

PROCESS FOR OBTAINING METAL ORGANIC FRAMEWORKS FROM POLYMERIC MATERIALS

FIELD OF INVENTION

- 5 The present invention provides a process for obtaining metal organic frameworks (MOFs) from polymeric materials.

BACKGROUND

- 10 The listing or discussion of a prior-published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

The widespread use of plastic materials derived from petroleum sources, such as polyethylene terephthalate (PET), poses significant environmental challenges. To mitigate these issues, biomass derived polymers like polyethylene furanoate (PEF) are being introduced as renewable alternatives to traditional plastics. However, with the increasing adoption of PEF, this material will inevitably become a prevalent component of post-consumer plastic waste. Consequently, the need for innovative and sustainable management strategies for the 'end of life' PEF plastics becomes crucial.

The current mechanical recycling techniques for PEF are analogous to those used for PET. While recycling represents a step towards sustainability, these methods bear significant limitations such as degradation of plastics during mechanical recycling. This leads to reduced material quality over time, thereby limiting the number of recycling cycles a given piece of plastic can undergo.

The upcycling of plastics, transforming them into products of greater value at the end of their life cycles, represents a viable solution to this problem. Metal-organic frameworks (MOFs) are porous materials with high commercial value due to their versatile applications in environmental remediation, carbon dioxide capture, gas separation and storage, as well as catalysis. Transforming post-consumer PEF into MOFs would provide a more valuable 'end of life' route for these plastics. However, current methods for MOF synthesis often employ toxic and expensive organic solvents such as *N,N*-dimethylformamide, which reduce the sustainability and cost-effectiveness of these processes.

Thus, there is a need for alternative and/or improved processes for upcycling such plastics, including polyethylene furanoate (PEF), into metal organic frameworks (MOFs).

SUMMARY

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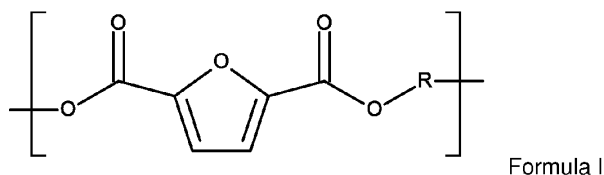
Aspects and embodiments of the current invention will now be described by reference to the following numbered clauses.

1. A one-pot process for obtaining a metal organic framework (MOF) from a polymeric material, the process comprising the steps of:

- 10 (i) subjecting an aqueous mixture comprising a polymeric material capable of being hydrolysed to provide 2,5-furandicarboxylic acid to hydrolysis conditions; and
(ii) adding a metal salt that comprises a metal capable of generating a MOF with 2,5-furandicarboxylic acid to the aqueous mixture to provide a reaction mixture and heating the
15 reaction mixture at an elevated temperature for a period of time to provide a MOF.

2. The process according to clause 1, wherein the hydrolysis in step (i) and the MOF generation in step (ii) occur simultaneously or sequentially in a reaction vessel.

20 3. The process according to clause 1 or clause 2, wherein the polymeric material comprises a polymer having the repeating unit shown in Formula I below



wherein R is a C₂₋₄ alkylene.

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4. The process according to clause 3, wherein the polymeric material comprises one or more of a group consisting of polyethylene furanoate (PEF), polypropylene furanoate (PPF) and polybutylene furanoate (PBF), optionally wherein the polymeric material comprises polyethylene furanoate (PEF).

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5. The process according to any one of the preceding clauses, wherein the hydrolysis conditions refer to an acidic and/or alkaline environment.

6. The process according to clause 5, wherein the hydrolysis conditions refer to a pH of from about 2 to about 8, such as from about 2.2 to about 7.5, such as from about 4 to about 7, such as about 2.2, such as about 4, such as about 7.

- 5 7. The process according to clause 5 or clause 6, wherein:
- (a) when the hydrolysis is conducted in an acidic environment, then a carboxylic acid is used, optionally wherein the carboxylic acid is formic acid and/or acetic acid; and
 - (b) when the hydrolysis is conducted in an alkaline environment, then sodium hydroxide and/or potassium hydroxide is used.

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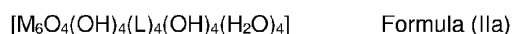
8. The process according to any one of the preceding clauses, wherein the period of time is from 30 minutes to 48 hours, such as from 1 hour to 36 hours, such as from about 2 hours to about 24 hours, such as about 2 hours or such as about 24 hours.

- 15 9. The process according to any one of the preceding clauses, wherein the elevated temperature is from 75 to 200 °C, such as from 90 to 180 °C, such as from about 100 °C to about 160 °C, such as about 100 °C, such as about 160 °C.

10. The process according to any one of the preceding clauses, wherein the metal salt comprises one or more of Ce, Zr, Al, Ga and In, optionally wherein the metal salt comprises:
- (i) one or both of Ce and Zr; or
 - (ii) one or more of Al, Ga and In.

- 25 11. The process according to any one of the preceding clauses, wherein the metal is Zr or Al.

12. The process according to any one of the preceding clauses, wherein the MOF has a Formula (IIa):



30 wherein M is one or both of Zr⁴⁺ and Ce⁴⁺; or

or a Formula (IIb):



where M' is selected from one or more of Al³⁺, Ga³⁺ and In³⁺,

where L in Formula (IIa) and Formula (IIb) is 2,5-furandicarboxylate.

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13. The process according to any one of the preceding clauses, wherein the MOF is a MIL-160 MOF or a CAU-28 MOF, optionally wherein the MOF is a MIL-160(AI) MOF or a CAU-28(Zr) MOF.

- 5 14. The process according to any of the preceding clauses, wherein a yield of the MOF is at least about 70%, optionally wherein the MOF yield is at least about 75%, based on the amount of 2,5-furandicarboxylic acid, optionally wherein the amount of 2,5-furandicarboxylic acid is based on a theoretical amount of 2,5-furandicarboxylic acid in the polymeric material.

10 BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic representation of the one-pot process for obtaining a MOF according to an embodiment of the present disclosure.

- 15 FIG. 2 includes a powder X-ray diffraction (PXRD) pattern of the MIL-160 synthesized according to Example 1 of the present disclosure (top), and that obtained from the Crystallographic Information File (CIF) of MIL-160 (bottom).

FIG. 3 is a N₂ adsorption isotherm of the MIL-160 synthesized according to Example 1 of the present disclosure, measured at 77 K.

FIG. 4 is a thermogravimetric analysis (TGA) curve of the MIL-160 synthesized according to Example 1 of the present disclosure (temperature ramp rate: 5°C/min, air flow rate: 40 ml/min).

- 25 FIG. 5 includes powder X-ray diffraction (PXRD) patterns of the CAU-28 synthesized according to Example 2A and 2B of the present disclosure (using formic acid and acetic acid as a modulator respectively), as well as the CAU-28 synthesized by a previously reported method from furan dicarboxylic acid.

30 DESCRIPTION

The present inventors have found an inexpensive, convenient and simple process for obtaining metal-organic frameworks (MOFs) from suitable plastics, such as polyethylene furanoate (PEF). The MOFs generated have comparable properties, such as crystallinity, porosity and thermal stability, to those synthesized from previously reported methods (i.e., from 2,5-furandicarboxylic acid) and are suitable for various applications depending on the MOF. The process is also able to achieve high yield (e.g., about ~76 %) which is higher than

previously reported methods. Furthermore, the process does not involve the use of toxic and expensive organic solvents such as *N,N*-dimethylformamide which are often employed in conventional MOF synthesis methods. The process also uses milder reaction conditions (e.g., temperature of about 100 °C and about 160 °C) when compared to these conventional methods.

Thus, in a first aspect of the invention, there is provided a one-pot process for obtaining a metal organic framework (MOF) from a polymeric material, the process comprising the steps of:

- (i) subjecting an aqueous mixture comprising a polymeric material capable of being hydrolysed to provide 2,5-furandicarboxylic acid to hydrolysis conditions; and
- (ii) adding a metal salt that comprises a metal capable of generating a MOF with 2,5-furandicarboxylic acid to the aqueous mixture to provide a reaction mixture and heating the reaction mixture at an elevated temperature for a period of time to provide a MOF.

In embodiments herein, the word “comprising” may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word “comprising” may also relate to the situation where only the components/features listed are intended to be present (e.g. the word “comprising” may be replaced by the phrases “consists of” or “consists essentially of”). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word “comprising” and synonyms thereof may be replaced by the phrase “consisting of” or the phrase “consists essentially of” or synonyms thereof and *vice versa*.

The phrase, “consists essentially of” and its pseudonyms may be interpreted herein to refer to a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure, such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

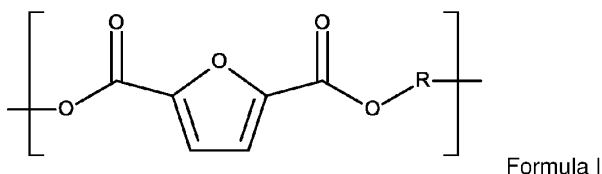
As disclosed herein, the term “one-pot process” refers to one that involves subjecting the reactant(s) to successive chemical reactions in just one reactor without the need for any separation/purification of the reaction intermediates. As demonstrated in the Examples of the present disclosure, the present process for obtaining a MOF is a one-pot process where it is not necessary to purify the reaction intermediates (i.e., 2,5-furandicarboxylic acid) by for example, removing the side products after the hydrolysis reaction (e.g., ethylene glycol from

the hydrolysis of polyethylene furanoate) – the presence of the side products do not affect the process efficiency.

In certain embodiments, the hydrolysis in step (i) and the MOF generation in step (ii) may occur simultaneously or sequentially in a reaction vessel. For example, when the hydrolysis in step (i) and MOF generation in step (ii) occur sequentially, the metal salt may be added after the hydrolysis is completed because the hydrolysis in step (i) occurs under conditions that may not be suitable for the introduction of a chelating metal salt (for example, due to the addition of a strong base to conduct the hydrolysis). In another example, when the hydrolysis in step (i) and MOF generation in step (ii) occur simultaneously, the metal salt may be added while the hydrolysis is still ongoing because the rate of the hydrolysis in step (i) may be slow (for example, due to the addition of a weak acid to conduct the hydrolysis). As demonstrated in the Examples, the MOF synthesized from the present method may achieve a higher crystallinity compared to those synthesized by conventional methods due to the relatively slower crystal growth rates attributed by the slow release of the 2,5-furandicarboxylic acid linker during the hydrolysis of the polymeric material (e.g. when the hydrolysis is conducted in the presence of a weak acid).

As disclosed herein, the term “polymeric material” refers to any suitable material that is capable of producing 2,5-furandicarboxylic acid upon hydrolysis. As the skilled person will appreciate, the polymeric material may contain other components, additives and/or impurities. For example, as discussed in the Examples of the present disclosure, the polymeric material may comprise residual polymerization catalyst which is shown to have negligible impact on the MOF synthesis.

In certain embodiments, the polymeric material may comprise a polymer having the repeating unit shown in Formula I below



wherein R is a C₂₋₄ alkylene.

In further embodiments, wherein the polymeric material may comprise one or more of a group consisting of polyethylene furanoate (PEF), polypropylene furanoate (PPF) and polybutylene

furanoate (PBF). In certain embodiments, the polymeric material may comprise polyethylene furanoate (PEF).

5 In certain embodiments, the hydrolysis conditions may refer to an acidic and/or alkaline environment. In certain embodiments, when the hydrolysis is conducted in an acidic environment, then a carboxylic acid may be used as the agent for hydrolysis. In such embodiments, the carboxylic acid may be, for example, formic acid and/or acetic acid. In other embodiments, when the hydrolysis is conducted in an alkaline environment, then sodium hydroxide and/or potassium hydroxide may be used as the agent for hydrolysis.

10 In certain embodiments, the hydrolysis conditions may refer to a pH of from about 2 to about 8, such as from about 2.2 to about 7.5, such as from about 4 to about 7, such as about 2.2, such as about 4, such as about 7. As the skilled person will appreciate, the pH depends on the concentration and nature of the hydrolysis agent used to hydrolyse the polymeric material.

15 In certain examples, the use of formic acid to hydrolyse the polymeric material may decrease the pH of the aqueous mixture to about pH 2.2 while the use of acetic acid may decrease the pH of the aqueous mixture to about pH 4. In other examples, formic acid may be used to neutralise any excess sodium hydroxide used to hydrolyse the polymeric material, thereby bringing the pH back from more than pH 7 to about pH 7.

20 As will be appreciated, the period of time for the method to be conducted may be determined by the skilled person based on their knowledge of the field (e.g., the nature of the MOF) and whether the reaction has been deemed to be completed or not. In certain embodiments, the period of time may be from 30 minutes to 48 hours, such as from 1 hour to 36 hours, such as

25 from about 2 hours to about 24 hours, such as about 2 hours or such as about 24 hours. In certain examples, the synthesis of MIL-160 may require a period of time of about 24 hours to provide the MOF. In other examples, the synthesis of CAU-28 may require a period of time of about 2 hours to provide the MOF.

30 The method disclosed herein may be conducted at any suitable elevated temperature. In certain embodiments, the elevated temperature may be from 75 to 200 °C, such as from 90 to 180 °C, such as from about 100 °C to about 160 °C, such as about 100 °C, such as about 160 °C. As will be appreciated, the temperature depends on the nature of the MOF. In certain examples, the synthesis of MIL-160 may require a temperature of about 100 °C to provide the

35 MOF. In other examples, the synthesis of CAU-28 may require a temperature of about 160 °C to provide the MOF.

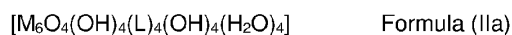
As disclosed herein, the term “metal salt” refers to any suitable salt which contains a metal capable of generating a MOF with 2,5-furandicarboxylic acid and an anion that does not interfere with the MOF synthesis. In certain examples, the metal salt may be aluminium chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) to obtain MIL-160. In other examples, the metal salt may be zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) to obtain CAU-28.

In certain embodiments, the metal salt may comprise one or more of Ce, Zr, Al, Ga and In, optionally wherein the metal salt may comprise:

- (i) one or both of Ce and Zr; or
- (ii) one or more of Al, Ga and In.

In further embodiments, wherein the metal may be Zr or Al.

In certain embodiments, the MOF may have a Formula (IIa):



wherein M is one or both of Zr^{4+} and Ce^{4+} ; or

or a Formula (IIb):



where M' is selected from one or more of Al^{3+} , Ga^{3+} and In^{3+} ,

where L in Formula (IIa) and Formula (IIb) is 2,5-furandicarboxylate. In further embodiments, wherein the MOF may be a MIL-160 MOF or a CAU-28 MOF. In certain exemplary embodiments, the MOF may be a MIL-160(Al) MOF or a CAU-28(Zr) MOF.

In certain embodiments, a yield of the MOF obtained from the process may be at least about 70% based on the amount of 2,5-furandicarboxylic acid. In further embodiments, the MOF yield may be at least about 75% based on the amount of 2,5-furandicarboxylic acid. In certain embodiments, the amount of 2,5-furandicarboxylic acid may be based on a theoretical amount of 2,5-furandicarboxylic acid in the polymeric material. Advantageously, the method disclosed herein achieves a higher MOF yield compared to other current state of the art methods for MOF synthesis.

The following Examples illustrate the invention.

EXAMPLES

Example 1: One pot conversion of PEF to MIL-160

NaOH pellets (2.6 g, 65 mmol) were completely dissolved in 14 mL of water, after which PEF resin pellets (4.0 g, 22 mmol based on repeating $C_6H_6O_5$ formula unit) were added. The mixture was refluxed for 2 hours, during which the solution turned dark purple. When all the PEF pellets were dissolved, the purple colour faded, leaving a light brown solution. The solution was allowed to cool to room temperature. An additional 50 ml of water was added, followed by 950 μ L of formic acid (~ 1.2 g, 26 mmol) to neutralize the excess NaOH and $AlCl_3 \cdot 6H_2O$ (5.2 g, 22 mmol). The solution was stirred at 100 $^{\circ}C$ for another 24 hours, during which a white precipitate was formed. The white solid was collected by filtration, washed with water, and dried in an oven.

Results and Discussion: Yield of MOF was found to be 4.04 g ($\sim 76\%$) based on the MOF formula unit $[Al(OH)(C_6H_2O_5) \cdot 2.5H_2O]$. Although the original report of MIL-160 synthesized from conventional starting materials did not report a yield¹ (Cadiou, A. *et al.*, "Design of Hydrophilic Metal Organic Framework Water Adsorbents for Heat Reallocation." *Adv. Mater.* **2015**, 27, 4775-4780), subsequent publications reported lower yields of about 55 %² (Tannert, N. *et al.*, "Robust synthesis routes and porosity of the Al-based metal-organic frameworks Al-fumarate, CAU-10-H and MIL-160" *Dalton Trans.* **2019**, 48, 2967-2976). The method according to the current disclosure thus has a higher yield of MOF. Furthermore, the properties of the MOF are still retained when compared to those synthesized by conventional methods as shown by the characterization data in FIG. 2 (powder X-ray diffraction), FIG. 3 (N_2 adsorption isotherm) and FIG. 4 (thermogravimetric analysis, TGA).

The powder X-ray diffraction (PXRD) pattern of the synthesized MOF was compared with the simulated PXRD pattern obtained from the Crystallographic Information File (CIF) of MIL-160.¹ The peaks in the experimental PXRD pattern perfectly align with the calculated pattern, confirming the structural identity of the synthesized MOF. Furthermore, the relative intensities of the peaks, which depends on the unit cell contents, match well with those of the simulated pattern. This not only corroborates the successful formation of the targeted MOF but also points towards its phase purity. The absence of any additional peaks not accounted for in the simulated pattern further verifies that the synthesized MOF is free from other crystalline impurities. Notably, the presence of ethylene glycol in solution, which is a side product from the depolymerization of PEF, had no noticeable effect on the crystallinity of the MIL-160. In addition, any residual polymerization catalyst in the PEF resin also had negligible impact on the MOF synthesis.

The N_2 adsorption isotherm measured at 77 K of the synthesized MIL-160 shows a characteristic Type I profile, indicative of microporous materials like MOFs, which aligns well

with the literature-reported isotherm. The steep rise in gas adsorption at low relative pressure (P/P_0) and the plateau at higher relative pressure show that the saturation limit for monolayer adsorption has been reached, which is characteristic of microporous MOFs. The rise close to $P/P_0 = 1$ is due to the condensation of N_2 in the interparticle spaces. Moreover, the specific surface area, calculated using the BET equation ($917.8 \text{ m}^2/\text{g}$), is in close agreement with the literature value ($1070 \text{ m}^2/\text{g}$).¹ This further confirms the successful synthesis of MIL-160 from plastic starting material and its comparable porosity to the literature-reported MIL-160. The high surface area and the associated high gas uptake capacity validate the efficiency of the MOF in gas storage and separation applications, as suggested by its literature counterpart.

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The TGA graph of MIL-160 shows a decrease in weight from room temperature to 100°C to about 80 wt%, which is due to the expulsion of water from the pores of the MOF. The material is then thermally stable until about 300°C , whereby it decomposed via oxidation/degradation of the organic linker, leaving behind an inorganic residue consisting of a mix of aluminium oxides and hydroxides. The thermal stability matches that of the MIL-160 synthesized using conventional starting materials.²

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Example 2A: One pot conversion of PEF to CAU-28 (using formic acid as a modulator)

Formic acid (5 mL) was added to a 30 mL microwave glass vessel, followed by 2 mL of water and 728 mg of PEF (4 mmol based on $\text{C}_8\text{H}_6\text{O}_5$ formula unit) resin pellets. The PEF resin began to swell under these conditions. The mixture was heated by microwave at 160°C for 20 minutes, during which time the PEF completely dissolved to give a homogenous brown solution. Upon cooling, the PEF precipitated as a white fine powder. This step was done to increase the surface area of the PEF, thereby increasing the rate of hydrolysis. Next, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (1990 mg) was added, followed by another 10 mL of water. The mixture was then heated by microwave at 160°C for 2 hours while stirring at 600 rpm. After cooling to room temperature, white powder formed was collected by centrifugation (8000 rpm, 10 minutes). The supernatant was discarded, and the white powder was redispersed in 20 mL of ethanol, and recentrifuged. This process was repeated three times to remove excess formic acid and unreacted starting material. Finally, the white powder was allowed to dry in air overnight. Yield of the MOF was found to be 2.01 g.

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Example 2B: One pot conversion of PEF to CAU-28 (using acetic acid as a modulator)

Acetic acid (7 mL) was added to a 30 mL microwave glass vessel, followed by 7 mL of water and 728 mg of PEF (4 mmol based on $\text{C}_8\text{H}_6\text{O}_5$ formula unit) resin pellets. The PEF resin did not swell in acetic acid, unlike in formic acid, and hence no pretreatment was performed. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (1990 mg, 6 mmol) was added and allowed to dissolve fully in the water-acetic

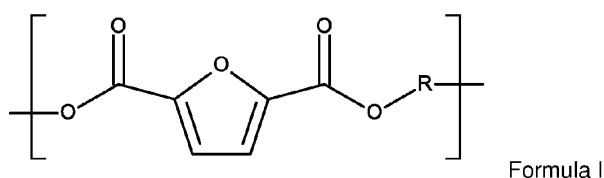
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acid mixture. The mixture was then heated by microwave at 160 °C for 2 hours with stirring at 600 rpm. After cooling to room temperature, white powder formed was collected by centrifugation (8000 rpm, 10 minutes). The supernatant was discarded, and the white powder was redispersed in 20 mL of ethanol, and recentrifuged. This process was repeated three
5 times to remove excess acetic acid and unreacted starting material. Finally, the white powder was allowed to dry in air overnight. Yield of the MOF was found to be 2.0 g.

Results and Discussion: Powder X-ray diffraction characterization of the CAU-28 synthesized from PEF in the one-pot synthesis using either acetic acid or formic acid as a modulator, as
10 well as the CAU-28 synthesized by the previously reported method from furan dicarboxylic acid are shown in FIG. 5.³ (Dreischarf, A. C. *et al.*, "Green Synthesis of Zr-CAU-28: Structure and Properties of the First Zr-MOF Based on 2,5-Furandicarboxylic Acid", *Inorg. Chem.* **2017**,
56, 4, 2270–2277). The unit cell matches that of the reported CAU-28. The CAU-28 synthesized according to the method of the present disclosure show a higher crystallinity
15 (sharper peaks) than the CAU-28 synthesized by the literature method, likely due to the slower crystal growth rates due to the slow release of the linker during polymer hydrolysis. Gas uptake and thermal characterization were not preformed, as CAU-28 is known to be unstable towards heat and evacuation.³

CLAIMS

1. A one-pot process for obtaining a metal organic framework (MOF) from a polymeric material, the process comprising the steps of:
 - (i) subjecting an aqueous mixture comprising a polymeric material capable of being hydrolysed to provide 2,5-furandicarboxylic acid to hydrolysis conditions; and
 - (ii) adding a metal salt that comprises a metal capable of generating a MOF with 2,5-furandicarboxylic acid to the aqueous mixture to provide a reaction mixture and heating the reaction mixture at an elevated temperature for a period of time to provide a MOF.
2. The process according to Claim 1, wherein the hydrolysis in step (i) and the MOF generation in step (ii) occur simultaneously or sequentially in a reaction vessel.
3. The process according to Claim 1 or Claim 2, wherein the polymeric material comprises a polymer having the repeating unit shown in Formula I below



wherein R is a C₂₋₄ alkylene.

4. The process according to Claim 3, wherein the polymeric material comprises one or more of a group consisting of polyethylene furanoate (PEF), polypropylene furanoate (PPF) and polybutylene furanoate (PBF), optionally wherein the polymeric material comprises polyethylene furanoate (PEF).
5. The process according to any one of the preceding claims, wherein the hydrolysis conditions refer to an acidic and/or alkaline environment.
6. The process according to Claim 5, wherein the hydrolysis conditions refer to a pH of from about 2 to about 8, such as from about 2.2 to about 7.5, such as from about 4 to about 7, such as about 2.2, such as about 4, such as about 7.
7. The process according to Claim 5 or Claim 6, wherein:
 - (a) when the hydrolysis is conducted in an acidic environment, then a carboxylic acid is used, optionally wherein the carboxylic acid is formic acid and/or acetic acid; and

(b) when the hydrolysis is conducted in an alkaline environment, then sodium hydroxide and/or potassium hydroxide is used.

8. The process according to any one of the preceding claims, wherein the period of time is from 30 minutes to 48 hours, such as from 1 hour to 36 hours, such as from about 2 hours to about 24 hours, such as about 2 hours or such as about 24 hours.

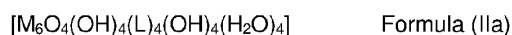
9. The process according to any one of the preceding claims, wherein the elevated temperature is from 75 to 200 °C, such as from 90 to 180 °C, such as from about 100 °C to about 160 °C, such as about 100 °C, such as about 160 °C.

10. The process according to any one of the preceding claims, wherein the metal salt comprises one or more of Ce, Zr, Al, Ga and In, optionally wherein the metal salt comprises:

- (i) one or both of Ce and Zr; or
- (ii) one or more of Al, Ga and In.

11. The process according to any one of the preceding claims, wherein the metal is Zr or Al.

12. The process according to any one of the preceding claims, wherein the MOF has a Formula (IIa):



wherein M is one or both of Zr^{4+} and Ce^{4+} ; or

or a Formula (IIb):



where M' is selected from one or more of Al^{3+} , Ga^{3+} and In^{3+} ,

where L in Formula (IIa) and Formula (IIb) is 2,5-furandicarboxylate.

13. The process according to any one of the preceding claims, wherein the MOF is a MIL-160 MOF or a CAU-28 MOF, optionally wherein the MOF is a MIL-160(Al) MOF or a CAU-28(Zr) MOF.

14. The process according to any of the preceding claims, wherein a yield of the MOF is at least about 70%, optionally wherein the MOF yield is at least about 75%, based on the amount of 2,5-furandicarboxylic acid, optionally wherein the amount of 2,5-furandicarboxylic acid is based on a theoretical amount of 2,5-furandicarboxylic acid in the polymeric material.