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Post-synthetic modification of zinc metal-organic frameworks through palladium-catalysed carbon-carbon bond formation

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Abstract

Post-synthetic Suzuki coupling reactions have been undertaken on the halide-functionalised metal-organic frameworks (MOFs) [Zn$_4$O(bdc-Br)$_3$] (bdc-Br = 2-bromo-1,4-benzenedicarboxylate, IRMOF-2) and [Zn$_4$O(bdc-I)$_3$] (bdc-I = 2-iodo-1,4-benzenedicarboxylate). Although the bulky catalyst employed leads to relatively low conversions, the use of core-shell MOFs demonstrates that the reactions are not confined to the crystal surfaces.

Keywords

1. Introduction

Post-synthetic modification has recently emerged as an important tool in the chemistry of metal-organic frameworks (MOFs), enabling access to functionalised materials that cannot be prepared by direct combination of the metal centres and ligands.[1, 2] Post-synthetic modifications can take place through exchange of metal centre[3] or linker,[4, 5] coordination of a metal centre[6] or ligand[7] to a MOF, or by formation or cleavage of a covalent bond. The majority of covalent post-synthetic modifications reported to date have involved transformations of amine groups, though a growing number of other functionalities have been shown to able to be modified in this manner, including alkenes,[8] sulfides[9] and halides.[10, 11] Reactions have also been shown to occur thermally[12, 13] or photochemically.[14, 15]

Post-synthetic modification reactions can occur with complete or partial conversion, and control over the degree of conversion is possible through variation of the steric bulk of the reagent and control over the number of reactive groups present on the MOF.[16] Use of a very bulky reagent would be expected to prevent access into the pores, and this can lead to modification only of the crystal surfaces, which allows the physical properties and reactivities of MOF crystals to be modified. Recently, Hupp, Nguyen and co-workers explored the surface-modification of MOFs using 'click' chemistry.[17] They used tetrabutylammonium fluoride to deprotect silyl-protected alkynes, before reacting the terminal alkyne products with azides. Their protocol relied on the fact that the bulky tetrabutylammonium cations limit the deprotection reaction to the surfaces. In a further study[18] they showed it was possible to obtain different triazoles on the surface and interior of the crystal. Kitagawa and co-workers have also investigated surface-modification reactions, though using coordination

bond formation as opposed to covalent bond formation.[19] They prepared carboxylates containing fluorescent dipyrromethene groups, and demonstrated that these react at the crystal surfaces terminated by zinc-carboxylate bonds, substituting dicarboxylate ligands on these surfaces by the fluorescent carboxylates.

Carbon-carbon bond forming reactions such as the Suzuki, Sonogashira and Heck reactions are extremely important synthetically, and although generally carried out in solution, they are also possible on solid-state supports such as resins.[20] We were interested in exploring whether such reactions could be carried out on a MOF, and if so whether modification would be limited to the crystal surfaces, given the steric bulk of the palladium complex catalyst which might be anticipated to be too bulky to penetrate into the pores. In this paper we explore the use of the Suzuki coupling reaction between a halide-containing MOF and a boronic acid.

Suzuki coupling reactions normally work best for iodides, and in this paper we investigate the post-synthetic modification reactions of $[Zn_4O(bdc\text{-}Br)_3]$ (IRMOF-2, bdc-Br = 2-bromo-1,4-benzenedicarboxylate) **1**[21] and $[Zn_4O(bdc\text{-}I)_3]$ (bdc-I = 2-iodo-1,4-benzenedicarboxylate) **2**[22] with a range of boronic acids under Suzuki coupling conditions. **1** and **2** have three-dimensional structures with a simple cubic topology, with linear dicarboxylate linkers inter-connecting Zn_4O nodes (Figure 1).
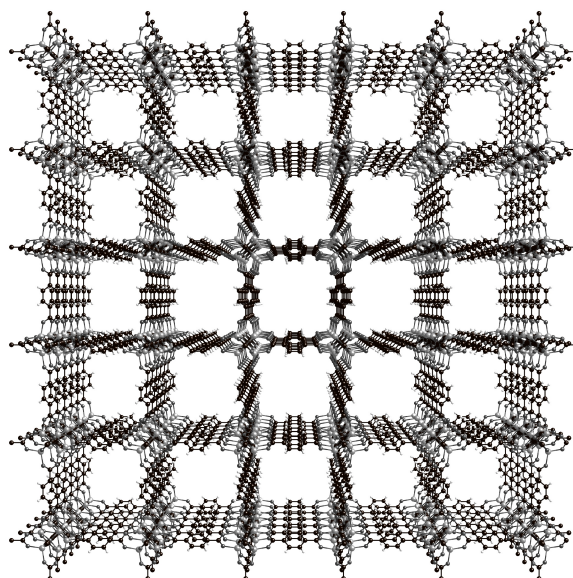

Figure 1. The 3-dimensional network structure that is observed in **1** and **2**. The figure was generated from the crystallographic data presented in ref. 21.

We also investigate analogous reactions with core-shell MOFs formed with either [Zn$_4$O(bdc)$_3$] (MOF-5, bdc = 1,4-benzenedicarboxylate) at the core, and one of [Zn$_4$O(bdc-I)$_3$] or [Zn$_4$O(bdc-Br)$_3$] as the shell, or with one of [Zn$_4$O(bdc-I)$_3$] or [Zn$_4$O(bdc-Br)$_3$] at the core and with [Zn$_4$O(bdc)$_3$] as the shell.

2.   Materials and Methods

2.1   General information

All MOF synthesis reactions were carried out in Ace pressure tubes purchased from Sigma Aldrich, in a Sanyo MOV-112 drying oven.   X-ray powder diffraction experiments were recorded on a Bruker AXS D8 Advance diffractometer with copper Kα radiation of wavelength 1.5406 Å at 298K.   Mass spectrometry data were recorded on a Bruker MicroTOF spectrometer, NMR data on a Bruker Avance 250 MHz or Bruker Ultrashield 300 MHz spectrometer, and infrared data on a Nicolet Nexus FT-IR spectrometer.   Atomic absorption measurements were recorded on a Perkin Elmer AAnalyst 100.   Solid-state NMR experiments were performed using a Bruker Avance III 600 spectrometer, equipped with a wide-bore 14.1 T magnet (ω_0 = 600.1, 564.7 and 150.9 MHz for ^{1}H, ^{19}F and ^{13}C, respectively).   Samples were packed in conventional 1.3 or 4 mm ZrO$_2$ rotors and rotated at a rate of 60 kHz (1.3 mm rotors) or 12.5 kHz (4 mm rotors) in standard Bruker double resonance probes.   The ^{19}F NMR spectrum (60 kHz MAS) was acquired with a Hahn-echo pulse sequence using a repeat interval of 3 s. ^{13}C spectra were acquired with cross polarisation from ^{1}H at 12.5 kHz MAS. A spin lock of 1 ms duration was used for ^{13}C, with a ramped (90-100%) pulse was applied to ^{1}H. TPPM-15 decoupling of ^{1}H was applied during acquisition. A repeat interval of 3 s was used. Signal averaging was carried out over 1024 transients for ^{19}F and 2048 transients for ^{13}C. [Zn$_4$O(bdc-Br)$_3$] **1** and [Zn$_4$O(bdc-I)$_3$] **2** were prepared followed the previously reported methods.[21, 22]

2.2   Suzuki couplings with **1** and **2**

The reactions of **1** and **2** with Ar^{1}B(OH)$_2$, Ar^{2}B(OH)$_2$, Ar^{3}B(OH)$_2$ and FcB(OH)$_2$ were carried out using the same method. **1** or **2** (0.68 mmol) was combined in a round-bottomed flask with the boronic acid (0.68 mmol), Pd(OAc)$_2$ (0.023 g, 0.10 mmol), PPh$_3$ (0.086 g, 0.33 mmol), NEt$_3$ (95 μl, 0.68 mmol) and DMF (15 cm^3). The mixture was heated under N$_2$ at 100 °C for 3 hours. The solid MOF was then separated by filtration and washed with 2 × 30 cm^3 fresh DMF to remove any unreacted or digested components.

The modified MOFs were digested and dissolved by sonication in 1.5 cm^3 of a solution of DMSO-d_6 and 200 µl of a DCl solution prepared by dissolving 23 µl of 35% DCl/D$_2$O solution in 1 cm^3 DMSO-d_6. This solution was used directly for ^{1}H, ^{13}C and ^{19}F NMR spectroscopy and was diluted by a factor of 10 in ethanol for mass spectrometry. Solid-state NMR spectroscopy was carried out directly on modified MOF samples after filtration.

2.3   Synthesis of core-shell MOFs

The following reactions were set up:

- 1,4-benzenedicarboxylic acid (0.025 g, 0.15 mmol) and Zn(NO$_3$)$_2$·6H$_2$O (0.149 g, 0.5 mmol) were dissolved in DEF (5 cm^3) in a pressure tube and heated at 95 °C for 48 hours (two separate batches).

- 2-bromo-1,4-benzenedicarboxylic acid (0.037 g, 0.15 mmol) and Zn(NO$_3$)$_2$·6H$_2$O (0.149 g, 0.5 mmol) were dissolved in DEF (5 cm^3) in a pressure tube and heated at 95 °C for 72 hours.

- 2-iodo-1,4-benzenedicarboxylic acid (0.044 g, 0.15 mmol) and Zn(NO$_3$)$_2$·6H$_2$O (0.149 g, 0.5 mmol) were dissolved in DEF (5 cm^3) in a pressure tube and heated at 95 °C for 48 hours.

The mother liquors were carefully decanted from each MOF reaction. 1.25 cm^3 of each solution was removed after stirring for 10 minutes and was mixed with 3.75 cm^3 of fresh DEF in order to dilute to a quarter of the original concentration. The diluted mother liquors from the H$_2$bdc reactions were added to the crystals from the H$_2$bdc-Br and H$_2$bdc-I reactions respectively. The diluted mother liquors from the H$_2$bdc-Br and H$_2$bdc-I reactions were added to the crystals from the H$_2$bdc reactions. These were heated at 80 °C for 2 weeks, then filtered and washed with fresh DEF.

2.4   Suzuki coupling on the core-shell MOFs

MOF-5@**1**, MOF-5@**2**, **1**@MOF-5 and **2**@MOF-5 were all modified in the same way using 4-methylsulfonylphenylboronic acid (Ar^{1}B(OH)$_2$) and ferroceneboronic acid. (FcB(OH)$_2$).

The MOF (0.68 mmol) was combined in a round-bottomed flask with the boronic acid (0.68 mmol), Pd(OAc)$_2$ (0.023 g, 0.10 mmol), PPh$_3$ (0.086 g, 0.33 mmol), NEt$_3$ (95 µl, 0.68 mmol) and DMF (15 cm^3). The mixture was heated under N$_2$ at 100 °C for 3 hours. The solid MOF was then filtered and washed with a generous amount of fresh DMF to remove any unreacted or digested components.

The modified MOFs were digested and dissolved by sonication in 1.5 cm^3 of a solution of DMSO-d_6 and 200 µl of a DCl solution prepared by dissolving 23 µl of 35% DCl/D$_2$O solution in 1 cm^3 DMSO-d_6. This solution was used directly for ^{1}H NMR spectroscopy and was diluted by a factor of 10 in ethanol for mass spectrometry.

3.   Results and Discussion

[Zn$_4$O(bdc-Br)$_3$] **1** and [Zn$_4$O(bdc-I)$_3$] **2** were both reacted with the boronic acids shown in Figure 2 in the presence of palladium(II) acetate, triphenylphosphine and triethylamine in *N,N*-dimethylformamide (DMF), at 100 °C under a nitrogen atmosphere for 3 h to give the materials **1**-Ar$^{1-3}$, **1**-Fc, **2**-Ar$^{1-3}$ and **2**-Fc (Scheme 1). After the reactions, the crystals had darkened from cream to pale brown (**1**-Ar$^{1-3}$ and **2**-Ar$^{1-3}$) or dark red (**1**-Fc and **2**-Fc). The crystals were separated by filtration, then washed several times with DMF to remove any reactants or soluble components.
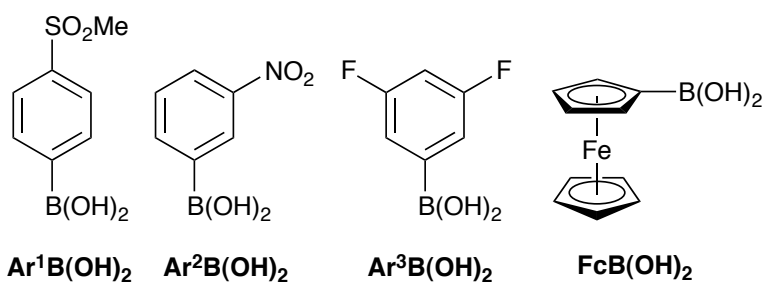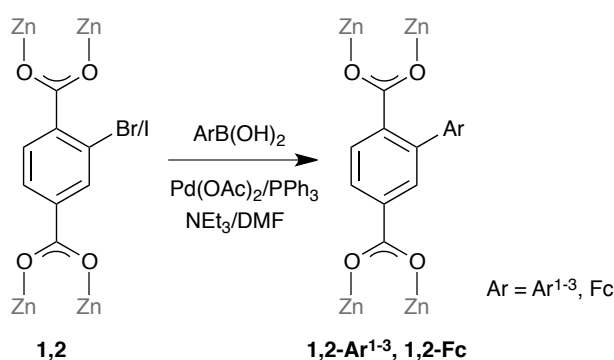

Figure 2. Boronic acids used in the post-synthetic modification of **1** and **2**.

Scheme 1

Compounds **2**, **2**-Ar^1 and **2**-Ar^3 were analysed by MAS NMR spectroscopy. Generally, only subtle differences could be observed between the ^{1}H and ^{13}C MAS NMR spectra of the starting material, **2**, and those of the modified products, which suggests low degrees of

conversion. However, observation of a broad resonance at δ −110 ppm in the ^{19}F MAS NMR spectrum of **2**-Ar[3] is indicative of successful modification, with the linewidth (~4000 Hz) consistent with the modified linker being present in a distribution of chemically similar but inequivalent environments rather than having a single crystallographic location. Other direct evidence of post-synthetic modifications include new stretching frequencies at 1147 cm^{−1} in the infrared spectra of **1**-Ar[1] and **2**-Ar[1], assigned to the $\nu(SO_2Me)$ group.

Further analysis of the Suzuki-modified products was undertaken by digesting samples with DCl/d_6-dmso, then analysing the resultant solutions by NMR spectroscopy and electrospray (ESI) mass spectrometry. The ^{1}H and ^{13}C NMR spectra are dominated by signals for the 2-halo-1,4-benzenedicarboxylic acids, consistent with the low degrees of conversion suggested by the MAS NMR experiments. However, the presence of lower intensity multiplets between δ 7.4 ppm and δ 7.7 ppm in all cases are consistent with additional aryl protons arising from successful coupling reactions. Further ^{1}H NMR evidence of coupling comes from peaks at δ 3.29 ppm for the methyl group in bdc-($C_6H_4SO_2Me$-4)-2 in digested samples of **1**-Ar[1] and **2**-Ar[1]. The ^{19}F NMR spectra for digested samples of **1**-Ar[3] and **2**-Ar[3] showed multiplets at δ −110.4 ppm, slightly shifted from the resonance for 3,5-difluorophenylboronic acid, which is observed at δ −111.2 ppm. The removal of the soluble reagents through the washing procedure was evidenced by the absence of these species from the ^{1}H NMR spectra of the digested products.

ESI mass spectra provided further evidence of successful coupling reactions, with peaks in the negative ion spectra at m/z 319.028 from **1**-Ar[1] and **2**-Ar[1] (calc. for [Hbdc-($C_6H_4SO_2Me$-4)-2][−], 319.027), 286.033 from **1**-Ar[2] and **2**-Ar[2] (calc. for [Hbdc-($C_6H_4NO_2$-3)-2][−], 286.035), 277.030 from **1**-Ar[3] and **2**-Ar[3] (calc. for [Hbdc-($C_6H_3F_2$-3,5)-2][−], 277.031) and 349.19 from **1**-Fc and **2**-Fc (calc. for [Hbdc-($C_5H_4Fe(C_5H_5)$)-2][−], 349.02). In each case, the observed mass spectrum has the expected isotope distribution pattern (see Supporting Information).

While the combination of NMR spectroscopy and ESI mass spectrometry has unambiguously confirmed the products contain linkers bearing Suzuki-coupled functionalities, it is difficult to quantify the conversions using these techniques, especially given the complex nature of the ^{1}H NMR spectra resulting from the number of non-equivalent aromatic protons. For **1**-Fc and **2**-Fc, the presence of the two metal centres suggested that atomic absorption spectroscopy could be used on digested samples to estimate the zinc : iron ratio, and hence quantify the degree of conversion. For **1**-Fc, the observed zinc : iron ratio was 22 : 1, giving a formula of [Zn_4O(bdc-Br)$_{2.82}$(bdc-$C_5H_4Fe(C_5H_5)$)$_{0.18}$], and a conversion of 6%. For **2**-Fc, the observed ratio was 12 : 1, giving a formula of [Zn_4O(bdc-Br)$_{2.66}$(bdc-$C_5H_4Fe(C_5H_5)$)$_{0.34}$], and a conversion of 11%. The greater conversion in the case of **2** is consistent with the well-

established ease of undergoing Suzuki coupling reactions for aryl iodides with respect to bromides. While still relatively low, these conversions are high enough to suggest that post-synthetic modification is not completely limited to the crystal surfaces. No further conversion was observed on an increase in reaction time.

Since palladium complexes, including palladium(II) acetate,[23] are known to interact with MOF-5 to form nanoparticles within the MOF,[24] it was important to establish whether such nanoparticles were formed under the reaction conditions here, as if so they could conceivably catalyse the Suzuki reaction. MOF-5 was observed to turn dark red on treatment with palladium(II) acetate and triphenylphosphine, consistent with the reported nanoparticle formation. In contrast, when a similar reaction was undertaken with **1** or **2**, no change in colour of the MOF was seen, though small black particles of palladium, not attached to the MOF crystals, were observed. These materials did not undergo reaction with any of the boronic acids, demonstrating the need for the homogeneous catalyst. Notably, atomic absorption spectroscopy on samples of digested **1** and **2** that had been treated with palladium(II) acetate and triphenylphosphine showed no evidence for palladium. This is consistent with the absence of colour change, and suggests that **1** and **2** do not form palladium nanoparticles under the same conditions as MOF-5.

In order to assess whether reactions were occurring only on the crystal surfaces, we focussed our attention on mixed-component MOFs,[16] and a particular class of mixed-ligand MOFs[25] known as core-shell MOFs.[16] These are materials in which one MOF crystallises on the external surfaces of another MOF. In the zinc-dicarboxylate system, core-shell MOFs have been previously reported using MOF-5 and $[Zn_4O(bdc-NH_2)_3]$ (IRMOF-3, bdc-NH$_2$ = 2-amino-1,4-benzenedicarboxylate).[26, 27] If Suzuki-coupling reactions are limited to crystal surfaces, core-shell MOFs such as **1**@MOF-5 and **2**@MOF-5, with halo-containing ligands on the surface would be expected to show evidence of post-synthetic Suzuki coupling, whereas MOFs such as MOF-5@**1** and MOF-5@**2**, with the halo-containing ligands in the interior, would not. The core-shell MOFs **1**@MOF-5, **2**@MOF-5, MOF-5@**1** and MOF-5@**2** were initially prepared following the method previously reported by Matzger and co-workers for core-shell MOFs containing IRMOF-3.[26] Once crystals of **1** (or **2**) and MOF-5 had started to form after 48 - 72 h in *N,N*-diethylformamide (DEF) at 95 °C, the mother liquors were swapped and the reactions continued for a further 72 h in DEF. Although the majority of the crystals formed after this time had the expected core-shell structure, under the microscope it was clear that the product was not homogeneous, and some crystals had formed that were simply **1**, **2** or MOF-5.

Previous observations had revealed that **1**, **2** and MOF-5 did not crystallise from the reaction

mixture in DEF at 80 °C, even after 2 weeks. Therefore, once the mother liquor exchange had taken place, the solutions were heated at 80 °C rather than 95 °C. The lower temperature was anticipated to prevent nucleation, with the intention that the MOF would only crystallise on the surfaces of already existing seed crystals. The reaction mixtures were left at 80 °C for two weeks in order to ensure that shells formed on all of the seed core crystals. After two weeks it was clear by microscopy that all of the crystals formed were core-shell crystals as expected, with the shell present as a thin layer on all of the crystals observed.

The powder X-ray diffraction patterns for these core-shell crystals were identical to those of the major component at the core. Thus **1**@MOF-5 and **2**@MOF-5 showed similar powder X-ray diffraction patterns to MOF-5, whereas MOF-5@**1** and MOF-5@**2** showed similar powder X-ray diffraction patterns to the isostructural MOFs **1** and **2**. Mass spectrometry of the acid digested core-shell crystals showed the presence of both the expected dicarboxylic acids.

Suzuki coupling reactions were carried out on all the core-shell MOFs with 4-methylsulfonylphenylboronic acid ($Ar^1B(OH)_2$) and ferroceneboronic acid ($FcB(OH)_2$). The reactions on the MOFs with MOF-5 as the shell were carried out to investigate whether the boronic acid and catalyst would penetrate the surface and the coupling would occur on the halogenated MOF core. The products were digested in DCl/DMSO-d_6 and analysed by mass spectrometry and ^1H NMR spectroscopy as before. In the mass spectra the *m/z* peaks for the Suzuki coupled products were seen but these were of very low intensity and in most cases the isotope patterns could not be distinguished. ^1H NMR spectroscopy revealed the presence of the Suzuki coupled products in all cases, including the methyl protons at δ 3.3 ppm for the 4-methylsulfonyl groups. These signals were of very low intensity in the ^1H NMR spectra suggesting low levels of conversion. Powder X-ray diffraction patterns suggested some reduction in crystallinity after the Suzuki coupling reactions (Fig. S9), though the retention of the major features suggests that the MOFs remain broadly intact.

As the Suzuki coupled products were seen in MOF-5@**1** and MOF-5@**2**, this suggests that the boronic acid and catalyst were able to penetrate into the interior of the crystals. In the case of ferroceneboronic acid, a change in colour of the interior of the crystals from pale yellow to orange is consistent with this observation, though notably the lower intensity of the colour with respect to reaction of **1** and **2** suggests a lower degree of modification. In other words, the MOF-5 shell decreases the extent of reaction, but does not completely stop it. Given the size of triphenylphosphine, the catalyst would not be expected to be small enough to diffuse through the pores, so it is likely that the diffusion only at defects.

4.   Conclusions

In conclusion, we have demonstrated that Suzuki couplings can be undertaken post-synthetically on MOFs. Using 'standard' Suzuki conditions of palladium(II) acetate, triphenylphosphine and triethylamine in DMF at 100 °C, post-synthetic modification was observed with four different boronic acids, though typically with low rates of conversion. Studies with core-shell MOFs revealed that conversion is not limited to the external crystal surfaces. The demonstration that carbon-carbon bond formation can be carried out post-synthetically on a MOF is significant, as the wide range of available boronic acids makes this a versatile method of adding functional groups to MOFs. Current work is focussed on determining whether reaction occurs due to the presence of defects in the shells or through a limited amount of penetration of the reagents through the shells. Furthermore, we are looking to increase levels of conversion by varying the catalyst and employing more robust halide-containing MOFs with larger pores than those in **1** and **2**.

5.   Acknowledgements

6.   References

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