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SYNTHESIS OF PHOTOACTIVE METAL-ORGANIC FRAMEWORKS

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Table of Contents

Introduction

Metal-organic frameworks (MOFs, also known as "coordination polymers"[1]) are inorganic-organic solids that form microporous crystalline solids, and can be synthesised by using a wide range of organic bridging ligands and metal ions.[2] Within the past two decades, MOFs have evolved rapidly in design, synthesis and characterisation, due to the potential applications of their structural and chemical diversity in gas storage, molecular separations and heterogeneous catalysis.[3-6]

Post-synthetic modification (PSM)[7] of MOFs has led to many interesting ideas, in terms of functionalising the pores for various applications. One unexplored strategy for the development of photo-active frameworks involves the grafting of light-responsive organic molecules, such as azobenzene (AZB) or spiropyran,[8-9] onto the internal surfaces of transparent MOFs, *via* covalent attachment to the bridging ligands.[10] The use of light to affect changes in the light-responsive molecules, thereby modulating the size and polarity of the pores, presents exciting new possibilities for the design of porous photoswitchable membranes.

Azobenzene is a photochromic compound which, upon photo-irradiation with UV-light (λ = 365 nm), undergoes reversible isomerisation from the stable *trans*-form to the meta-stable *cis*-form (refer to Figure 1).[3, 11] The *trans*-form can be recovered thermally, or *via* irradiation with blue light (λ > 440 nm). A post-synthetic functionalisation technique[12] was used to attach the amino group of the framework with a derivatised photoactive moiety, as shown in Figure 1.

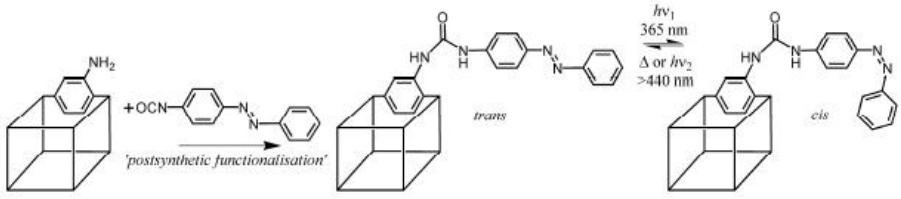
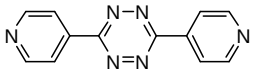
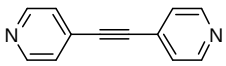
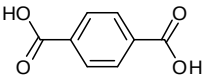
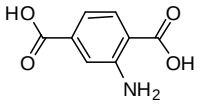
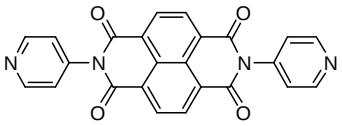
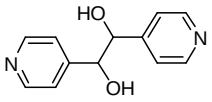
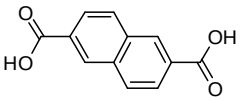
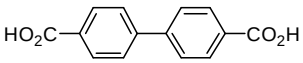
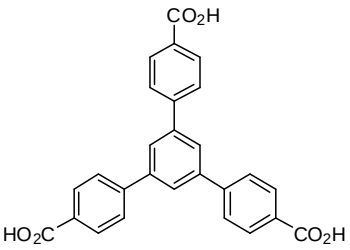
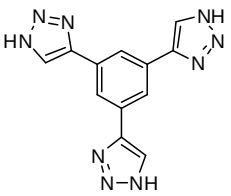


Figure 1. Scheme showing the post-synthetic grafting of azobenzene onto an amine-functionalised MOF. The structure of the photochromic membrane is altered by irradiation, which isomerises the azobenzene.

Our goal is to develop strategies for grafting azobenzene onto porous crystalline MOFs that consist of zinc(II) metal centres and mixed organic bridging ligands. Table 1 below contain names and structures of organic linkages mentioned in the report.

Table 1. Name abbreviation and structure of organic ligands referred to in the text.

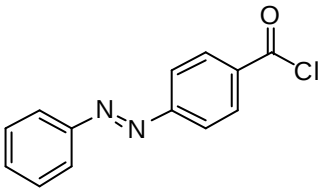
Name	Abbreviation	Structure
3,6-di(4-pyridyl)-1,2,4,5-tetrazine	BPTz	
1,2-bis(4-pyridyl)acetylene	BPA	
1,4-benezenedicarboxylic acid	BDC	
2-amino-1,4-benezenedicarboxylic acid	ABDC	
N,*N*'-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide	DPNI	
1,2-di(4-pyridyl)glycol	DPG	
2,6-naphthalenedicarboxylic acid	NDC	
biphenyl-4,4'-dicarboxylic acid	BPDC	
1,3,5-tris(4-carboxyphenyl)benzene	BTB	
1,3,5-tri(1*H*-1,2,3-triazol-4-yl)benzene	H_3BTTri	

Experimental Notes

- Melting points were obtained using the GALLEN KAMP Melting Point Apparatus.
- Infra-red spectra were recorded on a Bruker Tensor 27 spectrometer with compounds mixed in KBr. Absorption maxima are expressed in wavenumbers (cm^{-1}).
- ^1H Nuclear Magnetic Resonance spectra were acquired on either a Bruker Avance DPX 300 (300 MHz) or a Bruker Avance DPX 200 (200 MHz) spectrometer at 300 K. Chemical shifts (δ) are expressed in parts per million (ppm) downfield shift from tetramethylsilane (0 ppm). ^1H NMR signals are reported with multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), relative integral, coupling constant *J* (Hz) and assignment.
- X-ray powder diffraction (XRPD) patterns were obtained on a PANalytical X'Pert Powder diffractometer at 300 K. The diffraction angles are expressed in 2 theta (θ°) degrees.
- Chemicals were purchased from Sigma Aldrich, with the exception of the ligands, 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine (BPTz), 1,2-bis(4-pyridyl)acetylene (BPA), 1,3,5-tris(1H-1,2,3-triazol-5-yl)benzene) (H_3BTTri), which were generously sourced from Kepert and D'Alessandro *et al*.
- Solvents were purified and dried as required, as per the procedures of Perrin and Armarego.[13]

Experimental Procedures

Synthesis of 4-phenylazobenzoylchloride (1)[14]

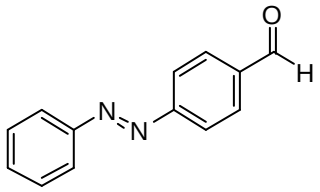


4-Phenylazobenzoic acid (0.5 g, 2.2 mmol) was added to anhydrous sodium carbonate (0.5 mg, 4.7 mmol) in a round bottomed flask. Thionyl chloride (10 mL, 34.4 mmol) was added to the mixture which was refluxed for 1.5h. The resulting HCl and SO_2 were quenched by bubbling through a solution of NaOH (100 mL, 1M). The reaction mixture was distilled to recover most of the thionyl chloride. The acid chloride was dissolved in petroleum spirit (30 mL), heated to 100 °C and filtered to remove the precipitated sodium carbonate. The product was concentrated by evaporation of the

solvent under reduced pressure, followed by drying in a desiccator overnight to give an orange/red solid (484.5 mg, 90%).

M.p. 93.5-95-5 °C (lit.94.5-95.5 °C). IR (KBr) *v* 1771 1742 1406 1197 877 775 685 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.22-8.2 (d, 2*H*, J 8.4 -C*H*CCOCl), 7.94-7.88 (m, 4*H,* -(C*H*)$_2$-N_2-(C*H*)$_2$-), 7.5-7.47 (t, 3*H*,*H*C(CH)$_2$-).

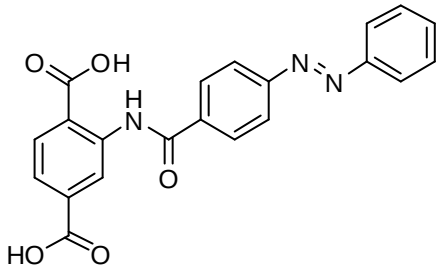
Synthesis of 4-phenylazobenzaldehyde (2)[15]



Lithium tri-*tert*-butoxyaluminium hydride (395 mg, 1.55 mmol) was dissolved in anhydrous THF (16 mL) and added dropwise, with stirring under Ar at -78 °C, to a solution of compound **1** (380 mg, 1.55 mmol) in anhydrous THF (12 mL). The reaction was stirred for a further 1 h and allowed to warm to room temperature. The reaction was quenched with HCl (10 mL, 1M), extracted with ether (3 x 15 mL), and dried over sodium sulfate. The solvent was evaporated and the resulting crude product was purified by flash chromatography (dichloromethane/cyclohexane, 5:3). The combined fractions were concentrated under reduced pressure, and dried in a desiccator overnight to yield an orange solid (280 mg, 86%).

R_f = 0.57. M.p. 120.5-121.5 °C (lit. 119-120 °C). ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 10.16 (s, 1*H*, -C*H*O), 8.08 (m, 4*H*, -(C*H*)$_2$-N_2-(C*H*)$_2$-), 8.04-7.99 (m, 2*H*, -C*H*CCHO), 7.61-7.59 (m, 3*H*, *H*C-(CH)$_2$-) ppm.

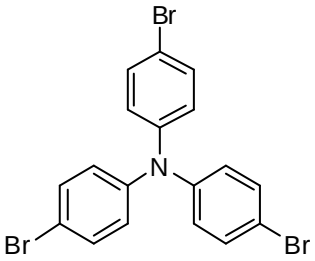
Synthesis of (*E*)-2-(4-phenyldiazenyl)benzimido)terephthalic acid (3)



Compound **1** (66.1, 0.21 mmol) and 2-amino-1,4-benezenedicarboxylic acid (49 mg, 0.27 mmol) was dissolved in DMF (10 mL). The solution was stirred at 80 °C for 30 min and quenched with water. The resulting precipitate was filtered and dried overnight in a desiccator to give an orange solid (95.7 mg, 91%).

IR (KBr) 3080 1679 1583 1429 1292 868 779 690 cm^{-1}.

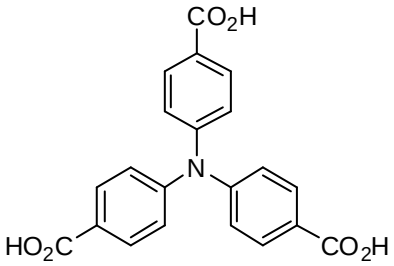
Synthesis of 4,4',4''-Tris(*p*-bromophenyl)amine (4)[16]



In a round-bottomed flask, triphenylamine (10 g, 40 mmol) was dissolved in chloroform (40 mL) and cooled in an ice bath. After covering the reaction flask with aluminium foil, bromine (6.3 mL, 122 mmol) was added dropwise to the cooled solution with stirring. The reaction was stirred for a further 1 h. Quenching with EtOH/H_2O (1:1, 100 mL) gave a white precipitate. The mixture was filtered and the residue was dissolved in hot chloroform (30 mL). After the addition of hot ethanol (50 mL) the product was allowed to crystallise overnight at -18 °C. The product was filtered and dried in a desiccator overnight to yield off-white crystals (10.5 g, 54%).

M.p. 145.5-146.5 °C (lit. 144-146 °C)[4,5]. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.39-6.36 (d, 6*H*), 6.96-6.93 (d, 6*H*) ppm.

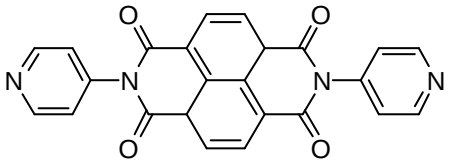
Synthesis of 4,4',4''-Nitrilotris-benzoic acid (5)[17]



4,4',4''-Tris(*p*-bromophenyl)amine (4.825 g, 10.0 mmol) was added to dry ether in a round-bottomed flask under Ar. *n*-Butyllithium in hexane (1.6 M, 21 mL, 33.6 mmol) was added dropwise to the solution in an ultrasonic bath at 0 °C. Dry carbon dioxide was bubbled through the resulting yellow mixture for 30 min. The ice bath was removed, and the bubbling of CO_2 was continued for a further 30 min. The green mixture was dissolved in ether and extracted with saturated $NaHCO_3$ solution (3 x 30 mL). HCl (1M) was added dropwise to the aqueous solution until a precipitate formed. The product was filtered and dried in a desiccator overnight to yield a green solid (1.1 g, 29%).

^{1}H-NMR (300 MHz,MeOD) δ = 7.98-7.94 (m, 2*H*), 7.55-7.52 (m, 1*H*), 7.19-7.08 (m, 4H) ppm.

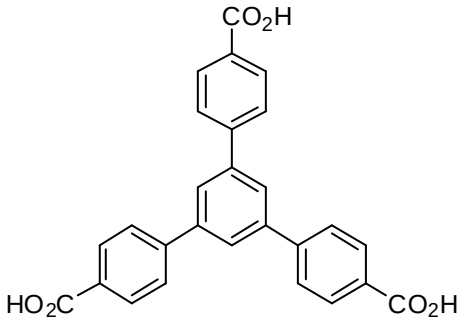
Synthesis of *N*,*N*'-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide (DPNI) (6)[18]



1,4,5,8-naphthalenetetracarboxylic dianhydride (2.1 g, 7.8 mmol) and 4-aminopyridine (2.0 g, 22 mmol) were dissolved in anhydrous DMF (100 mL) under nitrogen. The reaction mixture was refluxed overnight. The resulting white mixture was cooled in an ice bath and filtered. The residue was washed with acetone and dichloromethane, followed by drying in a vacuum desiccator overnight to yield an off-white solid (2.8 g, 81%).

IR(KBr) *v* 1715 1673 1578 1340 1246 cm^{-1}.^{1}H-NMR (200 MHz, TFA) δ 8.83-8.81 (d, 4*H*, *J* 4.0 Ar), 7.956 (s, 4*H*), 7.59-7.58 (d, 4*H, J* 3.8 NCC*H*) ppm.

Synthesis of 1,3,5-Tris(4-carboxyphenyl)benzene (BTB) (7)[19]



1,3,5-tris(4-carboxyphenyl)benzene (2g, 3.7 mmol) was dissolved in anhydrous THF (25 mL) under Ar and cooled to -78 °C. *n*-Butyllithium (1.6 M, 7 mL, 11.2 mmol) was added dropwise and stirred for 1 h resulting in a green reaction mixture. Dry carbon dioxide was bubbled through the lithiated mixture for 2 h to give a colourless precipitate of the lithium salt. The reaction was quenched with aqueous acetic acid (50% v/v, 100 mL) at room temperature and filtered. Recrystallisation of the residue from glacial acetic acid and drying in a desiccator overnight gave the product as white crystals (1.39 g, 86%).

IR(KBr) *v* 1596 1491 1441 1380 1076 1007 810 cm^{-1}. ^{1}H-NMR (200 MHz, DMSO-d_6) δ = 8.12 (s, 1*H*), 8.09 (m, 3*H*) ppm.

Synthesis of metal organic frameworks with zinc based clusters and mixed organic ligands

General preparation of MOF 1-11

$Zn(NO_3)_2 \cdot 6H_2O$, ligand 1 and ligand 2 were dissolved in DMF (reagent quantities as summarised). The solution was divided into 10 mL vials which were heated in a dry block heater at 85 °C for 48 h. The vials were cooled to room temperature and were decanted, leaving behind the resulting product as a solid or suspension. The crude products were combined (and for suspensions, centrifuged to obtain the solid), followed by washing with DMF (3 x 10 mL) and chloroform (3 x 10 mL). Residual DMF was removed by soaking the solid in chloroform, and exchanging the solvent for fresh chloroform every 24 h over 2 days. The chloroform was decanted, and the remaining solid was dried over a stream of nitrogen before recording mass yield (see table 2 below).

The Metal-organic framework products were stored in chloroform until needed. Metal-organic frameworks were characterized by X-ray powder diffraction.

*MOF 11-**b** (isothermal oven reaction)*

1,3,5-tris(4-carboxyphenyl)benzene (127.6 mg, 0.29 mmol), 2-amino-1,4-benezenedicarboxylic acid (146.7 mg, 0.81 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (963.9 mg, 3.24 mmol) were dissolved in DMF (30 mL). The solution was divided into three aliquots and heated in an isothermal oven at 85 °C for 48 h. The aliquots were cooled to room temperature and the solution was decanted leaving behind colourless crystals. The crystals were washed with DMF (3 x 10 mL), with chloroform (3 x 10 mL) and left to stand in chloroform for 2 days. The solvent was decanted and fresh chloroform was added every 24 h for 2 days. The crystals were characterized by Powder X-ray diffraction.

MOF 12

Compound **6** (340 mg, 0.78 mmol), NDC (174 mg, 0.80 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (600 mg, 2.0 mmol) were dissolved in DMF (400 mL)and heated in an isothermal oven at 80 °C for 48 h. The solution was cooled to room temperature and decanted to yield yellow crystals. The crystals were washed with DMF (3 x 20 mL), followed by chloroform (3 x 20 mL) and then left to stand in chloroform for 2 days. The solvent was decanted and fresh chloroform was added every 24 h for 2 days.

Photoactive modification by adding azobenzene to MOF 11-b (UMCM-1-NH_2)

Post-Synthetic Modification 1

Compound **1** (10.5 mg, 43 μmol) was dissolved in chloroform (1 mL) and was added to MOF 11-**b** (24 mg, 7.7 μmol) at room temperature. After 0.5 h, the resulting red solvent was decanted and the crystals were washed with chloroform (3 x 3 mL). The crystals were characterized by XRPD.

Post-Synthetic Modification 2

Compound **2** (20.6 mg, 98 μmol) was dissolved in chloroform (1 mL) and was added to MOF 11-**b** (100 mg) at room temperature. After one week, 1/3 of the crystals were removed from the solution, placed in another vial and washed with chloroform 3 times. The crystals were soaked in chloroform until needed. After additional 1 week, half of the crystals were subjected to the same washing procedure as mentioned above. A parallel washing procedure was carried out with toluene as solvent instead of chloroform. The crystals were characterized by XRPD and UV-Vis-NIR.

Grafting Method 1

Using the MOF 11-**b** procedure, compound **3** (95.7 mg, 0.25 mmol), compound **7** (42.5 mg, 97.0 μmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (321 mg, 1.08 mmol) were dissolved in DMF (10 mL) to produce red/orange-shaped needle crystals (33 mg).

Grafting Method 2

Using the MOF 11-**b** procedure, 1, 4-phenylazobenzoic acid (61 mg, 0.27 mmol), compound **7** (42.5 mg, 97.0 μmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (321 mg, 1.08 mmol) were dissolved in DMF (10 mL) to yield yellow needle-shaped crystals (31 mg).

Results and Discussion

Carboxylated organic compounds have been widely reported as suitable linkers between transition metals in the synthesis of MOFs. Hence, compounds **3**, **5** and **7** are likely to form stable organic frameworks with zinc(II), see figure 2.

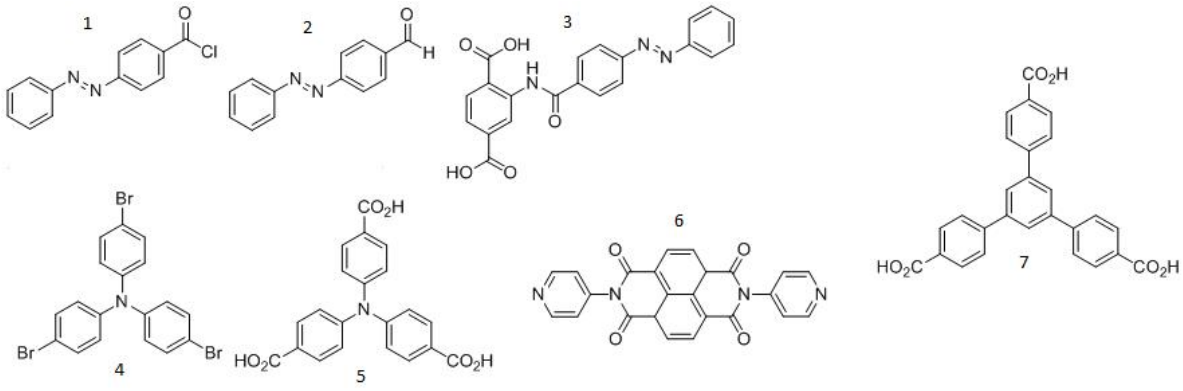


Figure 2. Illustration of the synthesised compound 1 to 7.

Compound **3** was made by *via* a nucleophilic attack of the 2-amino-1,4-benezenedicarboxylic acid on the electrophilic 4-phenylazo(benzoyl)chloride. Compound **3** was poorly purified and characterised, and to the best of our knowledge there are no reports of a previous synthesis and characterisation of this compound. The IR spectrum suggests that the desired compound was indeed synthesised, as it did not show peaks characteristic of the starting material, suggesting complete conversion. Additionally, the spectrum contained a N-H stretch at approximately 3080 cm^{-1}, as well as a C=O stretch at 1680 cm^{-1}, as expected for the desired product (see figure 3, below).

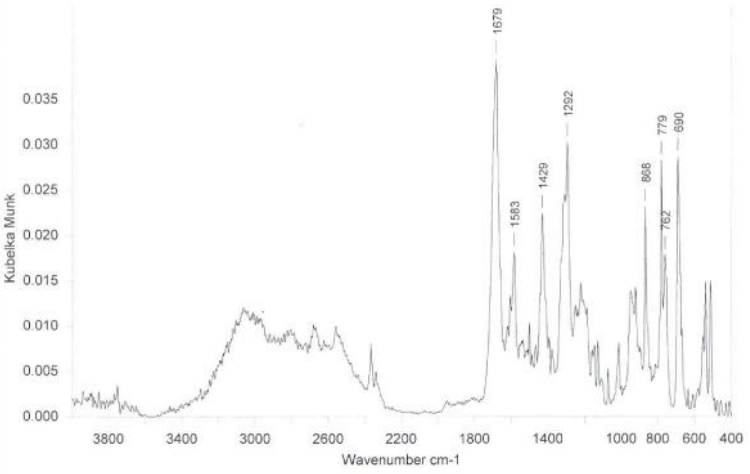


Figure 3. IR spectra of (*E*)-2-(4-phenyldiazenyl)benzimido)terephthalic acid (compound **3**).

University of Michigan Crystalline Material-1 (UMCM-1-NH_2) is consisting of compound **7** and 2-amino-1,4-benezenedicarboxylate coordinated to zink(II) clusters, this metal-organic framework is MOF11 in this report, see figure 4 below.

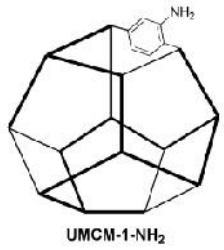


Figure 4. Structural illustration of MOF11.

We proceeded with the synthesis of MOF11 assuming that **3** was synthesised, however, we do not have sufficient characterisation to confirm the identity of this metal-organic framework.

Compound **5** is a ligand with interesting electronic properties and consists of a triangular tricarboxylate with an amine in the centre. Compound **7** is similar to compound **5**, with a benzene ring in place of the amino group. The characterisation of compound **5** showed the expected substitution group at the para position. The ^{1}H-NMR spectra revealed Ar–OH (δ 4.88 ppm) substitution with mono- and di-substituted carboxylates. The peaks ranging from 7-8 ppm are Ar-H and the signals below 4 ppm are ether and hexane. We could not, however, separate compound **5** from this mixture containing compounds with different substitutions (refer to figure 5 below). Therefore compound **5** was not used as an organic linker in MOF synthesis.

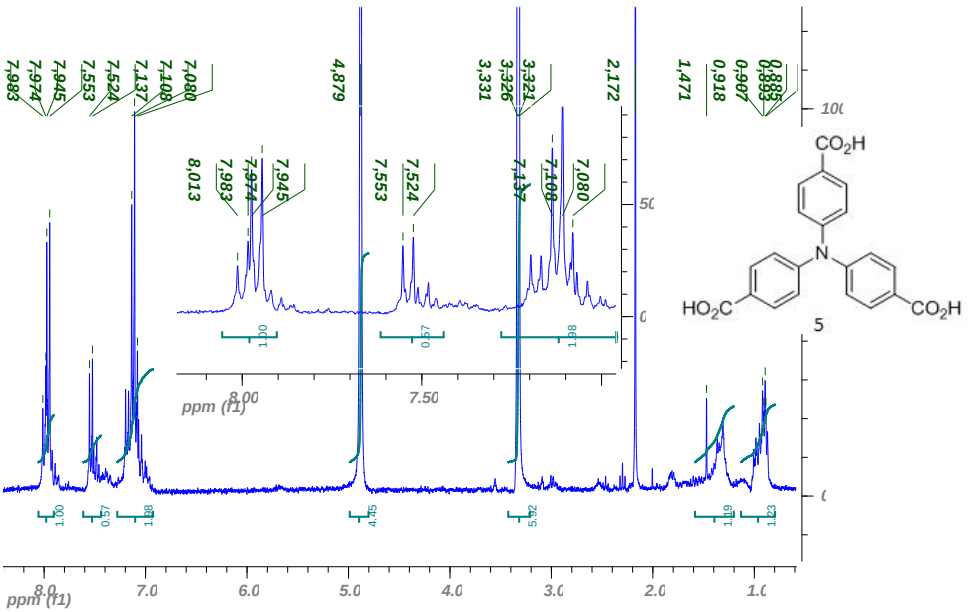


Figure 5. ^{1}H-NMR spectra of 4,4′,4′′-Nitrilotris-benzoic acid (compound **5**).

^{1}H-NMR characterisation of compound **7** showed two peaks at ≈8 ppm, although there should be three aryl proton environments. This may have arisen due to the low resolution of the ^{1}H-NMR acquisition (200 MHz) (figure 6).

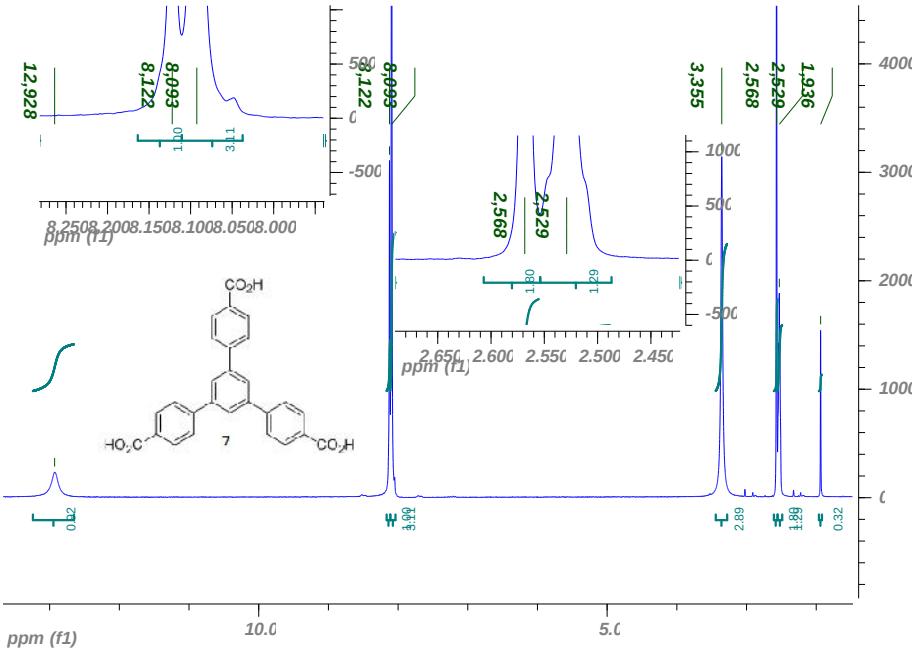


Figure 6. ^{1}H-NMR spectra of 1,3,5-Tris(4-carboxyphenyl)benzene (BTB) (compound **7**).

^{1}H-NMR characterisation of compound **1** revealed all nine protons in five proton environments in the region 7-8 ppm. The IR spectrum showed one peak at 1771 cm^{-1} (C=O stretch), see figure 7 below.

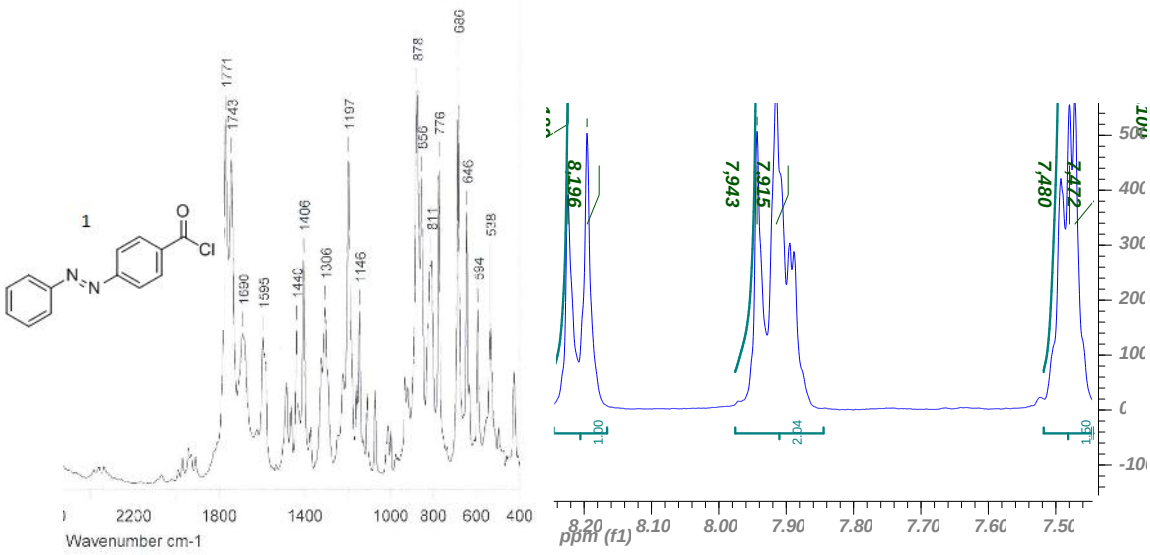


Figure 7. IR- and ^{1}H-NMR spectra of 4-phenylazobenzoylchloride (compound **1**).

Compound **2** showed a single aldehyde peak at 10.16 ppm and the remaining nine protons appear as five environments in the aryl region (7-8 ppm), refer to figure 8.

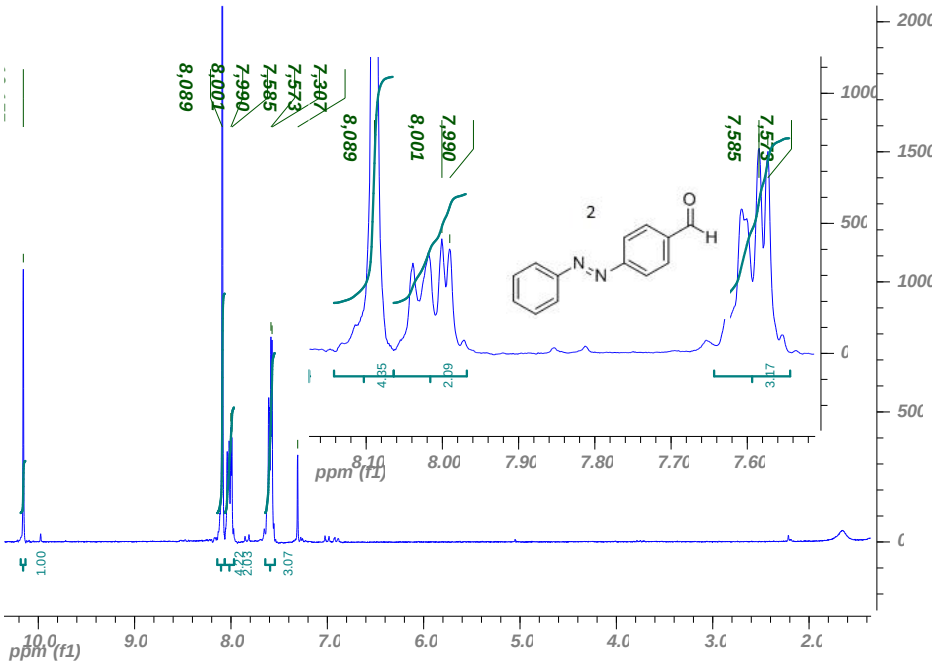
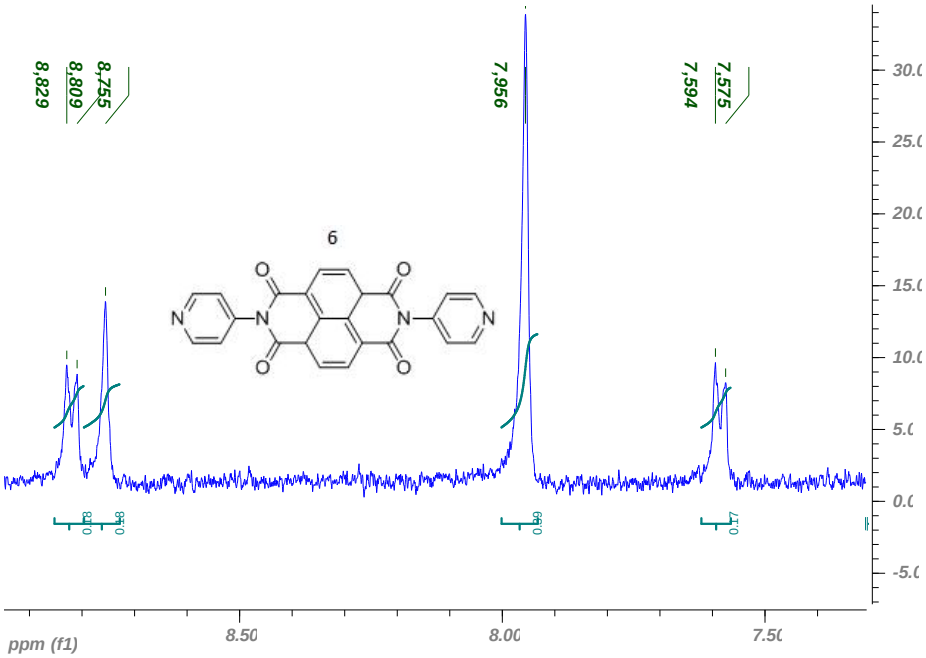


Figure 8. [1]H-NMR spectra of 4-phenylazobenzaldehyde (compound **2**).

Compound **6** is not a carboxylated ligand; rather, the amino groups are likely to coordinate to the metal centre. The [1]H-NMR spectrum shows three peaks in the 7.5 to 8.3 ppm range, which contains all 12 aryl protons for compound **6** (figure 9).



Figur 9. [1]H-NMR spectra of *N*,*N*'-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide (DPNI) (compound 6).

Our goal was to synthesise porous 3-dimensional zinc(II)-based metal-organic frameworks by selecting combinatorial pairs of the ligands, DPNI, BTB**,** BPA, H_3BTTri, DPG, DPNI and BPTz (1:1, see Table 1), followed by post-synthetic modifications facilitated by the OH or NH_2 groups on the ligands. The synthesis of MOF1 to 11 resulted in either single crystals or solids as products (see Table 2 and figure 10).

Table 2. This table provides a summary of the general synthesis of MOFs as mentioned above with the zinc based cluster, mixed ligands, mass yield and its appearance.

MOF	$Zn(NO_3)_2{\cdot}6H_2O$	Ligand 1		Ligand 2		MOF	Appearance
	Qty (mg, mmol)	Name	Quantity (mg, mmol)	Name	Quantity (mg, mmol)	Yield (mg)	
1	455, 1.53	DPNI	234, 0.55	ABDC	101, 0.56	102	Brown solid
2	206, 0.69	BPA	65, 0.36	ABDC	61, 0.34	53	Brown solid
3	18, 0.06	BPDC	4.8, 0.02	DPG	4.6, 0.02	10	Colourless solid
4	18, 0.06	H3BT-Tri	5.6, 0.02	ABDC	3.6, 0.02	3	Yellow suspension
5	18, 0.06	H3BT-Tri	5.6, 0.02	DPG	4.6, 0.02	-	White suspension
6	18, 0.06	BPTz	4.8, 0.02	ABDC	3.6, 0.02	-	Purple solution
7	18, 0.06	BPTz	3.6, 0.02	DPG	4.8, 0.02	-	Purple solution
8	18, 0.06	BPA	3.6, 0.02	BPDC	4.6, 0.02	1.1	White solid
9	18, 0.06	BPA	3.6, 0.02	DPG	4.8, 0.02	0.6	White solid
10	18, 0.06	BTB	8.8, 0.02	DPG	4.8, 0.02	1.9	White solid
11	1.61, 5.4	BTB	213, 0.49	ABDC	245, 1.4	213	Yellow/brown solid

The difficulty of producing crystalline products was most likely due to environmental disturbances. Attempts to promote crystal growth by heating in an oil bath resulted in non-crystalline product formation. On the other hand, heating in an isothermal oven gave single crystals for MOF11 and 12. Crystal growth is sensitive to environmental factors such as temperature, solvent and growth time.

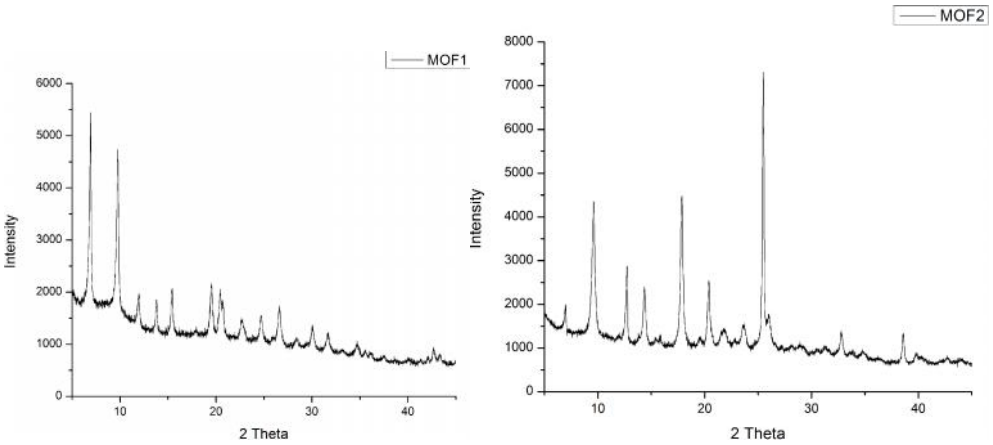


Figure 10. X-ray powder diffraction of MOF1-4 and MOF10. No XRPD characterization on MOF 5-9 due to difficulties of isolating the product or insufficient yield.

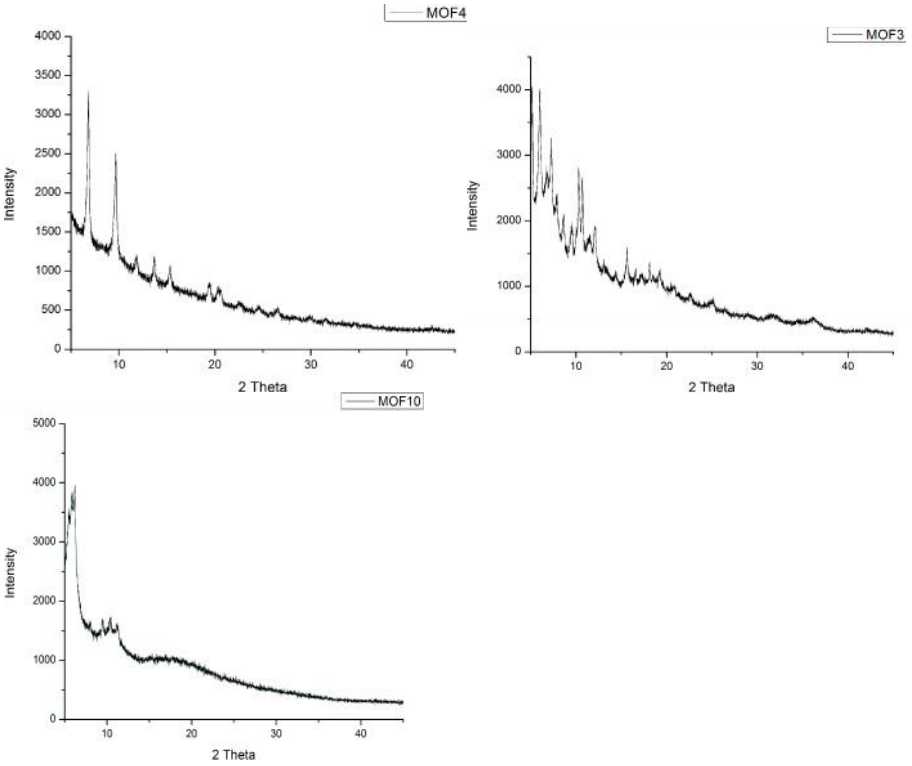


Figure 10. Continued.

MOF 11 was synthesised under two different conditions: in a dry heating block at 85 °C (MOF11-**a**), which produced a beige/brown solid, and in an isothermal oven (MOF11-**b**), which yielded colourless single crystals. The X-ray powder diffraction (XRPD) pattern patterns of the compound produced using method **a** (dry heat block) indicated that a MOF, other than the structure desired, was formed (see figure 11 below). The powder diffraction of MOF 11-**a** resembles a zinc(II) framework with only 2-amino-1,4-benzenedicarboxylic acid (ABDC) as ligands, based on data from the Cambridge Crystallographic Data Centre (CCDC).

Single crystals of MOF11-**b** and 12 were successfully grown, but only MOF11 underwent post-synthetic modification (PSM) since MOF12 did not have functional groups that could be modified. MOFs 5-9 were not characterised by powder X-ray diffraction because the attempted syntheses of these MOFs either gave no reaction or the product could not be isolated.

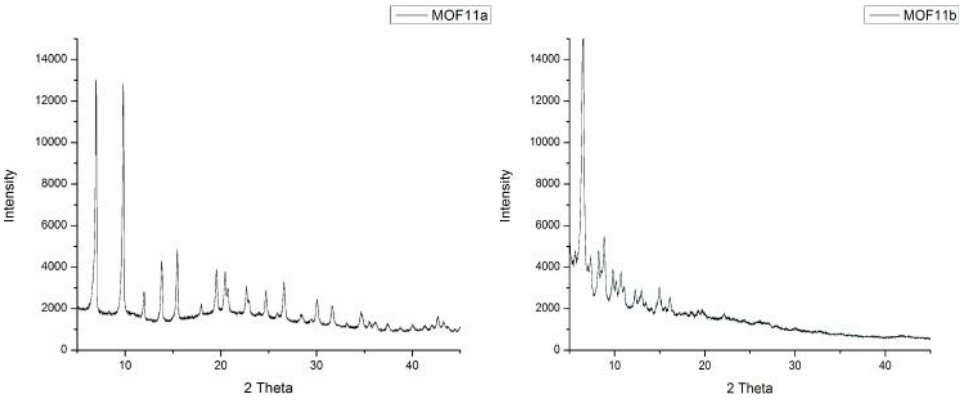


Figure 11. X-ray powder diffraction of MOF11a (heating block) and MOF11b (isothermal oven).

Post-synthetic modification of MOF11-**b**

Method 1

Post-synthetic modification of MOF11 (UMCM-1-NH_2) with compound **1** resulted in the degradation of the MOF's 3-dimensional structure, as shown from XPRD (Figure 12, brown pattern). This is most likely due to the reaction with the by-product, HCl, which may have protonated the carboxylate groups of the ligands, impeding coordination to the metal centres.

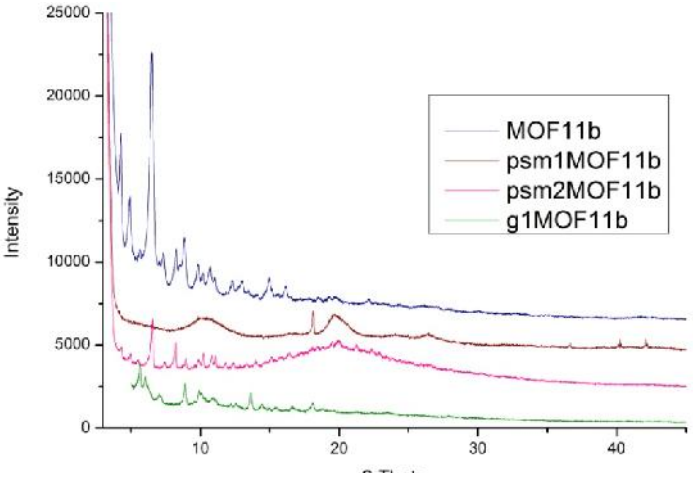


Figure 12. X-ray powder diffraction pattern of UMCM-1 (MOF11-**b**) after and before postsynthethic modification.

Method 2

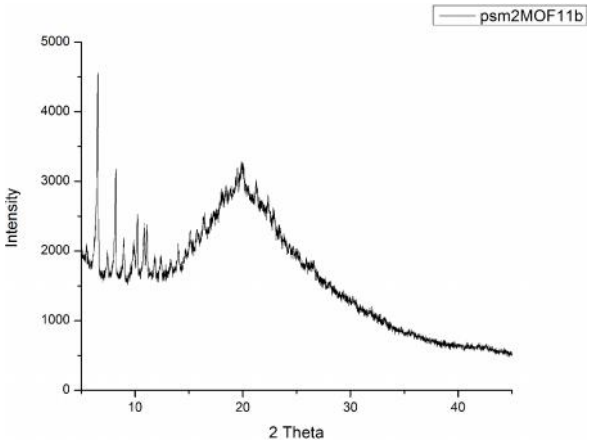


Figure 11. PXRD pattern of MOF11b post-synthetic modification method 2.

Orange crystals were anticipated from the post-synthetic modification of MOF11 by covalent attachment of 4-phenylazobenzaldehyde to the 2-amino-1,4-benezenedicarboxylate, since 4-phenylazobenzaldehyde is itself orange. The reaction gave, after one week, slightly orange-coloured crystals. The XRPD pattern showed no degradation of the MOF in this post-synthetic modification reaction (figure 11).

The colour of the product did not differ when the reaction was conducted in either chloroform or toluene. In both cases, the azobenzene (AZB) may have attached to ligands on the surface of the crystals.

Grafting azobenzene onto UMCM-1

Method 1

Another method of attaching azobenzene to the framework was to substitute 2-amino-1,4-benezenedicarboxylic acid with compound **3** to the synthesis of MOF11. Compound **3** is a modified benzenedicaboxylate with the azobenzene. This method gave orange needle-shaped crystals, the

colour and shape of which is consistent with Method 2. Single crystal X-ray diffraction confirmed the structure of UMCM-1, but did not confirm whether azobenzene was successfully attached to the network (processing of crystallographic data is not yet completed). The attachment of azobenzene must be confirmed by other methods such as UV-Vis spectrophotometry which is still in progress.

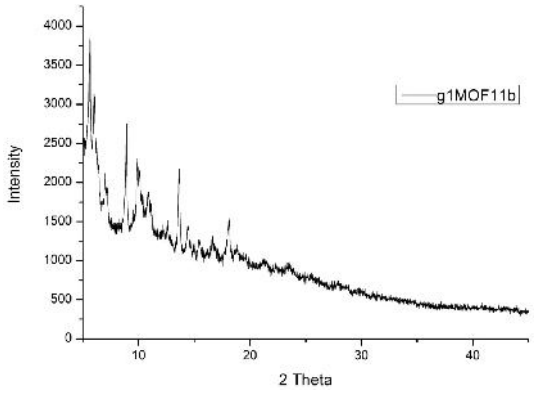


Figure 12. PXRD pattern of MOF11b grafting method 1.

Method 2

We also tried to graft azobenzene onto the framework bridging ligands by adding 4-phenyl(azo)benzoic acid to the synthesis mixture of MOF11. This procedure produced light orange needle-shaped crystals, as shown in Figure 13. Characterisation is still in progress.

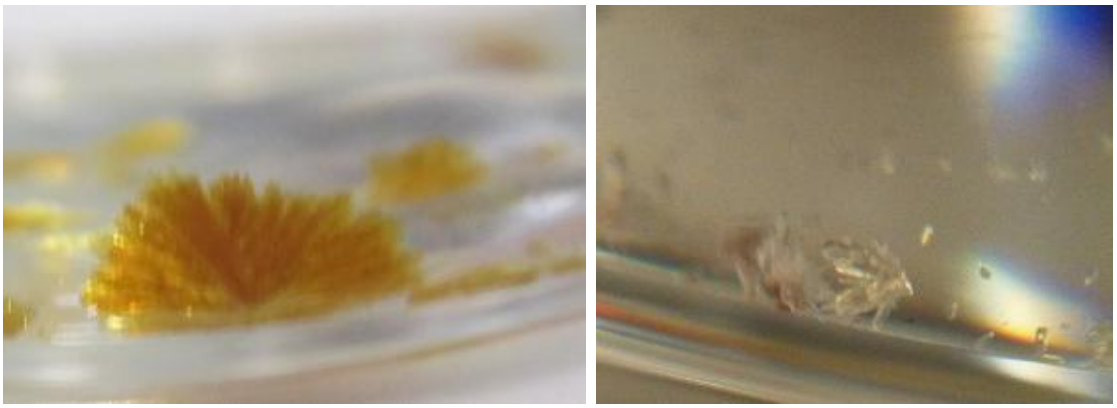


Figure 13. Synthesis of MOF 11 with a compound 3 yielded orange crystals, to the left. Slightly coloured crystals to the right were obtained by adding 4-phenylazobenzoic acid to the synthesis of MOF 11.

In conclusion, we have completed the early stages of synthesis of MOF1, 2, 3, 4 and 11 (Table 2). Early PXRD characterisation shows good quality diffraction patterns indicating that these MOFs have coherent structures. Further work is needed to grow these MOFs as single crystals to ascertain their exact structures. Further work is also needed to determine whether azobenzene was successfully grafted onto UMCM-1. Once the structures of these MOFs are accurately determined, they can be tested for applications such as gas separation, in addition to photoactivity.

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List of Abbreviations

2θ	X-ray powder diffraction scattering angle
Ar	aryl
$CDCl_3$	deuterated chloroform
$CHCl_3$	chloroform
d	doublet
DCM	dichloromethane
DMF	*N,N*-dimethylformamide
DMSO	dimethyl sulfoxide
DMSO-d_6	deuterated DMSO
h	hours
Hz	Hertz (frequency)
IR	infrared spectroscopy
J	^{1}H-^{1}H coupling constant in Hz
LC	liquid chromatography
lit.	literature value
M	metal
m	multiplet
M.p.	melting point
MeOD	deuterated methanol
MeOH	methanol
MOF	metal organic framework
NDC	2,6-naphthalenedicarboxylate
NIR	near infrared
NMR	nuclear magnetic resonance
ppm	parts per million
PSM	post-synthetic modification
PXRD/XRPD	powder X-ray diffraction / X-ray powder diffraction
R_f	retardation factor (thin layer chromatography)
s	singlet
t	triplet
TFA	trifluoroacetic acid
TLC	thin layer chromatography
THF	tetrahydrofuran
UMCM-1	University of Michigan Crystalline Material-1
v	wavenumber (cm^{-1})
δ	chemical shift in ppm, downfield from tetramethylsilane