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Cluster nuclearity control and modulated hydrothermal synthesis of functionalized Zr₁₂ metal-organic frameworks

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The synthesis of chemically stable metal-organic frameworks (MOFs) in benign solvents is a key step towards their scalable production and commercialization. Extending the modulated hydrothermal (MHT) synthesis approach for zirconium (Zr) MOFs, we herein demonstrate cluster nuclearity control over the secondary building units (SBUs) to target Zr_6 -based and Zr_{12} -based phases for the Zr terephthalate (Zr-BDC) system. Different functional groups (-NH₂, -NO₂, -Br, -F₄) can be incorporated into Zr₁₂-BDC, providing an avenue to further tune the chemical property of these promising MOFs.

MOFs are a class of porous materials which have garnered widespread research interests due to their tunable porosity, composition and functionality.^{1, 2} The prospect of the predictable combination of structurally encoded building blocks implies the engineering of novel MOFs to address global challenges in energy and environment.^{3, 4} To further align this goal of rational design with the demands of commercialization, increasing attention has been diverted towards the exploration of stable, high nuclearity building blocks as well as the compatibility of MOF synthesis with cheaper and greener solvents.⁵⁻⁷

Among the high connectivity inorganic building blocks, the hexanuclear SBU based on Group IV metals (herein M_6 , M = Zr, Hf, or Ce) is highly significant in the rational design of water-stable frameworks. Since the pioneering synthesis of the Zr_6 terephthalate MOF UiO-66 by a simple self-assembly of the constituent reactants,⁸ synthetic developments have revealed highly reproducible SBU formation conditions through the involvement of monocarboxylate additives (termed modulators).^{9, 10} Such robustness of the M_6 SBU has permitted commercially relevant solvent substitutions, in particular by water, and even solvent-free techniques for scale-up production.¹¹⁻¹³ Group IV MOFs incorporating linear ditopic linkers have exhibited interesting behaviours such as

other Group IV SBUs have been discovered, such as the chainbased SBU of the MIL-140 series, as well as dodecanuclear Zr₁₂ and Hf₁₂ SBUs.¹⁶⁻²⁰ Significantly, several isoreticular analogues have been isolated for these building blocks, extending the scope of molecular design for Group IV MOFs.²¹⁻²⁶ We have previously reported the use of modulated hydrothermal (MHT) synthesis approach to obtain functionalized variants of UiO-66 with different terephthalate-based ligands.¹² In the present contribution, we show the capability of MHT approach to tune the cluster nuclearity in the Zr-BDC MOF series by synthesizing dodecanuclear analogues bearing -NO2, -NH2, -Br, or -F4 functionalities. In particular, Zr₁₂-BDC-NH₂ shows improved catalytic performance over its Zr₆ counterpart (i.e. UiO-66-NH₂) in the tandem deacetylation-Knoevenagel condensation cascade reaction. Various topological outcomes exist for the self-assembly of

substoichiometric connectivity.14, 15 A further source of

structural diversity is through variations in cluster nuclearity.

While the hexanuclear SBU is found in majority of Zr structures,

Zr carboxylate clusters with linear ditopic linkers - including fcu, bcu, and reo structures.^{8, 27, 28} The fcu net is predicted by minimal transitivity principle upon the combining cubooctahedral Zr₆/Hf₆ clusters with linear ditopic linkers.^{9, 29} The reo topology is a derivative net arising from the systematic absence of ligands at the corner positions of the cubic unit cell.³⁰ The existence of reo nanodomains in UiO-66(Hf) was observed by Goodwin's group under high monocarboxylate concentrations.²⁸ Such systematic absences have also been reported for sulfonate-decorated linkers.³¹ The in-situ dimerization of Zr₆/Hf₆ clusters by bridging hydroxo ligands to form a distinct SBU – $(M_{12}(\mu_3-O)_8(\mu_3-OH)_8(\mu-OH)_6)$ – opens access to Zr/Hf MOFs exhibiting two additional topologies, namely hcp and hxl.^{25, 32} The resultant materials differ from the fcu structure in their stacking pattern, and consequently manifest distinct X-ray diffraction peaks for (002), (100), and (101) crystal planes in the low angle region. Based on the simulated structure of Zr₁₂-BDC (Fig. 1c), these occur at 5.0°, 7.2° and 7.6° respectively, which may be used for positive phase identification.

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Fig. 1. (a) Crystal structure representation of Zr₆-BDC. Left to right: View from [10¹] direction, [001] direction, and polyhedral representation. (b) Crystal structure representation of Zr₁₂-BDC. Left to right: View along [100] direction, [001] direction and polyhedral representation. (c) Simulated and experimental PXRD patterns of Zr₆- and Zr₁₂- BDC. Note: Zr₁₂-BDC may exhibit 2D layered **hxl** or 3D **hcp** topology. The optimized condition in this study yields **hcp** phase of Zr₁₂-BDC. (d) Experimental PXRD patterns of the synthesized Zr₁₂-BDC analogues. Herein, the notation Zr₁₂-BDC-X is used to acknowledge the nuclearity difference without making assumptions on the structure, due to the possible *in-situ* transformation between different phases.

Zr₁₂-BDC-H and Hf₁₂-BDC-F₄ were reported by our group previously.9, 17 These phases were attained by modified protocols, and the X-ray diffraction patterns were assigned to the hcp phase by Hartmann et al. and Grey et al., respectively.^{33, 34} In addition, the latter work reported the isolation of Hf₁₂-BDC and Zr₁₂-BDC-F₄. Building on these results, we have successfully incorporated $-NO_2$, $-NH_2$, -Br, and $-F_4$ functionalities into the Zr₁₂-BDC framework using the MHT method (Fig. 1d). Except Zr₁₂-BDC-F₄,³⁴ the remaining analogues are yet to be reported by solution-based synthetic processes. We note that an amino-functionalized UiO-66 thin film prepared by gas-phase deposition was observed to exhibit hexagonal morphology, but no bulk phase preparation was reported. ^35 The self-assembly of $\mathsf{Zr}_{12}\text{-}\mathsf{BDC}\text{-}\mathsf{X}$ involves two independent processes, specifically (1) the cluster dimerization of Zr₆ to form Zr₁₂ clusters, and (2) linker replacement of capping monocarboxylates to form the extended framework.²⁵ Considering the involvement of hydroxo ligands to bridge the clusters, it is likely that the progress of the first step is promoted under hydrolytic conditions. In this study, we thus increased simultaneously the reaction temperature (favoring hydrolysis) and modulator concentration (to reduce nucleation) to yield the desired hcp phase for four cases (X = H, NO₂, Br, and F₄, see ESI for optimized reaction conditions). For Zr₁₂-BDC-NH₂, although the product showed X-ray diffraction patterns consistent with the desired structure, the yield and quality were negatively affected.

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Considering the feasibility in synthesizing Zr₁₂-BDC at reflux temperature, a second round of optimization was performed at 120 °C. At this temperature, Zr₁₂-BDC-NH₂ crystallized within a narrow range of modulator concentration (60-90 eq. to linker, Fig. S1 and S2a). Moreover, the phase transition relative to the modulator concentration is inverted when compared to the solvothermal preparation of UiO-67(Hf). Specifically, the increase of modulator concentration above 120 eq. resulted in preferential formation of Zr₆-BDC-NH₂ over Zr₁₂-BDC-NH₂. This is presumably because the solubility effect of the liquid modulator (acetic acid, AA) is opposite in the two situations. 4'4-Biphenyldicarboxylic acid (BPDC, the linker for UiO-67 (Hf)) has a higher solubility in dimethylformamide (DMF) than in AA, whereas BDC has a higher solubility in AA than in water.³⁶ Thus, the increase of AA concentration under MHT conditions will elevate the linker concentration in the reaction mixture and accelerate nucleation of Zr₆-BDC-NH₂. To investigate the solubility hypothesis, we replaced varying portions of water by methanol (MeOH) as a 'good' solvent and investigated the phase behaviour under various modulator concentrations. At 90 eq. AA, replacement of half the solvent volume by MeOH led to the formation of Zr₆-BDC-NH₂ instead of Zr₁₂-BDC-NH₂ (Fig. S2b). In addition, we explored the use of dimethyl aminoterephthalate as an alternative precursor. The in-situ hydrolysis of ester based precursors has been used previously to improve the purity of specific kinetic MOF analogues, such as MIL-100(AI).37 Under the employed conditions, the use of ester precursor did not have a major effect on the phase domains (Fig. S1).



Fig. 2. (a) Scheme of functionalized Zr_{12} -BDC-X with indicative pore apertures (left to right: X = NO₂, NH₂, Br, F₄). (b) FT-IR spectra of Zr_{12} -BDC-X. (c) Nitrogen sorption isotherms at 77 K for functionalized Zr_{12} -BDC-X (adsorption, filled; desorption, empty).

Fourier-transform infrared (FT-IR) spectra (**Fig. 2b**) and N₂ sorption isotherms at 77 K (**Fig. 2c**) were collected for the functionalized Zr_{12} -BDC-X MOF samples. The linker carboxylates generate two sharp peaks at around 1400 cm⁻¹ and 1600 cm⁻¹ in the FT-IR spectra, corresponding to the symmetric and asymmetric C-O stretching vibrations respectively.^{8, 38} Given the increased nuclearity of the Zr_{12} cluster, the samples are less porous than Zr_6 cluster based analogues, with measured Brunauer-Emmett-Teller (BET)

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surface areas ranging from 272 m² g⁻¹ (Zr_{12} -BDC-F₄) to 622 m² g⁻¹ (Zr_{12} -BDC). The isotherms exhibit microporous feature for the most part, with some hystereses at high partial pressures, which can be attributed to interparticle voids from aggregated



Fig. 3. Morphological characterization of Zr_{12} -BDC-NH₂: (a-c) SEM images of Zr_{12} -BDC-NH₂. (d, e) TEM images of Zr_{12} -BDC-NH₂ (sonicated fragment). (f) Selected area electron diffraction (SAED) image of Zr_{12} -BDC-NH₂ (sonicated fragment).

Two-dimensional (2D) materials have been attracting wide research interests for diverse applications including electronics, catalysis and membrane separations.^{40, 41} The short diffusive lengths and readily accessible active sites, combined with the facile installation of chemical functionalities, make 2D MOFs ideal materials for catalytic applications.⁴² The spontaneous transformation of Hf₁₂-based hcp UiO-67(Hf) and hcp UiO-66-F₄(Hf) led Grey et al. to propose hcp-hxl transformation as a potential route to other 2D MOF nanomaterials.^{17, 34} We sought to test this hypothesis by examining the delamination characteristics of different functionalized Zr₁₂-cluster based MOFs. Fig. 3a shows the morphology of the Zr₁₂-BDC-NH₂. The as-prepared samples appear as intergrown florets of hexagonal nanoplates, which are clearly distinct from the typical octahedral morphology of Zr₆-BDC crystals.^{33, 43} However, the different functionalized samples exhibited differing stabilities with regards to delamination. The asprepared Zr₁₂-BDC-F₄ exhibited high X-ray diffraction peak intensity for the (100) reflection compared to the (101) reflection, suggesting a lower degree of ordering for the latter (Fig. 1d). The (002) and (101) reflections disappeared after storage of the sample in air for 4 weeks, yielding a characteristic pattern for 2D materials (Fig. S6a). The -Br and -NO₂ functionalized samples also underwent visible structural transformation according to their X-ray diffraction patterns (Fig. S3b). On the other hand, even after prolonged storage in air, no discernable change in powder X-ray diffraction (PXRD) patterns occurred in Zr₁₂-BDC and Zr₁₂-BDC-NH₂. Clearly, the easiness of 3D-to-2D structural transformation in Zr₁₂ cluster based MOFs depends strongly on the chemical nature of the bridging linkers. We postulate two possible contributions to rationalize the observed stability trend. Firstly, the presence of electron-withdrawing substituents stabilizes the conjugate base of the carboxylate linkers,44 thus weakening the coordination bond and favouring the exfoliation. Secondly, deviations from linearity in the bridging linkers may diminish

the likelihood of forming the **hcp** structure.⁴⁵ Specifically the carboxylates in BDC-F₄ and BDC-Br exhibit the spective of the and non-coplanar conformations.^{46,47}

To further investigate the feasibility of exfoliating Zr_{12} -BDC-X, the -NH₂ and -F₄ functionalized analogues were subject to sonication treatment in MeOH before morphological characterization. The sonically-treated Zr_{12} -BDC-NH₂ contained numerous particles with terraced morphology, evidencing their degradation under cavitation forces (**Fig. 3d**, left). Highresolution TEM and selected area electron diffraction (SAED) confirmed the retention of hexagonal order (**Fig. 3e-f**). Atomic force microscopy (AFM) for sonication-treated Zr_{12} -BDC-NH₂ revealed shape-similar particles of decreasing thicknesses (10 to 20 nm) and lateral size (**Fig. S7a**). Under the same treatment, Zr_{12} -BDC-F₄ separated into layers with thicknesses of 2-4 nm (**Fig. S7b**). Hence, the spontaneous 3D-to-2D transition may be a prerequisite to derive high aspect ratio materials from the Zr_{12} cluster-based MOFs.

The high aspect ratio morphologies, coupled with the small size of the dispersed particles, may be advantageous for catalysis.42 While access to the porous cages in the fcu structure is restricted by small window apertures, the 1D channels of the hcp structure (Fig. 2b) allow facile mass transfer of reagents. Recently, Momeni and Cramer predicted by simulation the superior hydrolytic activities of Zr₁₂-cluster based MOFs with coordinatively unsaturated metal sites, which function as Lewis acids.48 We used the tandem deacetalization-Knoevenagel condensation reaction to investigate the possible differences in catalytic activity between Zr₆-BDC-NH₂ and Zr₁₂-BDC-NH₂ arising from the change in SBU nuclearity.^{49, 50} First, benzaldehyde dimethyl acetal, a, is deprotected by Lewis acids into benzaldehyde, b, which is subsequently condensed with malononitrile under basic catalysis to form benzylidene malononitrile, c. Acetal protection is commonly adopted to protect aldehyde carbonyls from unwanted reactions, while products of the Knoevenagel condensation serve as important intermediates for various pharmaceuticals.51 The multi-step reaction hence facilitates the comparison of the node-specific Lewis acidity and the linker-centred Lewis basic activity for the two materials. The progress of the tandem reaction was monitored by ¹H NMR in deuterated chloroform. The overall conversion and yields for each step were calculated by integrating characteristic peak areas for **a**, **b**, and **c** (Table 1). The catalyst concentration was optimized at 55 °C. At 100 mg loading, Zr_{12} -BDC-H and Zr_{12} -BDC-NH₂ attained conversions of 94.5% and 99% after 24 h, respectively, which are slightly higher than that of Zr₆-BDC-NH₂ (92.7%). The catalyst-free control reflected a conversion of 6.5% to ${\bf b}$ due to the absence of catalyst, whereas no ${\bf c}$ was detected. With respect to a, the yield of final product c was only 31.6% under the catalysis of Zr₆-BDC-NH₂, which increased to 64.5% and 91.8%, respectively, when Zr₁₂-BDC-H and Zr₁₂-BDC-NH₂ was used. To study the contribution of Lewis acidic sites, digestion experiments in basic D₂O were performed on the Zr₁₂ MOFs to estimate the defects density. The modulator to linker ratio (m_R) was tabulated in Table S3. The density of Lewis acidic sites did not appear to be increased in the Zr₁₂

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reactions catalyzed by Zr-MOFs.

Recycle 1

Recycle 2

Recycle 3

framework (m_R = 0.05 for Zr₁₂-BDC-H vs. < 0.2 for acetic acidmodulated Zr₆-BDC-H). The improved accessibility to active sites and higher reactivity of the Zr₁₂ sites may have led to the superior activity.⁴⁸ Despite strong dependence of Knoevenagel condensation on the polarity of the reaction media, the efficiency of Zr₁₂-BDC-NH₂ for the same reaction remained comparable to the previously reported MOF catalysts (Table S4) even in deuterated chloroform ($\varepsilon = 4.8$) and nearly stoichiometric quantities of the starting reagents. The stability of the catalysts was ascertained by PXRD studies (Fig. S11). Zr₁₂-BDC-NH₂ did not show signs of degradation during recovery or immersion in aqueous solutions of varying pH values (1-10), indicating retention of the MOF structure.

Table 1. Conversions and yields of tandem deacetalization-Knoevenagel condensation

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OCH, Cat, CH₂(CN)₂ 2 CH. Conv. Catalyst Loading (mg) Yb Y_c (%) (%) (%) N.A. 0 6.5 6.5 -Zr₁₂ BDC-NH₂ 25 31.0 9.0 22.0 Zr12 BDC-NH2 50 49.5 0.5 49.0 Zr12 BDC-NH2 99.0 91.8 100 7.2 Zr12 BDC-H 100 94.3 29.8 64.5 Zr₆ BDC-NH₂ 100 92.7 61.1

Reaction conditions: benzaldehyde dimethyl acetal (1.0 mmol), malononitrile (1.1 mmol), CDCl_3 (1.5 mL), and catalyst; reaction temperature 55 °C; reaction time 24 h. The conversions and yields were determined by ¹H NMR.

98.4

95.3

95.1

100

100

100

In summary, we have prepared five functionalized Zr₁₂cluster based MOFs on the basis of functionalized terephthalate linkers using a modulated hydrothermal (MHT) synthesis approach, thus illustrating the feasibility of MHT in tuning the nuclearity of MOF SBUs. Spontaneous 3D-to-2D structure transformation was observed for certain variants. Zr₁₂-BDC-NH₂ was shown to exhibit distinct catalytic behaviour from Zr₆-BDC-NH₂ for the tandem deacetalization-Knoevenagel condensation reaction, due to the improved access to amine active sites in the MOF. The findings indicate that cluster condensation may be employed as a general strategy to finetune MOF properties without expending the linker degrees of freedom, paving a route to desired morphologies and porosities in Zr-MOFs.

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Conflicts of interest

The authors declare no competing financial interests.

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