The Chemistry behind Room Temperature Synthesis of Hafnium and Cerium UiO-66 Derivatives

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The Chemistry behind Room Temperature Synthesis of Hafnium and Cerium UiO-66 Derivatives

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As metal–organic framework (MOF) production scales up to meet industrial needs, the MOF field finds itself looking for less hazardous and more energy efficient synthetic protocols. Effective methods that operate at ambient conditions will be a huge production advantage that can promote MOF industrialization. To deepen our understanding of MOF room temperature (RT) synthesis, we investigate RT formation of Hf and Ce UiO-66 derivatives. We report the first successful RT synthesis of Hf UiO-66-X (X= -COOH, $-NO_2$, $-NH_2$, -Br and $-(OH)_2$) by first forming a Hafnium oxocluster at 80 °C in water or 120 °C in DMF and subsequently adding the linker at RT. Further, we present a green, one-step synthesis protocol for Ce UiO-66 derivatives in aqueous media either with or without a modulator. We compare the crystallinity, morphology, and yield of these one-step and two-step RT methods. This study advances current chemical understanding of RT synthesis of Hf and Ce UiO-66 structures and could help material chemists develop green RT synthesis protocols for other MOF structures.

1. Introduction

Room temperature (RT) synthesis is economically and environmentally advantageous in industrial scale production of metal-organic frameworks (MOFs).[1–4] RT synthesis not only benefits industrialization efforts but also opens the field to new applications such as bioaugmentation,[5] in which temperature-sensitive biological molecules are incorporated into abiotic structures like MOFs.[5–7] Despite the clear attraction of these sustainable protocols, MOF RT synthesis is rare and the mechanisms and kinetics are largely unexplored. The handful of MOF RT synthesis methods that have been reported can be categorized as one-step or multistep.[1] The one-step method is simple: a linker and a metal salt are combined in solution and the product forms spontaneously. The two-step method requires pre-treatment of either the inorganic or organic component before they are introduced and reacted at RT. Development of new RT synthesis methods for MOFs is of high demand and promises to advance this growing field.

Of the many different MOF structures,[8–10] the UiO-66 family is of particular interest as the structures are chemically stable, structurally robust, and highly porous, making them prime candidates for many practical applications.[11–15] Although UiO-66 is usually assembled with zirconium (Zr), variants using hafnium (Hf) and cerium (Ce) metal clusters not only offer advantageous chemical, thermal, and mechanical stability, but also boast acute Lewis acidity that results in interesting catalytic properties.[16] The similar chemical behaviour of Zr-, Hf- and Ce-ions[17] make it possible to synthesize isostructural Hf [18] and Ce [19] UiO-66 structures. The Hf analogue is actually more stable than Zr UiO-66 and has higher Lewis acidity,[20] making it especially useful in catalysis and gas separation.[16] Hf UiO-66 nanoparticles can also be used for cancer treatment[21,22] because they are relatively safe, exhibit high drug/gene loading capacities, and readily degrade in the body.[23–26] Ce UiO-66 exhibits photooxidative properties due to the facile switching of Ce^{4+}/ Ce^{3+} redox couple, making it useful in photocatalysis, oxidation catalysis, and redox reactions.[27]

The existing literature presents a few examples of one- and multistep RT syntheses of Zr UiO-66. One of the first one-step methods used ionic liquids to accelerate the reaction time, but ionic liquids are expensive and difficult to remove during the washing process.[28] In another work, acetylacetonate complexes were used as the metal source, but the resulting samples were poorly crystalline.[29] More recently, a straightforward and sustainable strategy that simply mixed the inorganic and organic components in aqueous media was used with appreciable success.[30] A scattering of solventless mechanochemical RT syntheses have also been reported,[31–34] but the appeal of these

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Electronic Supplementary Information (ESI) available: SEM and PXRD of the synthesized samples. See DOI: 10.1039/x0xx00000x straightforward methods is tempered by the low quality of the crystals they produce. Multistep RT syntheses of Zr UiO-66 are more variable, and generally involve either pre-heating of a Zr precursor (in DMF [35] or H_2O [36]), ligand pre-heating,[37] the use of linker salts,[36,38] or post-synthetic exchange.[39]

Only recently has the focus of UiO-66 RT synthesis shifted from Zr to other metals. The first RT synthesis of a Ce UiO-66 structure was reported in 2019,[40] when Gu and colleagues synthesized Ce UiO-66-X (X = -H, $-CH_3$, -Br, $-NO_2$) at RT by introducing solubility enhancing additives (NO_3^-, ClO_4^-, SCN^-, I^-). These ions are helpful in forming frameworks, but unfortunately necessitate strenuous washing to clean the final product. Another group has reported an additive-free RT synthesis of unfunctionalized Ce-UiO-66 synthesis,[41] but there are no reports of additive-free functionalized Ce UiO-66 synthesis. To the best of our knowledge, no studies of RT synthesis of Hf UiO-66 have been reported.

In this work, we present RT synthesis protocols for Hf and Ce UiO-66 derivatives. We began with the simplest and greenest methods: aqueous one-step reactions without any pre-heating, and progressed toward more complex two-step methods that involved pre-heating of the metal precursor (Fig. 1). During optimization of the one-step method, we probed the effects of various modulators (formic acid, acetic acid, benzoic acid, hydrochloric acid, or no modulator). In the case of two-step synthesis optimization, we explored metal cluster formation by pre-heating the inorganic precursor in water at 80 °C or in DMF at 80 °C or 120 °C. We compared the crystallinity, morphology, and yield of the products to evaluate the success of each method.

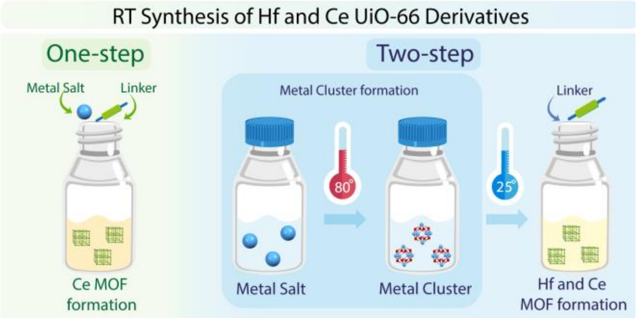

Fig. 1 Schematic illustration of the one-step and two-step RT synthesis methods of Hf and Ce UiO-66 derivatives.

2. Results and discussion

2.1 Synthesis of Hf UiO-66 derivatives

We began with RT synthesis of Hf UiO-66 derivatives because hafnium is a close analogue of zirconium; both are transition metals with similar atomic radii, physicochemical properties, and coordination chemistry.[17] However, they differ in one key regard: Hf has slower reaction kinetics and forms stronger M-O bonds than Zr, and this feature directly affects synthesis with these metals.[17]

The formation of the hexanuclear metal (IV) cluster is critical in the assembly of UiO-66 structures, so it is important to account for the many variables that impact this process, including solvent, solution acidity, and temperature.[42] Recently, Serre and co-workers demonstrated the formation of Zr UiO-66-NH_2 and Zr UiO-66-COOH derivatives in aqueous media in the presence of a formic acid modulator without any energy input.[30]

To probe whether it is possible to isoreticularly synthesize Hf UiO-66 analogues under similar synthetic conditions, we reacted equimolar amounts of $HfCl_4$ precursor and functionalized terephthalic acid linker in the presence of formic acid. We selected common derivatives of terephthalic acid with a range of acidities and nucleophilicities to represent a broad spectrum of chemical functionalities: nitro- ($-NO_2$), carboxy- (-COOH), amino- ($-NH_2$), bromo- (-Br), and hydroxy- ($(-OH)_2$). Functionalized derivatives of UiO-66 are particularly interesting for applications in catalysis and adsorption, where they outperform unsubstituted analogues.[43–45] The functionalization of terephthalic acid also greatly affects the physicochemical properties of the linkers, generally making them more reactive and soluble, therefore facilitating the reaction and permitting milder synthesis conditions. In this one-step aqueous RT method, Hf UiO-66 did not form from the nitro-, carboxy-, amino-, bromo-, or hydroxy-substituted terephthalic acid ligands. These results reflect the high energy barrier of Hf oxocluster formation, which exceeds the barrier of Zr clusters formation.[17,46] Consequently, we were unable to synthesize the functionalized Hf derivatives under the mild conditions that produce functionalized Zr derivatives[30]. Unsurprisingly, the Hf cluster also failed to form in DMF at RT, where the trace amounts of water present are insufficient to facilitate cluster formation. In short, the failure to synthesize Hf UiO-66 derivatives via one-step methods both in water and DMF indicates that the energy barrier of $[Hf_6O_4(OH)_4]^{12+}$ cluster formation is too high to occur without heating.

To overcome the high energy barrier of Hf oxocluster formation, we shifted our focus from one-step to two-step methods that pre-heat the inorganic precursor in water or DMF to form the clusters before MOF framework assembly. In pursuit of the greenest synthesis, we began with two-step synthesis in water, pre-heating the hafnium precursor at 80 °C for 2 hours. After the solution was cooled, an equimolar amount of linker was added at RT. PXRD patterns of the resulting material showed that this method was effective in producing two highly crystalline structures (Hf UiO-66-NO_2 and Hf UiO-66-COOH) at high yields (>90%), and with sharp morphologies (Fig. 2, 3a, S1). Unfortunately, this method failed to produce the amino-, bromo- and hydroxy-derivatives, presumably due to the low solubility of these linkers in the water/formic acid solution (Fig. S2).

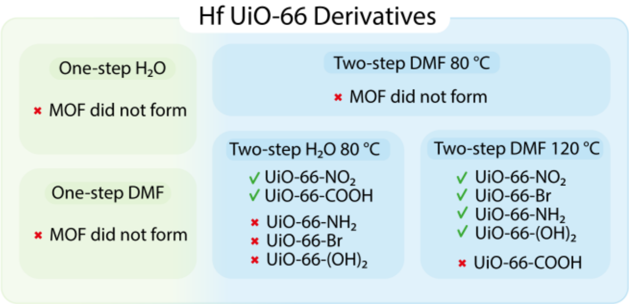

Fig. 2 Schematic overview of the one-step and two-step synthesis methods of Hf UiO-66-X (X= -NO_2, -COOH, -NH_2, -Br and -$(OH)_2$).

To overcome the linker solubility issue and accelerate metal cluster formation, we turned to a new solvent: DMF. Just as in the two-step water method, we began by pre-heating the Hf precursor at 80 °C in DMF and then introduced the linker at RT. However, the MOF did not form, which indirectly suggests that $[Hf_6O_4(OH)_4]^{12+}$ clusters did not form at 80 ºC during pre-heating. To facilitate Hf oxocluster formation, we increased the temperature to 120 °C. Using equimolar amounts of metal salt and linker, samples of low crystallinity were produced (Fig. S3). However, when we used 3-fold excess of a linker (as had been done in previous two-step Zr UiO-66 RT synthesis[35]), we obtained highly crystalline Hf UiO-66-NO_2, Hf UiO-66-NH_2, and low crystallinity Hf UiO-66-$(OH)_2$ structures with high yields (>90%) and highly crystalline Hf UiO-66-Br with slightly lower yield (51%) (Fig. 3b, S4). Failure to synthesize Hf UiO-66-COOH might be explained by the specific coordination chemistry of 1,2,4-benzenetricarboxilic acid;[47,48] the tridentate linker can transiently coordinate to metal centres in a number of geometries, complicating the formation of a MOF lattice. It should be noted that Hf UiO-66 with unfunctionalized terephthalic acid linker did not form in water or in DMF. Nonetheless, this two-step DMF method was very effective in synthesizing all of the other structures and we expect its versatility to extend to even more diverse linker classes.

After PXRD analysis was used to validate the crystallinity of the Hf UiO-66-X (X= -COOH, -NO_2, -NH_2, -Br and -$(OH)_2$) derivatives (Fig. 3a, b) and TGA (Fig. S5) confirmed their thermal stability, we examined the morphologies of the samples (Fig. S1, S4). The Hf UiO-66-NO_2 and Hf UiO-66-NH_2 nanoparticles were not only small (<100 nm) and uniformly sized (Fig. 4), but also highly crystalline (a felicitous combination that is difficult to achieve). The Hf UiO-66-NO_2 particles synthesized via the two-step method in water averaged 62±18 nm in diameter (Fig. 4a) and the analogous particles synthesized in DMF method averaged 30±9 nm in diameter (Fig. 4b). The Hf UiO-66-NH_2 nanoparticles averaged 77±27 nm (Fig. 4c). The other Hf UiO-66 derivatives produced slightly less uniform particles (Fig. S1, S4). Thus, we demonstrate that uniform, crystalline Hf UiO-66 nanoparticles can be obtained by RT synthesis.

To sum up, the synthesis of Hf UiO-66 derivatives at room temperature is only possible via the two-step method due to the high energy barrier of Hf oxocluster formation, but this synthesis (in water or DMF) generally produces UiO-66 derivatives with sharp morphologies and high yields (>90%).

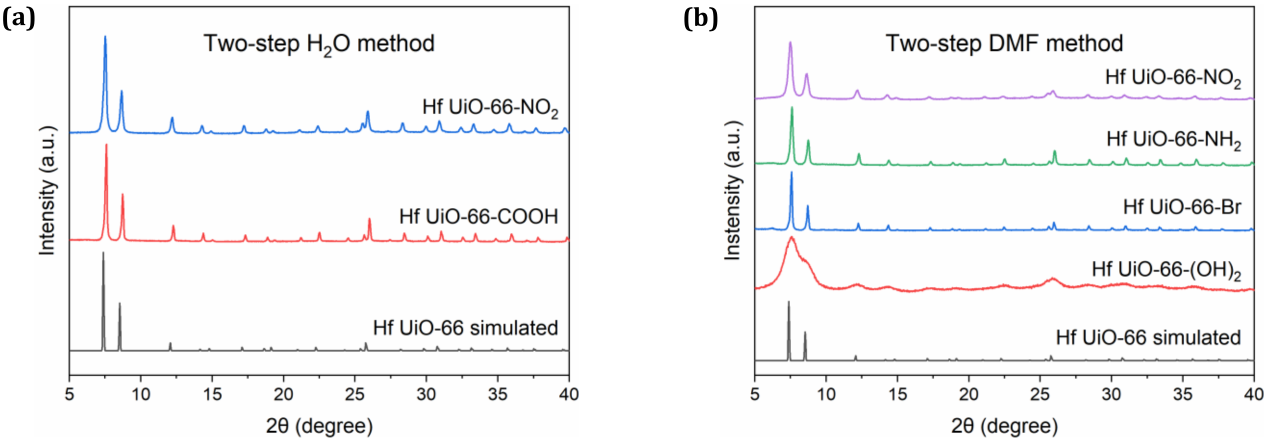

Fig. 3 Experimental PXRD of (a) Hf UiO-66-NO_2, Hf UiO-66-COOH formed by the two-step H_2O method with pre-heating at 80 °C; (b) Hf UiO-66-NO_2, Hf UiO-66-NH_2, Hf UiO-66-Br, Hf UiO-66-$(OH)_2$ synthesized by the two-step DMF method with pre-heating at 120 °C and simulated PXRD of Hf UiO-66.

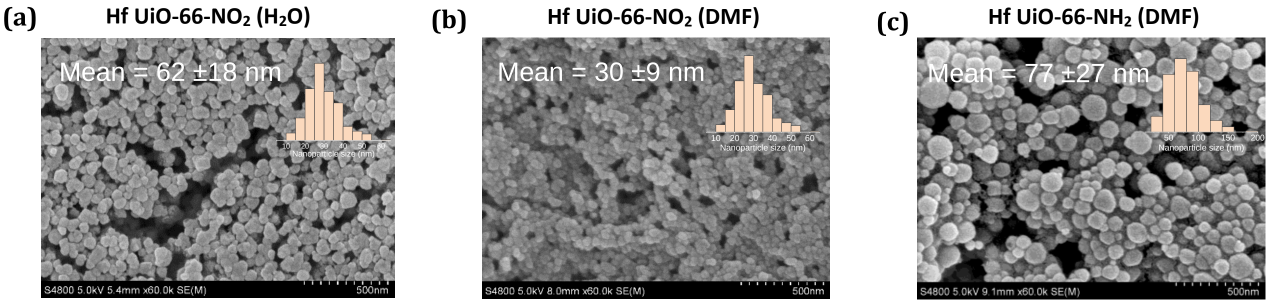

Fig. 4 SEM images of (a) Hf UiO-66-NO_2 synthesized by the two-step H_2O method with pre-heating at 80 °C; (b) Hf UiO-66-NO_2 and (c) Hf UiO-66-NH_2 synthesized by the two-step DMF method with pre-heating at 120 °C.

2.2 Synthesis of Ce UiO-66 derivatives

In contrast to Zr and Hf hexanuclear clusters, Ce oxoclusters readily self-assemble in aqueous media without heating or a modulator,[40,41] suggesting that the Ce-based MOFs are much more amenable to green, aqueous synthesis techniques. To test this, we performed timed experiments of Ce UiO-66-NO_2 formation in aqueous media with (Fig. S6) and without a modulator (Fig. S7). PXRD data evidenced that it is not only possible to form crystalline Ce UiO-66-NO_2 structures without a modulator, but that the MOF formation can be done with high yields (>90%) in just 15 min (Fig. 5a).

Synthesis of the other Ce UiO-66 derivatives in aqueous media without a modulator were also attempted. Under these conditions, Ce UiO-66-Br and Ce UiO-66-COOH were successfully synthesized, producing crystalline particles of small size and high yield (>90 %) (Fig. 5b, S8). Ce UiO-66-NH_2 and Ce UiO-66-$(OH)_2$ did not form in the absence of a modulator, probably due to low linker solubility in water. Nevertheless, the successful modulator-free syntheses of three MOFs at RT represent a valuable discovery.

In an attempt to better understand modulator effects on Ce UiO-66 formation at RT and to synthesize Ce UiO-66-NH_2 and Ce UiO-66-$(OH)_2$ structures, we performed a series of experiments with monocarboxylic acid modulators of different acidities,[49] namely formic acid (pKa ‒ 3.5), benzoic acid (pKa ‒ 4.2) and acetic acid (pKa ‒ 4.8), as well as the most common inorganic acid modulator for UiO-66 synthesis, hydrochloric acid (pKa ‒ -5.9).

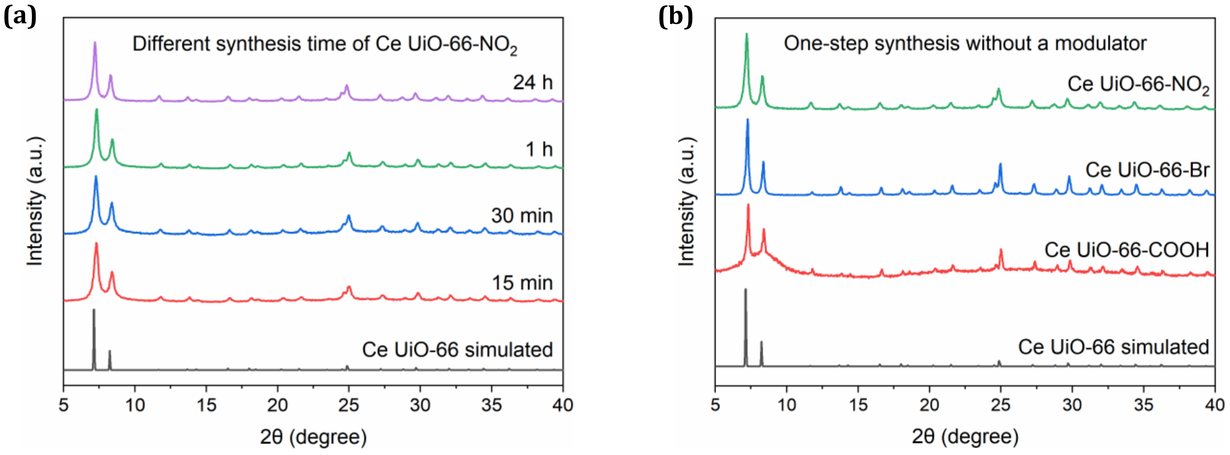

Fig. 5 Experimental PXRD of (a) Ce UiO-66-NO_2 synthesized by the one-step H_2O method without a modulator after 15 min, 30 min, 1 h, or 24 h; (b) Ce UiO-66-NO_2, Ce UiO-66-Br and Ce UiO-66-COOH synthesized by the one-step H_2O method without a modulator after 24h and simulated PXRD of Ce UiO-66.

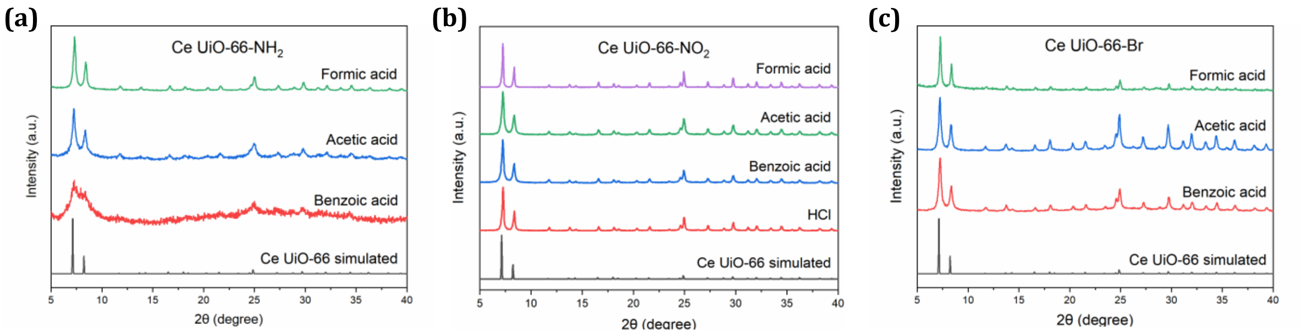

Fig. 6 Experimental PXRD of (a) Ce UiO-66-NH_2; (b) Ce UiO-66-NO_2 and (c) Ce UiO-66-Br synthesized with formic acid, acetic acid, benzoic acid or HCl and simulated PXRD of Ce UiO-66.

Ce UiO-66-NH_2 could be successfully synthesized when formic and acetic acid modulators were used, while a benzoic acid modulator resulted in poor quality crystals, likely due to the limited solubility of both benzoic acid and 2-aminoterephthalic acid (Fig. 6a, S9). Ce UiO-66-NH_2 did not form at all in the presence of HCl, possibly because this acid quickly protonated the linker, making it inaccessible for coordination to a metal cluster.

In the case of nitro- and carboxy-functionalized Ce UiO-66 derivatives, the PXRD patterns showed that carboxylic acid and inorganic acid modulators could be interchangeably used to reliably synthesize crystalline Ce UiO-66-NO_2 (Fig. 6b, S10) and UiO-66-COOH (Fig. S11) at high yields (>90%).

A different trend was observed in the case of Ce UiO-66-Br: the acidity of the modulator was found to be critical to MOF formation. Acetic acid and benzoic acid (both of moderate acidity) produced highly crystalline structures at high yields (>90%), similar to synthesis without a modulator (Fig. 6c, S12). In contrast, formic acid (higher acidity) inhibited MOF formation and resulted in low yields (8%) (Fig. 6c, S12), and synthesis attempts using the strongly acidic HCl modulator failed to produce any product at all.

Ce UiO-66-$(OH)_2$ was the only structure that could not be synthesized by the one-step methods, probably due to the chemistry of the linker: the dihydroxy groups can coordinate to Ce ions in many different ways, leading to a number of possible geometries[50,51] and complicating the formation of the targeted UiO-66 crystal structures. The two-step synthesis of Ce UiO-66-$(OH)_2$, (first pre-heating the Ce precursor at 80 °C in water) was also unsuccessful.

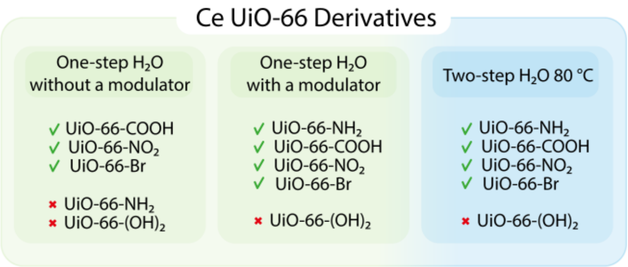

Fig. 7 Schematic overview of the one-step and two-step synthesis methods of Ce UiO-66-X (X= -COOH, -NO_2, -NH_2, -Br and -$(OH)_2$).

We tested the analogous two-step syntheses with amino-, carboxy-, nitro- and bromo- linkers and these experiments successfully produced structures of Ce UiO-66-NO_2, UiO-66-COOH, UiO-66-Br, UiO-66-NH_2 (Fig. 7, S13). When comparing the crystallinity, morphology, and yield of the products of the different methods (one-step synthesis with/ without a modulator and two-step synthesis with a modulator) several trends emerge: (1) modulator use results in more crystalline structures in both one-step and two-step methods; (2) modulator-free synthesis produces smaller particles; and (3) the yields of the two-step methods (~80%) are generally lower than the yields of the one-step methods (~90%). Therefore, both one-step and two-step strategies are viable methods to synthesize Ce UiO-66 derivatives, but one-step strategies are not just simpler and greener, but also result in the best balance of crystallinity, morphology, and yield.

3. Conclusions

In this work, we performed a systematic study of RT synthesis of Hf and Ce UiO-66-X (X=-NO_2, -COOH, -NH_2, -Br, -$(OH)_2$) using one-step or two-step methods. Based on our results, we show that Hf UiO-66 assembly is limited by metal cluster formation, making two-step synthesis methods that pre-form Hf metal clusters the only viable way to obtain the desired MOFs. Conversely, we demonstrate that Ce metal clusters self-assemble without the need for energy input or modulator, making quick, green and easily scalable one-step aqueous synthesis possible.

The synthesis protocols defined in this article are sustainable alternatives to standard MOF synthesis methods and have great potential for industrial scaling. We have proven that these room temperature protocols are reliable, versatile, and of general applicability. In case of specific physicochemical properties of the linkers, we investigated multiple possibilities of troubleshooting, showing how critical the role of the modulator can be in particular cases. We hope that these insights can and will be extended to other MOF families, advancing the RT synthesis in this unique and growing field.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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