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Robust and sustainable synthesis of Al-based MOFs form waste aluminium

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Aluminium MOFs have gained researchers attention for their applications in gas sequestration, water harvesting, drug delivery and chemical storage. Current synthetic methods, however, rely on a variety of aluminium salts for synthesis of MOFs within the same family and are not the most efficient sources of aluminium. Herein, we demonstrate a robust synthetic pathway to MOFs CAU-9, CAU-10 (-NO_2,-NH_2,-N_3), CAU-10-py, CAU-15, CAU-21, MIL-53(Al)-TCD, MOF-303 and Al-Fum from aluminium formate, a compound that we have previously synthesized from industrial aluminium waste. We replace commercial aluminium salts with sustainably sourced aluminium, reducing the amount of waste and harmful byproducts, all by using a common aluminium precursor.

Metal–organic frameworks (MOFs) are a class of porous materials that are becoming more industrially relevant due to their robust nature and porosity. MOFs have applications ranging from drug delivery, catalysts, gas sequestration, and water purification. They are made from the combination of Lewis basic organic ligands, and Lewis acidic metal cations. The combination of these two components leads to a porous, near infinite three-dimensional network. Aluminium based MOFs (Al-MOFs) are an important subclass to note; they have gained much attention for applications in gas phase water adsorption, CO_2, and SO_2 sequestration, H_2O purification, CH_4, and O_2 storage.[1–5] With these applications in mind, research has moved towards environmentally friendly and sustainable syntheses. These procedures involve the use of water as a solvent, reduce washing steps, and use sustainable reagents.[6–9] Recent work from Perbet *et al.* demonstrated the successful synthesis and large scale production of MIL-160 from aluminium isopropoxide, eliminating washing steps and toxic soluble byproducts from other commonly used aluminium precursors.[10]

The successful synthesis of Al-MOFs is quite elusive, even without sustainability or environmental considerations. Often to synthesize a series or family of Al-MOFs, a variety of aluminium salts are required. Modulators are often included in the synthesis but can be toxic or produce harmful byproducts.[11] We have developed a synthetic procedure that overcomes these challenges. We present the successful synthesis of 11 Al-MOFs directly from aluminium formate (ALF; $Al(COOH)_3$) as a common precursor. We have previously established ALF to be easily accessed from waste aluminium products, while generating hydrogen fuel as a convenient byproduct (1 L H_2 per 1 g aluminium).[12] Our most recent work has shown that in the digestion/processing of waste aluminium, the formation of ALF is a crucial purification step to remove any inclusion impurities (iron, copper, manganese, *etc.*) and prevent them from being incorporated into high value end products. We have indeed since validated these methods for other aluminium waste materials (*e.g.* beverage containers), providing multiple feedstocks for hydrogen and ALF generation.

A common strategy in MOF synthesis is to pre-form the metal cluster using a modulator.[13,14] Modulators are often mono carboxylate containing organic compounds that mimic ligands but cannot link one metal centre to the next.[14] Common examples in the literature include, benzoic acid, formic acid, trifluoracetic acid, and water.[15–18] ALF is comprised of Al^{3+} ions that are coordinated to formate capping groups. With this in mind, we envisioned using ALF as a precursor to many Al-MOFs. ALF can act as the pre-formed aluminium node, with a built-in modulator (formate) to encourage ligand exchange. Using ALF, compared to other commodity aluminium reagents common in MOF synthesis, provides an additional advantage. Approximately 16.7% of the mass of ALF is aluminium, making it an efficient aluminium source and reducing the mass of waste generated during synthesis. This work outlines the synthetic procedures to produce 11 different Al-MOFs (CAU family, MOF-303, Al-Fum, MIL-53(Al)-TDC) synthesized directly from the common starting reagent ALF, derived from waste aluminium, adding a layer of sustainability to the process.

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CAU MOFs

The CAU (Christian-Albrechts-Universität) family of MOFs are a series of MOFs with aluminium, magnesium, zinc, bismuth, or scandium metal centres coordinated to ditopic (terephthalic acid, isophthalic acid, phthalic acid, *etc.*) or tetratopic (1,2,4,5-tetrakis-(4-carboxylatophenyl)-benzene) linkers to form 3-dimenstional porous structures.[19–23] These materials have found applications in non-linear optics, water adsorption, size selective gas adsorption, and ultra-low-temperature cooling.[20,24–26]

The aluminium-based CAU MOFs are typically synthesized from $Al(NO_3)_3{\cdot}9H_2O$, $AlCl_3$, $AlCl_3{\cdot}6H_2O$, or $Al_2(SO_4)_3{\cdot}18H_2O$.[25–28] These compounds have low atom economy and indeed can produce undesirable, harmful side products; *e.g.* sulphates and nitrates are produced which present environmental hazards if not disposed of properly. We synthesized CAU-10, CAU-10-py, CAU-10-NO_2, CAU-10-N_3, CAU-15, CAU-21 and CAU-9 using the respective organic ligand (Fig. 1i–v), ALF as the aluminium source, and a mixture of DMF and water as the solvent (See SI for full experimental details). CAU-10 and its derivatives (-py, -NO_2, -NH_2) had PXRD patterns that matched the literature and simulated diffractograms quite well (Fig. 2) demonstrating the successful bulk synthesis of the material. N_2 gas adsorption measurements at 77 K confirmed the porosity of these MOFs (Table 1 and Fig. S9). CAU-10-N_3 matched the simulated CAU-10, and CAU-10 functionalized MOFs, indicating a similar structure. CAU-10-N_3 demonstrated a higher surface area to previously published literature, we hypothesize this difference is due to the different synthetic approaches to the MOF (Fig. S9).[29] The obtained PXRD patterns of CAU-9, CAU-15, and CAU-21 matched the simulated and previously reported

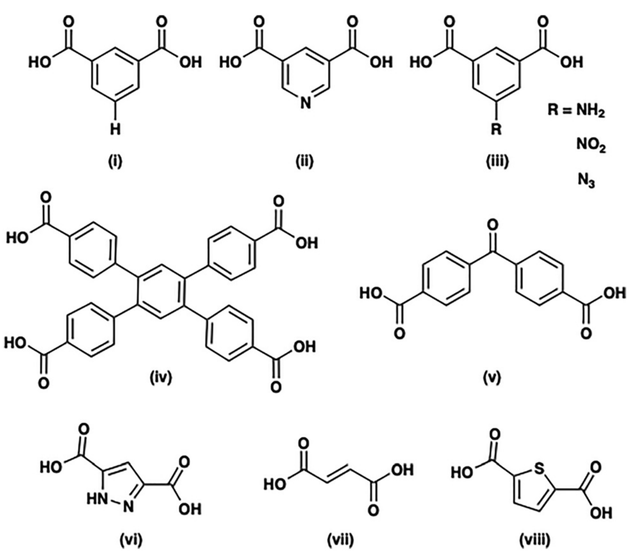

Fig. 1 Ligands used in the synthesis of MOFs from ALF. (i) isophthalic acid (CAU-10), (ii) pyridine-3,5-dicarboxylic acid (CAU-10-py), (iii) 5-aminoisophthalic acid, 5-nitroisophthalic acid, 5-azoisophthalic acid (CAU-10-NH_2, NO_2, N_3), (iv) 1,2,4,5-tetrakis(4-carboxyphenyl)benzene (CAU-9), (v) benzophenone-4,4′-dicarboxylic acid (CAU-15), (vi) pyrazole-3,5-dicarboxylic acid (MOF-303), (vii) fumaric acid (Al-Fum), (viii) thiophene-2,5-dicarboxylic acid (MIL-53(Al)-TDC).

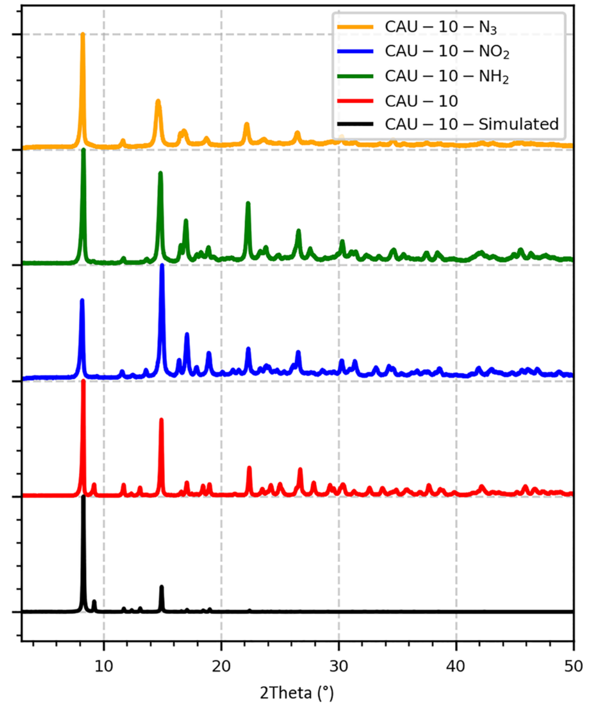

Fig. 2 Powder X-ray diffraction patterns of the series of CAU-10 MOFs. Simulated (black trace), CAU-10 (red trace), CAU-10-NO_2 (green trace), CAU-10-NH_2 (blue trace), CAU-10-N_3 (yellow trace).

Table 1 BET surface areas of Al-Based MOFs

	Experimental ($m^2\ g^{-1}$)	Literature ($m^2\ g^{-1}$)
CAU-10	575	635[25]
CAU-10-py	800	884
CAU-10-NO_2	380	440[25]
CAU-10-NH_2	33	409[20]
CAU-10-N_3	106	26[29]
CAU-15	30	—[a]
CAU-21	290	Non-N_2 accessible[30]
CAU-9	900	1118[27]
Al-TDC	730	395-1150[31]
MOF-303	930	1342[32]
Al-Fum	945	971[2]

[a] No surface area reported.[28]

patterns indicating their successful synthesis using ALF as the aluminium source. Nitrogen adsorption at 77 K of these MOFs matched the literature values, giving BET surface areas within *ca.* 10% (Table 1 and Fig. S11–S13), this is typical for varying synthetic conditions, indicating the porosity of the synthesized materials. CAU-10-NH_2 demonstrated a lower surface area than the reported literature, we attribute this to the lower synthesis temperature along with more concentrated reaction conditions. This can lead to a more defective material that reduces the overall surface area. Furthermore, the CAU MOFs in this study were analysed by scanning electron microscopy and thermogravimetric analysis (TGA) (see SI). The TGA confirmed the stability of the MOFs with decomposition temperatures ranging from *ca.* 763 K to 873 K.

MOF-303, MIL-53(Al)-TDC and Al-Fum

MOF-303 combines an aluminium centre with 1*H*-pyrazole-3,5-dicarboxylate ligand (Fig. 1vi), creating a porous material that has shown tremendous water adsorption capabilities from arid climates. Previous work from our group has synthesised MOF-303 from dross (Al waste from smelting) digest solution.[12] While effective, it does pose certain constraints including, storage of large amounts of digest solutions, uncertainty in the aluminium concentration caused by evaporation of process water, and inconsistent aluminium concentrations from waste materials varying in aluminium content. Using ALF as the aluminium source circumvents these obstacles and provides a sustainable source of aluminium for MOF synthesis. Furthermore, the synthesis from ALF in water, eliminates the need of $AlCl_3{\cdot}6H_2O$ traditionally used in MOF-303 synthesis, increasing the atom economy by increasing the aluminium weight per cent from 11 in $AlCl_3{\cdot}6H_2O$ to 16.7 in ALF. Obtained PXRD patterns and N_2 gas adsorption isotherms match previously reported literature (Fig. 3 and S16), along with a calculated BET surface area of 930 $m^2\ g^{-1}$ confirming the successful synthesis of MOF-303 (Table 1).

Al-Fum, also known as Basolite A520, combines fumaric acid (Fig. 1vii) linkers and aluminium salts to create a porous material that is produced industrially for its CO_2 sequestration capabilities.[2] BASF has optimized the synthesis using $Al_2(SO_4)_3{\cdot}18H_2O$, providing efficient synthesis in water. However, the aluminium content of the starting reagent is quite low, only accounting for roughly 8.1 per cent of its total mass. Using ALF, we use a more efficient source of aluminium (16.7 *vs.* 8.1 weight per cent) while still producing the MOF near quantitatively in water. The obtained PXRD patterns (Fig. 3) and N_2 adsorption data, giving a calculated BET surface area of 945 $m^2\ g^{-1}$, matches previously reported values (Fig. S15).[2,33]

MIL-53(Al)-TDC uses 2,5-thiophenedicarboxylate (Fig. 1viii) as the organic ligand, with an aluminium metal centre. MIL-53(Al)-TDC has applications in heat transformation, H_2S capture and water purification.[34,35] Literature methods for the synthesis use $AlCl_3$, $NaAlO_2$ or $Al_2(SO_4){\cdot}18H_2O$.[34,36] As previously indicated, these are not efficient sources of aluminium, but using the more atom economical ALF as the aluminium source, we were able to synthesize MIL-53(Al)-TDC. The successful synthesis was confirmed through N_2 gas adsorption, giving a calculated BET surface area of 730 $m^2\ g^{-1}$ (Fig. S14 and Table 1) and PXRD (Fig. 3). The PXRD pattern matches previously reported literature.[34]

In summary, we have further extended the number of high-value products stemming from the recycling of aluminium waste/salvage. In addition to the aluminium-based commodity chemicals ($Al(OH)_3$, Al_2O_3) and H_2 fuel,[12] we have now demonstrated a robust synthetic procedure for the synthesis of a library of academically and industrially relevant Al-MOFs (CAUs, MOF-303, Al-Fum, MIL-53(Al)-TDC). These MOFs can now be derived from waste or salvage aluminium sources, reducing the variety of aluminium salts, eliminating the production of harmful sulphates and nitrates, increasing the atom economy of the aluminium precursor, all by using a single common sustainable building block (ALF).

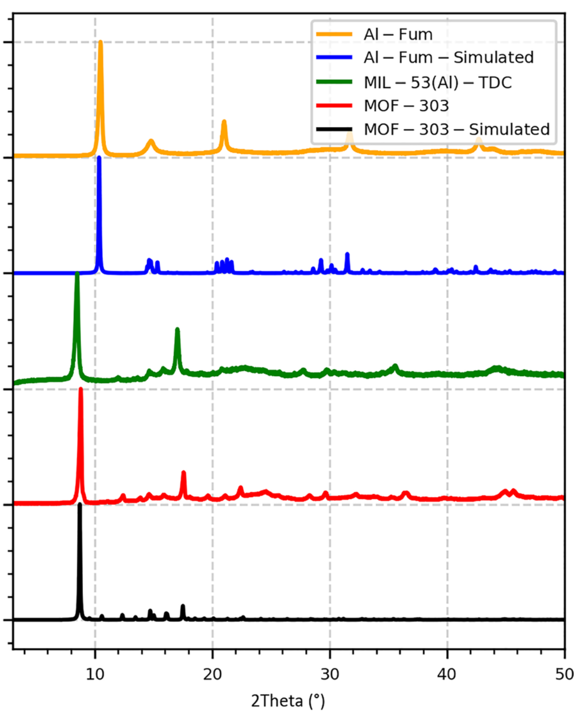

Fig. 3 Powder X-ray diffraction patterns of MOF-303 (simulated black trace, experimental red trace), MIL-53(Al)-TDC (blue trace), Al-Fum (simulated green trace, experimental yellow trace).

Author contributions

MCL: experimental, data collection and interpretation, conceptualization, manuscript preparation. RSH: experimental, data collection and interpretation, manuscript editing. MRH: data collection. BAB: funding procurement, conceptualization, manuscript preparation.

Conflicts of interest

Intellectual property protection has been filed by UNB, MCL, RSH, and BAB covering all novel aspects of the presented work.

Data availability

The raw data that underpins this work can be accessed through the University of New Brunswick data repository found here: https://doi.org/10.25545/KS9CKV.

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