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Selective incorporation of functional dicarboxylates into zinc metal–organic frameworks†

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Zinc(II) nitrate reacts with different ratios of 1,4-benzenedicarboxylic acid (H_2bdc) and 2-halo-1,4-benzenedicarboxylic acid (H_2bdc-X, X = Br or I) to give [$Zn_4O(bdc)_{3-x}(bdc\text{-}X)_x$], in which preferential incorporation of bdc is observed. The selective incorporation is related to crystal growth rates, and the proportion of incorporated bdc-X rises with increasing reaction time.

Over the past ten years, the study of materials in which bridging ligands connect metal centres or aggregates into extended coordination networks—commonly referred to as metal–organic frameworks (MOFs)—has become a major area of chemistry.[1–5] Many of these materials exhibit porosity, and applications such as hydrogen storage,[6] separations,[7] and catalysis[8] are attracting considerable attention.

While many MOFs contain just one type of linking ligand, MOFs containing two or more types of linker are becoming increasingly prevalent. In many of these MOFs, the two linking ligands play different structural roles. In [$Zn_2(bdc)_2(dabco)$] (bdc = 1,4-benzenedicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane),[9] for example, anionic bdc ligands connect the Zn_2 centres into sheets, whereas neutral dabco ligands act as pillars, connecting the sheets into a three-dimensional network. There is, however, another class of mixed-ligand MOF in which the linkers adopt similar structural roles, and are disordered within the crystal structures giving rise to solid solutions. For these materials, it may be possible to vary the ratio of the ligands within the mixed-ligand MOF, and even control it through variation of the reaction stoichiometry. We regard these materials as examples of mixed-component metal–organic frameworks (MC-MOFs),[10] a class of MOF which includes analogous systems with mixed metals as well as core–shell MOFs.[11,12] MC-MOFs are particularly relevant for post-synthetic modification,[13,14] since doping a small amount of a particular functional group in a MOF is essential for applications involving a controlled catalyst loading.

The first report of a mixed-ligand MC-MOF was by Kim and co-workers, who reacted zinc(II) with dabco and a combination of 1,4-benzenedicarboxylic acid (H_2bdc) and 2,3,5,6-tetramethyl-1,4-benzenedicarboxylic acid (H_2tmbdc) to form [Zn_2(bdc)(tmbdc)(dabco)].[15] Subsequently, MC-MOFs have been prepared in systems based on [$Zn_4O(bdc)_3$] (MOF-5),[11,16,17] [Zn_4O(4,4′-biphenyldicarboxylate)$_3$] (IR-MOF-9),[18] [Al(OH)(bdc)] (MIL-53),[19] [$Fe_3OCl(H_2O)_2(bdc)_3$] (MIL-101)[20] and [Zn(1,3-benzenedicarboxylate)(4,4′-bpy)].[21] Several of these studies have shown that there is preferential inclusion of one of the ligands, with equimolar mixtures of dicarboxylic acids leading to one of the dicarboxylates being incorporated to a greater extent into the structure. For example, we showed that the reaction between zinc(II) and a 1 : 1 mixture of 2-formyl-4,4′-biphenyldicarboxylic acid (H_2bpdc-CHO) and 2-methoxy-4,4′-biphenyldicarboxylic acid (H_2bpdc-OMe) gave [$Zn_4O(bpdc\text{-}CHO)_{0.3}(bpdc\text{-}OMe)_{2.7}$], with a 1 : 9 ratio of included ligands.[18] Yaghi and co-workers recently published an account of mixed-ligand MOFs based on [$Zn_4O(bdc)_3$] (MOF-5) but containing a range of bdc linkers substituted at the 2- and/or 5-positions, which they describe as multivariate MOFs (MTV-MOFs). They showed that up to eight different dicarboxylates could be introduced into a single MOF, and also demonstrated that the degree of incorporation of the different functional groups varied considerably.[16]

In other systems, the degree of incorporation of the ligands mirrors the ratios used in the syntheses. For example, Baiker and co-workers showed that reactions of zinc(II) with mixtures of H_2bdc and 2-amino-1,4-benzenedicarboxylic acid (H_2bdc-NH_2) gave [$Zn_4O(bdc)_{3-x}(bdc\text{-}NH_2)_x$] in which x could be controlled.[17] They term the mixed-ligand products as MIXMOFs.

Of course, these observations are not necessarily in conflict, as different systems may behave in different ways, and the degree of incorporation of a particular ligand into a MOF may depend on the reaction conditions. It is clear, however, that controlled incorporation of a particular functionality into a MOF is not yet universal, and more work is required in this field.

With the different observations based on MOF-5 and analogues with substituted bdc ligands in mind, we set out

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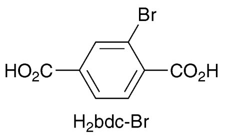
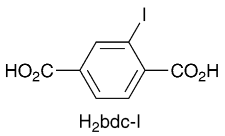
to investigate how changing the relative proportions of H_2bdc and either H_2bdc-Br (2-bromo-1,4-benzenedicarboxylic acid) or H_2bdc-I (2-iodo-1,4-benzenedicarboxylic acid) would affect the composition of the resultant zinc MOFs $[Zn_4O(bdc)_{3-x}(bdc\text{-}X)_x]$ (X = Br, I). $[Zn_4O(bdc\text{-}Br)_3]$ (IRMOF-2) has been previously reported,[22] but $[Zn_4O(bdc\text{-}I)_3]$ has not.



H_2bdc-Br



H_2bdc-I

The reaction of $Zn(NO_3)_2{\cdot}6H_2O$ with H_2bdc-I in DEF produces $[Zn_4O(bdc\text{-}I)_3]{\cdot}n$DEF in good yield. Single crystals of $[Zn_4O(bdc\text{-}I)_3]{\cdot}n$DEF did not diffract strongly enough for a structural determination, but the powder X-ray diffraction pattern for this compound confirms that it is isostructural with IRMOF-2.

Reactions were then carried out using mixtures of H_2bdc and H_2bdc-X (X = Br, I) in varying ratios to give $[Zn_4O(bdc)_{3-x}(bdc\text{-}X)_x]$. These reactions were carried out in DEF at 95 °C for 170 h, giving crystalline materials in all cases. The powder X-ray diffraction patterns revealed that the MC-MOFs are isostructural with each other, and with MOF-5. Portions of each of the products were digested fully in DCl/D_2O and d_6-DMSO and the resultant solutions analysed by ^{1}H NMR spectroscopy. The integrals for the aromatic protons were used to give the ratio of the different dicarboxylate ligands in the products. Individual single crystals were also digested in HCl (aq), and the observation of both monoanions in the negative mode ESI mass spectra showed that the products are truly MC-MOFs as opposed to physical mixtures of homoleptic MOFs.

20 reactions involving mixtures of H_2bdc and H_2bdc-I and 20 reactions involving mixtures of H_2bdc and H_2bdc-Br were undertaken. The results are summarised graphically in Fig. 1. In all cases, the proportion of bdc-I or bdc-Br observed in the product is less than that present in the reaction mixture, consistent with the report from Yaghi and co-workers that bdc is incorporated in preference to bdc-Br.[16] Notably, the incorporation of bdc-I is greater than that of bdc-Br. Nitrogen adsorption measurements on $[Zn_4O(bdc)_{3-x}(bdc\text{-}X)_x]$ showed that the BET surface areas of the materials decrease with increasing proportion of bdc-X (Fig. 2), as expected on steric grounds. In addition, the larger size of iodine than bromine is reflected in the lower values observed for the iodo-containing MOFs.

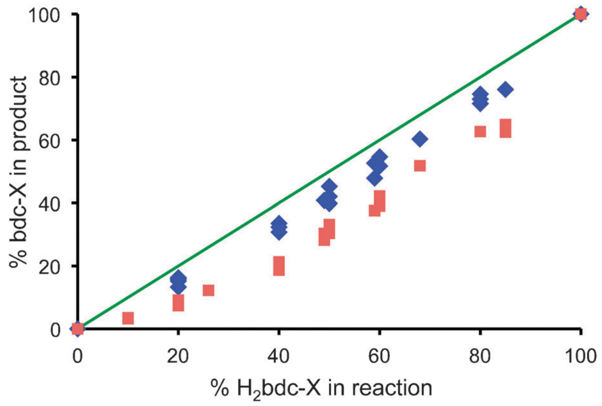


Fig. 1 The relationship between the percentage of bdc-X incorporated into $[Zn_4O(bdc)_{3-x}(bdc\text{-}X)_x]$ and the percentage of H_2bdc-X in the reaction mixture. For ◆, X = I, and for ■, X = Br. The green line represents what would be expected if the incorporation was not selective.

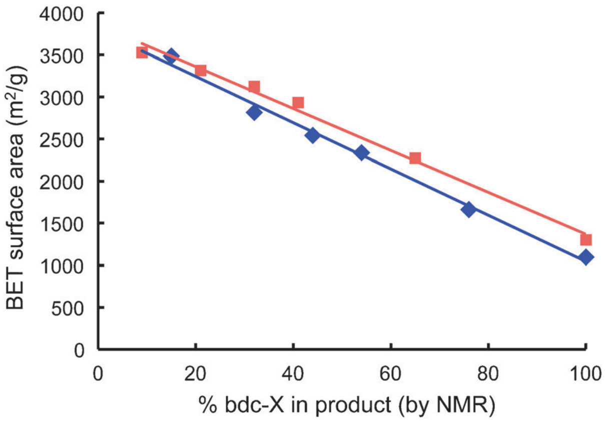


Fig. 2 The variation of BET surface areas with proportion of bdc-X incorporated into $[Zn_4O(bdc)_{3-x}(bdc\text{-}X)_x]$. For ◆, X = I, and for ■, X = Br.

10 reactions were also undertaken using mixtures of H_2bdc-I and H_2bdc-Br of different compositions. In these cases, the proportions of the 2-halo-1,4-benzenedicarboxylates observed in the NMR spectra are identical, within experimental error, to the proportions used in the synthesis. This is shown graphically in Fig. 3.

There are a number of potential factors that could influence the incorporation of the different dicarboxylates into the growing MOF structure. The presence of a bulky substituent might limit incorporation of the functionalised ligand, either through the potential for unfavourable steric interactions between anions and the framework or by lowering the diffusivity of the anions. This is not consistent with the observed results which show greater incorporation of the larger bdc-I into $[Zn_4O(bdc)_{3-x}(bdc\text{-}X)_x]$ than the smaller bdc-Br. It is also notable that in Yaghi's study 2,5-dimethyl-1,4-benzenedicarboxylate is included into the $[Zn_4OL_3]$ structure in preference to bdc, despite the greater bulk.[16]

Difference in pK_a between the acids is also a potential factor, though this is likely to give rise to two conflicting effects. The pK_a values for 2-halodicarboxylic acids would be

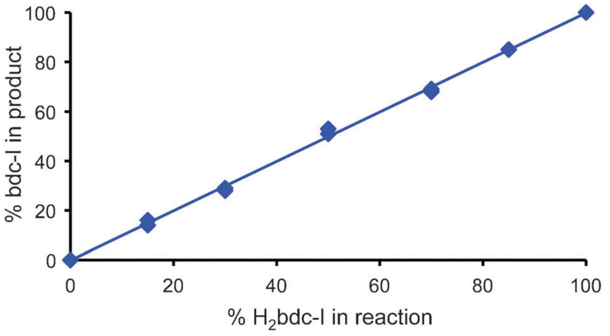


Fig. 3 The relationship between the percentage of bdc-I incorporated into $[Zn_4O(bdc\text{-}Br)_{3-x}(bdc\text{-}I)_x]$ and the percentage of H_2bdc-I in the reaction mixture.

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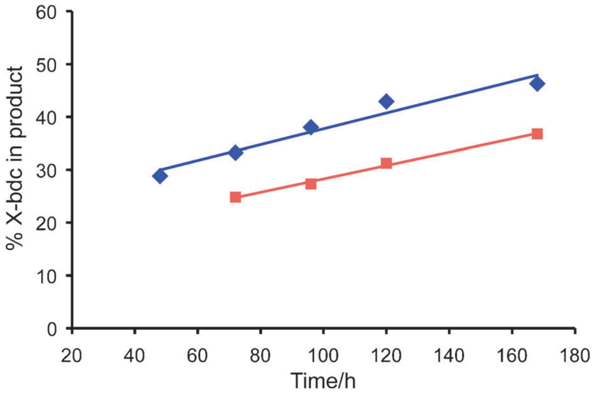

Fig. 4 The relationship between the percentage of bdc-X incorporated into $[Zn_4O(bdc)_{3-x}(bdc\text{-}X)_x]$ and the reaction time. For ◆, X = I, and for ■, X = Br.

expected to be lower than those for H_2bdc (pK_{a1} 3.51, pK_{a2} 4.82) given the inductive effect of the halo group. A similar effect is notable for the benzoic acids: compare benzoic acid (pK_a 4.20) with 2-iodobenzoic acid (pK_a 2.85) and 3-iodobenzoic acid (pK_a 3.86). This means that the concentration of the 2-halo-1,4-benzenedicarboxylates (and the $[Hbdc\text{-}X]^-$ monoanions) would be higher than that of bdc (and $[Hbdc]^-$). Given the greater inclusion of bdc over bdc-I and bdc-Br, the relative concentrations of the ions cannot be the major factor in their incorporation into the MOF crystals. However, the greater basicity of the anions derived from H_2bdc would be expected to make these anions better ligands, so it is conceivable that the greater ligating ability of the bdc ions wins out over the lower concentration.

Observations on the crystal growth rates of $[Zn_4O(bdc)_3]$ (MOF-5), $[Zn_4O(bdc\text{-}Br)_3]$ (IRMOF-2) and $[Zn_4O(bdc\text{-}I)_3]$ suggested another factor to be relevant too. When reactions to form $[Zn_4O(bdc)_3]$, $[Zn_4O(bdc\text{-}Br)_3]$ and $[Zn_4O(bdc\text{-}I)_3]$ were set up side by side using identical conditions, crystals were always observed first for $[Zn_4O(bdc)_3]$, with those of the the halo-containing products taking longer to form. This suggested that the faster crystal growth rate for $[Zn_4O(bdc)_3]$ might be a factor in the observed greater proportion of bdc in the mixed bdc/bdc-Br and bdc/bdc-I products.

In order to assess this, the reactions between zinc(II) and 50 : 50 mixtures of H_2bdc and H_2bdc-X (X = Br, I) were carried out for shorter periods of time, with the products analysed after 48 h, 72 h, 96 h, 120 h and 168 h. As expected, shorter reaction times led to lower yields, and indeed no product was observed for the reaction of zinc(II) with H_2bdc/H_2bdc-Br after 48 h. In all other cases, however, there was enough material to digest and analyse by ^{1}H NMR spectroscopy. These results are summarised graphically in Fig. 4. With shorter reaction times there is clearly a lower incorporation of bdc-Br or bdc-I into the MOF material, with the degree of incorporation going up with increasing reaction time. This is consistent with greater preferential inclusion of bdc at the early stages of crystal growth. As the reaction proceeds, the mother liquor will become enriched in bdc-X, which contributes to the growing proportion of bdc-X incorporated.

In conclusion, we have demonstrated that the preferential incorporatation of bdc over bdc-I and bdc-Br occurs in MOFs of the general formula Zn_4OL_3, and that this selectivity is related to the relative rates of crystallisation. An important implication of these results is that the composition of MC-MOFs is not necessarily uniform. In the system under study here, at least, the proportion of linkers that bear a halo group is lower towards the centre of the crystals than it is on the outside. This anisotropy will have an impact on the properties of these MC-MOFs, including post-synthetic modifications.

This work shows that the formation of MC-MOFs through control of the incorporation of ligands that have the same structural role provides opportunities to tailor the composition and function of MOFs. Current work is engaged in expanding the scope of MC-MOFs and assessing the generality of the results reported in this work.

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