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COMMUNICATION

Room Temperature Aqueous Synthesis of UiO-66 Derivatives via Postsynthetic Exchange

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Herein, we report the room temperature aqueous synthesis of the Zr(IV)-based metal-organic framework UiO-66 and a series of functionalized UiO-66 derivatives through postsynthetic exchange (PSE) from a perfluorinated UiO-66-F_4 precursor. All synthesized MOFs in this study were thoroughly characterized to verify formation of the desired MOF, porosity, crystallinity, and exchanged ligand content. This report represents a green, aqueous, room temperature synthesis of a highly valued series of Zr(IV)-based MOFs.

Metal-organic frameworks (MOFs) are three dimensional frameworks constructed from inorganic metal nodes, also termed secondary building units (SBUs), linked together by multitopic organic linkers.[1-2] Over the last two decades, MOFs have garnered significant attention due to their use in developing gas storage, separation and catalytic active materials.[1-2] Since the discovery of UiO-66 (UiO = University of Oslo) over a decade ago, Zr(IV)-based MOFs have been of great interest due to their inherently stable structures under a wide range of conditions.[3-5] The canonical UiO-66 MOF is composed of Zr(IV) oxide clusters that are connected by 12 1,4-benzenedicarboxylate (bdc^{2-}) ligands.[3] The stability of Zr(IV)-MOFs has been attributed to the strong coordination between the carboxylate linkers and the Zr(IV) metal centers.[3-4] Derivatization of the UiO-66 MOF with a wide range of pendant functional groups on the bdc^{2-} linkers has been demonstrated in an effort to develop MOFs with tailored properties.[6-7] This has prompted the synthesis of Zr(IV)-based MOFs using a wide range of linkers resulting in the synthesis of frameworks with varying connectivity at the SBU.[4-5, 8] The chemical tunability and stability of these MOFs has made them attractive for applications that include gas and liquid separations, toxic gas storage, and catalysis.[4, 9-11]

The synthetic conditions for Zr(IV)-based MOFs generally require high temperatures (80-150 °C) and environmentally unfriendly solvents such as DMF or DEF.[3, 8] Several groups have worked to develop methods to synthesize UiO-66 under more mild conditions. Some attempts to achieve mild conditions for UiO-66 and its derivatives have focused on dividing the synthesis into initial cluster formation and subsequent MOF assembly.[12-14] For example, Farha, Hupp, and co-workers initially synthesized the Zr(IV)-cluster at elevated temperatures and the resulting clusters were linked together at room temperature by terephthalate or terephthalate derivatives to form UiO-66 and functionalized derivatives in DMF.[13] In another approach, Szilágyi and coworkers reported the synthesis of UiO-66-NH_2 by first forming the Zr(IV) cluster in water at 50 °C and subsequently synthesizing the MOF with the disodium salt version of aminoterephthalate ($Na^+{}_2NH_2\text{-}bdc^{2-}$) in water at room temperature.[14] In both of these cases, elevated temperatures were required for the synthesis of the Zr(IV) cluster.[13-14] Subsequent MOF formation then occurs readily upon the introduction of a suitable dicarboxylic acid linker.[13-14]

Other groups have focused on synthesizing MOFs through either entirely aqueous or solvent-free conditions. Some aqueous, one-pot syntheses of UiO-66 have been reported successfully; however, these syntheses typically require high temperatures to form the MOF.[15-17] In a particularly interesting report, Maspoch and coworkers were able to successfully eliminate the use of heat in synthesizing UiO-66 MOFs.[18] They reported the room temperature aqueous synthesis of two UiO-66 derivatives (UiO-66-NH_2 and UiO-66-$(OH)_2$) in a one pot synthesis using acetylacetonate complexes as the metal source. The crystallinity of these frameworks was relatively poor compared to that of solvothermal synthesized UiO-66, whereas the surface area of the MOFs was not compromised. In a unique approach, Friscic and coworkers demonstrated a one-pot synthesis of UiO-66 through mechanochemical routes using a zirconium propoxide solution (70wt% in *n*-PrOH) with the

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[b] † Electronic Supplementary Information (ESI) available: Experimental procedures, ^1H NMR, ^{19}F NMR, PXRD, and SEM. See DOI: 10.1039/x0xx00000x

addition of MeOH grinding to achieve a crystalline UiO-66 MOF.[19] Finally, in a report of particular importance to our findings here, UiO-66-$(COOH)_2$ and UiO-66-F_4 were prepared via a room temperature synthesis under aqueous conditions; however, the canonical UiO-66 or UiO-66-NH_2 were not accessible via this method.[20]

Herein, we report a room temperature, aqueous, green synthesis of UiO-66 and several derivatives (UiO-66-NH_2, UiO-66-Br, UiO-66-I, and UiO-66-Napthalene) through postsynthetic exchange (PSE) from UiO-66-F_4, a UiO-66 derivative prepared from a tetrafluorinated bdc^{2-} (F_4-bdc^{2-}) ligand. UiO-66-F_4 was prepared in aqueous media using the aforementioned method (Figure 1).[20] The presence of four electron withdrawing fluorine atoms on the organic linker results in a weaker bond between the carboxylate linkers and Zr(IV) metal centers. This enables the use of PSE to replace the F_4-bdc^{2-} linker with bdc^{2-}, NH_2-bdc^{2-}, Br-bdc^{2-}, I-bdc^{2-}, and napth-bdc^{2-} (1,4-napthalenedicarboxylic acid). Nearly complete exchange of the F_4-bdc^{2-} linkers is achieved at room temperature, in water within the span of 4 h at a 1:1 linker ratio. The resulting MOFs were fully characterized for porosity and crystallinity.

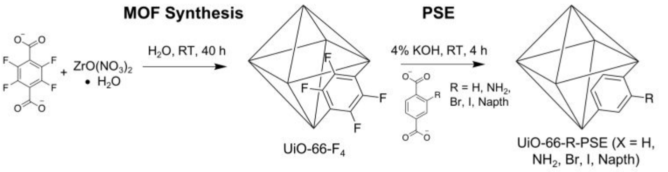

Figure 1. Synthetic scheme for UiO-66 and a range of derivatives at room temperature in aqueous media via PSE from UiO-66-F_4.

Typically, when synthesizing UiO-66 and its derivatives (-NH_2, -Br, -I, etc.), the ligand and metal salts are dissolved in DMF and subsequently heated >100 °C for 24+ h. Circumventing these harsh conditions (i.e., high temperature in nonaqueous solvent), a range of UiO-66 derivatives were synthesized in aqueous solutions at room temperature using PSE from UiO-66-F_4. UiO-66-F_4 was selected for PSE as the F_4-bdc^{2-} linker is labile and coordinates weakly to the Zr(IV) metal nodes as a consequence of the four electron withdrawing atoms on the benzene ring. UiO-66-F_4 was synthesized using an acetic acid modulated, aqueous synthesis (see ESI for details) previously reported by Farha and co-workers.[20]

PSE experiments were conducted by dissolving a R-bdc linker in a 4% KOH solution as previously reported.[21-22] The ligand solution was then neutralized to pH = 7 via the slow addition of 1M HCl (see ESI for details). A 1:1 ratio of UiO-66-F_4 was mixed with the ligand solution, and the mixture was then sonicated for 10 min and then left to stand at room temperature for 4 h. After incubation, the MOF was collected via centrifugation and thoroughly washed over the course of three days to ensure any excess ligand was removed. The product MOFs were then digested in dilute acid and characterized using ^1H and ^{19}F NMR. A coaxial tube with 40 μmol trifluorotoluene (CF_3-toluene, Figure 2) in DMSO-d_6 was used for quantification by NMR of the amount F_4-bdc^{2-} and the exchanged R-bdc^{2-} in each sample. The CF_3-toluene was used as an internal standard as it contains both F and H atoms with appropriate chemical shifts (Figure S1-S5). After the UiO-66-PSE MOF was digested, the coaxial tube of CF_3-toluene was added to the sample and both ^1H and ^{19}F NMR were used to analyze the sample. The amount of each linker in the MOF was quantified by comparing the PSE introduced R-bdc^{2-} (~7.0 - 8.0 ppm) linker to the CF_3-toluene peaks (7.3 – 7.7 ppm) in the ^1H NMR and also comparing the amount of F_4-bdc^{2-} remaining (-61.2 ppm) to the CF_3-toluene (-140.0 ppm) via the ^{19}F NMR (Figure 1a and b). This analysis allowed for the total quantity of ligand in the MOF to be determined, from which the fraction of F_4-bdc^{2-} and R-bdc^{2-} was calculated.

NMR data for the digested samples indicates that when exchanging the F_4-bdc^{2-} linker out for the canonical bdc^{2-} linker, we observe a 93±2% ligand exchange in the MOF in ~4 h (Figure 2). PSE of the UiO-66-F_4 with NH_2-bdc^{2-} gave 95±3% ligand exchange (Figure S2). PSE on UiO-66-F_4 with Br-bdc^{2-} and I-bdc^{2-} gave 89±3% and 80±2% PSE, respectively (Figure S3-4). The lower PSE conversion with Br-bdc^{2-} and I-bdc^{2-} is attributed to the electron withdrawing groups on these halogenated bdc^{2-} derivatives, making them bulkier, as well as weaker donors. PSE on UiO-66-F_4 using a sterically bulkier napth-bdc^{2-} linker gave a 77±3% ligand incorporation (Figure S5); the slightly less efficient PSE is attributed to the steric bulk of the napth-bdc^{2-} linker. Residual F_4-bdc^{2-} linkers in the PSE MOFs indicate that these materials are by definition multivariate (MTV) MOFs. MTV-MOFs have shown some interesting synergistic properties in making MOFs better sorbents or catalysts.[23-24] In this case, residual F_4-bdc^{2-} linkers could potentially be used for labeling purposes as a function of the F atoms characteristic spectroscopic properties.

All MOFs were characterized via PXRD to confirm the crystallinity of the UiO-66 framework after PSE. All of the MOFs synthesized via PSE display the characteristic UiO-66 reflections (Figure 3). The MOFs were also analyzed by scanning electron microscopy (SEM) to evaluate the particle size before and after PSE. As-prepared UiO-66-F_4 particles were small (~100 nm) and polydisperse in size.[20] Following PSE, SEM images verify that the crystallites are approximately the same size and dispersity as the parent UiO-66-F_4 (Figures S6-S11).

All MOFs were analyzed to determine the Brunauer-Emmett-Teller (BET) surface area of the materials using N_2 adsorption isotherms. The parent UiO-66-F_4 MOF displays a BET surface area of 628 ± 8 m^2/g, similar to previous reports.[20] Upon PSE of the MOF with other linkers we observe a general decrease in the BET surface area. For example, UiO-66-PSE displays a surface area of 463±46 m^2/g. Surface areas for other PSE MOFs were: 407±6 m^2/g for UiO-66-NH_2-PSE, 378±22 m^2/g for UiO-66-Br-PSE, 472±21 m^2/g for UiO-66-I-PSE, and 467±42 m^2/g for UiO-66-Napth-PSE. All of these UiO-66 derivatives, when synthesized by the typical hydrothermal method, display surface areas of >1000 m^2/g.[3, 7] We attribute the lower surface area of the PSE materials to the poorer porosity of the UiO-66-F_4 template. Nevertheless, the lower surface area of these materials does not detract from the value of these materials for many potential applications, especially if a greener synthetic route is desired.

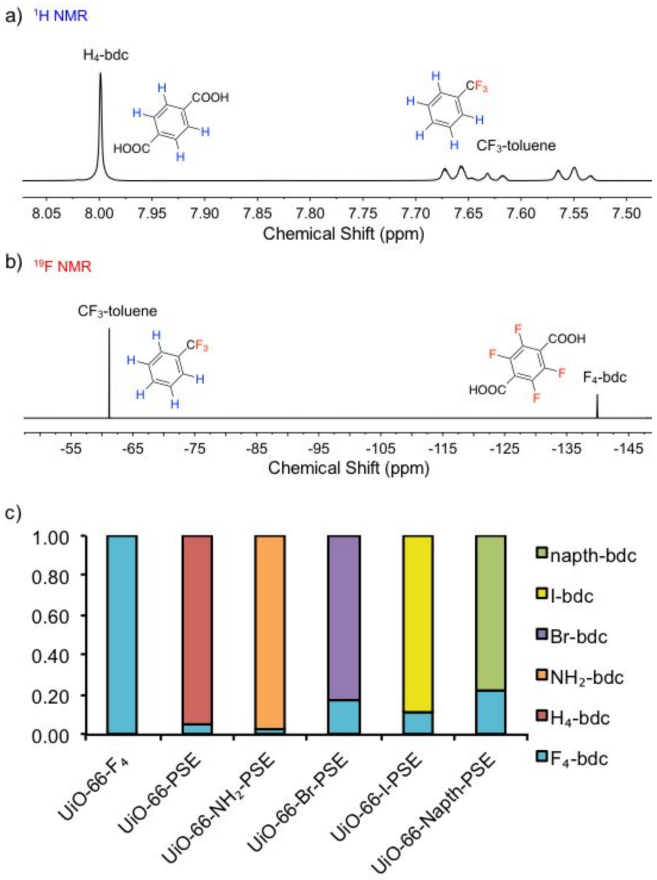

Figure 2. ^{1}H and ^{19}F NMR analysis of the PSE experiments performed with UiO-66-F$_4$. a) Representative ^{1}H and b) ^{19}F NMR spectra of digested UiO-66 formed by PSE (UiO-66-PSE). c) Relative amounts of the starting F$_4$-bdc^{2-} and the PSE R-bdc^{2-} derivatives in each of the PSE experiments performed.

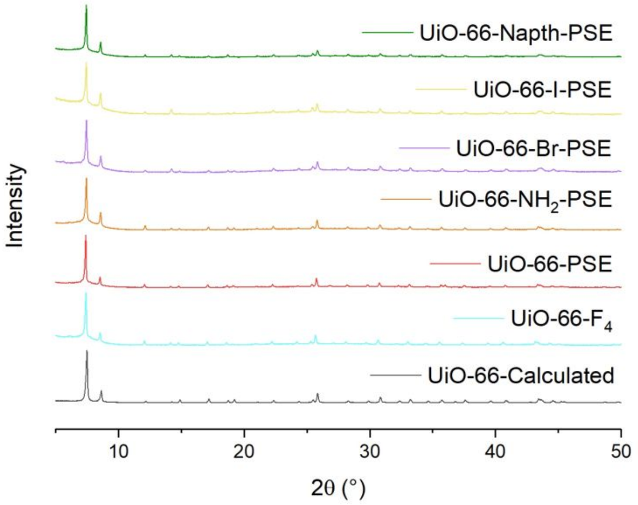

Figure 3. PXRD of the MOFs used in this study. The calculated UiO-66 pattern (black) is shown at the bottom; all other PXRD patterns are experimental results: UiO-66-F$_4$ (cyan), UiO-66-PSE (red), UiO-66-NH$_2$-PSE (orange), UiO-66-Br-PSE (purple), UiO-66-I-PSE (yellow), and UiO-66-Napth-PSE (green).

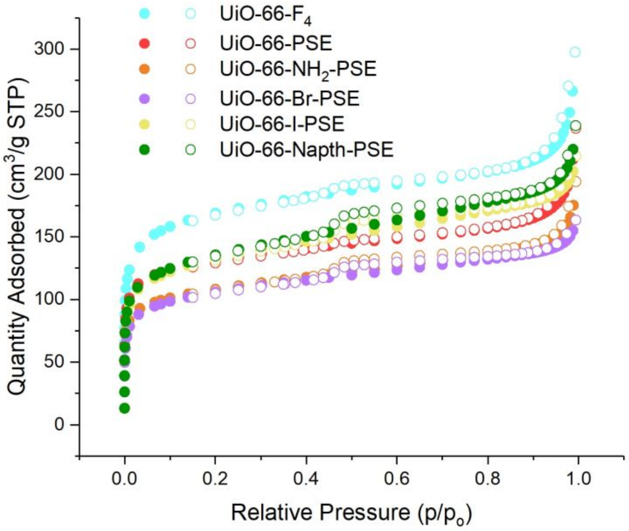

Figure 4. N_2 adsorption isotherms of UiO-66-F$_4$ and UiO-66-PSE MOFs: UiO-66-F$_4$ (cyan), UiO-66-PSE (red), UiO-66-NH$_2$-PSE (orange), UiO-66-Br-PSE (purple), UiO-66-I-PSE (yellow), and UiO-66-Napth-PSE (green).

Zr(IV)-based MOFs have been shown to be useful for the catalytic degradation of chemical warfare agents (CWAs) and their simulants.[24-25] Several factors have been suggested to affect activity toward CWAs such as particle size, defect sites, and ligand effects.[10, 24-27] As a proof of concept, we set out to screen a few of the MOFs in this study to show that variations in ligand functional groups effect catalytic activity, as previously reported.[24-25] To determine the catalytic activity of these MOFs, UiO-66-F$_4$, UiO-66-PSE, and UiO-66-NH$_2$-PSE were screened for the degradation of the CWA simulant dimethyl-4-nitrphenyl phosphate (DMNP). Because CWAs are extremely hazardous, we use the DMNP simulant as a safer alternative. MOFs were screened using a previously reported method.[27] The results indicate an increase in activity for both UiO-66-PSE and UiO-66-NH$_2$-PSE when compared to the as-synthesized UiO-66-F$_4$ MOF. The UiO-66-PSE and UiO-66-NH$_2$-PSE displayed >2-times the activity of the UiO-66-F$_4$ (Figure S12). It is important to note that the PSE MOFs (UiO-66-PSE and UiO-66-NH$_2$-PSE) were less active than hydrothermally synthesized UiO-66 and UiO-66-NH$_2$.[26] Overall, this result shows that we can use PSE to prepare materials under more mild, green conditions that display the expected MOF properties.

In conclusion, we have synthesized UiO-66 and a series of UiO-66 derivatives through a green aqueous and room temperature PSE route that uses UiO-66-F$_4$ as a template. These results highlight the power of postsynthetic chemistry to enhance not only the functionality, but synthetic accessibility of valuable MOF materials. Moreover, these mild synthetic conditions will allow researchers to more deeply analyze MOF formation through the use of instrumentation sensitive to harsh synthetic conditions.

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Conflict of Interest

There are no conflicts to declare.

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