Metal Acetylacetonates as a Source of Metals for Aqueous Synthesis of Metal-Organic Frameworks

Ceren Avci-Camur,[†]Javier Perez-Carvajal,[†] Inhar Imaz,*[†] and Daniel Maspoch*[†][‡]

[†]   Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain. E-mail: inhar.imaz@icn2.cat, daniel.maspoch@icn2.cat

[‡]   ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain

ABSTRACT

Demand continues for environmentally sound, high-yielding processes for the large-scale production of metal-organic frameworks (MOFs). Here we describe the use of metal acetylacetonate complexes as an alternative source of metals for the aqueous synthesis of MOFs. We have synthesized several carboxylate-based Zr(IV)- (UiO-66-NH$_2$, Zr-fumarate, UiO-66-(OH)$_2$, UiO-66-COOH and UiO-66-(COOH)$_2$), Fe(III)- (MIL-88A) and Al(III)- (CAU-10) porous MOFs from their corresponding metal acetylacetonates in good yields (typically > 85%) and, in some cases, at room temperature.
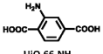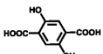
INTRODUCTION
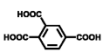
Metal acetylacetonate (acac) complexes that are formed of highly labile acetylacetonate linkers have found widespread use in industry,[1] including in vulcanisation of plastics for rubber;[2,3] curing processes for coatings (*e.g.* epoxy resins);[4-7] as oxidative reagents for degradation of organic pollutants[8] and also shelf-stable non-woven fabrics and films used in dippers, wipes, towels and bathmats;[9] as polyvinyl chloride (PVC) stabilisers;[10] and as catalysts in many polymerizations.[11-13] For example, $Zr(acac)_4$ is used to initiate lactide polymerization and co-polymerization for the production of b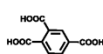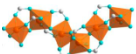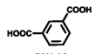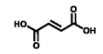ioresorbable materials; in drug-releasing processes; and to form scaffolds for tissue cultures and in biodegradable implants for surgical use.[14] In most of these processes, metal acetylacetonate complexes are considered green reagents due to their low toxicity and ease of handling in air.[15]

Metal-organic frameworks (MOFs) are among the most attractive porous materials known today, owing to their myriad potential industrial applications. However, their practical use has been limited by the paucity of environmentally friendly methods suitable for large-scale production.[16-19] The production process of MOFs generally needs high temperatures and the use of expensive, toxic, flammable and/or teratogenic organic solvents (such as DMF). Therefore, it is crucial to be able to fabricate MOFs in aqueous conditions, as water is safer and cheaper than using organic solvents. To date, some advances have been made in producing MOFs in water by mixing the organic linker, the metal salt (mainly nitrates, chlorides and oxochlorides) and acetic acid at high temperatures (Table 1). However, such salts can be problematic, as they present serious oxidative reactivity and toxicity hazards, and some of them are corrosive to metal-based reactors.[18,20] To overcome these drawbacks, De Vos *et al.* and Stock *et al.* replaced the above-mentioned metal salts with metal sulphates in the aqueous synthesis of diverse MOFs (UiO-type and CAU-

10) at high temperatures.[21, 22] Indeed, the sulphate ion is less corrosive, safer and greener than the corresponding anions of the aforementioned salts, and its use obviates the use of acetic acid. However, large concentrations of metal sulphates can compromise the framework rigidity and porosity of the resulting MOFs, due to interactions between the sulphate anions and the metal cations.[23, 24]

As part of our ongoing research to devise new methods for production of MOFs in water, we have sought alternatives to the metal sources cited above. Here we show that metal acetylacetonate complexes can serve as metal sources for aqueous synthesis of MOFs in good yields. As proof of concept, we used $Zr(acac)_4$ to prepare five members of the UiO-type family of MOFs, including UiO-66-NH_2, Zr-fumarate (also known as MOF-801), UiO-66-$(OH)_2$, UiO-66-COOH and UiO-66-$(COOH)_2$ (Table 1). We also extended our study to other metal acetylacetonates such as $Al(acac)_3$ (to produce CAU-10) and $Fe(acac)_3$ (to produce MIL-88A). Encouragingly, we found that many of these reactions proceed in high yields at room temperature (RT) - a remarkable finding, given that aqueous synthesis of MOFs without heating has scarcely been reported.[25,26]

Table 1. Summary of the aqueous syntheses of the selected MOFs reported in the literature.

Cluster	Ligand / MOF	Metal source	Solvent	T (ºC)	BET (m^2g^{-1})	Ref.
	UiO-66-NH$_2$	Zr(NO$_3$)$_4$	H$_2$O/AA	Reflux	833	27
		ZrOCl$_2$	H$_2$O/AA	90 °C	1150	24
		ZrOCl$_2$	H$_2$O/AA	150 °C	1261	28
		Zr(SO$_4$)$_2$	H$_2$O	Reflux	420	21
		Zr (acac)$_4$	H$_2$O/AA	RT	1106	This work
	Zr-fumarate	ZrOCl$_2$	H$_2$O/AA	90 °C	1200	24
		ZrOCl$_2$	H$_2$O/AA	150 °C	664	28
		Zr (acac)$_4$	H$_2$O/AA	RT	1249	This work
	UiO-66-(OH)$_2$	Zr(NO$_3$)$_4$	H$_2$O/AA	Reflux	705	27
		ZrOCl$_2$	H$_2$O/AA	95 °C	940	24
		Zr (acac)$_4$	H$_2$O/AA	RT	733	This work
	UiO-66-COOH	ZrCl$_4$	H$_2$O	100 °C	661	29
		Zr(acac)$_4$	H$_2$O/AA	90 °C	452	This work
	UiO-66-(COOH)$_2$	Zr(NO$_3$)$_4$	H$_2$O/AA	Reflux	494	27
		Zr(SO$_4$)$_2$	H$_2$O	Reflux	250	21
		ZrCl$_4$	H$_2$O	100 °C	516	29
		Zr(acac)$_4$	H$_2$O/AA	90 °C	538	This work
	CAU-10	Al$_2$(SO$_4$)$_3$ and NaAlO$_2$	H$_2$O/EtOH	130 °C	-	22
		Al(acac)$_3$	H$_2$O	90 °C	520	This work
	MIL-88A	FeCl$_3$	H$_2$O	85 °C	-	30
		Fe(acac)$_3$	H$_2$O	RT	-	This work

EXPERIMENTAL SECTION

General Procedures, Materials and Instrumentation

Zirconium acetylacetonate, iron (III) acetylacetonate, aluminium acetylacetonate, 2-aminoterephthalic acid, fumaric acid, 2-carboxyterephthalic acid, 2,5-dicarboxyterephthalic acid, isophthalic acid and acetic acid were purchased from Sigma-Aldrich. All reagents were used without further purification. All reactions were performed using deionised water, obtained from a Milli-Q system (18.2 MΩ.cm).

X-ray Powder Diffraction (XRPD) patterns were collected on an X'Pert PRO MPDP analytical diffractometer (Panalytical) at 45 kV and 40 mA using CuKα radiation (λ = 1.5419 Å). Nitrogen

and carbon dioxide adsorption and desorption measurements were performed at 77 K and room temperature respectively using an Autosorb-IQ-AG analyser (Quantachrome Instruments). Specific surface area (S_{BET}) was determined by applying the BET equation to the adequate region of the nitrogen isotherms: the range was taken between 0.025 and 0.06 P/P_0 for UiO-66-NH_2 and COOH, and between 0.05 and 0.1 P/P_0 for the others.[31] Prior to the measurements, samples were degassed inside the cell under primary vacuum at 200 °C for 6 h (UiO-66-NH_2) or at 150 °C for 10 h (Zr-fumarate) or at 100 °C for 3 h (UiO-66-$(OH)_2$) or at 70 °C for 12 h (UiO-66-COOH and UiO-66-$(COOH)_2$) or at 150 °C for 16 h (CAU-10). Gravimetric water vapour-sorption isotherms were measured using a DVS vacuum instrument (Surface Measurement Systems Ltd). The weight of the dried powder ($\approx$ 20 mg) was constantly monitored with a high-resolution microbalance ($\pm$ 0.1 µg) and recorded at 25 °C ($\pm$ 0.2 °C) under pure water vapour pressures. ^{1}H-NMR spectra were collected on a Bruker AVANCE III 400 MHz spectrometer. 10 mg of each sample were digested in 0.5 ml of 1.2% (wt) of HF solution prepared in DMSO-d6. From each spectrum, the amount of acetic acid per cluster was calculated. Field-emission scanning electron microscopy (FESEM) images were collected on a FEI Magellan 400 L scanning electron microscope at an acceleration voltage of 2.0 kV.

Synthesis of MOFs

Synthesis of UiO-66-NH_2 at room temperature:

Zr(acac)$_4$ (1169 mg, 2.4 mmol) and 2-aminoterephthalic acid (435 mg, 2.4 mmol) were mixed under stirring in 6 mL of a 50% (v/v) solution of acetic acid in water for 72 h at room temperature. The resulting yellow dispersion was washed once with water and three times with ethanol at room

temperature. The solid was dried for 12 h at 65 °C in a conventional oven to afford the final product (yield: 90%).

Synthesis of Zr-fumarate at room temperature:

Zr(acac)$_4$ (1169 mg, 2.4 mmol) and fumaric acid (278 mg, 2.4 mmol) were mixed under stirring in 6 mL of a 33% (v/v) or 50% (v/v) solution of acetic acid in water for 72 h at room temperature. The resulting white dispersion was washed once with water and three times with ethanol at room temperature. The solid was dried for 12 h at 65 °C in a conventional oven to afford the final product (yield: 83% to 88%).

Synthesis of UiO-66-(OH)$_2$ at room temperature:

Zr(acac)$_4$ (1169 mg, 2.4 mmol) and 2,5-dihydroxyterephthalic acid (476 mg, 2.4 mmol) were mixed under stirring in 6 mL of a 66% (v/v) solution of acetic acid in water for 72 h at room temperature. The resulting yellow dispersion was washed once with water and three times with ethanol at room temperature. The solid was dried for 12 h at 65 °C in a conventional oven to afford the final product (yield: 90%).

Synthesis of UiO-66-(COOH)$_2$ at 90°C:

Zr(acac)$_4$ (2194 mg, 4.5 mmol) and 2,5-dicarboxyterephthalic acid (1144 mg, 4.5 mmol) were mixed under stirring in 6 mL of a 33%, 50% or 66% (v/v) solution of acetic acid in water for 24 h at 90 °C. The resulting white dispersion was washed three times with water at room temperature. The solid was dried under vacuum to afford the final product (yield: 89% to 91%).

Synthesis of UiO-66-COOH at 90°C:

Zr(acac)$_4$ (2194 mg, 4.5 mmol) and 2-carboxyterephthalic acid (947 mg, 4.5 mmol) were mixed under stirring in 6 mL of a 66% (v/v) solution of acetic acid in water for 24 h at 90 °C. The resulting white dispersion was washed three times with water at room temperature. The solid was dried under vacuum to afford the final product (yield: 90%).

Synthesis of MIL-88A at room temperature:

Fe(acac)$_3$ (706 mg, 2.0 mmol) and fumaric acid (232 mg, 2.0 mmol) were mixed under stirring in 5 mL water for 72 h at room temperature. The resulting orange dispersion was washed once with water and three times with ethanol at room temperature. The solid was dried under vacuum to afford the final product (yield: 25%). In a subsequent synthesis, the yield was increased to 60% by running the reaction at 90 °C for 24 h.

Synthesis of CAU-10 at 90°C:

Al(acac)$_3$ (700 mg, 5.4 mmol) and isophthalic acid (947 mg, 4.5 mmol) were mixed in 6 mL water for 72 h at 90 °C under stirring. The resulting white dispersion was washed twice with water and several times with ethanol at room temperature. The solid was dried under vacuum to afford the final product (yield: 85%).

RESULTS & DISCUSSION

UiO-type MOFs are known for their large surface areas, chemical versatility and high hydrothermal, chemical and thermal stability, all of which make them good candidates for industrial applications such as catalysis, gas and pollutant capture, adsorption heat transformation

(AHT) and separation processes.[32-34] Among the different UiO-type MOFs, we started with a room-temperature aqueous batch synthesis of UiO-66-NH$_2$ from Zr(acac)$_4$. To this end, 0.4 M of Zr(acac)$_4$ and 0.4 M of 2-aminoterephthalic acid were added in 6 mL of a 50% (v/v) aqueous solution of acetic acid, and the resulting mixture (pH = 2.3) was stirred for 72 h at room temperature. Note that 0.4 M is the maximum useable concentration for Zr(acac)$_4$, which, at higher concentrations, becomes highly viscous and paste-like. For the synthesis of UiO-66-NH$_2$, the optimal concentration of acetic acid was 50% (v/v) (Table S1). Note that the concentration of acetic acid was crucial in this synthesis: the reaction only worked in the concentration range of 17% to 66% acetic acid (pH = 3.2 to 2.1). At lower concentrations, there was no reaction, whereas at higher concentrations, an amorphous solid was formed. After 72 h, the resulting yellow dispersion was washed once with water and three times with ethanol. Finally, the collected solid was dried for 12 h at 65 °C in a conventional oven to afford octahedral UiO-66-NH$_2$ submicron crystals (size: ~ 0.3-1μm) as a pure phase (yield: 90%) (Figure 1a), as confirmed by X-ray powder diffraction (XRPD) and N$_2$ sorption measurements (S$_{BET}$ = 1106 m^2 g^{-1}; (Figure 1b and 1d; Figure S1-S3). This S$_{BET}$ value is consistent with the literature values for UiO-66-NH$_2$ synthesized from other metal sources in water (Table 1).[24, 28] Moreover, the quality of the synthesized UiO-66-NH$_2$ was also assessed by analysing its water sorption capacity. The water sorption isotherm showed the expected S-type trend centred at 0.2 P/P$_0$, with a total water uptake of 0.44 g$_{water}$ g^{-1} (Figure 1e).[35] In this sample, the number of missing linkers per [Zr$_6$(OH)$_4$L$_6$] was found to be 0.9 (Figure S4), which is in agreement with reported values.[36]

The scalability of the room temperature aqueous synthesis of UiO-66-NH$_2$ submicron crystals using Zr(acac)$_4$ was demonstrated on the multigram-scale (Figure S5). For this, we stirred the precursors (0.4 M) in 500 ml of a mixture of water and acetic acid (50% (v/v)) for 72 h at room

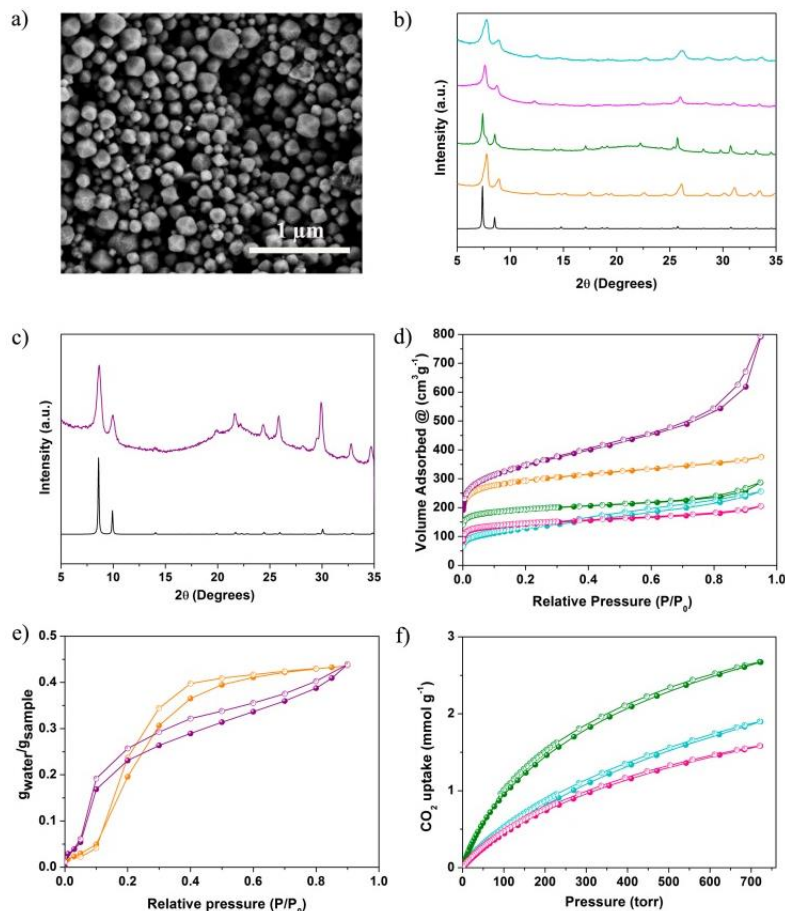temperature. After washing and drying, the resulting UiO-66-NH$_2$ powder (~53 g; yield: 95%) showed a S$_{BET}$ value of 1000 m^2 g^{-1}.

Figure 1. (a) Representative FESEM image of UiO-66-NH$_2$. (b) XRPD patterns for simulated UiO-66 (black) and synthesized UiO-66-NH$_2$ (orange), UiO-66-(OH)$_2$ (green), UiO-66-(COOH)$_2$ (pink) and UiO-66-COOH (blue). (c) XRPD patterns for simulated (black) and synthesized Zr-fumarate (purple). (d) N$_2$ adsorption (filled dots) and desorption (empty dots) isotherms at 77 K for UiO-66-NH$_2$ (orange), Zr-fumarate (purple), UiO-66-(OH)$_2$ (green), UiO-66-(COOH)$_2$ (pink) and UiO-66-COOH (blue). (e) Water sorption (filled dots) and desorption (empty dots) isotherms at room temperature for UiO-66-NH$_2$ (orange) and Zr-fumarate (purple) (f) CO$_2$ sorption (filled

dots) and desorption (empty dots) isotherms at room temperature of UiO-66-$(OH)_2$ (green), UiO-66-$(COOH)_2$ (pink) and UiO-66-COOH (blue).

We then extended our aqueous synthetic approach to two other UiO-66-type MOFs: Zr-fumarate and UiO-66-$(OH)_2$. For these syntheses, an aqueous mixture of acetic acid containing 0.4 M of $Zr(acac)_4$ and 0.4 M of either fumaric acid (for Zr-fumarate) or 2,5-dihydroxyterephthalic acid (for UiO-66-$(OH)_2$) was stirred for 72 h at room temperature. For Zr- fumarate, the optimal concentration of acetic acid was in the range of 33% to 50% (v/v); and for UiO-66-$(OH)_2$, it was 66% (v/v) (Table S2 and S3). Under these conditions, aggregates of nanocrystals (size: < 50 nm) of Zr-fumarate were synthesized in high yields (83% to 88%) and with an S_{BET} value of 1220-1249 m^2 g^{-1}. Note that these values are higher than most literature values (Figure 1c and 1d; Figure S6-S8).[24, 37-39] In Zr-fumarate, the number of missing linkers per $[Zr_6(OH)_4L_6]$ was calculated as 1.4 (Figure S9).[39] Given the promise of Zr-fumarate for water-related applications (*e.g.* delivery of drinking water from ambient air, storage of heat and/or refrigeration),[24, 37-41] we confirmed that synthesized Zr-fumarate retains the typical S-shaped isotherm, centred at 0.08 P/P_0, and high water uptake (0.43 g_{water} g^{-1}) (Figure 1e). The UiO-66-$(OH)_2$ was obtained (as aggregates of nanocrystals; size: < 100 nm) in high yield (94%), with a number of missing linkers per $[Zr_6(OH)_4L_6]$ of 1.3, and with an S_{BET} value of 733 m^2 g^{-1}. These results are consistent with the previously reported values for UiO-66-$(OH)_2$ synthesized in water (Figure 1b and 1d; Figure S10-S13).[27] Given the interest in UiO-66-$(OH)_2$ for CO_2-sorption application,[42] the quality of the prepared material was studied by measuring its CO_2 uptake capacity. Total CO_2 uptake was 2.6 mmol g^{-1} at 700 torr, which is consistent with the previously reported values (Figure 1f).[24, 37-40,]

Next, we performed aqueous syntheses of UiO-66-$(COOH)_2$ and UiO-66-COOH from $Zr(acac)_4$. Neither reaction worked at room temperature; they both required a temperature of 90 °C. To this

end, an aqueous mixture of acetic acid containing 0.75 M of Zr(acac)$_4$ and 0.75 M of either 2,5-dicarboxyterephthalic acid (for UiO-66-(COOH)$_2$) or 2-carboxyterephthalic acid (for UiO-66-COOH) was stirred for 24 h at 90 °C. An acetic acid concentration of 33% to 66% (v/v) gave submicrometre crystals (size: ~ 0.2-0.5 μm) of UiO-66-(COOH)$_2$ in high yield (89 to 91%) and with a good value S$_{BET}$ of 538 m^2 g^{-1} (Figure 1b and 1d; Table S4 and Figures S14-S16).[29] Similarly, an acid acetic concentration of 66% (v/v) afforded crystals of UiO-66-COOH (as aggregates of crystals; size: < 200 nm) in high yield (90%) and with a S$_{BET}$ value of 452 m^2 g^{-1} (Figure 1b and 1d; Table S4 and Figures S18-S20). The total CO$_2$ uptake at 700 torr was 1.6 mmol g^{-1} for UiO-66-(COOH)$_2$ and 1.9 mmol g^{-1} for UiO-66-COOH (Figure 1f).[29, 44] Here, the number of missing linkers per [Zr$_6$(OH)$_4$L$_6$] was 1.3 for UiO-66-(COOH)$_2$ and 1.8 for UiO-66-COOH (Figures S17, S21).[39] Note here that the slightly lower surface area observed in UiO-66-COOH[29] can be attributed to the presence of high amounts of defects.

Once we demonstrated that UiO-type MOFs could be synthesized in water using Zr(acac)$_4$, we then sought to prove the generality of our strategy by preparing MOFs based on other metal ions such as iron and aluminium. To this end, the Fe(III)-based MOF MIL-88A[44] was synthesized in water by stirring an aqueous mixture of 0.4 M of Fe(acac)$_3$ and 0.4 M of fumaric acid at room temperature for 72 h. After this period, the resulting orange dispersion was washed once with water and three times with ethanol. The collected solid was dried under vacuum to afford MIL-88A in the form of hexagonal rod-like crystals (yield: 25%; size: ~ 0.7-1.5 μm; Figure S22).[30] Interestingly, the yield could be increased up to 60% by simply heating the aqueous mixture at 90°C. Since this MOF is well-known for its structural breathing properties, this functionality was confirmed in the synthesized material by comparing the XRPD of the dry powder (closed form) to that of the material after it had been soaked in water for 20 minutes (open form) (Figure 2a).
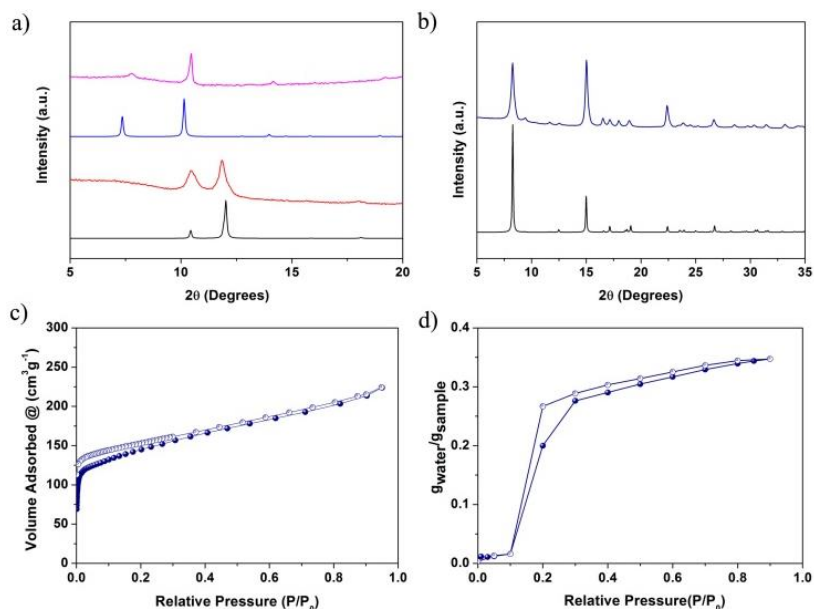
Figure 2. (a) XRPD patterns for the open (pink) and closed (red) forms of the synthesized MIL-88A, in comparison to the simulated patterns for the open (blue) and closed (blue) form. (b) XRPD patterns for simulated (black) and synthesized CAU-10 (blue). (c) N_2 adsorption (filled dots) and desorption (empty dots) isotherms at 77 K for CAU-10. (d) Water sorption (filled dots) and desorption (empty dots) isotherms at room temperature for CAU-10.

For an Al(III)-based MOF, we chose CAU-10, as it shows promise for many water sorption applications such as adsorption-driven heat pumps and chillers.[45] This MOF was synthesized by heating an aqueous mixture of 0.36 M of Al(acac)$_3$ and 0.30 M of isophthalic acid at 90 °C under continuous stirring for 72 h. The resulting white dispersion was then washed twice with water and four times with ethanol, and the collected solid dried under vacuum to afford submicrometre crystals of CAU-10 (size: ~ 0.2-0.5 μm) in good yield (85%; Figure 2b; Figure S23). N_2 and water sorption experiments revealed an S_{BET} value of 520 m^{2}g^{-1} and total water uptake of 0.34 g$_{water}$ g^{-1},

with the expected S-type trend centred at 0.2 P/P_0 (Figure 2c, 2d). These values are all in agreement with the reported values.[22]

CONCLUSION

We have shown that metal acetylacetonate complexes can be used as an alternative source of metals to synthesize MOFs in water. We used metal acetylacetonates to synthesize various MOFs at either RT (UiO-66-NH_2, Zr-fumarate, UiO-66-OH_2 and MIL-88A) or 90 °C (UiO-66-$(COOH)_2$, UiO-66-COOH and CAU-10). The yields were all good, ranging from 60% for MIL-88A to > 85% for all the others. Since metal acetylacetonate complexes are considered green reagents for numerous industrial processes, our strategy should enable the development of a simple, environmentally sound process for production of MOFs in water and consequently, accelerate their commercialization.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Additional synthetic details, XRPD patterns, surface area measurements, FESEM images (PDF)

AUTHOR INFORMATION

Corresponding Author

* E-mail: inhar.imaz@icn2.cat, daniel.maspoch@icn2.cat

Notes

There are no conflicts to declare.

REFERENCES

1.   Sodhi, R. K.; Paul, S. An Overview of Metal Acetylacetonates: Developing Areas/Routes to New Materials and Applications in Organic Syntheses. *Catal. Surv. Asia*, **2017,** *22*, 31-62.

2.   Nor, H. M.; Ebdon, J. R. Telechelic Liquid Natural Rubber: A Review. *Prog. Polym. Sci.*, **1998**, *23*, 143-177.

3.   Przybyszewska, M.; Zaborski, M.; Jakubowski, B.; Zawadiak, J. Zinc Chelates as New Activators for Sulphur Vulcanization of Acrylonitrile-Butadiene Elastomer. *eXPRESS Polym. Lett.*, **2009,** *3*, 256-266.

4.   Yamada, K.; Chow, T. Y.; Horihata, T.; Nagata, M. J. A. Low Temperature Synthesis of Zirconium Oxide Coating using Chelating Agents. *Non-Cryst. Solids*, **1988**, *100*, 316-320.

5.   Ibe, T.; Frings, R. B.; Lachowicz, A.; Kyo, S.; Nishide, H. Nitroxide Polymer Networks Formed by Michael Addition: on Site-Cured Electrode-Active Organic Coating. *Chem. Commun.*, **2010,** *46*, 3475-3477.

6.   Shimp, D. A. Metal Acetylacetonate/Alkylphenol Curing Catalyst for Polycyanate Esters of Polyhydric Phenols. US Patent 4 847 233, July 27, 1987.

7.   Smith, J. D. B. Metal Acetylacetonates as Latent Accelerators for Anhydridehyphen;Cured Epoxy Resins. *J. Appl. Polym. Sci.*, **1981**, *26*, 979-986.

8.   Sannino, F.; Pernice, P.; Imparato, C.; Aronne, A.; D'Errico, G.; Minieri, L.; Perfetti, M.; Pirozzi, D. Hybrid TiO$_2$-Acetylacetonate Amorphous Gel-Derived Material with Stably Adsorbed Superoxide Radical Active in Oxidative Degradation of Organic Pollutants. *RSC Advances*, **2015**, *5*, 93831-93839.

9.   Hudson, R. L. Shelf Stable Nonwoven Fabrics and Films. US Patent 5 393 831, June 5, 1993.

10.   Preparation Method for High-Brightness Calcium Acetylacetonate for PVC (Polyvinyl Chloride) Heat Stabilizer. CN Patent 103 086 857, June 5, 2013.

11.   Gorczynski, J. L.; Chen, J.; Fraser, C. L. Iron Tris(dibenzoylmethane)-Centered Polylactide Stars: Multiple Roles for the Metal Complex in Lactide Ring-Opening Polymerization. *J. Am. Chem. Soc.*, **2005**, *127*, 14956-14957.

12.   Czech, Z.; Wojciechowicz, M. The Crosslinking Reaction of Acrylic PSA Using Chelate Metal Acetylacetonates. *Eur. Polym. J.*, **2006**, *42*, 2153-2160.

13.   Wu, J.; Jiang, X.; Zhang, L.; Cheng, Z.; Zhu, X. Iron-Mediated Homogeneous ICAR ATRP of Methyl Methacrylate under ppm Level Organometallic Catalyst Iron(III) Acetylacetonate. *Polymers*, **2016,** *8*, 29.

14.   Dobrzynski, P. Mechanism of ε-Caprolactone Polymerization and ε-Caprolactone/Trimethylene Carbonate Copolymerization Carried out with Zr(Acac)$_4$. *Polymer* **2007,** *48*, 2263-2279.

15.   Levis, R. J. *Sax's Dangerous Properties of Industrial Materials (8th ed.)*. Van Nostrand Reinhold, New York, 1992.

16.   (a) Julien, P. A.; Mottillo, C.; Friscic, T. Metal-Organic Frameworks Meet Scalable and Sustainable Synthesis. *Green Chem.* **2017,** *19*, 2729-2747.

17.   (a) Rubio-Martinez, M.; Avci-Camur, C.; Thornton, A. W.; Imaz, I.; Maspoch, D.; Hill, M. R. New Synthetic Routes Towards MOF Production at Scale. *Chem. Soc. Rev.* **2017**, *46* (11), 3453-3480; (b) Zhang, J.; White, G. B.; Ryan, M. D.; Hunt, A. J.; Katz, M. J. Dihydrolevoglucosenone (Cyrene) As a Green Alternative to N,N-Dimethylformamide (DMF) in MOF Synthesis. *ACS Sustainable Chem. Eng.* **2016**, *4* (12), 7186-7192; (c) Paseta, L.; Potier, G.; Sorribas, S.; Coronas, J. Solventless Synthesis of MOFs at High Pressure. *ACS Sustainable Chem. Eng.* **2016**, *4* (7), 3780-3785; (d) Doan, H. V.; Fang, Y.; Yao, B.; Dong, Z.; White, T. J.; Sartbaeva, A.; Hintermair, U.; Ting, V. P. Controlled Formation of Hierarchical Metal–Organic Frameworks Using CO$_2$-Expanded Solvent Systems. *ACS Sustainable Chem. Eng.*, **2017**, *5* (9), 7887-7893.

18.   Reinsch, H. "Green" Synthesis of Metal-Organic Frameworks. *Eur. J. Inorg. Chem.* **2016,** 2016, *27*, 4290-4299.

19.   Reinsch, H.; Stock, N. Synthesis of MOFs: a Personal View on Rationalisation, Application and Exploration. *Dalton Trans.*, **2017**, *46*, 8339-8349.

20.   Gaab, M.; Trukhan, N.; Maurer, S.; Gummaraju, R.; Müller, U. The Progression of Al-Based Metal-Organic Frameworks − From Academic Research to Industrial Production and Applications. *Microporous Mesoporous Mater.* **2012,** *157*, 131-136.

21.   Reinsch, H.; Bueken, B.; Vermoortele, F.; Stassen, I.; Lieb, A.; Lillerud, K. P.; De Vos, D. Green Synthesis of Zirconium-MOFs. *CrystEngComm* **2015,** *17*, 4070-4074.

22.   Lenzen, D.; Bendix, P.; Reinsch, H.; Fröhlich, D.; Kummer, H.; Möllers, M.; Hügenell, P. P. C.; Gläser, R.; Henninger, S.; Stock, N. Scalable Green Synthesis and Full-Scale Test of the Metal–Organic Framework CAU-10-H for Use in Adsorption-Driven Chillers. *Adv. Mater.* **2018,** *30*, 1705869.

23.   Reinsch, H.; Stassen, I.; Bueken, B.; Lieb, A.; Ameloot, R.; De Vos, D. First Examples of Aliphatic Zirconium MOFs and the Influence of Inorganic Anions on their Crystal Structures. *CrystEngComm* **2015,** *17*, 331-337.

24.   Reinsch, H.; Waitschat, S.; Chavan, S. M.; Lillerud, K. P.; Stock, N. A Facile "Green" Route for Scalable Batch Production and Continuous Synthesis of Zirconium MOFs. *Eur. J. Inorg. Chem.* **2016**, 4490-4498.

25.   Sanchez-Sanchez, M.; Getachew, N.; Diaz, K.; Diaz-Garcia, M.; Chebude, Y.; Diaz, I. Synthesis of Metal-Organic Frameworks in Water at Room Temperature: Salts as Linker Sources. *Green Chem.* **2015,** *17*, 1500-1509.

26.   Garzon-Tovar, L.; Carne-Sanchez, A.; Carbonell, C.; Imaz, I. and Maspoch, D. Optimised Room Temperature, Water-Based Synthesis of CPO-27-M Metal-Organic Frameworks with High Space-Time Yields. *J. Mater. Chem. A*, **2015**, *3*, 20819-20826.

27.   Hu, Z.; Peng, Y.; Kang, Z.; Qian, Y.; Zhao, D. A Modulated Hydrothermal (MHT) Approach for the Facile Synthesis of UiO-66-Type MOFs. *Inorg. Chem.* **2015,** *54*, 4862-4868.

28.   Avci-Camur, C.; Troyano, J.; Perez-Carvajal, J.; Legrand, A.; Farrusseng, D.; Imaz, I.; Maspoch, D. Aqueous Production of Spherical Zr-MOF Beads via Continuous-Flow Spray-Drying. *Green Chem.* **2018,** *20*, 873-878.

29.   Ragon, F.; Campo, B.; Yang, Q.; Martineau, C.; Wiersum, A. D.; Lago, A.; Guillerm, V.; Hemsley, C.; Eubank, J. F.; Vishnuvarthan, M.; Taulelle, F.; Horcajada, P.; Vimont, A.; Llewellyn, P. L.; Daturi, M.; Devautour-Vinot, S.; Maurin, G.; Serre, C.; Devic, T.; Clet, G. Acid-Functionalized UiO-66(Zr) MOFs and their Evolution After Intra-Framework Cross-Linking: Structural Features and Sorption Properties. *J. Mater. Chem. A* **2015**, *3*, 3294-3309.

30.   Wang, J.; Wan, J.; Ma, Y.; Wang, Y.; Pu, M.; Guan, Z. Metal-Organic Frameworks MIL-88A with Suitable Synthesis Conditions and Optimal Dosage for Effective Catalytic Degradation of Orange G Through Persulfate Activation. *RSC Advances* **2016,** *6*, 112502-112511.

31.   (a) Llewellyn, P.; Maurin, G.; Rouquerol J. *Adsorption by Powders and Porous Solids (2nd Edition)*. Academic press, Poland, 2012. (b) Gomez-Gualdro, D. A.; Moghadam, P. Z.; Hupp, J.

T.; Farha, O. K.; Snurr, K. Q. Application of Consistency Criteria To Calculate BET Areas of Micro- And Mesoporous Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2016**, 138, 215−224.

32.   (a) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. *J. Am. Chem. Soc.* **2008,** *130*, 13850-13851; (b) Bai, Y.; Dou, Y.; Xie, L. H.; Rutledge, W.; Li, J. R.; Zhou, H. C. Zr-based Metal–Organic Frameworks: Design, Synthesis, Structure, and Applications. *Chem. Soc. Rev.*, **2016**, *45*, 2327-2367; (c) Han, Y.; Li, J. R.; Xiea, Y.; Guo G. Substitution Reactions in Metal–Organic Frameworks and Metal–Organic Polyhedra. *Chem. Soc. Rev.*, **2014**, *43*, 5952-5981.

33.   Liu, X.; Demir, N. K.; Wu, Z.; Li, K., Highly Water-Stable Zirconium Metal–Organic Framework UiO-66 Membranes Supported on Alumina Hollow Fibers for Desalination. *J. Am. Chem. Soc.* **2015**, *137*, 6999-7002.

34.   (a) Kim, H.; Yang, S.; Rao, S. R.; Narayanan, S.; Kapustin, E. A.; Furukawa, H.; Umans, A. S.; Yaghi, O. M.; Wang, E. N. Water Harvesting from Air with Metal-Organic Frameworks Powered by Natural Sunlight. *Science* **2017,** *356*, 430-434; (b) Garzón-Tovar, L.; Pérez-Carvajal, J.; Imaz, I.; Maspoch, D. Composite Salt in Porous Metal-Organic Frameworks for Adsorption Heat Transformation. *Adv. Funct. Mater.*, **2017**, *27*, 1606424.

35.   Jeremias, F.; Lozan, V.; Henninger, S. K.; Janiak, C. Programming MOFs for Water Sorption: Amino-Functionalized MIL-125 and UiO-66 for Heat Transformation and Heat Storage Applications. *Dalton Trans.* **2013**, *42*, 15967-15973.

36.   DeStefano, M. R.; Islamoglu , T.; Garibay, S. J.; Hupp, J. T.; Farha, O. K. Room-Temperature Synthesis of UiO-66 and Thermal Modulation of Densities of Defect Sites. *Chem. Mater.* **2017**, *29*, 1357-1361.

37.   Furukawa, H.; Gándara, F.; Zhang, Y.-B.; Jiang, J.; Queen, W. L.; Hudson, M. R.; Yaghi, O. M. Water Adsorption in Porous Metal–Organic Frameworks and Related Materials. *J. Am. Chem. Soc.* **2014,** *136*, 4369-4381.

38.   Canivet, J.; Bonnefoy, J.; Daniel, C.; Legrand, A.; Coasne, B.; Farrusseng, D. Structure-Property Relationships of Water Adsorption in Metal-Organic Frameworks. *New J. Chem.* **2014,** *38*, 3102-3111.

39.   Hu, Z.; Castano, I.; Wang, S.; Wang, Y.; Peng, Y.; Qian, Y.; Chi, C.; Wang, X.; Zhao, D. Modulator Effects on the Water-Based Synthesis of Zr/Hf Metal–Organic Frameworks: Quantitative Relationship Studies between Modulator, Synthetic Condition, and Performance. *Cryst. Growth Des.* **2016,** *16*, 2295-2301.

40.   Yang, H.; Zhu, H.; Hendrix, M. M. R. M.; Lousberg, N. J. H. G. M.; With, G. d.; Esteves, A. C. C.; Xin, J. H. Temperature Triggered Collection and Release of Water from Fogs by a Sponge Like Cotton Fabric. *Adv. Mater.* **2013**, *25*, 1150-1154.

41.   Kalmutzki, M. J.; Diercks, C. S.; Yaghi, O. M. Metal–Organic Frameworks for Water Harvesting from Air. *Adv. Mater.*, **2018**, 1704304.

42.   Rada, Z. H.; Abid, H. R.; Shang, J.; Sun, H.; He, Y.; Webley, P.; Liu, S.; Wang, S. Functionalized UiO-66 by Single and Binary $(OH)_2$ and NO_2 Groups for Uptake of CO_2 and CH_4. *Ind. Eng. Chem. Res.* **2016,** *55*, 7924-7932.

43.   Biswas, S.; Zhang, J.; Li, Z.; Liu, Y.-Y.; Grzywa, M.; Sun, L.; Volkmer, D.; Van Der Voort, P. Enhanced Selectivity of CO_2 over CH_4 in Sulphonate-, Carboxylate- and Iodo-Functionalized UiO-66 Frameworks. *Dalton Trans.* **2013,** *42*, 4730-4737.

44.   Ferey, G.; Serre, C. Large Breathing Effects in Three-Dimensional Porous Hybrid Matter: Facts, Analyses, Rules and Consequences. *Chem. Soc. Rev.* **2009,** *38*, 1380-1399.

45.   de Lange, M. F.; Zeng, T.; Vlugt, T. J. H.; Gascon, J.; Kapteijn, F. Manufacture of Dense CAU-10-H Coatings for Application in Adsorption Driven Heat Pumps: Optimization and Characterization. *CrystEngComm* **2015,** *17*, 5911-5920.