Role of Modulators in Controlling the Colloidal Stability and Polydispersity of the UiO-66 Metal–Organic Framework

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1. INTRODUCTION

Nanoscale porous structures, namely, infinite coordination polymers (ICPs) and metal–organic frameworks (MOFs), constructed from metal-containing moieties connected in three dimensions by rigid organic ligands, are becoming topics of significant interest in nanoscience.1–6 Solvothermal control techniques, microwave methods, and chemical modulator guided routes have been developed for synthesizing them.7–9 Additionally, studies have been performed to better understand how particle size affects the gas adsorption, ion exchange, and catalytic properties of MOFs.10–12

In 2011, Behrens and co-workers first reported that chemical modulators could be used in the size-controlled synthesis of UiO-66.13 Such modulators, which are typically acids have been proposed to compete for metal binding sites, thereby controlling the number of nucleation sites available for crystal growth, which in turn impacts crystallite size.14 Since that initial work, modulators have been employed extensively in the size-controlled synthesis of UiO-66 and its analogues, which led to the first single crystal X-ray diffraction structure determination of UiO-66.15 Structural characterization carried out by Wu et al.

ABSTRACT: Nanoscale UiO-66 Zr6(OH)4O4(C8O4H4)6 has been synthesized with a series of carboxylic acid modulators, R-COOH (where R = H, CH3, CF3, and CHCl2). The phase purity and size of each MOF was confirmed by powder X-ray diffraction, BET surface area analysis, and scanning transmission electron microscopy (STEM). Size control of UiO-66 crystals from 20 nm to over 1 μm was achieved, and confirmed by STEM. The colloidal stability of each MOF was evaluated by dynamic light scattering and was found to be highly dependent on the modulator conditions utilized in the synthesis, with both lower pKA and higher acid concentration resulting in more stable structures. Furthermore, STEM was carried out on both colloidal stable samples and those that exhibited a large degree of aggregation, which allowed for visualization of the different degrees of dispersion of the samples. The use of modulators at higher concentrations and with lower pKas leads to the formation of more defects, as a consequence of terephthalic acid ligands being replaced by modulator molecules, thereby enhancing the colloidal stability of the UiO-66 nanoparticles. These findings could have a significant impact on nanoscale MOF material syntheses and applications, especially in the areas of catalysis and drug delivery.

KEYWORDS: metal–organic frameworks, coordination modulation, nanoparticle, size control, colloidal stability

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Therefore, we have set out to systematically investigate the role that modulators play in altering the colloidal stability of UiO-66.

Colloidal stability of nanoparticles is important for applications in biology, materials assembly, and catalysis. With MOF nanoparticles, colloidal stability typically has been realized by surface functionalization with polymers, silica, DNA, and lipids. These methods can be complicated and often block access to the pores. Therefore, simpler methods for controlling colloidal stability while maintaining porosity are required. Herein, we evaluate a strategy to stabilize MOF colloids using acidic synthetic modulators that typically are used to control crystallite size, catalytic activity, and shape uniformity. Specifically, we evaluate how the type, pH, and concentration of the modulator can be used to control the surface charge on the MOF nanoparticle, which directly corresponds to colloidal stability.

In this report, we present the first systematic study of the role of modulators, type, and concentration, in controlling the size dispersity and colloidal stability of nanoscale UiO-66. Samples of UiO-66, Zr₆(OH)₄O₄(C₈O₄H₄)₆, were synthesized using four different modulating acids (acetic acid (AA), formic acid (FA), dichloroacetic acid (DCA), and trifluoroacetic acid (TFA)) across a range of concentrations (Scheme 1). Powder each vial. The concentration ranges studied were 1.2–6.7 M for acetic acid, 1.8–6.4 M for formic acid, 0.3–1.1 M for dichloroacetic acid, and 0.62–1.18 M for trifluoroacetic acid. The solution was heated at 90 °C for 18 h to yield UiO-66 Zr₆O₄(OH)₄(C₈O₄H₄)₆.

Characterization. To determine the crystallinity of each MOF nanoparticle, powder X-ray diffraction data (PXRD) were collected at Argonne National Laboratory using the Dow-Northwestern-Dupont Collaborative Access team (DND-CAT) Beamline S-1D-D at the Advanced Photon Source (APS). A wavelength of 1.239 Å with an exposure time of 1 s was used for each measurement. Two-dimensional scattering data were converted to one-dimensional spectra by taking a radial average of the two-dimensional data. Prior to data collection, as-synthesized MOF nanoparticles were centrifuged at 15 000 rpm for 1 h and washed sequentially with DMF three times and then water three times. Air-dried samples for PXRD were placed in quartz capillaries (Charles Supper Company) (1.5 mm) for measurement. The size and dispersity of UiO-66 were evaluated using a Hitachi HD-2300 scanning transmission electron microscope in SE or TE modes depending on the crystallite size with an accelerating voltage of 200 kV. Samples were dispersed onto TEM grids by drop-casting a dilute solution containing MOF crystals. The average crystal size for each synthesis was determined by measuring at least 50 crystals. Zeta potential and DLS size measurements of hydrodynamic radii were made on a Malvern Zetasizer Nano-ZS (Malvern Instruments). Results were averaged over ten measurements.

3. RESULTS AND DISCUSSION

Initially, reaction conditions were systematically screened to select for UiO-66 particles between the 20 nm and 1 μm size range. Over 20 different samples of UiO-66 were synthesized in this study by utilizing four modulators over a range of concentrations (Table S1). The four modulators and the concentration ranges utilized were formic acid (FA) (1.8–6.9 M), acetic acid (AA) (1.2–6.7 M), dichloroacetic acid (DCA) (0.3–1.1 M), and trifluoroacetic acid (TFA) (0.62–1.2 M). Each sample of UiO-66 was synthesized in a solvothermal reaction at 90 °C for 18 h, employing the selected modulator at the given concentration (Scheme 1). At concentrations above 1.1 and 1.2 M for TFA and DCA, respectively, no product was observed after 18 h at 90 °C. In reactions where product was formed, analysis by PXRD was carried out after solvent exchange and drying (Figure 1). PXRD data collected from each sample was successfully indexed to simulated patterns generated from the reported structure of UiO-66, which confirmed the expected fcu topology (Scheme 1). At low concentrations of modulator, peak broadening was observed, which is indicative of nanoscale crystallites.

To evaluate the role of modulators on crystallite size and polydispersity, we utilized STEM to visualize the synthesized samples (Figure 2). For each acidic modulator, the size of the MOF crystallites increased as a function of acid concentration (Figure 2). The morphologies of the crystals changed as a function of acid concentration, with low concentrations producing UiO-66 with a quasi-spherical morphology and higher concentrations leading to the formation of octahedral UiO-66 crystals (Figure 2). To evaluate the size and polydispersity of each sample, the dimensions (diameter for quasi-spherical particles, and edge length for octahedral shape particles) of 50 crystals from one synthesis were determined from the STEM images (Figure 3). Depending on acid concentration, the size of the crystals varied from 17(2)–721 (56) nm, 17(4)–1174 (258) nm, 19(5)–550 (51), and 38(7)–227 (46) for AA, FA, DCA, and TFA, respectively (Table S1). Therefore, we have determined that by using analogous synthetic conditions and simply changing the modulator and...
its concentration, one can realize size control from 20 nm to over one micron (Table S1). To further evaluate the dispersity of the MOF crystals, a coefficient of variation (CV) was calculated for each sample (Figure 3) and determined to be between 20 and 30%. Significantly, acetic acid was shown to produce samples with the narrowest size distribution at both high and low concentrations of modulator (Figure 3).

To characterize the porosity of each MOF synthesized, we performed N2 isotherms and evaluated their surface area by BET analysis (Figure 4). Prior to the surface area measurements, the samples were activated to remove solvent from the pores of the MOF (see the Supporting Information). In each case, the MOFs synthesized using higher modulator concentrations, exhibited higher surface areas compared to the ones prepared with lower modulator concentrations (Figure 4A). Similarly, UiO-66 nanocrystals of comparable size (~20 nm) synthesized with strong modulators, DCA and TFA, exhibited higher porosity as compared to those synthesized with the weaker modulator, acetic acid (Figure 4B). Compared to terephthalic acid linkers, deprotonated strong modulators have higher binding affinities for Zr clusters, resulting in a high concentration of missing cluster defects in the MOF structures. Since the pKₐ values of formic acid (3.77) and acetic acid (4.76) are similar to that of terephthalic acid (1st 3.51 and second 4.82), they compete with terephthalic acid to form coordination bonds with available Zr (in solution and on the surface of the growing MOF), which in turn slows down particle nucleation and promotes slow growth of the MOF, favoring larger crystals with fewer defects.²⁶ This is important because BET area analysis of UiO-66 shows that the number of defects in the MOF correlate with the modulator used in the synthesis.¹⁵,¹⁶,¹⁸,²³,²⁴,²⁶

To investigate how modulator type and concentration affect the colloidal stability of the MOF nanoparticles, we carried out DLS measurements to evaluate the average hydrodynamic radius of each MOF nanoparticle sample in water as well as the absence of aggregates. As shown in Figure 5A, B, the hydrodynamic radius of MOF nanoparticles increases as modulator concentration increases, and in general DLS measurements are in agreement with particle size measurements obtained from microscopy images. Samples synthesized with FA, DCA, and TFA were colloidally stable, as probed by DLS, with average particle sizes closely reflecting those measured by STEM (Table S1). When acetic acid was used as a modulator, similar behavior was observed, however, when UiO-66 was synthesized with acetic acid as the modulator at low concentrations (1.2 and 1.9 M), significant particle aggregation occurred (Figure 5B, purple). The MOF nanoparticle sizes were determined to be 17(2) and 34(22) nm from STEM measurements, respectively, but no meaningful determinations could be made by DLS measurements on these samples due to aggregation (Figure 5C). In contrast, the sample that was prepared with DCA did not show any visible aggregation (DCA = 0.58 M, Figure 5D), and when dispersed and dried on a TEM grid, STEM measurements revealed well-formed particles and no evidence of aggregation (Figure 5D).
Therefore, by simply choosing the appropriate modulator used during synthesis, one can deliberately generate colloids of stable UiO-66 particles across a wide size range.

To further understand the surface chemistry and colloidal stability of the MOF nanoparticles, we evaluated the zeta potential of each sample (Figure 5E). The zeta potential of the MOF nanoparticles can be altered by varying the number of defects introduced in the samples, which can be accomplished by (i) changing the concentration of modulator or (ii) using modulators with different acid strengths. For all particles synthesized with acetic acid as the modulator, zeta potential measurements spanned the broadest range from ~−5 to 41 mV. Samples of UiO-66 synthesized with low concentrations of acetic acid were colloidally unstable with zeta potentials close to zero, while samples synthesized with high concentrations of acetic acid were colloidally stable with zeta potentials of approximately +40 mV. These results suggest that as the concentration of acetic acid modulator is increased, more surface defects are incorporated which increases the surface charge and hence the repulsion between neighboring nanoparticles. The zeta potential was also dramatically altered by using modulators with different acid strength, which also

Figure 4. Impact of modulator concentration and acid utilized on porosity. BET adsorption isotherm for (A) three concentrations of acetic acid modulated UiO-66 colloids, 1.2 M (black), 3.5 M (blue) and 6.7 M (red), respectively. (B) Three different acid modulated UiO-66 colloids, AA (1.2 M, black), DCA (0.58 M, red), and TFA (0.62 M, blue), respectively.

Figure 5. Summary of MOF nanoparticle size measurements determined by (A) STEM and (B) DLS, as a function of modulator relative acidity and molar concentration. The acids utilized are FA (black), AA (green), DCA (red), and TFA (blue). The purple region in B corresponds to highly aggregated samples where particle size cannot be determined by DLS. STEM image and digital photographs of UiO-66 dispersed in H2O synthesized with different modulators: (C) UiO-66 synthesized with AA (1.2 M) and (D) UiO-66 synthesized with DCA (0.58 M). (E) Zeta potential measurements as a function of modulator relative acidity and molar concentration. Scale bars C = 200 nm and D = 500 nm.
controls the number of defects introduced into the nanoparticles. Moreover, the use of strong acid modulators allows for the synthesis of sub-50 nm nanocrystals that are highly defective and colloidal stable. Colloidal stability is in large part a consequence of the repulsion between MOF nanoparticles, which can be controlled by tuning the zeta potential of the particles. Indeed, the zeta potential is correlated with the stability (in the context of a colloid), and size dispersity. Furthermore, in principle, the methodology can be extended to related MOF and ICP architectures, thereby allowing them to be compared to more conventional classes of nanoparticles based upon noble metals, metal oxides, and quantum dots.31–36 Indeed, convenient methods for preparing colloidal stable MOF nanoparticles will set the stage for using such particles and surface modified forms of them in a variety of areas spanning the life sciences and energy conversion.

4. CONCLUSION

In summary, the work described herein shows that modulators can be used to control UiO-66 nanoparticle surface charge, stability (in the context of a colloid), and size dispersity. Indeed, through systematic studies, we have identified conditions suitable for making colloidal stable UiO-66 particles that are sub-50 nm in size and relatively monodisperse. Furthermore, in principle, the methodology can be extended to related MOF and ICP architectures, thereby allowing them to be compared to more conventional classes of nanoparticles based upon noble metals, metal oxides, and quantum dots.31–36

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