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Postsynthetic Ligand and Cation Exchange in Robust Metal–Organic Frameworks

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Supporting Information

ABSTRACT: Postsynthetic ligand and metal ion exchange (PSE) processes are shown to readily occur in several "inert" metal–organic frameworks (MOFs), including zeolitic imidazolate frameworks (ZIFs). Ligand exchange can occur between solid samples, as was demonstrated under relatively mild conditions with two robust, topologically distinct MOFs, MIL-53(Al) and MIL-68(In). Interestingly, ligand PSE is not observed with MIL-101(Cr), which is attributed to the kinetic inertness of the Cr(III) ion. In addition to ligand exchange, metal ion (cation) PSE was also studied between intact MOF microcrystalline particles. Metal ion transfer between MIL-53(Al) and MIL-53(Fe) was readily observed. These PSE reactions were monitored and the products characterized by a number of techniques, including aerosol time-of-flight mass spectrometry, which permits single-particle compositional analysis. To show the potential synthetic utility of this approach, the PSE process was used to prepare the first Ti(IV) analogue of the robust UiO-66(Zr) framework. Finally, experiments to rule out mechanisms other than PSE (i.e., aggregation, dissolution/recrystallization) were performed. The results demonstrate that PSE, of either ligands or cations, is common even with highly robust MOFs such as UiO-66(Zr), MILs, and ZIFs. Furthermore, it is shown that PSE is useful in preparing novel materials that cannot be obtained via other synthetic methods.

INTRODUCTION

Metal–organic frameworks (MOFs, also referred to as porous coordination polymers, PCPs) are crystalline materials with high porosity that have garnered substantial attention for use in gas storage,[1,2] separation,[3] molecular shuttling,[4] sensing,[5] and catalysis.[6] Unlike other porous materials such as zeolites, active carbons, and mesoporous silicas, the organic linker/ligand component of MOFs can be easily functionalized, allowing for great structural and functional diversity. A variety of functional groups can be introduced on the organic ligand through direct solvothermal synthesis[7] or through postsynthetic approaches,[8] such as postsynthetic modification (PSM)[9,10] and postsynthetic deprotection (PSD).[11−15]

Recently the metathesis of metal ions or ligands from intact MOFs has been reported. This has important implications for the stability of these materials, but it can also be viewed as a type of postfunctionalization method, which we recently termed postsynthetic exchange (PSE).[16] Analogous cation and anion exchange reactions have been observed with nanoparticles[17] and other inorganic materials,[18−20] but observation of such phenomena in MOFs is relatively recent. For example, the exchange of metal cations from MOF crystals was reported with several systems,[21−26] where MOFs exposed to solutions containing metal ions were found to exchange the secondary building unit (SBU) metals with those from the solution without signficant changes in the framework structure. Similarly, ligand exchange between a MOF and a "competing" ligand in solution has also been recently studied. For example, neutral pyridine-based pillaring ligands in a MOF could be fully exchanged with a different pyridine-based ligand to achieve "stepwise" MOF synthesis.[27−29] In these cases, ligand and metal ion exchange in MOFs was observed in less chemically robust MOF materials where the metal–ligand bonding can be considered somewhat labile.

The complete exchange of anionic carboxylate ligands has been utilized in the stepwise synthesis of MOFs from metal–acid clusters[30] and has been observed during the surface modification of MOFs,[31] as well as in metal–organic polyhedra (MOP).[32] However, only very recently was it reported that anionic carboxylate ligand exchange was observed (both from solution and between two intact solids) in MOF materials.[16] Surprisingly, carboxylate ligand exchange was observed with a microcrystalline MOF that is considered to possess high chemical stability, namely, UiO-66(Zr) (UiO = University of Oslo, Zr(IV)-based MOF). UiO-66(Zr) is prepared from $ZrCl_4$ and 1,4-benzenedicarboxylic acid (BDC), producing a material reported to be inert and robust under a variety of chemical conditions.[33] Despite the structural stability of UiO-66(Zr), ligand PSE was observed in a solid–solid reaction between microcrystals suspended in solvent and also in a solid–liquid ligand exchange with free anionic ligand from solution (Scheme 1). PSE from ligand in solution proved to be a useful synthetic approach for modifying the UiO-66(Zr) framework with

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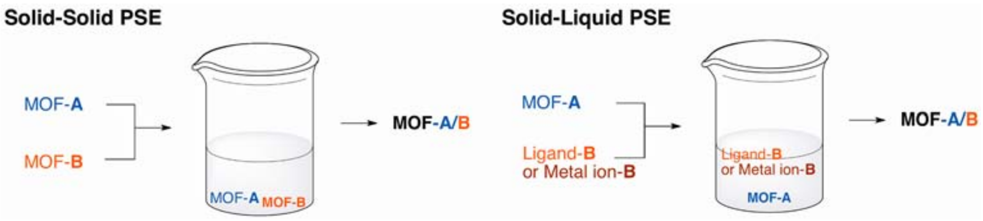
Scheme 1. Two PSE Scenarios: Solid−Solid and Solid−Liquid



functionalized ligands (e.g., azide- and hydroxyl-functionalized BDC ligands). Overall, PSE appeared promising as a postfunctionalization method for MOFs, as well as an important phenomenon when considering the assumed stability of robust MOFs.[16]

Herein, it is established that ligand and metal ion PSE can occur in a variety of the most chemically robust MOFs, including ZIFs. Aerosol time-of-flight mass spectrometry (ATOFMS) was used to monitor ligand or metal ion PSE processes in MOFs on a single-particle basis. It is also demonstrated that new MOFs, unavailable by other synthetic methods, can be accessed via metal ion PSE. Finally, mechanistic experiments support the hypothesis that the data obtained are best explained by a PSE process, allowing us to rule out other processes such as particle aggregation or bulk dissolution/recrystallization. These findings are important for understanding the stability and dynamics of MOFs, as well as providing new routes to the synthesis of unprecedented, mixed-component MOF materials.

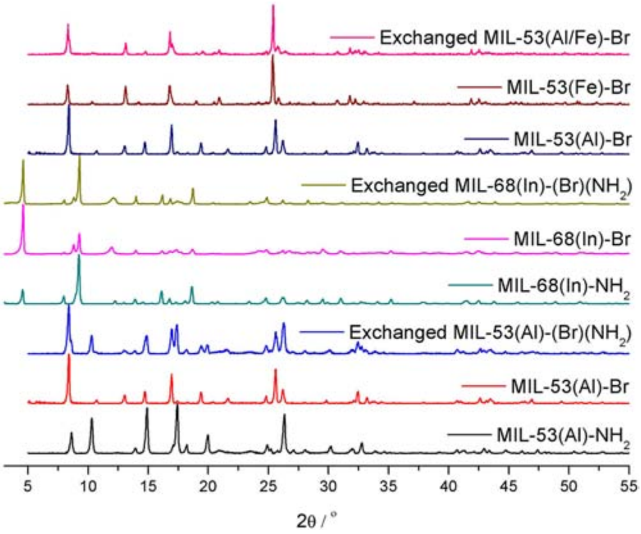


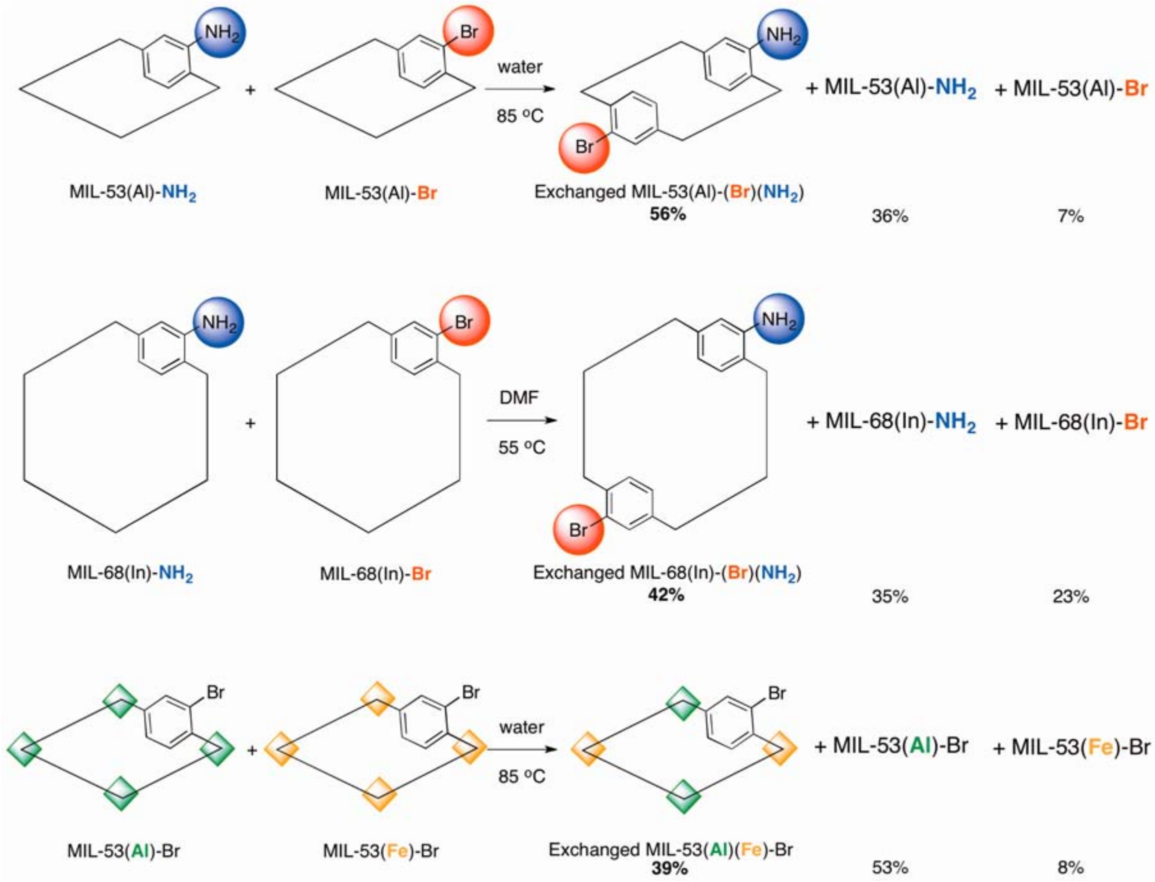
Figure 1. PXRD patterns of MIL materials examined in this study.

RESULTS AND DISCUSSION

Ligand PSE with Robust MOFs. Given the intriguing results from previous PSE reports, an attempt to determine if PSE was a widespread phenomenon was undertaken. Several reportedly water-stable MOFs were examined for ligand exchange. Water stability is essential for the technological use of MOFs, and many robust MOFs have been reported to have good moisture stability.[34] Water-resistant MOFs such as the MIL series (MIL = Materials of the Institut Lavoisier)[35] and ZIF series (ZIF = Zeolitic Imidazolate Framework)[36] form very stable but generally microcrystalline materials (not large single crystals). MIL-53 was developed by the Ferey group and exhibits high thermal and chemical stability.[35] For example, the stable aluminum-based MIL-53(Al) was successfully used for PSM experiments involving phosgene reagents without loss of the framework structure.[37]

MIL-53(Al)-NH$_2$ and MIL-53(Al)-Br were prepared from the combination of 2-amino-1,4-benzendicarboxylic acid (NH$_2$-BDC) or 2-bromo-1,4-benzendicarboxylic acid (Br-BDC) with an aluminum salt and water at 150 °C.[38,39] After isolation, the two MOFs were mixed together (as dry powders), suspended in water, and incubated for 5 d at 85 °C (well below the temperature required for solvothermal synthesis of the material, Scheme 1). The solid was then collected by centrifugation and washed with methanol. As expected, powder X-ray diffraction (PXRD) confirmed that the structure of the MIL-53(Al) frameworks was unchanged (Figure 1). However, ATOFMS analysis verified that the chemical composition of the MOF had changed, revealing that ligand-based PSE had occurred in these MIL-53(Al) derivatives. The dynamic exchange of ligands between solid MOFs while maintaining bulk crystallinity recapitulated that observed with UiO-66(Zr) (Scheme 2). The positive-ion ATOFMS spectra showed Al and Al$_2$O ions from the SBUs. More importantly, the negative-ion ATOFMS spectra showed both bromide- (m/z = −79 and −81) and nitrogen-containing ions (m/z = −26) in a single particle (Figure S1), indicative of PSE. Approximately 56% of single particles among the ~500 particles analyzed contained both a bromide ion and a nitrogen-containing ion (Table S1); that is, PSE occurred between more than half of the particles.

Ligand-based PSE was also examined in MIL-68(In). MIL-68(In) has a Kagome-like lattice with infinite chains of metal clusters linked through a BDC ligand.[40] MIL-68(In)-NH$_2$ and MIL-68(In)-Br were synthesized by modifying a previously reported method,[40] and similar to other PSE experiments, the two solids were mixed together as dry powders and incubated in *N*,*N*-dimethylformamide (DMF) for 5 days at 55 °C (Scheme 2). Because MIL-68(In) requires a lower temperature (100 °C) for solvothermal synthesis than the MIL-53(Al) series, the PSE incubation temperature was decreased to avoid MOF dissolution/recrystallization. Also, DMF was used as the reaction medium, instead of water, due to the instability of MIL-68(In) in water at elevated temperatures. Consistent with the other systems, PXRD shows that the crystallinity of the mixed MIL-68(In) powder is retained (Figure 1), but the negative-ion ATOFMS spectra show both bromide- and nitrogen-containing ions in a single particle, clearly indicating that PSE has occurred. The positive-ion ATOFMS spectra showed the expected In ion from the SBUs (Figure S2). Around 42% of particles contain both bromide- and nitrogen-containing ions in negative mode, unambiguously demonstrating that PSE occurs for MIL-68(In) in DMF solvent (Table S1). These findings highlight that many MOFs that are considered highly robust and "inert", including MIL-53(Al), Scheme 2. Postsynthetic Ligand and Cation Exchange in MIL Materials



MIL-68(In), and UiO-66(Zr), can undergo PSE in water or DMF. Although the degree of PSE in the MIL series is slightly lower than found with UiO-66(Zr) under the same conditions, the results demonstrate that PSE is a phenomenon relevant to many MOFs.

Another chemically robust MOF, MIL-101(Cr), was examined with respect to ligand PSE.[41] PSE for MIL-101(Cr) could be very valuable as a functionalization method, as there are few reported methods for functionalizing this material, and derivatives are difficult to synthesize directly due to the high temperature required for preparing this MOF (>220 °C).[42] Biphasic (solid–liquid, Scheme 1) PSE was attempted with activated MIL-101(Cr) incubated in a water solution of 2-bromobenzenedicarboxylate at 85 °C for 5 days. After centrifugation and washing with water, the green MIL-101(Cr) solid was recovered. The crystallinity of MIL-101(Cr) was totally retained, as evidenced by PXRD (Figure S3); however, no ligand PSE was detected, as Br-BDC was not detected in the ^{1}H NMR spectrum after base digestion of MIL-101(Cr). This is in contrast to the other robust MOFs studied, which do show ligand-based PSE. With respect to PSE, MIL-101(Cr) appears to be more inert compared to the other robust MOFs investigated. This finding is consistent with the very low ligand exchanges rates of Cr(III)[43,44] and suggests that the kinetic lability and/or inertness of a metal ion may play a significant role in the chemical stability of MOFs. This is consistent with the solvothermal conditions under which MOFs are synthesized; the ability to obtain crystalline or microcrystalline materials is dependent on the inherit reversibility of coordinate covalent bonds.

In order to examine other anion- but non-carboxylate-based stable MOFs, we chose to examine PSE in the highly robust ZIFs. Dichloro-substituted Zn(II)-based RHO-type ZIF-71 was synthesized as previously reported[45] and exposed to a MeOH solution of 4-bromo-1*H*-imidazole. 4-Bromo-1*H*-imidazole was selected as a model system for PSE because there are no ZIFs reported with this ligand. The solid–liquid mixture was incubated at 55 °C for 5 days, separated by centrifugation, and washed with MeOH. The bulk stability of the material was verified by PXRD, which confirmed that the crystallinity was retained after exchange. However, ^{1}H NMR spectra of digested samples showed that 4-bromo-1*H*-imidazole was incorporated into the ZIF by PSE (Figures 2 and S4). Approximately 30% of the ZIF was comprised of 4-bromo-1*H*-imidazole after the PSE reaction. Hence, again it was found that ligand PSE could be performed on a canonical "inert" MOF, in this case based on imidazolate ligands, resulting in the formation of a new material that could not be obtained by conventional solvothermal or other postsynthetic methods.

Metal Ion PSE with Robust MOFs. Cation exchange (i.e., metal ion PSE) in MOFs has become a growing area of interest, with several papers now published;[21−26] however, those studies have focused largely on MOFs that are not considered highly robust. In addition, metal cation exchange has only been reported on the basis of exchange between the MOF framework and a metal salt in solution (solid–liquid, Scheme 1) and never between two MOF solids.[16] It might be expected that robust MOFs would not readily exchange their structural metal ions in either a solid–liquid or solid–solid PSE process. To test this hypothesis, metal ion PSE of several robust,

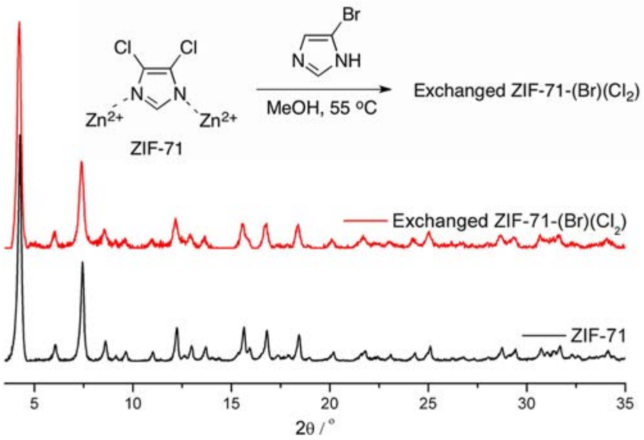


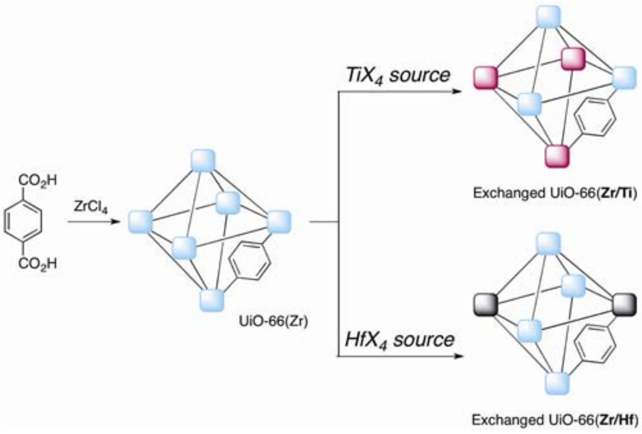
Figure 2. PXRD patterns of ZIF-71 and exchanged ZIF-71-(Br)(Cl_2).

microcrystalline MOFs was examined and monitored by using positive-ion ATOFMS spectra.

MIL-53 is a versatile material that has been synthesized with several metal salts, including Fe(III), Al(III), and Cr(III).[46] As described earlier, MIL-53(Al)-Br and MIL-53(Fe)-Br could be synthesized and activated as previously reported.[39,47] The purity and homogeneity of the materials was confirmed by the ATOFMS positive-ion spectra of pristine MIL-53(Al)-Br, which showed only Al and Al_2O ions (m/z = 27 and 70). Similarly, the ATOFMS positive-ion spectra of MIL-53(Fe)-Br showed only Fe isotopes (m/z = 54 and 56, Figure S5). MIL-53(Al)-Br and MIL-53(Fe)-Br were mixed as dry solids and then incubated in water for 5 days at 85 °C (Scheme 2). After incubation, the solid was collected by centrifugation, and PXRD confirmed that the crystallinity of the MOFs was unchanged (Figure 1). However, positive-ion ATOFMS spectra of the resulting solid showed that many particles contain both Fe and Al ions. Approximately 40% of the particles were shown to contain both metal ions (i.e., MIL-53(Al/Fe), Table S2). As expected, all negative-ion spectra showed bromide ions (m/z = −79 and −81, Figure S5), consistent with the presence of the Br-BDC ligand. In addition, scanning electron microscopy and energy-dispersed X-ray spectroscopy (SEM-EDAX) confirmed the presence of both Fe and Al in exchanged MIL-53(Al/Fe)-Br particles (Figure S6). These experiments provided direct evidence of metal ion PSE between two intact MOF solids. Importantly, sizing analysis of the particles by ATOFMS confirmed no change in particle size, ruling out particle aggregation as the source of these results (Figure S7).

Having observed that metal ion PSE could occur between two MOF solids, we sought to explore whether deliberate cationic exchange could be used to prepare new mixed-metal materials that were inaccessible by other synthetic methods. Specifically, the Ti(IV) analogue of the UiO-66(Zr) MOF has been elusive, as Ti(IV) is not known to form the SBU metal cluster found in UiO-66(Zr) ($M_6O_4(OH)_4(CO_2)_{12}$). In contrast, the heavier Hf(IV) analogue, which is known to make such a cluster, has been recently described (UiO-66(Hf)).[48] Ti(IV) would be attractive as a lighter, highly oxophilic metal that should impart a lower density with improved stability as well as unique photochemical properties.[49] Few Ti-based MOFs have been reported, and most show high reactivity with water and oxygen.[50,51] Therefore, the introduction of the Ti(IV) cation into the UiO-66 MOF was an attractive target and substantial challenge (Scheme 3).

Scheme 3. Postsynthetic Cation Exchange of UiO-66



UiO-66(Zr) was prepared, isolated, and then exposed to DMF solutions of Ti(IV) salts, such as $TiCp_2Cl_2$, $TiCl_4(THF)_2$, or $TiBr_4$ (Cp = η^5-cyclopentadienyl, THF = tetrahydrofuran), for 5 days at 85 °C . After separating the solid by centrifugation and washing with fresh DMF, the presence of the Ti(IV) ion in the MOF was confirmed by positive-ion ATOFMS spectra (Figure 3). The number of particles containing Ti(IV) is dependent on the metal salt used in the PSE reaction (Table S3). $TiBr_4$ showed the lowest level of PSE via ATOFMS when compared with $TiCp_2Cl_2$ and $TiCl_4(THF)_2$, which was likely due to the reactivity and instability of $TiBr_4$, making it more difficult to handle. The amount of incorporated Ti(IV) was quantified by inductively coupled plasma mass spectrometry (ICP-MS, Table 1). The best incorporation was achieved with $TiCl_4(THF)_4$, which resulted in >90% of the microcrystalline MOF particles incorporating Ti(IV), with Ti(IV) constituting ~38 wt% of the metal ion present in the whole sample (Table 1, entry 4). Importantly, the crystallinity of exchanged UiO-66(Zr/Ti) was retained, as evidenced by PXRD, and thermogravimetric analysis (TGA) showed a thermal decomposition temperature similar to that of UiO-66(Zr) (>400 °C, Figures S8 and S9). A Brunauer−Emmett−Teller (BET) surface area of ~1200 m^2/g was obtained using dinitrogen, which supports the arguments that the Ti(IV) metal was incorporated into the SBU clusters and that no Ti ions or particles are blocking the pores (Table 1). As further evidence of SBU inclusion, UiO-66(Zr/Ti) is colorless, while $TiCl_4(THF)_2$ is a pale yellow solid, suggesting that the Ti(IV) found in the MOF is not trapped starting material. Similar experiments were performed with $HfCl_4$, which showed very little PSE at room temperature, with only ~20% of the particles incorporating Hf(IV) even at elevated temperatures (Tables 1 and S3). Nonetheless, by using metal ion PSE, we have discovered a synthetic route to the long-sought Ti(IV)-containing analogue of UiO-66 and found that the MOF shows excellent stability, crystallinity, and porosity.

Exploring PSE in Rigorously Separated Samples. In our previous PSE studies,[16] the ligand PSE process occurred with two solid MOF samples that were physically mixed together and incubated in a solution (as described above). ATOFMS data showed both ligands in a single particle, which we attribute to PSE between the solid samples; however, we sought to provide additional evidence to rule out other phenomena that might explain these observations. Other plausible mechanisms might include dissolving/re-forming of

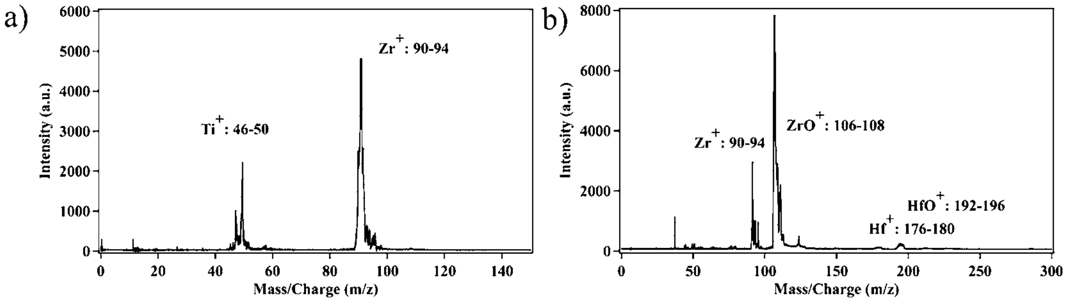


Figure 3. ATOFMS positive-ion spectra for the PSE products: (a) UiO-66(Zr/Ti) and (b) UiO-66(Zr/Hf).

Table 1. Postsynthetic Cation Exchange of Titanium and Hafnium in UiO-66(Zr)[a]

entry	Ti or Hf salt	temp	exchanged % (ATOFMS)[b]	wt% of Ti or Hf (ICP-MS)	BET surface area (m^2/g)
1	$TiCp_2Cl_2$[c]	rt	<5 ± 5.0	–	–
2	$TiCp_2Cl_2$[c]	85 °C	94 ± 0.7	12.0	1259
3	$TiCl_4(THF)_2$	rt	54 ± 5.0	–	–
4	$TiCl_4(THF)_2$	85 °C	93 ± 0.7	37.9	1365
5	$TiBr_4$	rt	57 ± 5.0	–	–
6	$TiBr_4$	85 °C	73 ± 1.4	1.4	1291
7	$HfCl_4$	rt	10 ± 0.9	–	–
8	$HfCl_4$	85 °C	18 ± 1.2	–	1289

[a] UiO-66(Zr) (0.1 mmol) and Ti salt (0.1 mmol) were placed in a dram vial with 2 mL of DMF for 5 days. [b] (Number of particles of Ti or Hf)/(total number of particles). [c] $TiCp_2Cl_2$ = dichloridobis(η^5-cyclopentadienyl) titanium(IV).

the framework or particle aggregation. MOF dissolving/re-forming was ruled out because UiO-66(Zr) cannot be directly synthesized under the exchange conditions utilized. In addition, particle size analysis by ATOFMS, SEM, and DLS before and after the PSE reaction shows no change in crystallite size, which argues against particle aggregation.[16] Nonetheless, to further clarify the details of the PSE process, experiments were performed where the microcrystalline MOFs were not physically mixed (i.e., never placed in direct physical contact). A small (2 mL) vial containing UiO-66(Zr)-Br was placed into a larger (20 mL) vial containing UiO-66(Zr) and water (Scheme S1, Figure S10). After incubation, the two vials were separated and analyzed by ^{1}H NMR and ATOFMS to determine whether PSE had occurred (see Supporting Information for experimental details). Under these conditions, a much larger volume of water (~22 mL vs ~2 mL) was used in order to fill the two vials, and no PSE was observed.[16] We attribute this observation, in part, to the much higher dilution and lack of stirring/agitation of the samples (which might be required to promote diffusion of exchanging ligands).

Recently, the use of acidic additives have been reported for the synthesis of MOFs, including UiO analogues.[52,53] In these reports, the organic acid (benzoic or acetic acid) can modulate crystal growth by metastasis with the BDC ligand, resulting in better control over the crystallization process.[53] We speculated that this equilibrium between the acid additive and BDC ligand could promote PSE by exchanging with and labilizing ligands in the MOF. Performing the same vial-separated experiment described above, but with the addition of with 2% AcOH(aq), resulted in PSE between the materials, as confirmed by ^{1}H NMR and ATOFMS (Table S4), with a retention of crystallinity, as determined by PXRD (Figure S11). After PSE, ~90% of the UiO-66(Zr) particles contained a bromide ion, as revealed by negative-ion ATOFMS, which originates from PSE with the isolated UiO-66(Zr)-Br sample. Recall that,

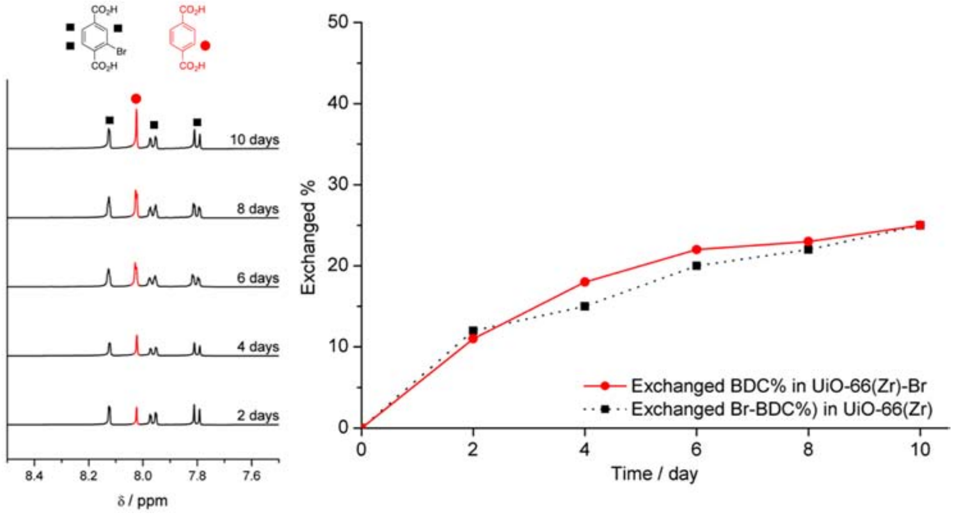


Figure 4. Time course of vial-separated PSE experiment with UiO-66(Zr) and UiO-66(Zr)-Br. ^{1}H NMR spectra of exchanged UiO-66(Zr)-Br after acid digestion at several time points (left). Percentage of particles show ligand PSE (right) as a function of time: percentage of UiO-66(Zr)-Br containing BDC (red solid line), and percentage of UiO-66(Zr) containing Br-BDC (black dotted line).

under these conditions, the UiO-66(Zr) and UiO-66(Zr)-Br microcrystals are never in physical contact. ^{1}H NMR was used to show that the exchanged UiO-66(Zr) sample contained 25% Br-BDC and 75% BDC after 10 days of incubation. Kinetic studies confirm that the amount of exchanged ligand increases over time (Figure 4 and Table S4), and the percentage of PSE for each MOF is complementary (that is, the amount of Br-BDC in UiO-66(Zr) and the amount of BDC in UiO-66(Zr)-Br are the same), as would be expected (determined by ^{1}H NMR, Figure 4). It should be noted that incubation with ≥5% AcOH(aq) decreased the crystallinity of UiO-66(Zr) significantly.

In summary, these experiments strongly suggest that PSE is a true ligand-exchange mechanism and that particle aggregation is not the origin of the mixed-ligand particles we observe by ATOFMS. Furthermore, UiO-66(Zr) cannot be directly synthesized under the PSE reaction conditions (i.e., water, 85 °C); thus, the mechanism of PSE cannot be attributed to a bulk-scale dissolution and recrystallization process of the MOF. Rather, we assert that the transfer process is due to the reversible nature of the coordination bonds in these materials, resulting in classic ligand-exchange reactions between solids or a solid−solution mixture that we refer to as PSE.

■ CONCLUSION

The findings presented here show that PSE of anionic ligands or cationic metal ions is a general phenomenon in even the most “inert” MOFs. These results, combined with other recent exchange/substitution studies, strongly suggest that PSE is nearly universal in MOFs and that the chemical bond between the metal cluster SBUs and ligand linkers is reversible. Of all the systems examined, only MIL-101(Cr) appeared to be resistant to PSE, which we attribute to the high kinetic inertness of the Cr(III) ion. Although MOFs are solid-state materials that are thermally, structurally, and chemically stable, it appears that they can be quite dynamic. Experiments were performed that confirm the data obtained are the result of PSE and not other mechanisms.

The unique ability of ATOFMS to analyze the chemical composition of a single microcrystalline particle has now been applied to reveal metal cation PSE. Metal ion PSE was observed between MIL-53(Al) and MIL-53(Fe). More significantly, biphasic (solid−liquid) PSE was used to produce Ti(IV)-exchanged UiO-66(Zr/Ti) materials. This demonstrates the utility of PSE to access materials that cannot be obtained by other synthetic methodologies currently available. The results presented here with robust MOFs provide important information on MOF dynamics important for their technological applications and yet also provide a route to new functional materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details of MOF synthesis and PSE, ATOFMS, TGA, and ^{1}H NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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