</sup> at 5.6 kg h<sup>-1</sup> and *ca*. 1000-1100 m<sup>2</sup>g<sup>-1</sup>.<sup>8</sup> Other synthetic routes comprise for example spray drying,<sup>11</sup> and our recently proposed technique or microwave assisted-dry gel conversion, MW-DGC.<sup>12</sup>

Aluminum fumarate is one of the most promising MOFs for application,<sup>4,13,14</sup> mostly due to its hydrothermal stability and water sorption properties, but also due to an environmentally friendly synthesis route with water as single solvent, inexpensive and abundant metal cation, and a "green" linker from renewable biomass.<sup>15,16</sup> Gaab *et al.* proved its applicability as storage container for natural gas, used as fuel in a vehicle, with 40% increased cruising distance.<sup>16</sup> Moreover, Alfum was proven to be a very promising candidate for implementation as adsorbent in heat transformation applications,<sup>14,17</sup> since it displays suitable water sorption characteristics (desired s-shaped isotherm with steep loading lift, absence of hysteresis, reasonable isosteric heat of adsorption).<sup>4,14</sup> Alfum is applicable as adsorbent for removal of fluoride from water,<sup>18</sup> in desalination processes,<sup>7</sup> in mixed-

matrix-membranes (MMMs)<sup>19</sup> and it was proposed to be the best porous solid for mechanical energy storage.<sup>20</sup> Latest contributions to Alfum included defective engineering/modulation,<sup>21</sup> modelling,<sup>22</sup> adsorption of volatile organic compounds,<sup>6</sup> and kinetics of water sorption.<sup>23</sup>

# CAU-10-H

In 2012 Reinsch and co-workers described the synthesis of CAU-10-H (Fig. S3) (CAU = *Christian-Albrechts-Universität*) out of a water-dimethylformamide (DMF) mixture of isophthalic acid and aluminum sulfate, applying solvothermal conditions (135 °C, 12 h).<sup>24</sup>



**Figure S3** Structural elements in CAU-10-H. (a) Extended asymmetric unit with full Al coordination spheres and full ligand bridging mode. Symmetry transformations i = 1-x, y, z; ii = x, -y, -z; iii = 0.25+y, 0.25-x, -0.25+z; iv = 0.25+y, -0.25+x, 0.25-z; v = 0.25-y, -0.25+x. (b) The inorganic building unit, a fourfold helical chain of cis vertex-bridged {AlO<sub>6</sub>}-polyhedra winding around the four-fold axis (yellow line). (c) The 3D framework structure exhibits square shaped one-dimensional channels. Graphic produced by software Diamond<sup>3</sup> from cif-file for CAU-10-H (CSD-Refcode OQOBUT).<sup>25</sup>

CAU-10-H features *cis*- $\mu$ -OH connected {AlO<sub>6</sub>}-polyhedra, that form helical chains, running along the crystallographic *c* direction. Along *a* and *b* the chains are connected by the isophthalate linkers. The material builds up one-dimensional channels, resulting in a surface area of 535-625 m<sup>2</sup> g<sup>-1</sup> (BET) and a pore volume of 0.25 cm<sup>3</sup> g<sup>-1</sup>.<sup>24</sup> The latter is in good agreement with single point adsorption simulation by force-field methods (0.23 cm<sup>3</sup> g<sup>-1</sup>),<sup>26</sup> although theoretical calculations suggested a surface area of 713 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 0.43 cm<sup>3</sup> g<sup>-1</sup> (Cadiau *et al.* <sup>27</sup>: 0.35 cm<sup>3</sup> g<sup>-1</sup>).<sup>28</sup> The 5-position of the aromatic ring can bear various substituents, yielding chemical formulas corresponding to [Al(OH)(O<sub>2</sub>C-C<sub>6</sub>XH<sub>3</sub>-CO<sub>2</sub>) · *n* H<sub>2</sub>O]<sub>m</sub> (with X = -H, -OH, -OCH<sub>3</sub>, -NH<sub>2</sub>, -NO<sub>2</sub>, -CH<sub>3</sub>, -F, -Br, -SO<sub>3</sub>H),<sup>24,29,30,31</sup> going along with variegated properties of the resulting material (*e.g.* sorption characteristics of water vapor, CO<sub>2</sub>- and H<sub>2</sub>). Also various mixed-linker approaches were carried out.<sup>30,31,32</sup>

In terms of different synthesis routes, CAU-10-MOFs were always obtained out of water-DMF mixtures under solvothermal conditions (135 °C, 12 h). Besides the common approach, de Lange *et al.* obtained CAU-10-H in a microwave synthesis within 1 h heating.<sup>33</sup> Although the synthesis requires DMF, both aluminum sources and isophthalic acid are produced on an industrial scale, are toxicologically harmless and rather inexpensive.<sup>33,34</sup> Therefore, CAU-10-H represents a most marketable material.<sup>33</sup> To the best of our knowledge, there is no report for alternative synthesis routes to the solvothermal and microwave conditions.

CAU-10-H is a very good candidate for heat transformation applications,<sup>17</sup> as it represents nearly perfect hydrothermal stability,<sup>35</sup> which is underlined by no structural degradation of the material over 700 repeated adsorption/desorption cycles.<sup>35</sup> It has a higher volumetric adsorption capacity (0.38 cm<sup>3</sup> g<sup>-1</sup> at pp<sub>0</sub><sup>-1</sup> = 0.26)<sup>24</sup> and thermodynamic efficiency for water than commercially adsorbents (*e.g.* SAPO-34),<sup>33,36</sup> possessing an isosteric heat of adsorption of *ca.* 54 kJ mol<sup>-1</sup> (theoretically -49 kJ mol<sup>-1</sup>, predicted by GCMC simulations.<sup>37</sup> Accordingly, dense coatings of CAU-10-H were employed on different substrates with the purpose of heat transformation.<sup>38</sup> Due to its properties, it was also addressed to be suitable for humidity sensing by impedance spectroscopy,<sup>31</sup> investigated in terms of proton conductivity and catalytic activity,<sup>32</sup> as well as gas adsorption and separation.<sup>39</sup>

#### **MIL-160**

A rather new Al-MOF material is MIL-160 (*Matériaux Institut Lavoisier*), which was described by Cadiau *et al.* in 2015.<sup>27</sup> They obtained the MOF by applying reflux conditions for aqueous solutions of 2,5-furandicarboxylic acid, sodium hydroxide and aluminum chloride. MIL-160 is constructed identical to CAU-10-H by cis- $\mu$ -OH-connected, vertex-sharing {AlO<sub>6</sub>} octahedra, that form helical chains, which are then joined by the linker 2,5-furandicarboxylate (Fig. S4).



**Figure S4** Structural elements in the framework of MIL-160: (a) Extended asymmetric unit with full Al coordination spheres and full ligand bridging mode. Symmetry transformations i = 1-x, y, z; ii = x, -y, -z; iii = 0.25+y, 0.25-x, -0.25+z; iv = 0.25+y, -0.25+x, 0.25-z; v = 0.25-y, -0.25+x, 0.25+z. (b) Helical chains of cis vertex-bridged {AlO<sub>6</sub>}-polyhedra and (c) surrounded by the carboxylates ligands, to yield square-shaped one dimensional channels; compare to the closely related structure of CAU-10-H in Fig. S3. Graphic produced by software Diamond<sup>3</sup> from cif-file for MIL-160 (CSD-Refcode PIBZOS).<sup>40</sup>

MIL-160 is reported to be isostructural to CAU-10-H, having chains of {AlO<sub>6</sub>}-polyhedra that are surrounded by linker molecules.<sup>27</sup> This results in a chemical formula of [Al(OH)(O<sub>2</sub>C-C<sub>4</sub>H<sub>2</sub>O<sub>-</sub>CO<sub>2</sub>)  $\cdot n$  H<sub>2</sub>O]<sub>m</sub> and microporous square-shaped channels of 5 Å edge length.<sup>27,41</sup> The material exhibits a surface

area of 1070 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 0.40 cm<sup>3</sup> g<sup>-1</sup> from AlCl<sub>3</sub> and NaOH (theoretically: 1250 m<sup>2</sup> g<sup>-1</sup>, 0.48 cm<sup>3</sup> g<sup>-1</sup>),<sup>27</sup> respectively 1150 m<sup>2</sup> g<sup>-1</sup> and 0.46 cm<sup>3</sup> g<sup>-1</sup>, from Al(OH)(CH<sub>3</sub>COO)<sub>2</sub>,41 although very recent theoretical calculations suggested a surface area of 776 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 0.45 cm<sup>3</sup> g<sup>-1</sup>,<sup>28</sup>

The hydrophilic character of the MOF is also due to the heteroatom in the furan moiety of the linker. This resulted in a highly hydrothermally stable material with promising water sorption characteristics. Very recently, the MOF was advantageously synthesized from basic aluminum acetate (*i.e.* Al(OH)(CH<sub>3</sub>COO)<sub>2</sub>) in a scale-up.<sup>41</sup> The synthesis route of MIL-160 is environmentally friendly, since the linker is already on the way to being produced from renewable biomass *via* oxidation of 5-(hydroxy-methyl)furfural (5-HMF) on a very large industrial scale and water is the single solvent.<sup>42,43</sup> Hence, the production costs for MIL-160 may decline further within the next years. MIL-160 is quite a new material, there are – to the best of our knowledge - only the aforementioned two reports for different synthesis routes, mainly varying in the aluminum source and scale of synthesis.<sup>27,41</sup> A most recent and third report on MIL-160 focusses on structural refinements and flexibility upon N<sub>2</sub> and H<sub>2</sub>O sorption.<sup>40</sup>

Cadiau *et al.* denoted MIL-160 as the most promising Al-MOF for heat pump applications.<sup>27</sup> In comparison to CAU-10-H, slightly higher desorption temperatures are required; nevertheless, it outperforms both Alfum and CAU-10-H in terms of gravimetric water loadings.<sup>27</sup> In detail, it submits distinctively higher performance in terms of the loading spread (*i.e.* mass of adsorbed water vapor per mass of adsorbent) for the desired lift phase 1 (*i.e.* according to Henninger *et al.*: desired loading at low pp<sub>0</sub><sup>-1</sup>, depending on driving temperature).<sup>27,44,45,46</sup> Permyakova *et al.* investigated MIL-160 with respect to shaping into granules and heat reallocation.<sup>41</sup> Their report suggests similar properties to the ones reported by Cadiau *et al.* and underlines the suitability of the material for heat transformation application.

#### S3. Reflux-based syntheses for comparison

**Alfum** was synthesized according to the patented approach:<sup>1,2</sup> for solution 1, sodium hydroxide (0.2803 g, 7.01 mmol, 4 eq) and fumaric acid (0.3863 g, 3.33 mmol, 2 eq) were dissolved in water (6 mL). For solution 2, aluminum sulfate octadecahydrate (1.171 g, 1.76 mmol, 1 eq) was diluted in water (5 mL) at 60 °C. Over the course of 30 min, solution 1 was dropped into solution 2 and further stirred (60 °C, 2 h). The product was centrifuged (2000 U/min, 15 min) and decanted, subsequently washed with water (50 mL). The latter step was repeated. Subsequently, the product was dried overnight (80 °C, 1 - 10 mbar), yielding a white powder (0.4104 g, 74% yield, BET = 1131 m<sup>2</sup> g<sup>-1</sup>).

**CAU-10-H** was synthesized according to a protocol by Reinsch *et al.*: Aluminum sulfate octadecahydrate (0.8005 g, 4.82 mmol, 1 eq) and isophthalic acid (0.2000 g, 5.00 mmol, 1 eq) were transferred into a Teflon-lined autoclave (37 mL reactor volume) with water (4 mL) and DMF (1 mL). After 5 min of stirring, the autoclave was closed and heated (3 h heating, 12 h at 135 °C, 1 h cooling). Afterwards, the reaction mixture was decanted, washed with water three times (30 mL each), centrifuged (2000 U/min, 30 min), decanted and re-dispersed each time. Subsequently, the product was dried overnight (80 °C, 1 - 10 mbar), yielding a white powder (0.2122 g, 42% yield, BET = 435 m<sup>2</sup> g<sup>-1</sup>).

**MIL-160** was synthesized in a modified protocol of Cadiau *et al.*, who used 1 eq NaOH, whereas we used 2 eq NaOH to deprotonate the linker fully: 2,5-furandicarboxylic acid (0.3123 g, 2.0 mmol, 1 eq) and sodium hydroxide (0.1603 g, 4.0 mmol, 2 eq) were converted in water (10 mL, 2 h). Aluminum chloride hexahydrate (0.4826 g, 2.0 mmol, 1 eq) was added and reflux (24 h, 100 °C) was initiated. After decantation, the product was washed with water three times (30 mL each), centrifuged (2000 U/min, 30 min), decanted and re-dispersed each time. Subsequently, the product was dried overnight (80 °C, 1 - 10 mbar), yielding a white powder (0.2184 g, 55% yield, BET = 1178 m<sup>2</sup> g<sup>-1</sup>).

# S4. Dry-gel conversions: Syntheses optimizations

In order to find reliable DGC synthesis routes for the three presented MOFs, we carried out profound synthesis optimizations for each MOF individually: In a first approach, we assumed the stated synthesis temperatures and conversion times according to the reflux-based syntheses described in the literature for each MOF. Subsequently, we varied the temperature to one elevated and one lower level to find an optimal synthesis temperature. By applying the most suitable temperature, we varied time by choosing one longer and one shorter protocol.

The details and results of these time and temperature variations are summarized in Table S2, S4 and S7 for Alfum, CAU-10-H and MIL-160, respectively.

In each synthesis, one approach was carried with dry starting materials, another with wetted reactants. Thereby, we checked if wetting of the precursor mixture before conversion may be supportive for crystallinity and/or BET surface areas of the presented MOFs (*cf.* Figures S5-S12 and Figures S17-S19). Thereby, we were able to assure best and most efficient DGCs of the presented MOFs. The criteria yield, crystallinity, BET surface area and pore volume, as well as water sorption behavior were taken into account for synthesis optimizations towards first DGCs of Al-MOFs in general.

For CAU-10-H the DGC synthesis is based on the autoclave solution synthesis of Reinsch *et al.* using the same molar ratios of aluminum sulfate and isophthalic acid.<sup>24</sup> The reaction conditions of 135 °C for 12 h were taken as a starting point and the time and temperature were systematically varied.

For MIL-160 we have used the reaction conditions of Cadiau *et al.* as a starting point, that is 100 °C and 24 h.<sup>27</sup> From this starting point we have chosen a higher and lower temperature and at the medium temperature we varied the reaction to longer and shorter times than the literature. Furthermore, we investigate the use of 1 or 2 eq NaOH.

PXRD plots and nitrogen sorption isotherms that were taken into account as key-factors for synthesis optimizations are depicted in the respective Sections S4.1, S4.2 and S4.3.

# Alfum

In a typical synthetic procedure, we rapidly ground aluminum sulfate octadecahydrate  $(Al_2(SO_4)_3 \cdot 18H_2O)$  (159 mg, 0.24 mmol, 1 eq), fumaric acid (H<sub>2</sub>fum) (53 mg, 0.48 mmol, 2 eq) and sodium hydroxide (NaOH) (40 mg, 1.02 mmol, 4 eq) in a mortar and placed the mixture on a DGC sieve with water (5 mL) at the bottom of a Teflon reactor. DGCs were carried out at varying temperatures and conversion times. The white products were washed three times with water (10 mL each), recovered by centrifugation each time and finally dried under vacuum (80 °C, 24 h).

#### CAU-10-H

In a typical synthetic procedure, we rapidly ground aluminum sulfate octadecahydrate  $(Al_2(SO_4)_3 \cdot 18H_2O)$  (169 mg, 0.25 mmol, 1 eq), isopththalic acid  $(H_2BDC)$  (42 mg, 0.25 mmol, 1eq) in a mortar and placed the mixture on a DGC sieve with water/DMF (4:1, 5 mL) at the bottom of a Teflon reactor. DGCs were carried out at varying temperatures and conversion times. The white products were washed three times with water (10 mL each), recovered by centrifugation each time and finally dried under vacuum (80 °C, 24 h).

In a typical synthetic procedure, we rapidly ground aluminum chloride hexahydrate (AlCl<sub>3</sub>·6H<sub>2</sub>O) (144 mg, 0.60 mmol, 1 eq), 2,5-furandicarboxylic acid (H<sub>2</sub>FDC) (93 mg, 0.60 mmol, 1 eq) and sodium hydroxide (NaOH) (1 or 2 eq) in a mortar and placed the mixture on a DGC sieve with water (5 mL) at the bottom of a Teflon reactor. DGCs were carried out at varying temperatures and conversion times. The white products were washed three times with water (10 mL each), recovered by centrifugation each time and finally dried under vacuum (80 °C, 24 h).

# S4.1. Dry-gel conversions: Synthesis optimizations -- Alfum

Aluminum fu	ımarate					
Conditions	Not Moistened					
80 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1559 g	0.23 mmol	1 eq	Yield	0.0516 g (70 %)
	Fumaric acid	0.0542 g	0.47 mmol	2 eq		
	NaOH	0.0400 g	1.00 mmol	4 eq	Surface	630 m <sup>2</sup> /g
	Water	2 ml	-	-		
100 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1597 g	0.24 mmol	1 eq	Yield	0.0524 g (69 %)
	Fumaric acid	0.0555 g	0.48 mmol	2 eq		
	NaOH	0.0409 a	1.02 mmol	4 eq	Surface	795 m <sup>2</sup> /g
	Water	2 ml	-	-		
120 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1571 g	0.24 mmol	1 eq	Yield	0.0609 g (82 %)
	Fumaric acid	0.0546 g	0.47 mmol	2 eq		
	NaOH	0.0403 g	1.01 mmol	4 eq	Surface	749 m <sup>2</sup> /g
	Water	2 ml	-	-		Ű
100 °C; 6 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1573 g	0.24 mmol	1 eq	Yield	0.0500 g (67 %)
	Fumaric acid	0.0547 g	0.47 mmol	2 eq		
	NaOH	0.0404 a	1.01 mmol	4 eq	Surface	1037 m <sup>2</sup> /g
	Water	2 ml	-	-		<u> </u>
100 °C; 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1590 g	0.24 mmol	1 eg	Yield	0.0532 g (71 %)
	Fumaric acid	0.0553 g	0.48 mmol	2 eq		
	NaOH	0.0408 q	1.02 mmol	4 eq	Surface	1129 m²/g
	Water	2 ml	-	-		
	•		•			
Conditions	Moistened					
80 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1550 g	0.23 mmol	1 eq	Yield	0.0468 g (64 %)
	Fumaric acid	0.0539 g	0.46 mmol	2 eq		
	NaOH	0.0397 g	0.99 mmol	4 eq	Surface	1004 m²/g
	Water	1.8 + 0.2 ml	-	-		
100 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1593 g	0.24 mmol	1 eq	Yield	0.0460 g (61 %)
	Fumaric acid	0.0554 g	0.48 mmol	2 eq		
	NaOH	0.0408 g	1.02 mmol	4 eq	Surface	604 m²/g
	Water	1.8 + 0.2 ml	-	-		
120 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1564 g	0.23 mmol	1 eq	Yield	0.0663 g (89 %)
	Fumaric acid	0.0544 g	0.47 mmol	2 eq		
	NaOH	0.0402 g	1.01 mmol	4 eq	Surface	577 m²/g
	Water	1.8 + 0.2 ml	-	-		
100 °C; 6 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1591 g	0.24 mmol	1 eq	Yield	0.0435 g (58 %)
	Fumaric acid	0.0553 g	0.48 mmol	2 eq		
	NaOH	0.0409 g	1.02 mmol	4 eq	Surface	1284 m²/g
	Water	1.8 + 0.2 ml	-	-		
100 °C; 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1590 g	0.24 mmol	1 eq	Yield	0.0280 g (37 %)
	Fumaric acid	0.0553 g	0.48 mmol	2 eq		
	NaOH	0.0408 q	1.02 mmol	4 eq	Surface	575 m²/g

Table S2. Listing of DGC synthesis conditions for Alfum with variation of time and temperature.

# Section S4.1.1. Dry-gel conversions: Synthesis optimizations -- Alfum solvent re-use

Aluminum fu	Imarate					
Conditions	Not moistened					
100 °C; 6 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1676 g	0.25 mmol	1 eq	Yield	0.0386 g (49 %)
	Fumaric acid	0.0587 g	0.51 mmol	2 eq		
	NaOH	0.0406 g	1.02 mmol	4 eq	Surface	924 m²/g
	Water	2 ml	-	-		
100 °C; 6 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1670 g	0.25 mmol	1 eq	Yield	0.0326 g (41 %)
	Fumaric acid	0.0579 g	0.50 mmol	2 eq		
	NaOH	0.0423 g	1.06 mmol	4 eq	Surface	1076 m <sup>2</sup> /g
	Water	2 ml	-	-		
100 °C; 6 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1672 g	0.25 mmol	1 eq	Yield	0.0390 g (49 %)
	Fumaric acid	0.0588 g	0.51 mmol	2 eq		
	NaOH	0.0405 g	1.01 mmol	4 eq	Surface	1045 m <sup>2</sup> /g
	Water	2 ml	-	-		
100 °C; 6 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1673 g	0.25 mmol	1 eq	Yield	0.0364 g (46 %)
	Fumaric acid	0.0582 g	0.50 mmol	2 eq		
	NaOH	0.0437 g	1.09 mmol	4 eq	Surface	1032 m <sup>2</sup> /g
	Water	2 ml	-	-		5
			-	· · · · · · · · · · · · · · · · · · ·		
Conditions	Moistened					
100 °C; 6 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1673 g	0.25 mmol	1 eq	Yield	0.0377 g (48 %)
	Fumaric acid	0.0592 g	0.51 mmol	2 eq		
	NaOH	0.0410 g	1.02 mmol	4 eq	Surface	983 m²/g
	Water	1.8 + 0.2 ml	-	-		
100 °C; 6 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1650 g	0.25 mmol	1 eq	Yield	0.0413 g (53 %)
	Fumaric acid	0.0579 g	0.50 mmol	2 eq		
	NaOH	0.0422 g	1.06 mmol	4 eq	Surface	991 m²/g
	Water	1.8 + 0.2 ml	-	-		
100 °C; 6 h	Starting Materials		Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1661 g	0.25 mmol	1 eq	Yield	0.0180 g (23 %)
	Fumaric acid	0.0586 g	0.50 mmol	2 eq		
	NaOH	0.0401 g	1.00 mmol	4 eq	Surface	1189 m²/g
	Water	1.8 + 0.2 ml	-	-		
100 °C; 6 h	Starting Materials		Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1691 g	0.25 mmol	1 eq	Yield	0.0404 g (50 %)
	Fumaric acid	0.0590 g	0.51 mmol	2 eq		/
	NaOH	0.0427 g	1.07 mmol	4 eq	Surface	1089 m <sup>2</sup> /g
	Water	1.8 + 0.2 ml	-	-		, v

 Table S3. Listing of DGC synthesis conditions for Alfum and solvent re-use.

# S4.2. Dry-gel conversions: Synthesis optimizations -- CAU-10-H

Table S4. Listing of DGC synthesis	conditions for CAU-10-H with	h variation of time and	temperature.

CAU-10-H						
Conditions	Not Moistened				_	
115 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.2065 g	0.31 mmol	1 eq	Yield	-
	Isophthalic Acid	0.0517 g	0.31 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	-
	Water	1.6 ml	-	-		
135 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.2001 g	0.30 mmol	1 eq	Yield	0.0362 g (29 %)
	Isophthalic Acid	0.0509 g	0.31 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	33 m²/g
	Water	1.6 ml	-	-		
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1920 g	0.29 mmol	1 eq	Yield	0.0783 g (65 %)
	Isophthalic Acid	0.0481 g	0.29 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	13 m²/g
	Water	1.6 ml	-	-		
135 °C; 6 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.2002 g	0.30 mmol	1 eq	Yield	-
	Isophthalic Acid	0.0502 g	0.30 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	-
	Water	1.6 ml	-	-		
135 °C; 24 h	Starting Materials	<b>Initial Weight</b>	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1642 g	0.25 mmol	1 eq	Yield	0.0487 g (48 %)
	Isophthalic Acid	0.0411 g	0.25 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	1 m²/g
	Water	1.6 ml	-	-		
Conditions	Moistened					
115 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.2062 g	0.31 mmol	1 eq	Yield	0.0460 g (36 %)
	Isophthalic Acid	0.0517 g	0.31 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	168 m²/g
	Water	1.6 ml	-	-		
135 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1999 g	0.30 mmol	1 eq	Yield	0.0590 g (47 %)
		0.0508 g	0.31 mmoi	1 eq		000 2/.
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	398 m /g
455 °C1 42 h	Starting Matariala	I.0 IIII	- Molor Amount	-	Droduct	
155 C, 12 II	Aluminum Sulfato				Viold	0.0552 g (52 %)
	Isonhthalic Acid	0.1030 g	0.25 mmol	1 eq	Tielu	0.0002 g (02 /0)
	N N Dimothylformamida	0.0420 g	0.20 11110	i cq	Surface	$472 \text{ m}^2/\text{a}$
	Water	0.4 ml			Surface	472 m /g
135 °C: 6 h	Starting Materials	Initial Weight	Molar Amount	Fauivalents	Product	
	Aluminum Sulfate	0.2015 g	0.30 mmol	1 eq	Yield	0.0373 g (30 %)
	Isophthalic Acid	0.0506 a	0.30 mmol	1 ea		(cc / c)
	N.N-Dimethylformamide	0.4 ml	_	- 1	Surface	255 m²/a
	Water	1.61	-	<u> </u>		
135 °C: 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
,	Aluminum Sulfate	0.1707 a	0.26 mmol	1 ea	Yield	0.0484 a (45 %)
	Isophthalic Acid	0.0427 g	0.26 mmol	1 eq		g(.c,0)
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	250 m <sup>2</sup> /g
	Water	1.6 ml	-	-		<u> </u>

# S.4.2.1. Dry-gel conversions: Synthesis optimizations -- CAU-10-H solvent re-use

CAU-10-H						
Conditions	Not Moistened					
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1987 g	0.30 mmol	1 eq	Yield	0.0643 g (52 %)
	Isophthalic Acid	0.0502 g	0.30 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	67m <sup>2</sup> /g
	Water	1.6 ml	-	-		
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1998 g	0.30 mmol	1 eq	Yield	0.0606 g (49 %)
	Isophthalic Acid	0.0500 g	0.30 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	23 m²/g
	Water	1.6 ml	-	-		
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1982 g	0.30 mmol	1 eq	Yield	0.0387 g (31 %)
	Isophthalic Acid	0.0505 g	0.30 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	232 m <sup>2</sup> /g
	Water	1.6 ml	-	-		
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1990 g	0.30 mmol	1 eq	Yield	0.0408 g (33 %)
	Isophthalic Acid	0.0503 g	0.30 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	20 m²/g
	Water	1.6 ml	-	-		
Conditions	Moistened					
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.2008 g	0.30 mmol	1 eq	Yield	0.0071 g (6 %)
	Isophthalic Acid	0.0503 g	0.30 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	285 m²/g
	Water	1.6 ml	-	-		
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1994 g	0.30 mmol	1 eq	Yield	0.0376 g (30 %)
	Isophthalic Acid	0.0496 g	0.30 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	348 m²/g
	Water	1.6 ml	-	-		
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1974 g	0.30 mmol	1 eq	Yield	0.0362 g (29 %)
	Isophthalic Acid	0.0503 g	0.30 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	560 m <sup>2</sup> /g
	Water	1.6 ml	-	-		
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.2005 g	0.30 mmol	1 eq	Yield	0.0114 g (9 %)
	Isophthalic Acid	0.0515 g	0.31 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	42 m <sup>2</sup> /g
	Water	1.61	-	-		

 Table S5. Listing of DGC synthesis conditions for CAU-10-H and solvent re-use.

# S4.2.2. Dry-gel conversions: Synthesis optimizations -- CAU-10-H solvent re-use (less DMF)

CAU-10-H						
Conditions	Not Moistened					
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.2023 g	0.30 mmol	1 eq	Yield	0.0706 g (56 %)
	Isophthalic Acid	0.0515 g	0.31 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	8 m²/g
	Water	1.6 ml	-	-		
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.2008 g	0.30 mmol	1 eq	Yield	0.0588 g (47 %)
	Isophthalic Acid	0.0492 g	0.30 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	15 m²/g
	Water	1.6 ml	-	-		
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1999 g	0.30 mmol	1 eq	Yield	0.0565 g (45 %)
	Isophthalic Acid	0.0502 g	0.30 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	0 m²/g
	Water	1.6 ml	-	-		
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.2004 g	0.30 mmol	1 eq	Yield	0.0547 g (44 %)
	Isophthalic Acid	0.0505 g	0.30 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	10 m²/g
	Water	1.6 ml	-	-		
Conditions	Moistened					
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.2000 g	0.30 mmol	1 eq	Yield	0.0547 g (44 %)
	Isophthalic Acid	0.0484 g	0.29 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	317 m <sup>2</sup> /g
	Water	1.6 ml	-	-		
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.2008 g	0.30 mmol	1 eq	Yield	0.0434 g (35 %)
	Isophthalic Acid	0.0496 g	0.30 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	497 m²/g
	Water	1.6 ml	-	-		
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.1998 g	0.30 mmol	1 eq	Yield	0.0093 g (7 %)
	Isophthalic Acid	0.0500 g	0.30 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	10 m²/g
	Water	1.6 ml	-	-		
155 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Sulfate	0.2026 g	0.30 mmol	1 eq	Yield	0.0277 g (22 %)
	Isophthalic Acid	0.0500 g	0.30 mmol	1 eq		
	N,N-Dimethylformamide	0.4 ml	-	-	Surface	312 m <sup>2</sup> /g
	Water	1.61	-	_		

Table S6. Listing of DGC synthesis conditions for CAU-10-H and solvent re-use with less DMF.

# S4.3. Dry-gel conversions: Synthesis optimizations -- MIL-160

Table S7. Listing of DGC synthesis conditions for MIL-160 with variation of time and temperature.

MIL-160						
Conditions	Not Moistened					
80 °C; 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminium Chloride	0.1391 g	0.58 mmol	1 eq	Yield	0.0313 g (27 %)
	2,5-Furandicarboxylic Acid	0.0899 g	0.58 mmol	1 eq		
	NaOH	0.0230 g	0.58 mmol	1 eq	Surface	264 m²/g
	Water	2 ml	-	-		
100 °C; 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminium Chloride	0.1927 g	0.80 mmol	1 eq	Yield	0.0416 g (26 %)
	2,5-Furandicarboxylic Acid	0.1242 g	0.80 mmol	1 eq		
	NaOH	0.0326 g	0.82 mmol	1 eq	Surface	57 m²/g
	Water	2 ml	-	-		
120 °C; 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminium Chloride	0.1439 g	0.60 mmol	1 eq	Yield	0.0162 g (14 %)
	2,5-Furandicarboxylic Acid	0.0929 g	0.60 mmol	1 eq		
	NaOH	0.0238 g	0.60 mmol	1 eq	Surface	101 m²/g
	Water	2 ml	-	-		
100 °C; 12 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminium Chloride	0.1465 g	0.61 mmol	1 eq	Yield	0.0227 g (19 %)
	2,5-Furandicarboxylic Acid	0.0947 g	0.61 mmol	1 eq		
	NaOH	0.0243 g	0.61 mmol	1 eq	Surface	394 m²/g
	Water	2 ml	-	-		
100 °C; 48 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminium Chloride	0.1395 g	0.58 mmol	1 eq	Yield	0.0237 g (21 %)
	2,5-Furandicarboxylic Acid	0.0902 g	0.58 mmol	1 eq		0
	NaOH	0.0232 g	0.58 mmol	1 eq	Surface	119 m²/g
	Water	2 ml	-	-		
-						
Conditions	Moistened					
80 °C; 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminium Chloride	0.1402 g	0.58 mmol	1 eq	Yield	0.0216 g (19 %)
	2,5-Furandicarboxylic Acid	0.0906 g	0.58 mmoi	1 eq		405 24
	NaOH	0.0232 g	0.58 mmol	1 eq	Surface	135 m <sup>-</sup> /g
400 °O: 04 h	vvater	1.8 + 0.2 mi	-	-	Due du et	
100 °C; 24 n	Starting Materials			Equivalents	Product	$0.0705 \approx (40.0/)$
	2.5 Eurandicarboxulic Acid	0.1931 g	0.80 mmol	1 eq	Tielu	0.0765 y (46 %)
		0.1244 g	0.00 mmol	1 eq	Surface	$254 \text{ m}^2/\text{g}$
	Water	1.0327 g	0.62 1111101	i eq	Surface	554 m /g
120 °C · 24 h	Starting Materials	Initial Weight	Molar Amount	Fauivalente	Product	
120 0, 24 11	Aluminium Chloride	0 1444 a		1 equivalents	Yield	0 0902 g (76 %)
	2.5-Furandicarboxylic Acid	0.0933	0.60 mmol	1 eq	Tiera	0.0002 g (10 /0)
	NaOH	0.0239	0.60 mmol	1 eq	Surface	$402 \text{ m}^2/\text{q}$
	Water	18+02ml	-	-	Surface	402 11 /g
100 °C: 12 h	Starting Materials	Initial Weight	Molar Amount	Fouivalents	Product	
	Aluminium Chloride	0 1475 g	0.61 mmol	1 eq	Yield	0 0099 g (7 %)
	2,5-Furandicarboxvlic Acid	0.0954 a	0.61 mmol	1 ea		5.0000 g (1 /0)
	NaOH	0 0245 g	0.61 mmol	1 eq	Surface	249 m <sup>2</sup> /a
	Water	$1.8 \pm 0.2$ ml	-	-	Juilace	2.0 m /g
100 °C: 48 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminium Chloride	0.1391 a	0.58 mmol	1 eq	Yield	0.0066 g (6 %)
	2,5-Furandicarboxvlic Acid	0.0899 a	0.58 mmol	1 ea	11010	5.0000 g (0 /0)
	NaOH	0.0231 g	0.58 mmol	1 eq	Surface	451 m²/a
	Water	1.8 + 0.2 ml	-	-		

# S4.3.1. Dry-gel conversions: Synthesis optimizations -- MIL-160 solvent re-use

MIL-160						
Conditions	Not Moistened					
100 °C; 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Chloride	0.0980 g	0.41 mmol	1 eq	Yield	0.0336 g (42 %)
	2,5-Furandicarboxylic Acid	0.0637 g	0.41 mmol	1 eq		
	NaOH	0.0332 g	0.83 mmol	2 eq	Surface	438 m <sup>2</sup> /g
	Water	2 ml	-	-		
100 °C; 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Chloride	0.0993 g	0.41 mmol	1 eq	Yield	0.0294 g (36 %)
	2,5-Furandicarboxylic Acid	0.0646 g	0.41 mmol	1 eq		
	NaOH	0.0343 g	0.85 mmol	2 eq	Surface	435 m²/g
	Water	2 ml	-	-		
100 °C; 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Chloride	0.1005 g	0.42 mmol	1 eq	Yield	0.0413 g (50 %)
	2,5-Furandicarboxylic Acid	0.0622 g	0.40 mmol	1 eq		
	NaOH	0.0323 g	0.81 mmol	2 eq	Surface	370 m²/g
	Water	2 ml	-	-		
100 °C; 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Chloride	0.0988 g	0.41 mmol	1 eq	Yield	0.0295 g (36 %)
	2,5-Furandicarboxylic Acid	0.0624 g	0.40 mmol	1 eq		
	NaOH	0.0315 g	0.79 mmol	2 eq	Surface	891 m²/g
	Water	2 ml	-	-		
Conditions	Moistened					
100 °C; 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Chloride	0.0966 g	0.40 mmol	1 eq	Yield	0.0302 g (38 %)
	2,5-Furandicarboxylic Acid	0.0614 g	0.40 mmol	1 eq		
	NaOH	0.0337 g	0.84 mmol	2 eq	Surface	995 m²/g
	Water	1.8 + 0.2 ml	-	-		
100 °C; 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Chloride	0.0987 g	0.41 mmol	1 eq	Yield	0.0244 g (30 %)
	2,5-Furandicarboxylic Acid	0.0659 g	0.42 mmol	1 eq		
	NaOH	0.0333 g	0.83 mmol	2 eq	Surface	968 m²/g
	Water	1.8 + 0.2 ml	-	-		
100 °C; 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Chloride	0.1010 g	0.42 mmol	1 eq	Yield	0.0379 g (46 %)
	2,5-Furandicarboxylic Acid	0.0625 g	0.40 mmol	1 eq		
	NaOH	0.0344 g	0.86 mmol	2 eq	Surface	1180 m²/g
	Water	1.8 + 0.2 ml	-	-		
100 °C; 24 h	Starting Materials	Initial Weight	Molar Amount	Equivalents	Product	
	Aluminum Chloride	0.0989 g	0.41 mmol	1 eq	Yield	0.0177 g (22 %)
	2,5-Furandicarboxylic Acid	0.0631 g	0.40 mmol	1 eq		_
	NaOH	0.0321 g	0.80 mmol	2 eq	Surface	980 m²/g
	IWater	18+02ml	-	-		

Table S8. Listing of DGC synthesis conditions for MIL-160 and solvent re-use.

### S5. Solvent re-use for Alfum, CAU-10-H and MIL-160

We carried out solvent re-use experiments over four repeated DGC runs with the same solvent and fresh reactant mixture on the sieve at the head of the DGC autoclave (*cf.* Figure S1).

The details and results of these solvent re-use experiments are summarized in Table S3, S5, S6 and S8 for Alfum, CAU-10-H and MIL-160, respectively.

Figure S5-S8 graphically depict the results of solvent re-use with respect to BET surface area and yield.

# Alfum



**Figure S5** Solvent re-use over four DGC runs for Alfum, with BET surface area (red bars) and yields (blue squares). Left: wetted precursor mixture, right: dry precursor mixture. Minor yields, e.g. 20% in run 3, due to washing off/falling down of the product during handling of the DGC setup.



#### CAU-10-H, repetition with wetting of neat DMF

**Figure S6** Solvent re-use over four DGC runs for CAU-10-H, with BET surface area (red bars) and yields (blue boxes). A wetted (neat DMF) precursor mixture was used. Minor yields, due to washing off/falling down of the product during handling of the DGC setup.



**Figure S7** Solvent re-use over four DGC runs for MIL-160, with BET surface area (red bars) and yields (blue boxes). A wetted precursor mixture was used. Minor yields, due to washing off/falling down of the product during handling of the DGC setup.

#### S6. PXRD measurements

Crystallinity was proven with powder X-ray diffractometry (PXRD), using a *Bruker D2 Phaser* diffractometer with a flat silicon, low background sample holder and Cu-K<sub> $\alpha$ </sub> radiation ( $\lambda$  = 1.54184 Å) at 30 kV and 0.04 ° s<sup>-1</sup> in the 2 $\theta$  = 5-50 ° range.

Figure S8-S12 depict PXRD patterns of all obtained samples Alfum, CAU-10-H and MIL-160 samples within solvent re-use in comparison with each simulated pattern.

#### Alfum



**Figure S8** PXRD patterns of Alfum samples obtained by synthesis runs with solvent re-use, in comparison with simulated pattern (CDS-Refcode DOYBEA).<sup>4</sup> Left: wetted precursor mixture, right: dry precursors. Figure 1 in the main manuscript shows a comparison with the industrial benchmark Basolite A520.



#### CAU-10-H, repetition with wetting of neat DMF

**Figure S9** PXRD patterns of aluminum CAU-10-H samples obtained by synthesis runs with solvent reuse, in comparison with simulated pattern (CCDC CSD-Refcode QQOBUT).<sup>25</sup> A wetted (neat DMF) precursor mixture was used.



**Figure S10** PXRD patterns of MIL-160 samples obtained by synthesis runs with solvent re-use, in comparison with simulated pattern (CCDC PIBZOS).<sup>40</sup> A wetted precursor mixture was used.

#### S7. Thermogravimetric Analysis (TGA)

Exemplarily, we performed thermogravimetric analyses (TGA) of samples obtained *via* DGC of each of the presented MOFs. Figure S11-S15 depict TGA curves of Alfum, CAU-10-H and MIL-160 samples.

# Alfum



**Figure S11** TG curve of Alfum samples from DGC (blue) and from solution-based synthesis (red) in comparison with industrial benchmark *Basolite A520*.



CAU-10-H

Figure S12 TG curve of CAU-10-H samples from DGC (blue) and from solution-based synthesis (red).



Figure S13 TG curve of MIL-160 samples from DGC (blue) and from solution-based synthesis (red).

## S8. Scanning electron microscopy (SEM)

For control of morphology we recorded SEM images using a JEOL JSM-6510 advanced electron microscope with a  $LaB_6$  cathode at 20 keV.

Figure S14-S18 exemplarily depict SEM images of selected samples of the three presented MOFs.

# Alfum





**Figure S14** SEM images of different Alfum samples at different magnifications (left: overview, right: close-up). Top: Basolite A520. Middle: Alfum from DGC. Bottom: Alfum from solution-based synthesis

CAU-10-H



**Figure S15** SEM images of different CAU-10-H samples at different magnifications (left: overview, right: close-up). Top: CAU-10-H from DGC. Bottom: CAU-10-H from solution-based synthesis.



**Figure S16** SEM images of MIL-160 samples at different magnifications (left: overview, right: close-up). Top: MIL-160 from DGC. Bottom: MIL-160 from solution-based synthesis.

## S9. Nitrogen sorption experiments solvent re-use (T = 77 K)

Surface areas (BET) were determined by nitrogen (purity 99.999%) sorption experiments at 77.35 K using a *Quantachrome NOVA-4000e* instrument within a partial pressure range of  $pp_0^{-1} = 10^{-3}$ -1 bar. Each sample was degassed under vacuum (<  $10^{-2}$  mbar) at 100 °C (MIL-100(Fe)), respectively 150 °C (Alfum) for *ca*. 3 h, prior to measurement. All surface areas (BET) were calculated from five adsorption points in the pressure range  $pp_0^{-1} = 0.009 - 0.041$  bar for samples of Alfum,  $pp_0^{-1} = 0.004 - 0.125$  bar for samples of CAU-10-H and  $pp_0^{-1} = 0.014 - 0.052$  bar for samples of MIL-160. This range is indeed not recommended by IUPAC (International Union of Pure and Applied Chemistry) for BET surface determination, but rather suitable for microporous materials.<sup>47</sup>

Figure S17-S19 depict the nitrogen sorption isotherms of all obtained MOF samples during DGCs with solvent re-use over four DGC runs.



#### Aluminum fumarate

**Figure S17** Nitrogen sorption (77 K) isotherms of aluminum fumarate samples obtained by synthesis runs with solvent re-use. Left: wetted precursor mixture, right: dry precursor mixture.

#### CAU-10-H, repetition with wetting of neat DMF



**Figure S18** Nitrogen sorption (77 K) isotherms of CAU-10-H samples obtained by synthesis runs with solvent re-use. A wetted (neat DMF) precursor mixture was used.



**Figure S19** Nitrogen sorption (77 K) isotherms of MIL-160 samples obtained by synthesis runs with solvent re-use. A wetted (neat DMF) precursor mixture was used.

Table S9 summarizes repeated  $N_2$  sorption results of the industrial benchmark *Basolite A520* using the same batch, but not the same sample.

**Table S9** Repeated determination of BET areas of Basolite A520 using nitrogen sorption (T = 77 K).

Benchmark	No. of	BET
	measurement	[m² g <sup>-1</sup> ]
	1	1030
	2	1038
Basolite A520	3	999
	4	1040
	5	1026

# S10. Water sorption experiments (T = 20 °C)

Water sorption experiments were carried out on a *Quantachrome VStar4* (QUANTACHROME, Odelzhausen, Germany) instrument within a partial pressure range of  $pp_0^{-1} = 10^{-3}$ -1 bar. Each sample was degassed under vacuum (<  $10^{-3}$  mbar) at 150 °C for *ca*. 3 h prior to measurement, using a *FloVac* (QUANTACHROME, Odelzhausen, Germany) degasser.

All water sorption isotherms are depicted in Figures 2c) ,3c),4c) in the main manuscript.



Fig. S20 Water uptake (at  $p/p_0 = 0.95$ ) versus the total pore volume (at  $p/p_0 = 0.95$ ) for solution and DGC samples.

Fable S10 Microporosity cho	aracteristics for solution a	and DGC samples from	V-t-plot method.
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Sample	Micropore surface area [m <sup>2</sup> g <sup>-1</sup> ]	External and mesopore surface area [m <sup>2</sup> g <sup>-1</sup> ]	Micropore volume [cm³ g⁻1]
Alfum solution-based	1112	141	0.427
DGC	941	104	0.367
CAU-10-H solution-based	378	192	0.089
DGC	437	129	0.173
MIL-160 solution-based	1067	30	0.403
DGC	899	81	0.279

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