Upcycling a Plastic Cup: One-Pot Synthesis of Lactate Containing Metal Organic Frameworks from Polylactic Acid

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Abstract: Waste PLA can be upcycled to metal organic frameworks of potential high value in a one-pot synthesis scheme, where PLA depolymerisation occurs in-situ. Three lactate based frameworks were successfully synthesised and characterised from PLA as a feed source, including homochiral framework ZnBLD. The chiral separation ability of ZnBLD was maintained.

Keywords: metal-organic framework; upcycling; waste polymer; chiral MOF; enantioselective

Metal Organic Frameworks (MOFs) are a series of porous coordination polymers consisting of metal nodes coordinated to organic ‘linker’ ligands.[1] MOFs have several promising applications from sensing,[2] to separations,[3,4] including chiral separations.[5,6] A significant number of reported frameworks are synthesised from terephthalic acid as an organic linker.[7,8] A search of the Cambridge Structural Database (Conquest) for all structures containing 1,4-benzenedicarboxylate revealed 2,028 reported structures, of which a very high proportion are MOFs.[9,10] Polyethylene terephthalate is a polyester consisting of terephthalic acid and ethylene glycol in a 1:1 molar ratio. Research efforts have focused on uses for excess PET in the environment, and alternative recycling methods, for example, utilisation of PET in asphalt pavement,[11] and biological based recycling.[12]

This is likely to have been influenced by growing concerns about the environmental impact of plastic where it is estimated that as of 2015, 8300 million metric tons of virgin plastic was produced, 76% of which is now waste.[13] Recently, PET has been used as a terephthalic acid source for the synthesis of several MOFs. PET was successfully depolymerised under microwave irradiation before being used as a linker source in hydrothermal synthesis of two terephthalate based MOFs including MOF-5.[14] Subsequently, reports highlighted the synthesis of several MIL based MOFs directly from PET as terephthalate source (without a prior depolymerisation step), utilising either microwave,[15] or conventional heating techniques.[16,17] This process of upcycling waste polymer receptacles such as PET bottles and cups can potentially be applied to other waste polymer materials for the synthesis of MOFs. ZnBLD [Zn2(bdc)(L-lactate)(dmf)](DMF) (bdc=1,4-benzenedicarboxylate), (dmf=N,N-dimethylformamide) is a homochiral metal organic framework synthesised from zinc nitrate hexahydrate, terephthalic and L-lactic acids in a 2:1:1 molar ratio respectively.[5] Potentially, ZnBLD could be synthesised from PET as terephthalic acid source and polylactic acid (PLA) as the lactic acid source. However, hydrolysis of PET requires higher temperatures (above 200 °C) than the synthesis temperature of ZnBLD (110 °C) and is typically performed in aqueous media.[18] MOFs 1201 [Ca4(3-lactate)2(acetate)6(C2H5OH)(H2O)] and 1203 [Ca6(3-lactate)3(acetate)9(H2O)] are synthesised from calcium acetate and L-lactic acid in a 1:2 and 1:1 molar ratio respectively.[19] In addition to ZnBLD, these frameworks can potentially be synthesised from PLA as the lactic acid source. Schemes S1 and S2 (Supplementary Information) depict the depolymerisation schemes for PET and PLA to
the corresponding monomers. Like PET, PLA is a polyester formed from the polymerisation of lactic acid. The polymer is commonly found in biodegradable single use plastic items such as plastic cups. Although PLA is often considered as a recyclable polymer, PLA waste is typically treated by methods such as composting, hydrolysis and natural decomposition.\[20\]

Pure lactic acid is stable as a solid below its melting point of 16.8 °C,[21] but under standard conditions will melt and absorb water. Consequently, the price of pure L-lactic acid (required for the synthesis of ZnBLD and MOFs 1201 and 1203) is considerably more expensive than the more stable but lower purity aqueous solution.\[1\]

PLA-MOF composites have been previously synthesised; nano sized ZIF-8 particles were dispersed in a chloroform solution of PLA which was then cast to a thin film for disposable electronics applications.[22] To the best of our knowledge, PLA has not been used as lactic acid ligand source for MOF preparation.

In the polymerisation process of both PLA and PET, one water molecule is removed in each ester linkage formed (1 mole of water per mole of lactic acid/1 mole of water per 1 mole of terephthalic acid). Therefore, the minimum molar quantity of water must be present in the 1-pot polymer based MOF syntheses procedures in order to successfully depolymerise the polymers. Both frameworks have a molar excess of water from the metal salts (calcium acetate monohydrate and zinc nitrate hexahydrate). However, ZnBLD is synthesised from DMF with no requirement for this to be anhydrous. As DMF is hygroscopic, having DMF seasoned by atmospheric water vapour can significantly increase the water content. Contrastingly, MOFs 1201 and 1203 require anhydrous ethanol and methanol respectively. Therefore, it is expected that PLA will show considerably different depolymerisation behaviours in each solvent.

We attempted the synthesis of ZnBLD, MOF-1201 and MOF-1203 by replacing L-lactic acid with the equivalent molar ratio of PLA. Table S1 (Supplementary Information) shows the composition of the frameworks synthesised based on the adjusted molar ratios for the PLA synthesised MOFs. The suffix dPLA is used to describe MOFs synthesised from waste PLA (dPLA=depolymerised polylactic acid). Additional unsuccessful attempts were made to synthesise ZnBLD from waste PET, this is outlined in the Supplementary Information.

The dPLA powder X-ray diffraction (PXRD) traces were recorded and compared with the predicted and experimental patterns using pure L-lactic acid as feed source, these results are displayed

\[1\] Prices of lactic acids on the UK Sigma Aldrich website on the 21/02/2019: 1 L 80 % aqueous solution L-lactic acid= £38.50 (GBP), 10 g 98% L-lactic acid= £121 (GBP)
in Figure 1. The phases of ZnBLD and MOFs 1201 and 1203 were obtained. There were slight variations in the PXRD traces of ZnBLD and ZnBLD-dPLA. The relative intensity of the Zn(bdc)-xH$_2$O (8.6° 2θ) phase (caused by partial hydrolysis of the framework), had a relatively higher intensity in the ZnBLD-dPLA crystals. We suspected that this was caused by a higher concentration of this phase in the ZnBLD-dPLA crystals than that of ZnBLD, which may be a consequence of using PLA as feed source instead of L-lactic acid.

In order to ensure consistency with our results, the same batch of as-synthesised crystals were used for all characterisation and separation experiments. The PXRD traces of MOFs 1201-dPLA and 1203-dPLA were less crystalline than the pure lactic acid synthesised counterparts. Additionally, the product was obtained as a mixture with a gel like by-product, which is commonly prepared from calcium acetate and alcohol. The crystal structure of ZnBLD-dPLA is reported in the Supplementary Information, this structure is isostructural with ZnBLD (previously reported) with the same unit cell and space group (P2_12_2_1).[5]

As-synthesised MOF crystals of ZnBLD, MOFs 1201 and 1203 and their dPLA counterparts were digested in DMSO-d$_6$/DCl before nuclear magnetic resonance (NMR) spectra were recorded to determine the organic composition of the frameworks. Comparing the spectra of ZnBLD and ZnBLD-dPLA, (Figure 2) there was a slight difference in the ratio of terephthalic acid:lactic acid (1:0.89 and 0.73 respectively). We can therefore conclude that there is a higher concentration of Zn(bdc)-xH$_2$O in ZnBLD-dPLA as observed in the PXRD traces. As-synthesised MOFs 1201 and 1203 produced consistent organic compositions with the expected formulas for these MOFs but the dPLA synthesised counterparts contained higher concentrations of acetate and solvent (Figures S1 and S2, Supplementary Information). This is caused by the formation of the amorphous gel like phase.

The chiral separation ability of ZnBLD-(dPLA) was compared with ZnBLD for four racemates (1-phenylethanol, 2-butanol, limonene and 2-methyl-2,4-pentanediol) using an adsorption, desorption method. Whereby, each framework was soaked in neat solutions of the racemates, filtered and soaked in dichloromethane to desorb the adsorbed guest species. Subsequent analysis of the supernatant by chiral gas chromatography revealed the enantiomeric excess of the separation process, and using Table S3 (Supplementary Information), the preferentially adsorbed enantiomers can be determined.

Figure 3 shows that the separation ability of the dPLA synthesised frameworks were not negatively impacted by the modified synthesis method for the racemates tested. Interestingly,
there was a significant increase in the enantiomeric excess for the limonene separation when using the ZnBLD-dPLA framework. The ZnBLD 1-phenylethanol and 2-butanol enantiomeric excess values are previously reported.[23] Further investigation is required to better understand the selectivity increase effecting limonene. We hypothesise that this is caused by the reduction in crystal size of ZnBLD-dPLA (see images S3 and S4, Supplementary Information). The enantiomeric excess for a mandelate based homochiral MOF has been shown to increase with time from 1-7 days. However, the influence of the crystal size was not taken into consideration in this study,[24] and to the best of our knowledge, has not been investigated in other studies, our hypothesis is based on the assumption that smaller crystals will reach maximum separation capacity faster than larger ones.

Additionally the loading of the four adsorbed racemates was determined by $^1$H NMR spectroscopy in the ZnBLD and ZnBLD-dPLA frameworks. In this process, after adsorption of each racemate, the MOF crystals were filtered and subsequently dissolved in DMSO-d6/DCl before NMR spectra were recorded. Characteristic proton resonances of the framework terephthalic acid and selected peaks from each racemate were integrated in order to determine the loading (where the loading of racemates was compared with 1 molecule of the framework terephthalic acid), further details are reported in the Supplementary Information. Figure 4 displays the loading results from the adsorbed chiral guest molecules. There were slight variations in guest molecule loading when comparing the two frameworks, but overall, neither framework consistently outperformed the other.

**Conclusions**

To summarise, we have shown for the first time that polylactic acid can be utilised as a feed source for the synthesis of lactate containing MOFs such as ZnBLD and MOFs 1201 and 1203. By using this method, we were able to upcycle post-consumer use PLA products into potentially high value materials. We demonstrate that it is possible to bypass the requirement to purchase expensive high purity lactic acid and instead use waste plastic drinking cups. The ZnBLD homochiral framework upholds the equivalent or enhanced chiral separation properties as its counterpart synthesised from pure chemicals without an overall reduction in loading. This can considerably reduce the cost of manufacturing of these products. We expect that by altering the synthesis of MOFs 1201 and 1203, to increase the PLA depolymerisation efficiency, these MOFs can be synthesised effectively without obtaining the amorphous gel.

**Acknowledgements**

Benjaim Slater acknowledges CSIRO and Imperial College London for financial support, and thanks Professor Jason Hallett for discussions on PLA waste. The authors acknowledge Dr Charles Romain for providing PLA cups.

**Conflicts of interest**

There are no conflicts to declare.
Data Repository

Raw XRD spectra and other supporting data are available from the open data repository: https://doi.org/10.5281/zenodo.2638093

References


Supplementary Information

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Experimental Section

Materials and Methods

All materials and solvents were used without further purification and obtained from commercial suppliers unless otherwise stated. All experiments were conducted at room temperature.

ZnBLD Synthesis

ZnBLD was synthesised following an adaptation of the previously reported procedure.\textsuperscript{1} Zinc nitrate hexahydrate (8mmol), terephthalic acid (4mmol) and \(\ell\)-lactic acid (4mmol) were dissolved in 80ml of dimethylformamide and heated in a 200ml sealed reaction vessel at 110°C for 2 days. Needle crystals were obtained which were vacuum filtered and washed with fresh DMF.

ZnBLD-EG Synthesis

ZnBLD-EG was synthesised based on the ZnBLD procedure with the addition of 4mmol of ethylene glycol in the synthesis. Needle crystals were obtained which were vacuum filtered and washed with fresh DMF.

ZnBLD-dPLA Synthesis

ZnBLD-dPLA was synthesised based on the above ZnBLD procedure except \(\ell\)-lactic acid was replaced for the molar equivalent of PLA. PLA was obtained from plastic drinking cups (Natureworks\textsuperscript{®} 500ml single use cups, Image S 1), the cups were cut into small (mm sized flakes) with a pair of scissors (Image S 2). Needle crystals were obtained which were vacuum filtered and washed with fresh DMF.

ZnBLD-dPET synthesis

ZnBLD-dPET synthesis was attempted based on the above ZnBLD procedure. Terephthalic acid was substituted for the equivalent molar quantity of PET. PET was obtained from a waste Coca-Cola\textsuperscript{®} 2L bottle. The bottle was cut into small (mm sized flakes) with a pair of scissors. No product was obtained and undigested PET remained in the vessel.

ZnBLD-dPET-dPLA synthesis

ZnBLD-dPET-dPLA synthesis was attempted based on the above procedures, terephthalic and lactic acids were substituted for the equivalent molar quantity of PET and PLA respectively. PLA was obtained from plastic drinking cups (Natureworks\textsuperscript{®} 500ml single use cups, Image S 1), the cups were cut into small (mm sized flakes) with a pair of scissors. PET was obtained from a waste Coca-Cola\textsuperscript{®} 2L bottle. The bottle was cut into small (mm sized flakes) with a pair of scissors (Image S 2). No product was obtained and undigested PET remained in the vessel.

MOFs 1201 and 1203 Synthesis

MOFs 1201 and 1203 were synthesised based on the previously reported procedure.\textsuperscript{2} Ethanol was dried over magnesium ethoxide and distilled under argon atmosphere to obtain anhydrous ethanol.

MOF1201-dPLa and MOF1203-dPLA Synthesis

The procedure previously reported,\textsuperscript{2} was adapted to replace the molar ratio of \(\ell\)-lactic acid with PLA. PLA was obtained from plastic drinking cups (Natureworks\textsuperscript{®} 500ml single use cups, Image S 1), the cups were cut into small (mm sized flakes) with a pair of scissors (Image S 2). Ethanol was dried over magnesium ethoxide and distilled under argon atmosphere to obtain anhydrous ethanol.
**Table S 1 Composition of all synthesised MOFs**

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Terephthalic acid source</th>
<th>L- Lactic acid source</th>
<th>Ethylene glycol source</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnBLD</td>
<td>Terephthalic acid</td>
<td>L- Lactic acid</td>
<td>-</td>
</tr>
<tr>
<td>ZnBLD-EG</td>
<td>Terephthalic acid</td>
<td>L- Lactic acid</td>
<td>Ethylene glycol (1mmol)</td>
</tr>
<tr>
<td>ZnBLD-dPET</td>
<td>Waste PET</td>
<td>L- Lactic acid</td>
<td>Waste PET</td>
</tr>
<tr>
<td>ZnBLD-dPLA</td>
<td>Terephthalic acid</td>
<td>Waste PLA</td>
<td>-</td>
</tr>
<tr>
<td>ZnBLD-dPET,dPLA</td>
<td>Waste PET</td>
<td>Waste PLA</td>
<td>Waste PET</td>
</tr>
<tr>
<td>MOF-1201</td>
<td>-</td>
<td>L- Lactic acid</td>
<td>-</td>
</tr>
<tr>
<td>MOF-1201-dPLA</td>
<td>-</td>
<td>Waste PLA</td>
<td>-</td>
</tr>
<tr>
<td>MOF-1201</td>
<td>-</td>
<td>L- Lactic acid</td>
<td>-</td>
</tr>
<tr>
<td>MOF-1203-dPLA</td>
<td>-</td>
<td>Waste PLA</td>
<td>-</td>
</tr>
</tbody>
</table>

**Chiral Adsorption**

Either 100mg or 30mg (chiral separation for gas chromatography and guest loading for NMR respectively) of MOF material was soaked in 1ml/0.3ml of either 1-phenylethanol, 2-butanol, limonene or 2-methyl-2,4-pentanediol for 24 hours. The crystals were filtered under vacuum filtration and washed with 5ml of dichloromethane. Guest molecules were then either desorbed or digested with framework based on the below procedures.

**Chiral Desorption**

Crystals were placed in 8ml of dichloromethane and left for 24 hours to desorb guest molecules. Supernatant was then removed and analysed by chiral gas chromatography.

**Digestion for NMR spectroscopy**

20-30mg of MOF material was dissolved in 0.6ml of DMSO-d₆ and two drops of DCl. ¹H NMR spectra were recorded and processed in Mestrenova. Characteristic peaks were selected and used to determine the relative composition of each sample as a ratio. Table S 2 describes the proton resonances selected for integration and calculation of a material’s composition.

**Table S 2 Assignment of chemical shifts for NMR spectra**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Chemical shift (ppm)</th>
<th>Multiplicity</th>
<th>Integral per molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lactic acid</td>
<td>4.02</td>
<td>Quartet</td>
<td>1</td>
</tr>
<tr>
<td>Terephthalic acid</td>
<td>8.02</td>
<td>Singlet</td>
<td>4</td>
</tr>
<tr>
<td>N,N’-dimethylformamide</td>
<td>7.92</td>
<td>Singlet</td>
<td>1</td>
</tr>
<tr>
<td>1-phenylethanol</td>
<td>4.66</td>
<td>Quartet</td>
<td>1</td>
</tr>
<tr>
<td>2-butanol</td>
<td>3.45</td>
<td>Sextet</td>
<td>1</td>
</tr>
</tbody>
</table>
Characterisation

Gas Chromatography

Gas chromatographs were recorded on a Shimadzu 2010-plus gas chromatograph fitted with an FID detector and autosampler, all analytes were separated on a Supelco Beta-Dex 120 capillary column. The analysis conditions were as follows: 1-phenylethanol; injection 1µl, split ratio of 100:1, injector port isothermal at 200°C, oven temperature isothermal at 120°C for 19 minutes before ramping (post-elution of both enantiomers) at 10°C/min to 170°C for 6 minutes to condition the column for the next run, He carrier gas 30 cm/sec, FID detector at 210°C. 2-butanol; injection 1µl, split ratio of 40:1, injector port isothermal at 200°C, oven temperature isothermal at 30°C for 40 minutes before ramping (post-elution of both enantiomers) at 10°C/min to 170°C for 6 minutes to condition the column for the next run, He carrier gas 15 cm/sec, FID detector at 210°C. Limonene; injection 1µl, split ratio of 15:1, injector port isothermal at 250°C, oven temperature isothermal at 80°C for 26 minutes before ramping (post-elution of both enantiomers) at 10°C/min to 170°C for 6 minutes to condition the column for the next run, He carrier gas 25 cm/sec, FID detector at 250°C. 2-methyl-2,4-pentanediol; injection 1µl, split ratio of 100:1, injector port isothermal at 200°C, oven temperature isothermal at 100°C for 60 minutes before ramping (post-elution of both enantiomers) at 10°C/min to 170°C for 6 minutes to condition the column for the next run, He carrier gas 30 cm/sec, FID detector at 210°C.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>1st eluting peak</th>
<th>2nd eluting peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-phenylethanol</td>
<td>R</td>
<td>S</td>
</tr>
<tr>
<td>2-butanol</td>
<td>R</td>
<td>S</td>
</tr>
<tr>
<td>2-methyl-2,4-pentanediol</td>
<td>S</td>
<td>R</td>
</tr>
<tr>
<td>limonene</td>
<td>S</td>
<td>R</td>
</tr>
</tbody>
</table>

Enantiomeric Excess

Each sample was injected into the gas chromatograph three time and the standard deviation was used to calculate error bars, the value displayed is the mean. The chiral separation was quantified by calculating the enantiomeric excess (ee%) using Equation 1, where R and S correspond to the concentration of the R and S enantiomer (where the S enantiomer is in excess, the order of R and S in the equation is reversed). The retention time of each enantiomer was characterised by injecting enantiopure samples of each isomer.

\[
ee(\%) = \left( \frac{R - S}{R + S} \right) \times 100\%
\]

Powder X-ray diffraction
Samples were ground using a ceramic mortar and pestle before traces were recorded on a PANalytical X-Pert Pro MPD X-ray diffractometer CuKα X-ray source (40 kV, 20 mA) and a reflection-transmission spinner sample stage at ambient conditions.

**Single Crystal X-ray Diffraction**

Diffraction patterns were recorded on an Agilent Xcalibur PX Ultra A diffractometer, see below for further details.

**Nuclear Magnetic Resonance Spectroscopy**

$^1$H NMR spectra were recorded on a Bruker Av400MHz solution state spectrometer, integrals were calculated in Mestrenova software.

**Optical Microscopy**

Optical microscope images were taken on a Leica MC120 HD camera fitted to a Leica M60 stereo microscope.

**Further Results and Discussion**

**Depolymerisation Schemes**

![Scheme 1 Depolymerisation of PET](image)

**Scheme S 1 Depolymerisation of PET**

![Scheme 2 Depolymerisation of PLA](image)

**Scheme S 2 Depolymerisation of PLA**

**Organic Composition of MOFs 1201 and 1203**

MOFs 1201 and 1203 were digested before NMR spectra were recorded. The resulting spectra were integrated and peaks assigned according to Table S 2. The organic composition of each framework (acetic acid, lactic acid and methanol or ethanol) were compared between each framework. The expected composition of each MOF is referenced from the formulae of these MOFs. The as synthesised and DPLA synthesised counterparts were compared with the expected composition. The composition of as synthesised MOF 1201 and MOF-1201-DPLA are presented in Figure S 1. A significantly higher concentration of acetic acid and ethanol is present in MOF-1201-dPLA than expected. This is caused by the formation of the gel phase of calcium acetate in ethanol due to low
solubility of calcium acetate in ethanol. Additionally, a higher concentration of ethanol is present in MOF-1201 than expected as it was not dried under vacuum. Therefore MOF-1201 was digested with solvated ethanol in the pores of the framework.

![Figure S1 Composition of synthesised MOF-1201 compared with the expected composition](image)

Figure S 1 Composition of synthesised MOF-1201 compared with the expected composition

Figure S 2 shows the composition of as synthesised MOF-1203 and MOF-1203-dPLA compared with the expected composition. Like the composition of MOF-1201-dPLA, MOF-1203-dPLA contains a higher composition of methanol and acetic acid than expected due to the formation of the gel phase.
Synthesis and characterisation of ZnBLD-EG

ZnBLD-EG was synthesised to establish whether ethylene glycol was detrimental to the synthesis of ZnBLD. The PXRD trace (Figure S 3) shows that the MOF was obtained in phase purity and we could therefore conclude that this did not hinder the formation of the MOF.
Figure S 3 Powder X-ray diffraction trace of ZnBLD-EG compared with predicted ZnBLD

Formation of gel phase

The products obtained from the synthesis of MOFs 1201-dPLA and 1203-dPLA only contained one crystalline phase as shown by the phase purity when compared with the predicted and non-PLA synthesised versions. We also compared the PXRD traces of the dPLA synthesised frameworks with the predicted pattern of calcium acetate in order to ensure that crystalline calcium acetate was not present in the product (Figure S 4 PXRD traces of MOFs 1201-dPA and 1203-dPLA compared with the predicted pattern of calcium acetate Figure S 4).
Figure S4 PXRD traces of MOFs 1201-dPA and 1203-dPLA compared with the predicted pattern of calcium acetate.
Gas Chromatograms

Figure S5 Chromatogram of limonene desorbed from ZnBLD
Figure S6 Chromatogram of 2-methyl-2,4-pentanediol desorbed from ZnBLD
Figure S7 Chromatogram of 1-phenylethanol desorbed from ZnBLD-dPLA
Figure S8 Chromatogram of 2-butanol desorbed from ZnBLD-dPLA
Figure S 9 Chromatogram of limonene desorbed from ZnBLD-dPLA
Figure S 10 Chromatogram of 2-methyl-2,4-pentanediol desorbed from ZnBLD-dPLA
Nuclear Magnetic Resonance Spectra

Figure S 11 NMR spectra of digested ZnBLD
Figure S 12 NMR spectrum of digested ZnBLD-dPLA
Figure S 13 NMR spectrum of digested ZnBLD-limonene
Figure S 14 NMR spectrum of digested ZnBLD-2-methyl-2,4-pentanediol
Figure S 15 NMR spectrum of digested ZnBLD-dPLA-1-phenylethanol
Figure S16 NMR spectrum of digested ZnBLD-dPLA-2-butanol
Figure S17 NMR spectrum of digested ZnBLD-dPLA-limonene
Figure S 18 NMR spectrum of digested MOF-1201
Figure S 19 NMR spectrum of digested MOF-1201-dPLA
Figure S 20 NMR spectrum of digested MOF-1203
Figure S 21 NMR spectrum of digested MOF-1203-dPLA
Single Crystal X-ray Diffraction

Crystal data for ZnBLD-dPLA: C_{14}H_{15}NO_{2}Zn_{2}·1.5(C_{3}H_{7}NO), M = 565.65, orthorhombic, P2_{1}2_{1}2_{1} (no. 19), a = 10.3034(4), b = 11.7652(9), c = 20.3570(7) Å, V = 2467.7(2) Å^{3}, Z = 4, D_{c} = 1.523 g cm^{-3}, μ(Cu-Kα) = 2.850 mm^{-1}, T = 173 K, colourless blocky needles, Agilent Xcalibur PX Ultra A diffractometer; 4699 independent measured reflections (R_{int} = 0.0369), F^2 refinement, \textit{R}_{1}(obs) = 0.0441, \textit{wR}_{2}(all) = 0.1209, 4140 independent observed absorption-corrected reflections \(|F_{o}| > 4\sigma(|F_{o}|), completeness to \theta_{\text{full}}(67.7°) = 99.3\%\), 245 parameters. The absolute structure of ZnBLD-dPLA was determined by use of the Flack parameter [x^* = +0.08(3)]. CCDC 1908241.

Both the C_{6} ring of the terephthalate group and the O30-based coordinated dimethylformamide molecule in the structure of ZnBLD-dPLA were found to be disordered, and in each case two orientations were identified, of ca. 59:41 and 55:45% occupancy respectively. The geometries of each pair of orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (those of the minor occupancy orientations were refined isotropically).

The included solvent was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON.\textsuperscript{5} This suggested a total of 248 electrons per unit cell, equivalent to 62 electrons per asymmetric unit. Before the use of SQUEEZE the solvent most resembled dimethylformamide (C_{3}H_{7}NO, 40 electrons), and 1.5 dimethylformamide molecules corresponds to 60 electrons, so this was used as the solvent present. As a result, the atom list for the asymmetric unit is low by 1.5(C_{3}H_{7}NO) = C_{4.5}H_{10.5}N_{1.5}O_{1.5} (and that for the unit cell low by C_{18}H_{42}N_{6}O_{6}) compared to what is actually presumed to be present. Figure S 22 depicts the asymmetric unit of ZnBLD-dPLA.
Figure S 22 The crystal structure of ZnBLD-dPLA showing the asymmetric unit and how it links to adjacent atoms (50% probability ellipsoids).
Photographs

Image S 1 Natureworks PLA plastic cups used as PLA source
Image S 2 Example of size and shape of PET and PLA polymer flakes used
Image S3 Optical microscope image of as-synthesised ZnBLD crystals
Image S 4 Optical microscope images of as-synthesised ZnBLD-dPLA crystals
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