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ARTICLE

Isorecticular Chemistry of Scandium Analogues of the Multicomponent Metal-Organic Framework MIL-142

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Interpenetrated multicomponent MIL-142(Sc) MOFs were synthesised using the planar tritopic (4,4',4''-(1,3,5-triazine-2,4,6-triyl)tribenzoate, TATB, or 4,4',4''-(pyridine-2,4,6-triyl)tribenzoate, PTB)) and linear ditopic (1,4-benzenedicarboxylate, BDC, or 2-amino or 2-nitro-1,4-benzenedicarboxylate (NH₂- or NO₂-BDC) linkers. Structure solution of the MIL-142(Sc)-TATB series from single crystal X-ray diffraction in space group $R\bar{3}m$ reveals regioselective ordering of bulky NO₂ groups in MIL-142(Sc)-TATB-NO₂. Use of 1,3,5-benzenetribenzoate (BTB) favours instead the mesoporous Sc-BTB, the PTB analogue of which forms in the absence of BDC. The materials are highly porous: MIL-142(Sc)-TATB-BDC has a pore volume of 0.70 cm³ g⁻¹.

Introduction

The substitution of metal cations and organic linkers within metal-organic frameworks (MOFs) of a given topology type by other cations or linkers of similar coordination geometry is the basis of isorecticular chemistry. It permits tuning of physical properties (adsorption, flexibility, catalytic activity, magnetism, luminescence) in an analogous way to that widely practised for solid solutions in dense solid-state materials.¹ Many trivalent metal carboxylate MOFs have been shown to display wide compositional variety, including the prototypical MOFs MIL-53², -88³, -100⁴ and -101⁵. The most commonly studied metals within all these structures are Fe and Cr,^{6,7} with Al,⁸ V,⁹ Ga,¹⁰ In¹¹ and Sc^{12–14} forms of some or all of them also having been reported. Of these, Sc³⁺ has the largest ionic radius (0.745 Å), and forms some MOFs not observed with the other metals.¹⁵ Scandium MOFs possess favourable attributes: when present as coordinatively unsaturated centres they possess exceptional Lewis acidic catalytic activity^{16–18} and they often form as crystals of suitable quality for study by single crystal diffraction.^{19–22} They therefore present an excellent opportunity for structural study.^{23–25}

Like many of the trivalent cation carboxylate MOFs, the fully interpenetrated MIL-142(Fe) (Figure 1),²⁶ general formula Fe₃O(X)(OH)₂(LDC)(BTB)_{4/3} (where X = OH⁻, Cl⁻; LDC is a linear dicarboxylate; BTB is benzenetribenzoate)^{6–11} contains Fe₃O-based trimeric clusters as the metal-oxy nodes, but it is one of relatively few mixed-linker carboxylate MOFs that contain both dicarboxylate and

tricarboxylate linkers.^{27–30} It was first prepared as small crystals and its structure was solved by single crystal diffraction at a synchrotron source. It was found to accept a wide range of isorecticular replacement of dicarboxylate linkers of differing length.²⁶ The structure is chemically and thermally stable, and a recent report describes its adsorptive selectivity for ethylene over ethane.³¹ Although only the iron analogue has been prepared directly, the more kinetically stable chromium form has been prepared by cation exchange from solution.³² Here we report the direct crystallisation of scandium members of the MIL-142 family, and show that it is possible to prepare these MOFs in highly porous form *via* chemical variation of both the dicarboxylate and tricarboxylate linkers, although the prototypical 1,3,5-benzenetribenzoate (BTB) linker, used in the synthesis of MIL-142(Fe), shows different product selectivity. Single crystal X-ray diffraction reveals hitherto unresolved details of the MIL-142 structure and also the regioselectivity of substitution for different functionalised linkers.

Figure 1: (Above) The MIL-142(Fe) structure when viewed along the z-axis. (Below) The Fe₃O trimer and linkers of MIL-142(Fe). The structure for MIL-142(Fe) is adapted from MIL-142(Sc). Colour code: Fe, orange; C, black; O, red.

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Experimental

Synthesis of 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tribenzoic acid (H₃TATB) and 4,4',4''-(pyridine-2,4,6-triyl)tribenzoic acid (H₃PTB)

TATB was synthesised in two steps following literature procedures (Scheme S1, Figure S1).^{33,34}

PTB was synthesised in two steps using a modified procedure.

Scheme 1: Synthesis of H₃PTB

4-(2,6-bis(4-cyanophenyl)pyridine-4-yl)benzoic acid (BCPB): 5.08 g (34.9 mmol) 4-acetylbenzonitrile and 2.62 g (17.4 mmol) 4-carboxybenzaldehyde was weighed out in to a 500 mL round-bottom flask occupied with a magnetic stirrer. 145 mL methanol was added with stirring at room temperature until the solution became clear. 160 mL of 15 wt % aqueous KOH was added slowly followed by the addition of 18.6 mL of aqueous ammonia solution after 30 minutes. The solution changed colour from orange to black and then back to orange. After stirring at room temperature for 72 h, the resulting solid was filtered, washed multiple times with chloroform and the solid obtained was dissolved in methanol. After the complete dissolution of solid, the pH of the solution was adjusted to 3 by the addition of 1 M HCl solution to precipitate the product as white solid. The product was filtered and washed multiple times with water and dried overnight at 80 °C. Yield = 4.413 g (63%). ¹H NMR (400MHz, DMSO) δ(ppm): 8.59 (d, 4H, *J* = 8.38Hz), 8.51 (s, 2H), 8.25 (d, 2H, *J* = 8.36Hz), 8.12 (d, 2H, *J* = 8.38Hz), 8.05 (d, 4H, *J* = 8.38Hz) (Figure S2).

4,4',4''-(pyridine-2,4,6-triyl)tribenzoic acid (H₃PTB): 4.413 g (10.99 mmol) 4-(2,6-bis(4-cyanophenyl)pyridine-4-yl)benzoic acid (BCPB) was added to 250 mL of 2 M NaOH solution in a round bottom flask and stirred at reflux until the complete dissolution of the solid. After cooling to room temperature, the product was acidified to pH 1 using 1M HCl solution resulting in the precipitation of H₃PTB as an off-white coloured solid. H₃PTB was separated by filtration and washed multiple times with water before drying at 100 °C overnight. Yield = 4.05 g (84%). ¹H NMR (400MHz, DMSO) δ(ppm): 8.51 (d, 4H, *J* = 8.23Hz), 8.44 (s, 2H), 8.25 (d, 2H, *J* = 8.17Hz), 8.13 (d, 6H, *J* = 8.53Hz) (Figure S3) in accordance with literature.³⁵

MIL-142(Sc)-TATB, MIL-142(Sc)-TATB-NH₂, MIL-142(Sc)-TATB-NO₂

In the synthesis of **MIL-142(Sc)-TATB**, 83.1 mg (0.5 mmol) BDC and 220.6 mg (0.5 mmol) TATB were weighed out into a Teflon liner (~ 30 mL total volume) containing a magnetic stirrer. 3 mL of DMF was added to the precursors followed by the addition of 0.3 mL aqueous ScCl₃ (1.45 M) solution. After stirring at room temperature for 50 min, the Teflon-liner was transferred to a stainless-steel autoclave

and heated to 150 °C at a ramp rate of 5 °C min⁻¹ in a programmable oven. After keeping at the same temperature for 30 h, the autoclave was cooled down to 30 °C (at 25 °C min⁻¹). The crystalline solid obtained was washed multiple times with DMF and kept in DMF for 24 h, followed by DMF exchange with methanol and immersion in methanol for 24 h before being filtered and dried overnight at 80 °C. Yield = 144.1 mg. **MIL-142(Sc)-TATB-NH₂** was synthesised by replacing BDC with 90.6 mg (0.5 mmol) of NH₂-BDC in the synthesis procedure for MIL-142(Sc)-TATB. Yield = 121.0 mg. **MIL-142(Sc)-TATB-NO₂** was synthesised by replacing BDC with 105.6 mg (0.5 mmol) of NO₂-BDC in the synthesis procedure for MIL-142(Sc)-TATB. Yield = 134.7 mg.

MIL-142(Sc)-PTB, MIL-142(Sc)-PTB-NH₂, MIL-142(Sc)-PTB-NO₂

MIL-142(Sc)-PTB was synthesised by replacing TATB with PTB in the synthesis of MIL-142(Sc)-TATB. 83.1 mg (0.5 mmol) BDC and 219.6 mg (0.5 mmol) PTB were weighed out into a Teflon-liner (~ 30 mL total volume) containing a magnetic stirrer. 3 mL of DMF was added to the precursors followed by the addition of 0.3 mL aqueous ScCl₃ (1.45 M) solution. After stirring at room temperature for 50 min, the Teflon-liner was transferred to a stainless-steel autoclave and heated to 150 °C at a ramp rate of 5 °C min⁻¹ in a programmable oven. After keeping at the same for 30 h, autoclave was cooled down to 30 °C (at 25 °C min⁻¹). The crystalline solid obtained was washed multiple times with DMF and kept in DMF for 24 h, followed by DMF exchange with methanol and kept in methanol for 24 h before being filtered and dried overnight at 80 °C. Yield = 122.6 mg.

MIL-142(Sc)-PTB-NH₂ was synthesised by replacing BDC with 90.6 mg (0.5 mmol) of NH₂-BDC in the synthesis procedure for MIL-142(Sc)-PTB. Yield = 131.5 mg. **MIL-142(Sc)-PTB-NO₂** was synthesised by replacing BDC with 105.6 mg (0.5 mmol) of NO₂-BDC in the synthesis procedure for MIL-142(Sc)-PTB. Yield = 142.7 mg.

Sc-BTB and Sc-PTB

Sc-BTB was initially obtained in this study in our attempt to synthesise the Sc analogue of MIL-142(Fe) using BDC, BTB and aqueous ScCl₃ solution as the precursors. The powder X-ray diffraction (PXRD) pattern of the product was similar to that of a Sc-MOF, isorecticular to InPF-110,³⁶ that we reported elsewhere, formed by the incorporation of BTB (Figure S4).³⁷ Single crystals of Sc-BTB suitable for SCXRD (Figure S5) were obtained by the modification of our reported procedure: 76 mg (0.33 mmol) Sc(NO₃)₃·xH₂O (after drying at 105 °C overnight) and 66 mg (0.15 mmol) BTB were placed into a Teflon-liner containing a magnetic stirrer. 2.5 mL DMF was added to the precursors followed by the 0.8 mL nitric acid. After stirring at room temperature for 1 h, the Teflon-liner was placed in a stainless-steel autoclave and heated in a preheated oven at 150 °C for 4 h. After cooling to room temperature at 25 °C min⁻¹, single crystals obtained were washed multiple times with DMF and kept in DMF for 24 h, followed by DMF exchange with methanol and immersion in methanol for 24 h before being filtered and dried overnight at 80 °C prior to analysis. Yield = 70.0 mg.

Table 1 Crystallographic data for MIL-142(Sc)-BDC-TATB and its functionalised derivatives and of MIL-142(Sc)-PTB.View Article Online
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	MIL-142(Sc)-TATB	MIL-142(Sc)-TATB-NH ₂	MIL-142(Sc)-TATB-NO ₂	MIL-142(Sc)-PTB
Formula	C ₄₀ H ₂₁ N ₄ O ₁₆ Sc ₃	C ₄₀ H ₂₂ N ₅ O ₁₆ Sc ₃	C ₄₀ H ₂₀ N ₅ O ₁₈ Sc ₃	C _{42.67} H _{23.67} N _{1.33} O ₁₆ Sc ₃
Formula weight (g mol ⁻¹)	948.49	963.51	993.49	944.85
Temperature (K)	125(2)	173(2)	125(2)	125(2)
Crystal system	Trigonal	Trigonal	Trigonal	Trigonal
Space group	<i>R</i> $\bar{3}m$	<i>R</i> $\bar{3}m$	<i>R</i> $\bar{3}m$	<i>R</i> $\bar{3}m$
a (Å)	28.8613(2)	28.8727(19)	28.8170(7)	28.7845(15)
c (Å)	47.8704(4)	47.845(3)	47.9423(7)	48.405(3)
V (Å ³)	34532.6(6)	34542(4)	34478.4(13)	34733(3)
Z	18	18	18	18
ρ (calcd) (g cm ⁻³)	0.821	0.834	0.861	0.814
μ (mm ⁻¹)	2.580	2.589	2.625	2.554
F(000)	8640	8784	9036	8640
Reflections collected	134096	122628	135506	134806
Unique reflections (<i>R</i> _{int})	8445 (0.0645)	7429 (0.1205)	8414 (0.1862)	8495 (0.2803)
GoF	1.031	1.076	1.008	0.919
Final <i>R</i> ₁ values [<i>I</i> > 2 σ (<i>I</i>)]	0.0559	0.0566	0.0653	0.1208
Final <i>wR</i> ₂ values (all data)	0.1701	0.1842	0.2103	0.4338

Sc-PTB was synthesised by replacing BTB with 65.9 mg (0.15 mmol) of PTB in the optimised synthesis procedure of Sc-BTB. Yield = 68.3 mg.

Characterisation

The identity and phase purity of products was determined using PXRD in Debye-Scherrer geometry using Stoe STAD i/p diffractometers with primary monochromation (Cu K α , λ = 1.54056 Å), using 0.7 mm quartz glass capillaries. Patterns were measured over the 2 θ range of 2–25° (Sc-BTB and Sc-PTB)/2–30° (MIL-142) for 1 h 30 min unless otherwise mentioned.

Single-crystal X-ray diffraction (SCXRD) data were collected at 173 or 125 K by using a Rigaku MM-007HF High Brilliance RA generator/confocal optics with a XtaLAB P100 or P200 diffractometer [Cu K α radiation (λ = 1.54187 Å)]. Intensity data for all compounds were collected using either both ω and ϕ steps or just ω steps, accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects. A multiscan absorption correction was applied by using either CrysAlisPro³⁸ or CrystalClear.³⁹ Structures were solved by dual-space methods (SHELXT),⁴⁰ and refined by full-matrix least-squares against *F*² (SHELXL-2018/3).⁴¹ Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. The capping molecules of the Sc-clusters in the MIL-142(Sc) structures could not be identified beyond the coordinating oxygen. One of these sites should be anionic (presumably OH⁻) for charge balance, and the necessary proton has been included in the formulae. The amino groups in MIL-142(Sc)-TATB-NH₂ are disordered over all four equivalent positions, while the nitro groups in MIL-142(Sc)-TATB-NO₂ are disordered only over two adjacent, equivalent positions. The pyridyl group of one of the PTB ligands in MIL-142(Sc)-

PTB is disordered by symmetry across all three potential positions. All five structures structure showed high proportions of void space (MIL-142(Sc)-TATB: 19760 Å³ [57 % of unit cell volume), MIL-142(Sc)-TATB-NH₂: 18888 Å³ (55 %), MIL-142(Sc)-TATB-NO₂: 18721 Å³ (54 %), MIL-142(Sc)-PTB: 19801 Å³ (57 %), Sc-BTB: 7895 Å³ (53 %)] and the SQUEEZE⁴¹ routine implemented in PLATON⁴² was used to remove the contribution to the diffraction pattern of the unordered electron density in the void spaces. All calculations except SQUEEZE were performed using the CrystalStructure interface.⁴³ The topological analysis of MIL-142(Sc) was carried out with the ToposPro package.⁴⁴ Selected crystallographic data are presented in Tables 1 and ST1. Deposition numbers 2039587-2039591 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

N₂ adsorption isotherms were measured volumetrically on a Micrometrics Tristar at –196 °C. CO₂ adsorption-desorption isotherms were measured gravimetrically on Hiden IGA porosimeter at 25 °C. All samples were activated at 160 °C overnight prior to measurements unless otherwise stated. Thermogravimetric analysis (TGA) of all the MOF samples were carried out on a Netzsch TGA 209 F1 or Rheometrics system interface with Stanton Redcroft STA-780 for a temperature range of 20 - 800 °C at a heating rate of 5 °C min⁻¹ in a continuous air flow using argon as the protective gas.

Scanning electron micrographs of MIL-142(Sc) series materials were obtained using a JEOL JSM-6700 FE SEM. All samples were sputter coated (3×) with gold in a Quorum Q150R ES (10 mA, 30 s). For elemental analysis, a JEOL JSM-5600 SEM combined with an Oxford INCA Energy 200 EDX was used.

Table 2 Synthesis optimization for MIL-142(Sc)-TATB. (Metal Source is 1.5 M aqueous ScCl₃ solution.)View Article Online
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1.5M Aq.ScCl ₃ (mL)	BDC (mmol)	TATB (mmol)	DMF (mL)	Temperature (°C)	Time (h)	Phase	BET Surface Area (m ² g ⁻¹)
0.2	0.2	0.66	3	150	30	Impurity	-
0.3	0.2	0.66	3	150	30	MIL-142(Sc) + impurity	-
0.2	0.4	0.66	3	150	30	MIL-142(Sc), poorly crystalline	593
0.3	0.4	0.66	3	150	30	MIL-142(Sc), poorly crystalline	-
0.2	0.5	0.66	3	150	30	MIL-142(Sc), poorly crystalline	1032
0.3	0.5	0.66	3	150	30	MIL-142(Sc), poorly crystalline	1211
0.6	0.5	0.66	3	150	30	MIL-142(Sc), poorly crystalline	-
0.9	0.5	0.66	3	150	30	MIL-142(Sc), poorly crystalline	-
1.24	0.5	0.66	3	150	30	Impurity	-
0.4	0.5	0.5	3	150	30	MIL-142(Sc), crystalline	-
0.5	0.5	0.5	3	150	30	MIL-142(Sc), crystalline	1516
0.3	0.5	0.5	3	150	30	MIL-142(Sc), highly crystalline	1753

For catalytic studies, MOF samples were activated at 150 °C for 16 h under vacuum. In the test imine synthesis, 4'-fluoroacetophenone (1 mmol) and benzylamine (1 mmol) in dry, degassed toluene (5 mL) were added to the activated MOF (1.5 mol%) and heated with stirring at 90 °C for 24 h under argon and the conversions determined by ¹⁹F NMR.

Results and Discussion

Initial attempts using BDC as the dicarboxylate linker to access MIL-142(Sc), gave MIL-142(Sc) with TATB and PTB but not with BTB (see Figure 2, S6). In that case, only the structure reported in our previous study was observed, where the framework was formed by preferential incorporation of BTB as identified by PXRD (with exclusion of BDC) - here labelled Sc-BTB. On further examination of the Sc-BTB SCXRD structure (Figure 3, Tables ST1 and ST2), the Sc₃ trimers were found to be bridged by formate groups, forming 1D rod like SBUs, unlike the isolated Sc₃ trimers in ScMOF reported by Ibarra *et. al.*⁴⁵

Figure 2. Simulated PXRD patterns of (a) MIL-142(Sc)-TATB and (b) Sc-BTB, compared with the experimental PXRD pattern for (c) Sc-BTB.

Since no formic acid was used in the synthesis, decomposition of DMF aided by HNO₃ (used as the synthesis promoter), may have

resulted in its formation. The Sc-BTB framework was found to be isostructural to that of the indium MOF (*npo-e* topology) reported by Reinos-Fisac *et. al* with overall framework formula Sc₃O(HCO₂)₂(DMF)(BTB)₂.³⁶ Similar to the indium version, Sc-BTB possesses mesoporous channels of free diameter 2.5 nm (taking into account the van der Waals radii of the channel wall atoms) running along the *c*-axis. For comparison, we tried to prepare this structure using each of the tricarboxylic acids (BTB, TATB and PTB) alone, using the conditions given in the Table ST3. Whereas it was possible to prepare the structure with BTB and (for the first time) PTB, similar reactions with TATB (reported elsewhere to give PCN-333⁴⁶) did not give well-defined crystalline products (Figure S7, S8).

Figure 3. (Left) Polyhedral and ball-stick representation of Sc-BTB structure with *npo-e* topology and (Right) the rod-like SBU of Sc-BTB consisting of Sc₃ trimers bridged by formate groups and cluster-coordinated DMF molecules. Hydrogen atoms are omitted for clarity. Colour code: Sc, pink; C, black; N, green; O, red.

On replacing BTB with TATB under similar synthetic conditions, single crystals with three-fold symmetry were obtained, along with some unidentified impurities. SCXRD of a selected crystal revealed a structure with trigonal symmetry, space group *R* $\bar{3}m$, that was found to be isostructural to MIL-142A, where the Fe₃O trimers were replaced with Sc₃O trimers and BTB with TATB. Further synthesis

Figure 4: SEM images of (A) MIL-142(Sc)-TATB, (B) MIL-142(Sc)-TATB-NH₂, (C) MIL-142(Sc)-TATB-NO₂, (D) MIL-142(Sc)-PTB, (E) MIL-142(Sc)-PTB-NH₂, (F) MIL-142(Sc)-PTB-NO₂.

optimization in DMF (Table 2, Figures S9 and S10), gave bulk samples of phase pure MIL-142(Sc)-TATB with 1,4-benzene dicarboxylate and its amino- and nitro-functionalised derivatives as single crystals suitable for SCXRD (Figures 4 and S11).

The geometry of the tricarboxylate linkers plays the major role in controlling whether the mesoporous or the interpenetrated phase forms,⁴⁷ but the size of the Sc³⁺ ions may also play a part, as observed previously in related syntheses.¹⁵ Interactions between the central ring (benzene, pyridine, triazine) and the benzoic acid groups are optimized, permitting TATB to attain a planar geometry, in contrast to the slightly out-of-plane geometry of BTB (Figure S12). While TATB and BTB form interpenetrated and mesoporous phases, respectively, the PTB ligand, which because of its pyridine core has intermediate geometry, can form both phases. Under optimised synthesis conditions of MIL-142(Sc)-TATB, synthesis with PTB gave single crystals of sufficient quality for structure determination (Figure 4). SCXRD studies revealed a structure isostructural to MIL-142(Sc)-TATB labelled MIL-142(Sc)-PTB. For MIL-142(Sc)-PTB prepared with functionalised BDC, roughly spherical crystal agglomerates resulted.

MIL-142(Sc)-TATB and MIL-142(Sc)-PTB are isostructural, the only difference being the substitution of TATB with PTB (Figure 5a, S13).

They adopt space group $R\bar{3}m$ rather than the lower symmetry $R3c$ reported for the iron form and the unit cells are larger than those reported for the Fe form. The MIL-142(Sc)-TATB framework consists of distorted superoctahedra with overall framework formula, $\text{Sc}_3\text{O}(\text{H}_2\text{O})_2(\text{OH})(\text{BDC})(\text{TATB})_{4/3}$, in which the vertex-occupying Sc_3O trimers are connected *via* three BDC and four TATB linkers (Figure 5b). This is agreement with the EDX studies confirming the MOFs are

free from halogen impurities from the metal precursor used in their synthesis (Figure S14, S15). While TATB linkers occupy four faces of the superoctahedron, the remaining three edges are occupied by BDC. The superoctahedral cage of MIL-142(Sc)-TATB is a hybrid between the supertetrahedra of MIL-101(Sc) and PCN-333(Sc) structures with an internal diameter of 1.1 nm. Substitution of a Sc_3O trimer on one of the corners of the PCN-333(Sc) supertetrahedron by one face of the MIL-101(Sc) supertetrahedron, in which the Sc_3O trimers are bridged by BDC, gives the superoctahedra of MIL-142(Sc)-TATB. The framework possesses an overall two-fold interpenetrated 3D structure via catenane-like intertwining of superoctahedra at their intergrown base triangles (Figure 5c) while TATB connects the top triangles of the nearby superoctahedra (Figure S16). In addition to the larger cages within the superoctahedra, there are smaller cages between the top triangles of non-interpenetrating neighbouring superoctahedra, with internal diameter 0.9 nm (Figure 5D, blue sphere). In addition to the narrow windows between large voids (radius about 0.34 nm) through the base triangles along the *c*-axis, there is 2D connectivity along the *ab*-plane through 0.6 nm pores (Figure S17). The Sc-O bond lengths in Sc_3 trimers of MIL-142(Sc)-TATB are in good agreement with the values reported previously for the Sc analogues MIL-126 and MIL-88 (Table ST4, ST5). The MIL-142(Sc)-PTB is refined with the position of one pyridine N atom ordered, and the other disordered by symmetry across all three possible positions (Figure S18).

Figure 5: Crystal structure of MIL-142(Sc)-TATB. (a) The overall two-fold interpenetrated structure of MIL-142(Sc)-TATB, (b) the distorted superoctahedra of MIL-142(Sc)-TATB in which the Sc_3 trimers are connected by BDC and TATB linkers, (c) the interpenetrated superoctahedra and (d) the superoctahedra with a small cage between them. Cages are represented by yellow and blue spheres. Colour code: Sc, pink; C, black; N, green; O, red.

In a second series of syntheses, BDC was replaced by nitro- or amino-functionalised BDC with each of the TATB and PTB linkers and the conditions adjusted to give crystalline MIL-142(Sc). For the TATB-containing samples, single crystals were obtained as single crystals similar in morphology to those of the parent MOF, and the structures were solved by SCXRD (Table 1). One structural feature of the functionalised derivatives of MIL-142(Sc)-TATB is the regioselectivity of amino and nitro groups in the structure. Whereas amino groups are disordered over all available *meta* and *ortho* positions of BDC with equivalent probability in MIL-142(Sc)-TATB-NH₂, nitro groups are located only on one side of the linker (with equal probability on both positions) in MIL-142(Sc)-TATB-NO₂ (Figure 6a, 6b, S19, S20). The bulky amino and nitro groups pointing into the cage between the superoctahedra reduce the cage size to 0.7 nm. Since there are no functional groups hindering the pore openings, the pore diameter remains the same in all these structures. The MIL-142(Sc) series is the first reported instance of multicomponent Sc MOFs that contain geometrically-distinct linkers (see Table ST6 for other multicomponent MOFs).^{48–51} Furthermore, MIL-142(Sc) permits the substitution of both di- and tricarboxylate linkers in addition to the dicarboxylate substitution already reported for the Fe form.

Topological analysis of MIL-142(Sc) was carried out with the ToposPro package. The $Sc_3-\mu_3O(O_2C)_6$ SBU is considered as a six-coordinating node (in form of a triangular prism), the TATB linker as a three-coordinating node; however, the BDC linker is only a 2-c node and therefore not a node but only an edge. The outcome of the

simplification procedure is that MIL-142(Sc)-TATB builds a 2-fold interpenetrated structure of two independent underlying nets with the topology **nht**, which is a (3,3,6)-c trinodal net (topological type 3,3,6T99) with the stoichiometry $(3-c)(3-c)_3(6-c)_3$. Note, that there are two 3-c vertices, which are not symmetry-related to each other. Figure 6c shows the **nht** net in its augmented version (i.e. **nht-a**), looking along the crystallographic *c* direction.

PXRD patterns of the multicomponent MIL-142(Sc)-TATB series showed good general agreement with the pattern simulated from the SCXRD structure of MIL-142(Sc)-TATB (Figure 7A) confirming the phase type and purity. TGA of as-synthesised MOF samples showed all structures were stable up to 450 °C before linker disintegration resulted in structural degradation (Figure 7B). N₂ adsorption at -196 °C for MIL-142(Sc)-TATB after activation at 160 °C for 16 h showed type I adsorption isotherm with BET surface area of 1768 m² g⁻¹ and 0.70 cm³ g⁻¹ pore volume. The surface area of MIL-142(Sc)-TATB is close to that of Sc-BTB (1865 m² g⁻¹ and 0.70 cm³ g⁻¹) and relatively high when compared to known Sc MOFs.^{52–55} Similarly, MIL-142(Sc)-TATB-NH₂ and MIL-142(Sc)-TATB-NO₂ showed BET surface areas and pore volumes of 1497 m² g⁻¹ and 1468 m² g⁻¹ and 0.57 cm³ g⁻¹ and 0.56 cm³ g⁻¹, respectively (Figure 7B). The pore volumes of the parent and the functionalised MOFs are in fair agreement with the theoretical values (Table ST7). The materials were also investigated for their CO₂ uptake at 25 °C after activation under similar conditions (Figure S21). While both MIL-142(Sc)-TATB and MIL-142(Sc)-TATB-

Figure 6: (a) Smaller cage of MIL-142(Sc)-TATB-NH₂ with amino groups disordered over all the *meta* and *ortho* positions of the BDC, (b) Smaller cage of MIL-142(Sc)-TATB-NO₂ with nitro groups disordered over meta and ortho positions on one side of the linker and (c) *nht-a* topology of MIL-142(Sc)-TATB. Colour code: Sc, pink; C, black; N, green; O, red. H atoms not shown.

Figure 7: PXRD patterns, TGAs and N₂ adsorption isotherms (–196 °) for the MIL-142(Sc)-TATB (A, B, C, respectively) and MIL-142(Sc)-PTB (D, E, F) families. In each case the plots are (red) with BDC, (blue) with NH₂-BDC and (green) with NO₂-BDC. PXRD patterns are compared with the simulated pattern for MIL-142(Sc)-TATB.

NH₂ showed an uptake of ca. 7 mmol g^{–1} at 5 bar, MIL-142(Sc)-TATB-NO₂ exhibited lower uptake (6.65 mmol g^{–1}).

For the MIL-142(Sc)-PTB series, PXRD showed good agreement with the simulated pattern of MIL-142(Sc)-TATB confirming the isorecticular nature of the frameworks (Figure 7). TGA of as-synthesised MOF samples showed that the parent and nitro functionalised MOFs were stable up to 450 °C while the amino derivative degraded at 400 °C.

N₂ adsorption at –196 °C for MIL-142(Sc)-PTB after activation gave a Type I adsorption isotherm with BET surface area of 1688 m² g^{–1} and 0.66 cm³ g^{–1} pore volume. MIL-142(Sc)-PTB-NH₂ and MIL-142(Sc)-PTB-NO₂ showed BET surface areas and pore volumes of 1508 m² g^{–1} and 1415 m² g^{–1} and 0.59 cm³ g^{–1} and 0.57 cm³ g^{–1}, respectively (Figure 7). Again, CO₂ adsorption of the MOFs was measured at 25 °C after activation under similar conditions. As was seen with the TATB series, higher uptakes of 6.63 and 8.16 mmol g^{–1} were observed at 5 bar for MIL-142(Sc)-PTB and MIL-142(Sc)-PTB-NH₂, respectively and MIL-142(Sc)-PTB-NO₂ exhibited a lower uptake of 5.73 mmol g^{–1} (Figure S22).

The Lewis acidity of the coordinatively unsaturated Sc^{3+} metal-sites in MIL-142(Sc)-TATB generated *via* the removal of cluster coordinated solvent molecules was examined by testing the MOF as a Lewis acid catalyst in the imine condensation reaction between 4'-fluoroacetophenone and benzylamine (Scheme S2). MIL-142(Sc)-TATB showed only 63% conversion towards the desired imine. Since this is much lower than reported for Sc-BTB and MIL-100(Sc) under identical conditions from our previous studies, no further investigations were carried out on the stability and recyclability of the catalyst.³⁷ The reduced activity of MIL-142(Sc)-TATB when compared to other Sc MOFs with similar coordinatively unsaturated Sc^{3+} sites is attributed to the restricted access resulting from the full 2-fold interpenetration of the framework.

Conclusions

A series of porous MIL-142(Sc) MOFs were synthesised solvothermally using mixed linkers of distinct connectivity namely BDC, NH_2 -BDC, NO_2 -BDC, TATB and PTB. Initial attempts to synthesise interpenetrated MIL-142(Sc) using BTB as the tricarboxylic linker resulted in the formation of mesoporous Sc-BTB *via* the incorporation of BTB alone, even in the presence of BDC. By contrast, synthesis using the more closely planar TATB gave the scandium-TATB analogue, MIL-142(Sc)-TATB, of the previously-reported MIL-142(Fe). The importance of linker geometry in guiding the formation of either interpenetrated or mesoporous frameworks with Sc^{3+} ions was subsequently emphasised by synthesising MIL-142(Sc)-PTB and Sc-PTB using the PTB linker. The MIL-142(Sc) series comprises the first Sc MOFs possessing mixed linkers of distinct connectivity. Furthermore, the framework permits substitution of both di- and tricarboxylate linkers, whereas for the Fe form only dicarboxylate replacement is reported. The isorecticular materials exhibit high crystallinity, permanent porosity and good temperature stability.

Conflicts of Interest

There are no conflicts of interest to declare.

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MIL-142(Sc) is prepared and the limits of the isorecticular substitution of each linker type are explored and characterised by single-crystal XRD

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