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Electronic Supplementary Information (ESI) for the manuscript:

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

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Contents

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.[1] zinc nitrate hexahydrate (8mmol), terephthalic acid (4mmol) and $_{\mathrm{L}}$-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 $_{\mathrm{L}}$-lactic acid was replaced for the molar equivalent of PLA. PLA was obtained from plastic drinking cups (Natureworks® 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® 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® 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® 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.[2] Ethanol was dried over magnesium ethoxide and distilled under argon atmosphere to obtain anhydrous ethanol.

MOF1201-dPLa and MOF-1203-dPLA Synthesis

The procedure previously reported,[2] was adapted to replace the molar ratio of $_{\mathrm{L}}$-lactic acid with PLA. PLA was obtained from plastic drinking cups (Natureworks® 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

Sample code	**Terephthalic acid source**	**L-lactic acid source**	**Ethylene glycol source**
ZnBLD	Terephthalic acid	L-lactic acid	-
ZnBLD-EG	Terephthalic acid	L-lactic acid	Ethylene glycol (1mmol)
ZnBLD-dPET	Waste PET	L-lactic acid	Waste PET
ZnBLD-dPLA	Terephthalic acid	Waste PLA	-
ZnBLD-dPET,dPLA	Waste PET	Waste PLA	Waste PET
MOF-1201	-	L-lactic acid	-
MOF-1201-dPLA	-	Waste PLA	-
MOF-1201	-	L-lactic acid	-
MOF-1203-dPLA	-	Waste PLA	-

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-d_6 and two drops of DCl. ^{1}H 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

Molecule	Chemical shift (ppm)	Multiplicity	Integral per molecule
Lactic acid	4.02	Quartet	1
Terephthalic acid	8.02	Singlet	4
N,N'-dimethylformamide	7.92	Singlet	1
1-phenylethanol	4.66	Quartet	1
2-butanol	3.45	Sextet	1

limonene	4.63	Singlet	1
Acetic acid	1.88	Singlet	3
Ethanol	3.39	Quartet	2
Methanol	3.11	Singlet	3

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 S 3 elution orders of the analytes on a Supelco Beta-Dex 120 column using the above conditions

Analyte	1st eluting peak	2nd eluting peak
1-phenylethanol	*R*	*S*
2-butanol	*R*	*S*
2-methyl-2,4-pentanediol	*S*	*R*
limonene	*S*	*R*

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.

1

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

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

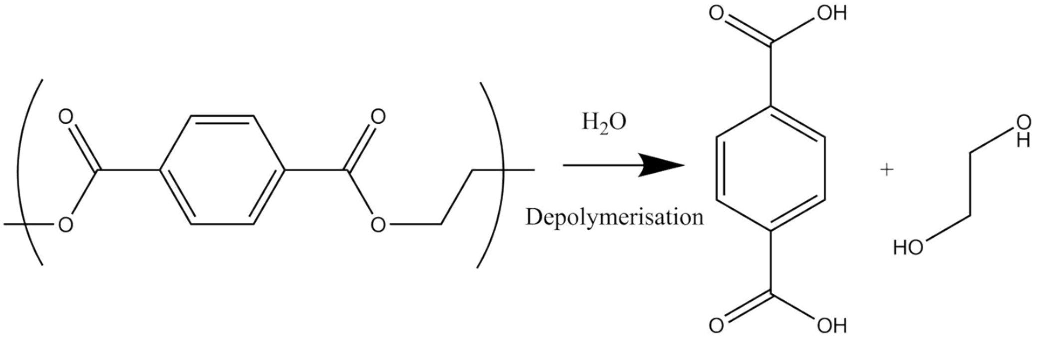
^{1}H NMR spectra were recorded on a Bruker Av400MHz solution state spectrometer, integrals were calculated in Mestrenova software.

Optical Microscopy

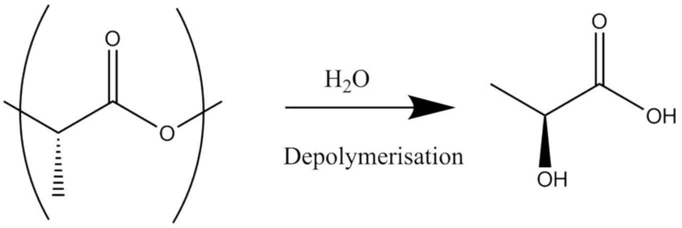
Optical microscope images were taken on a Leica MC120 HD camera fitted to a Leica M60 stereo microscope.

Further Results and Discussion

Depolymerisation Schemes



Scheme S 1 Depolymerisation of PET



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.

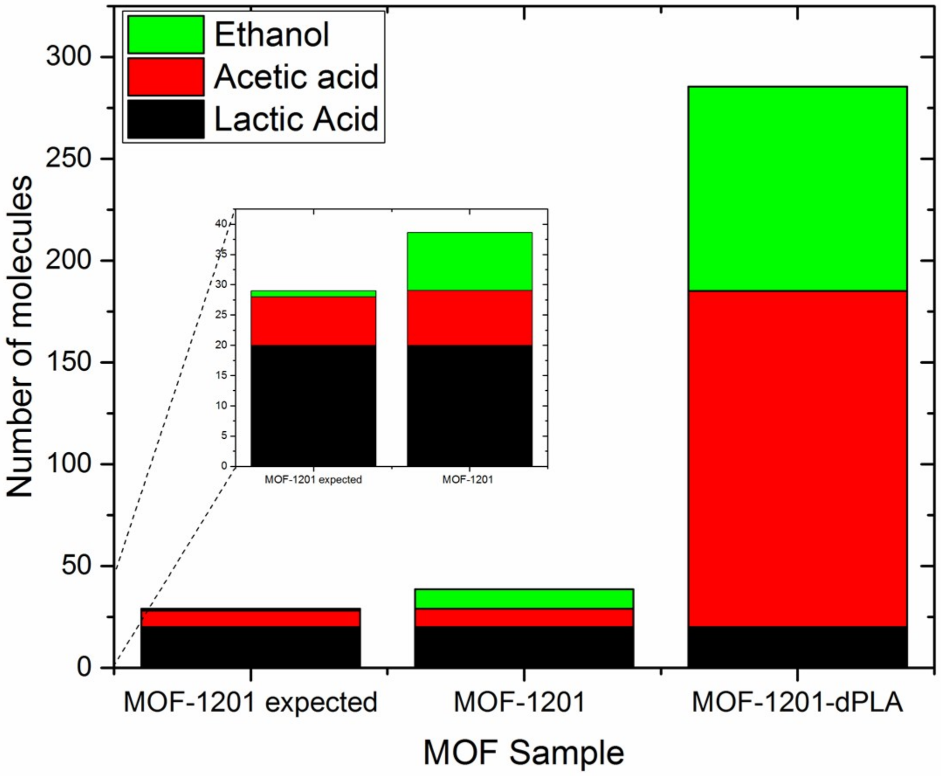


Figure S 1 Composition of synthesised MOF-1201 compared with the expected composition

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.

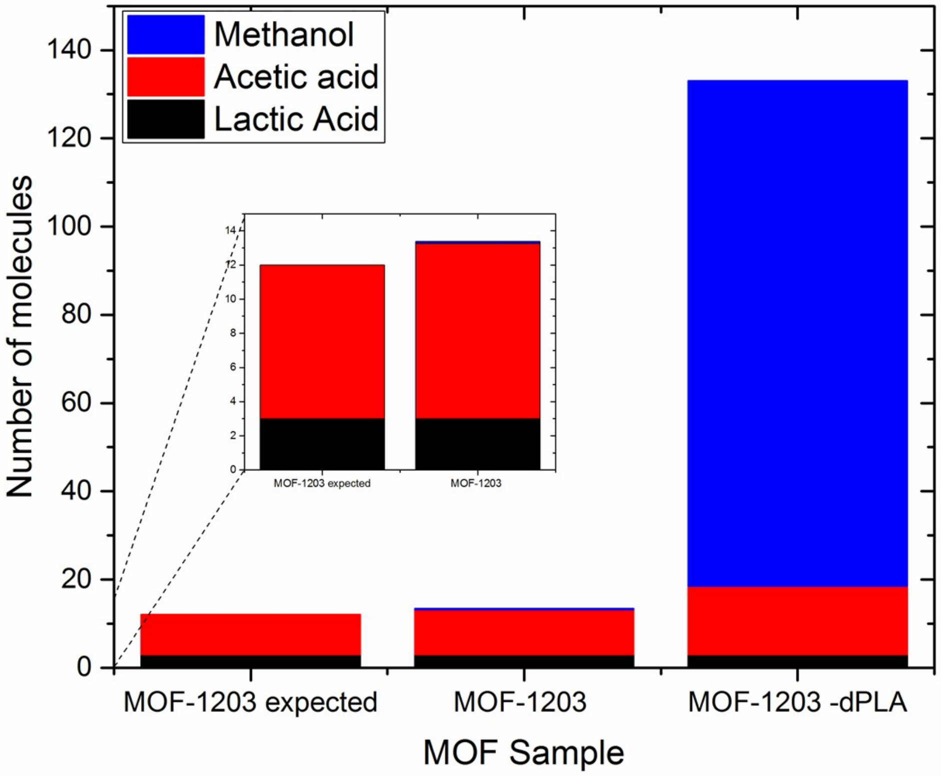


Figure S 2 Composition of synthesised MOF-1203 compared with the expected composition

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.

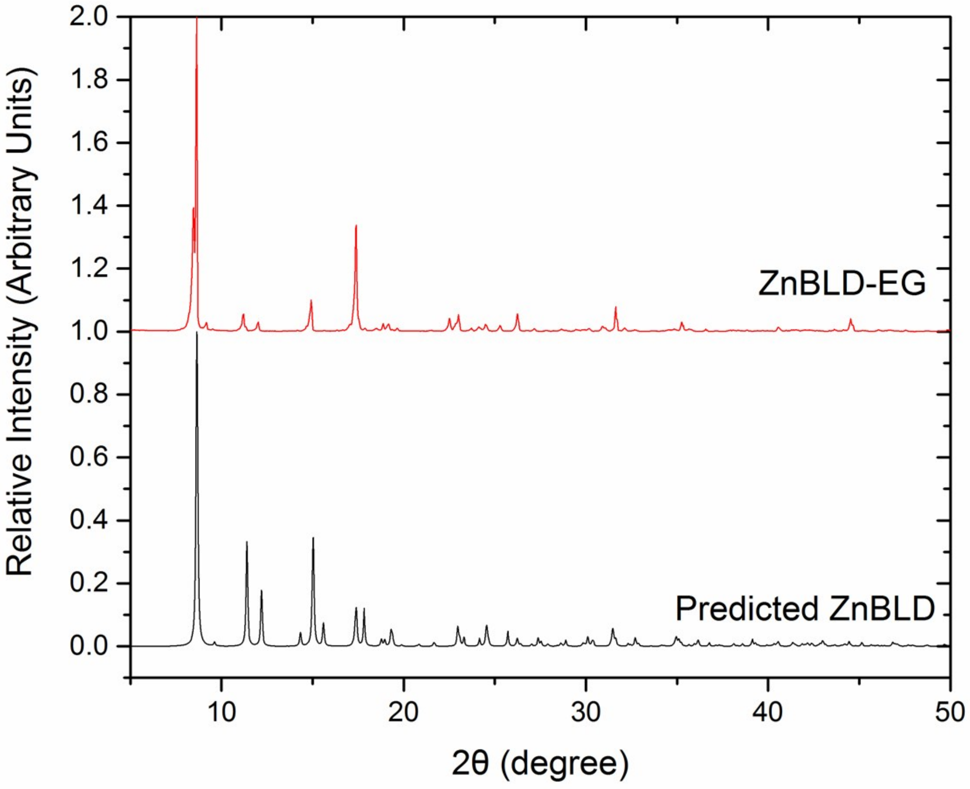


Figure S 3 Powder X-ray diffraction trace of ZnBLD-EG compared with predicted ZnBLD

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).

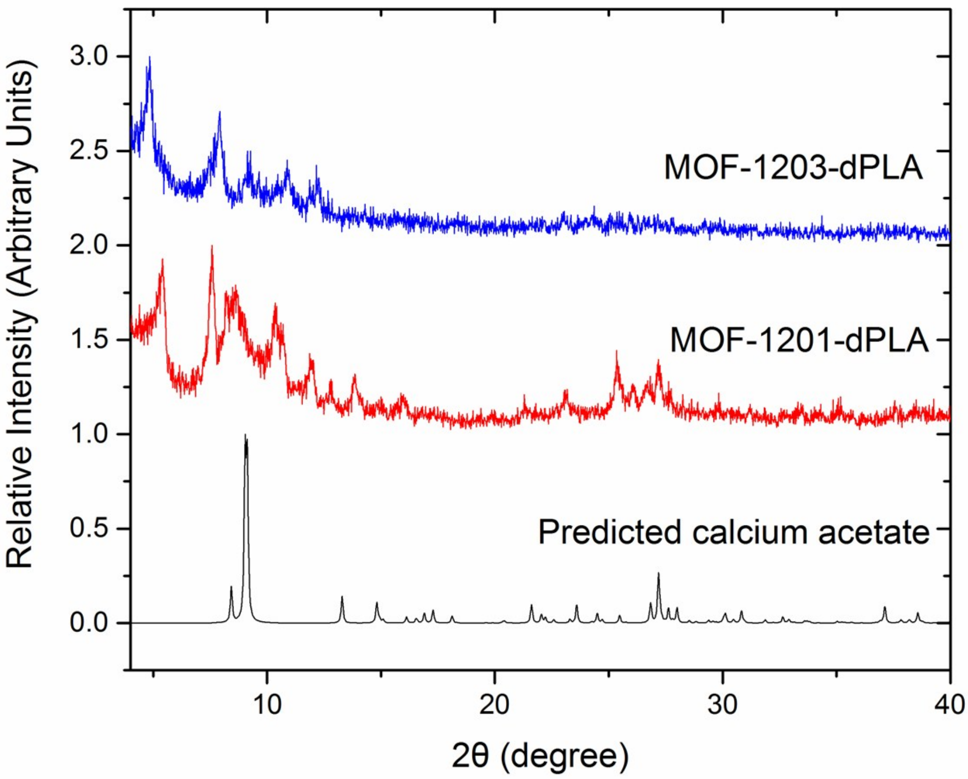


Figure S 4 PXRD traces of MOFs 1201-dPA and 1203-dPLA compared with the predicted pattern of calcium acetate

Loading of Guest Molecules

The loading of guest molecules was determined by ^{1}H NMR spectroscopy and the results are compared between ZnBLD and ZnBLD-dPLA. These results are displayed in Figure S 5.

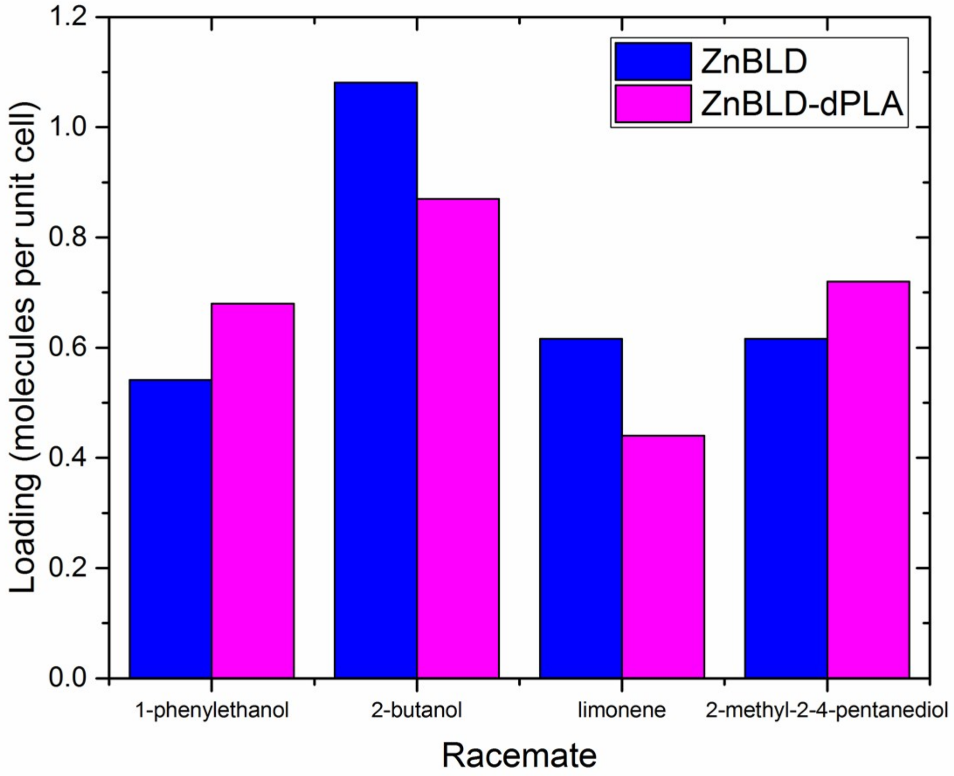


Figure S 5 Loading of guest molecules in ZnBLD and ZnBLD-dPLA determined from NMR spectra of digested crystals

Gas Chromatograms

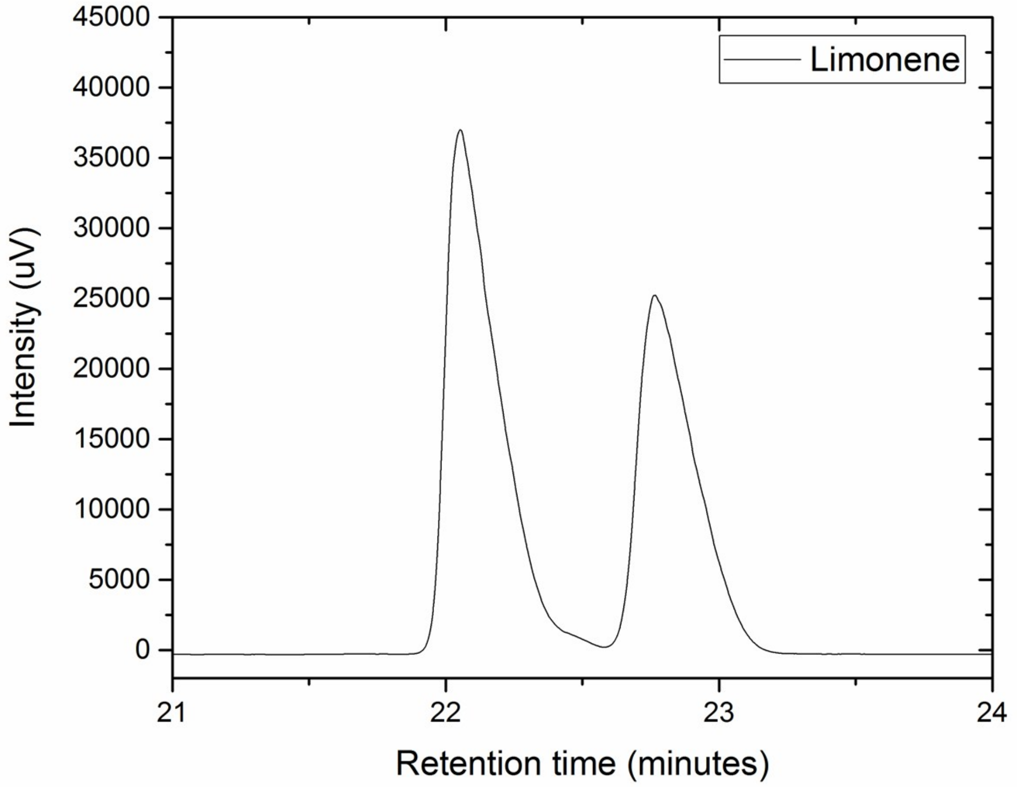


Figure S 6 Chromatogram of limonene desorbed from ZnBLD

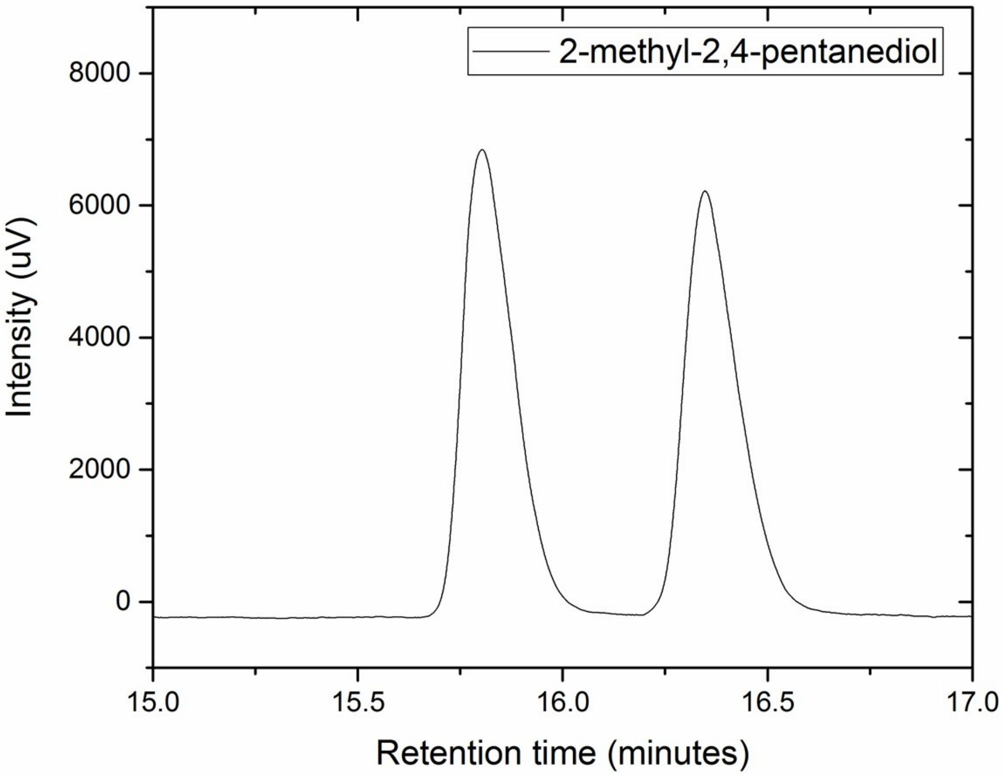


Figure S 7 Chromatogram of 2-methyl-2,4-pentanediol desorbed from ZnBLD

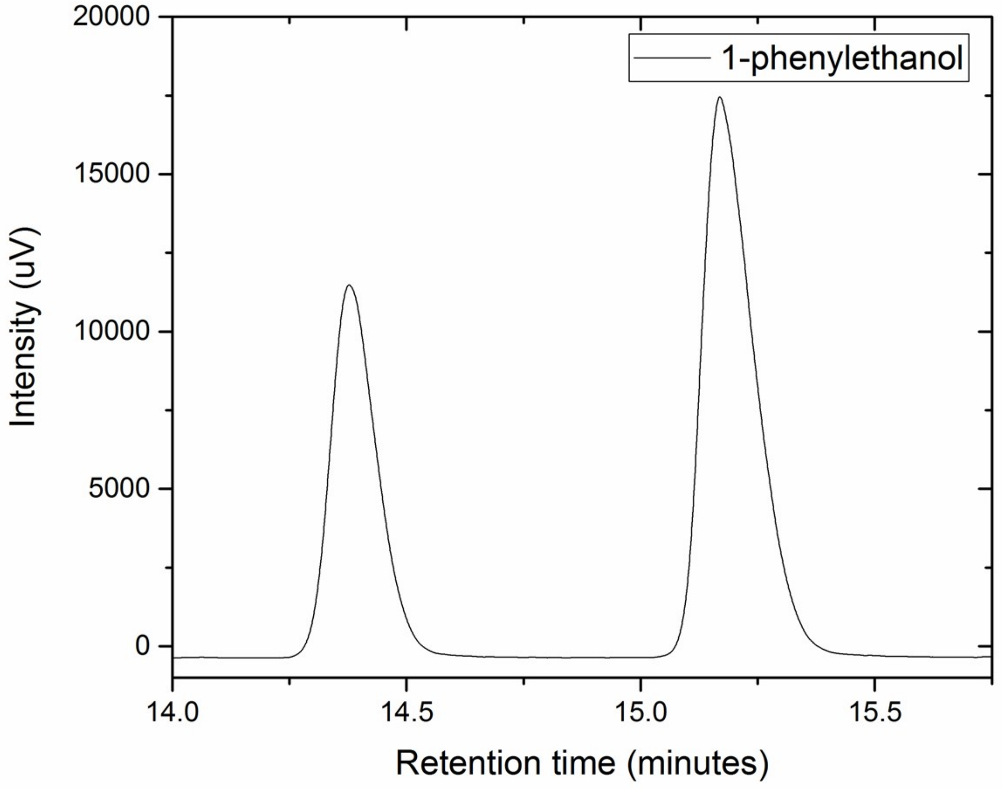


Figure S 8 Chromatogram of 1-phenyletyhanol desorbed from ZnBLD-dPLA

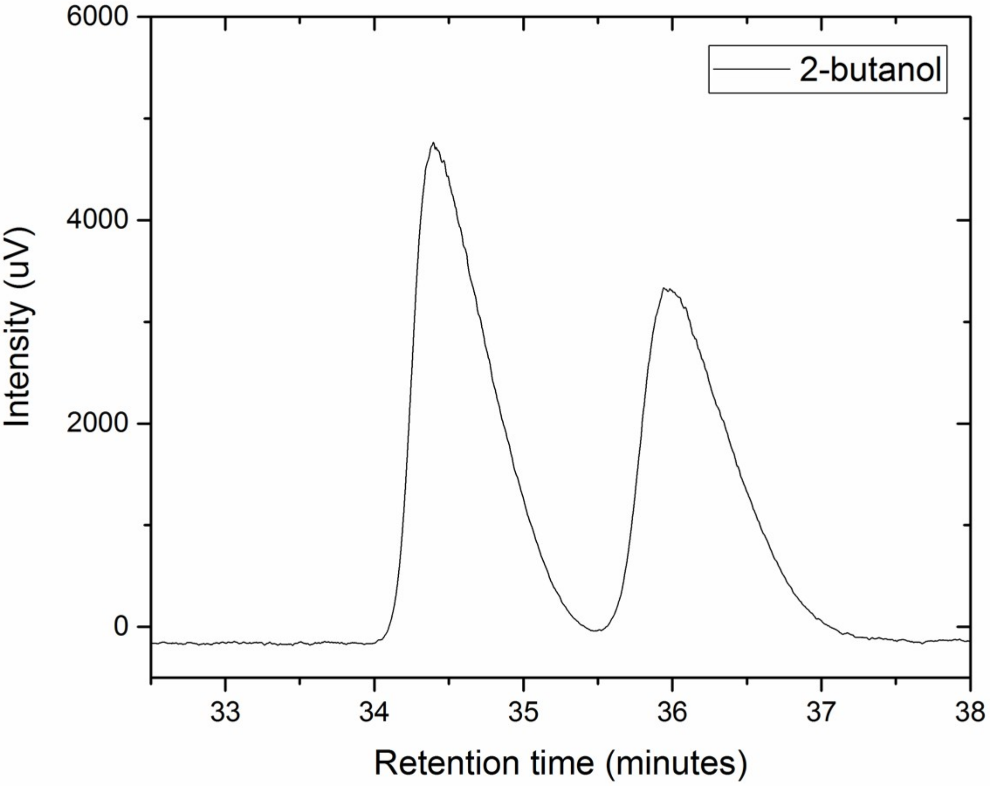


Figure S 9 Chromatogram of 2-butanol desorbed from ZnBLD-dPLA

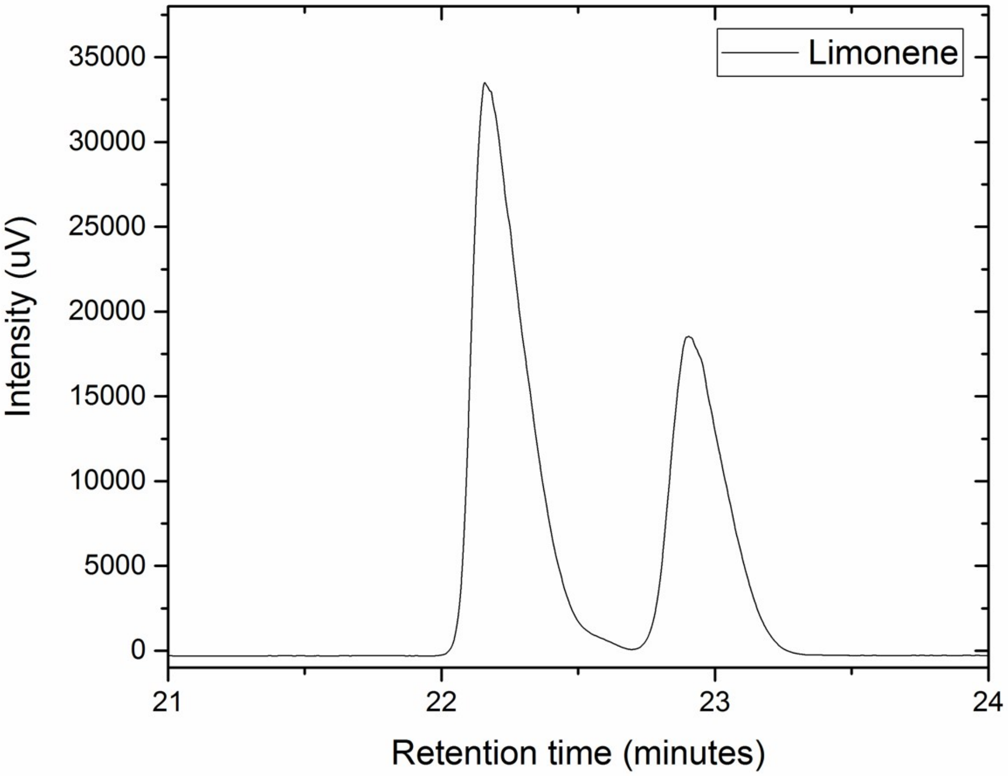


Figure S 10 Chromatogram of limonene desorbed from ZnBLD-dPLA

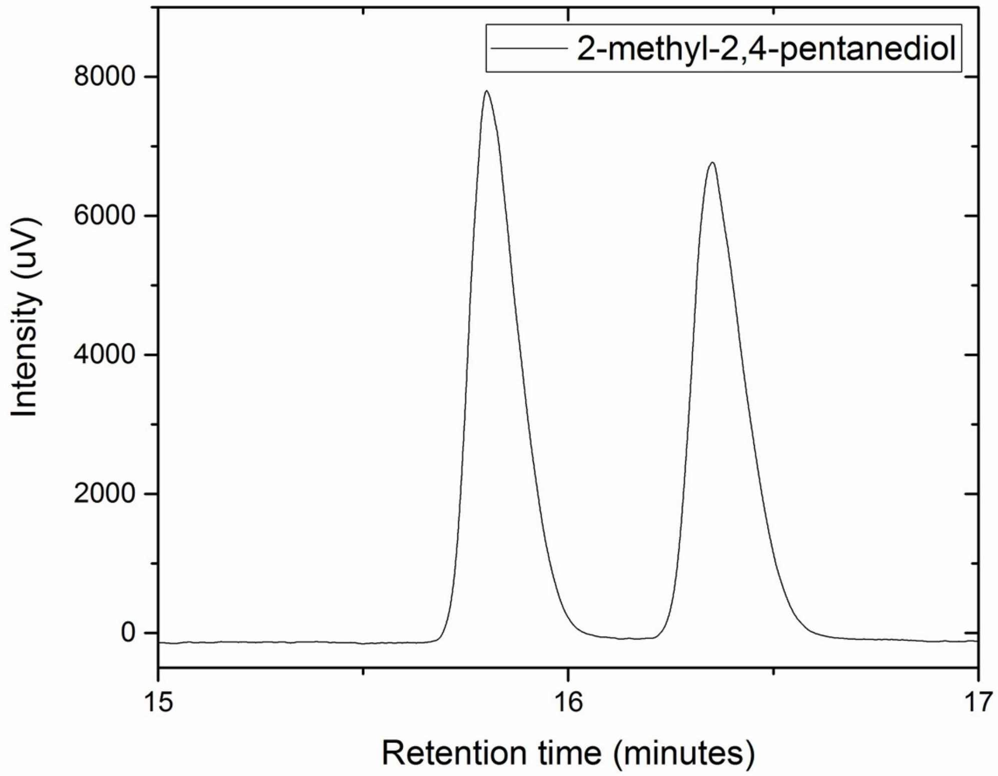


Figure S 11 Chromatogram of 2-methyl-2,4-pentanediol desorbed from ZnBLD-dPLA

Nuclear Magnetic Resonance Spectra

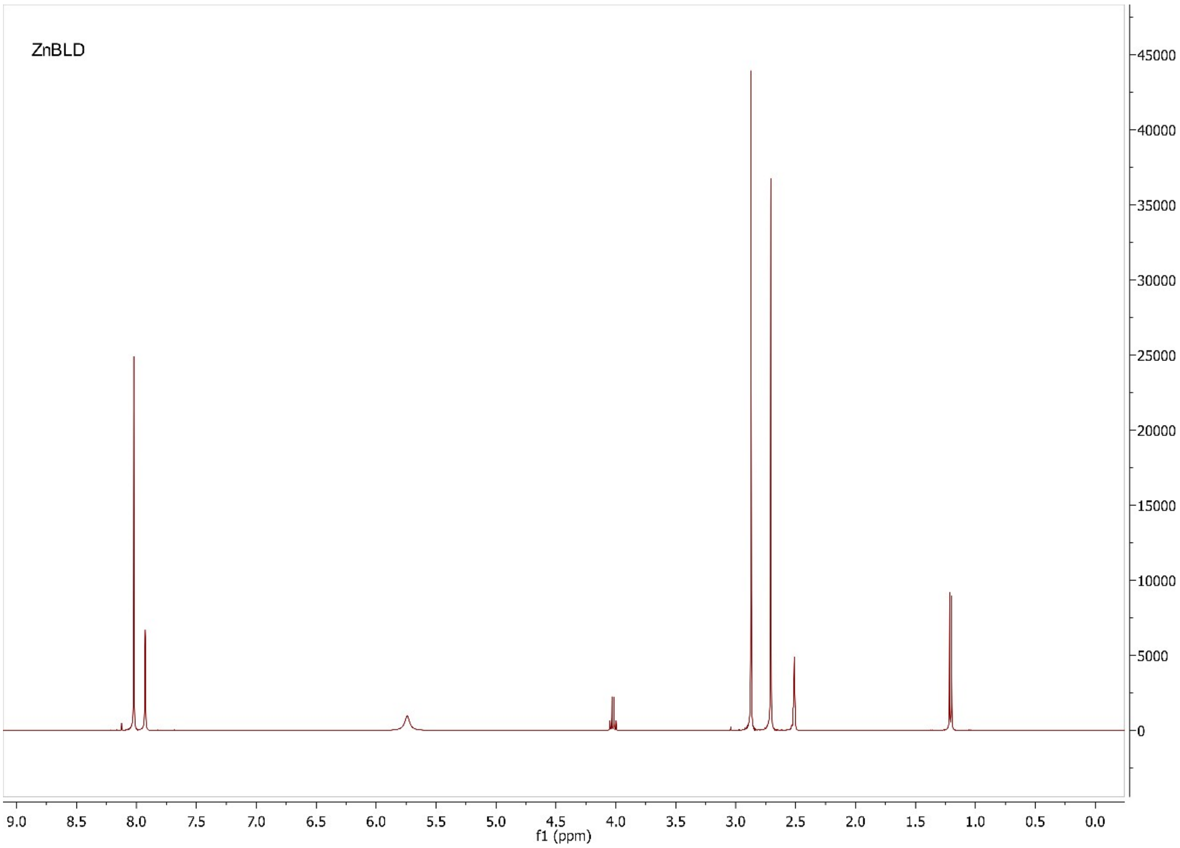


Figure S 12 NMR spectra of digested ZnBLD

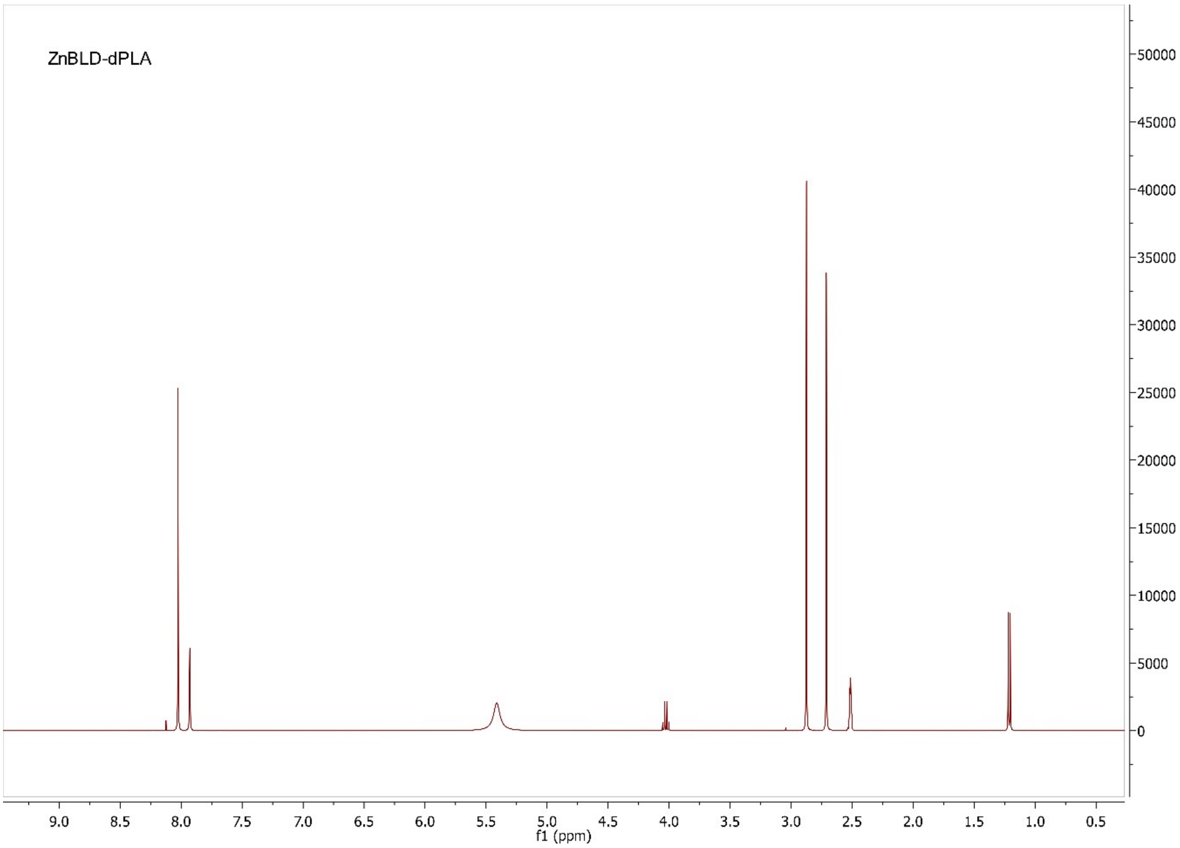


Figure S 13 NMR spectrum of digested ZnBLD-dPLA

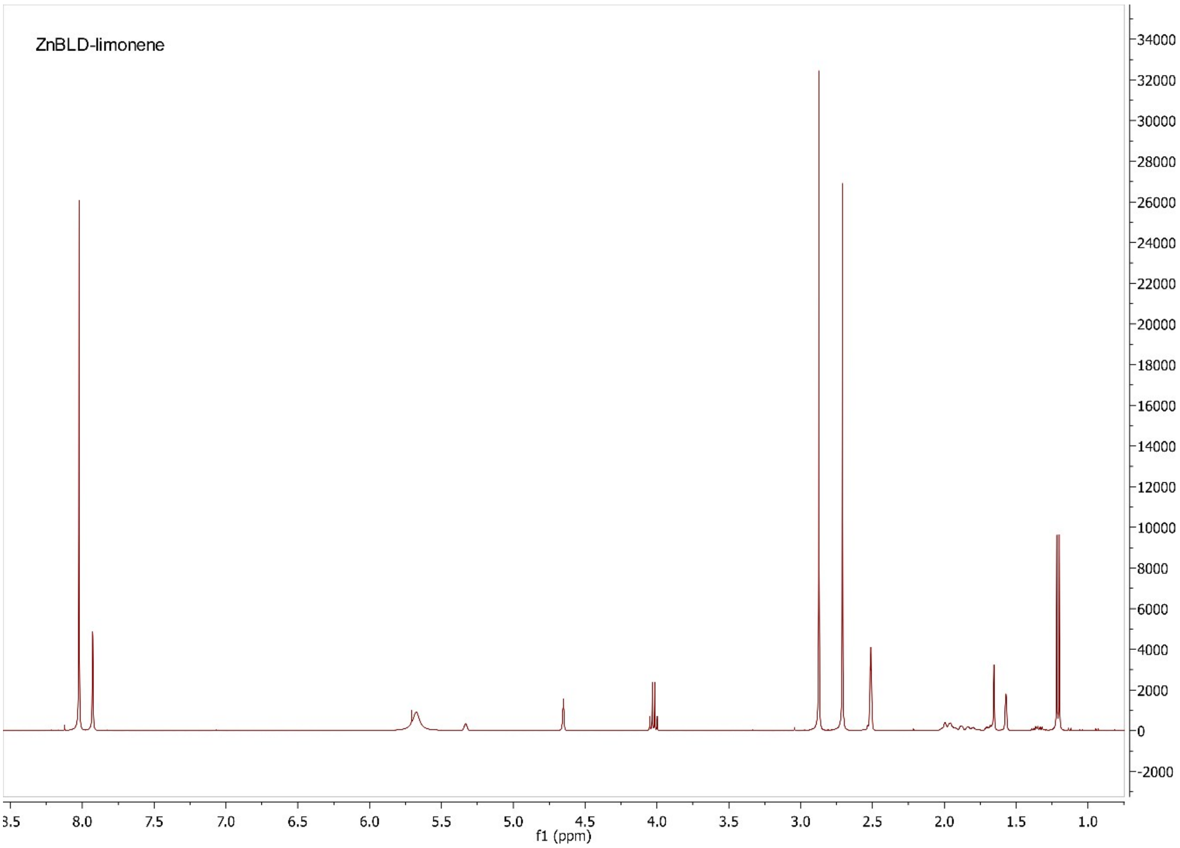


Figure S 14 NMR spectrum of digested ZnBLD-limonene

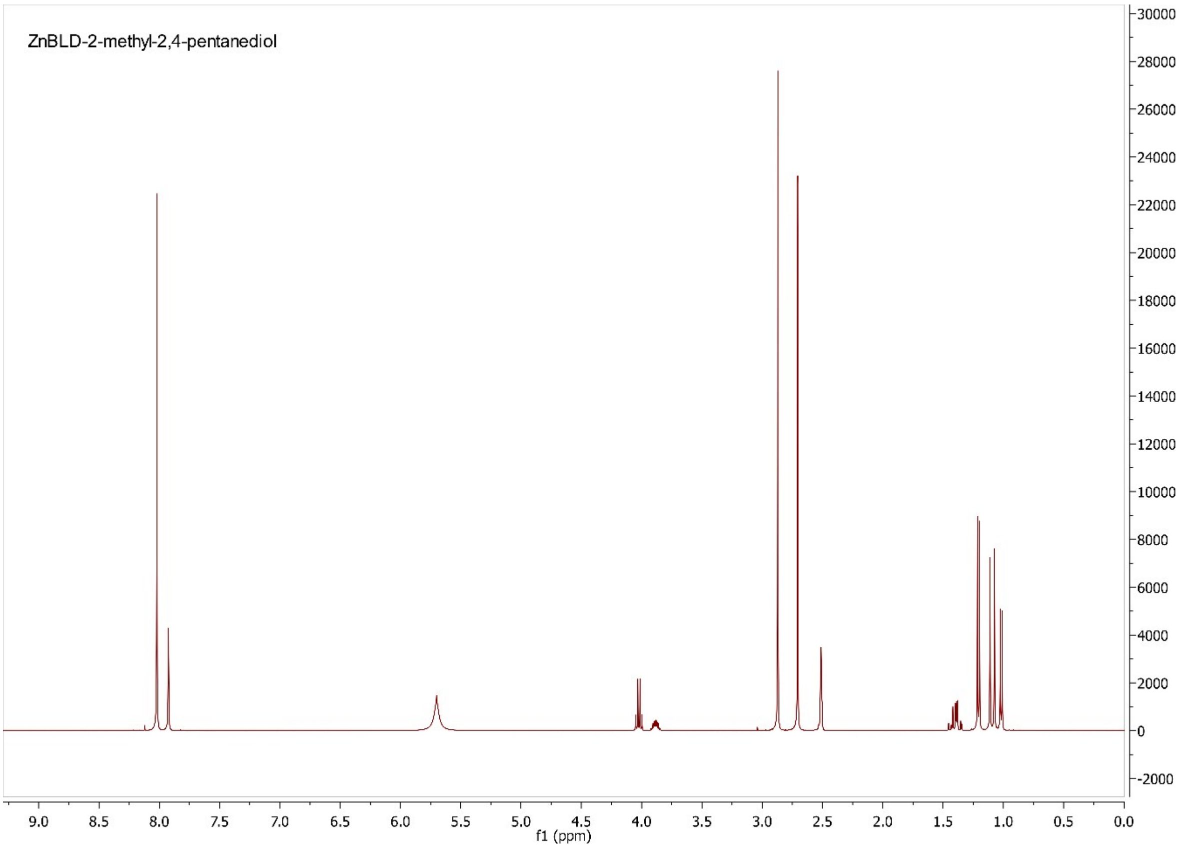


Figure S 15 NMR spectrum of digested ZnBLD-2-methyl-2,4-pentanediol

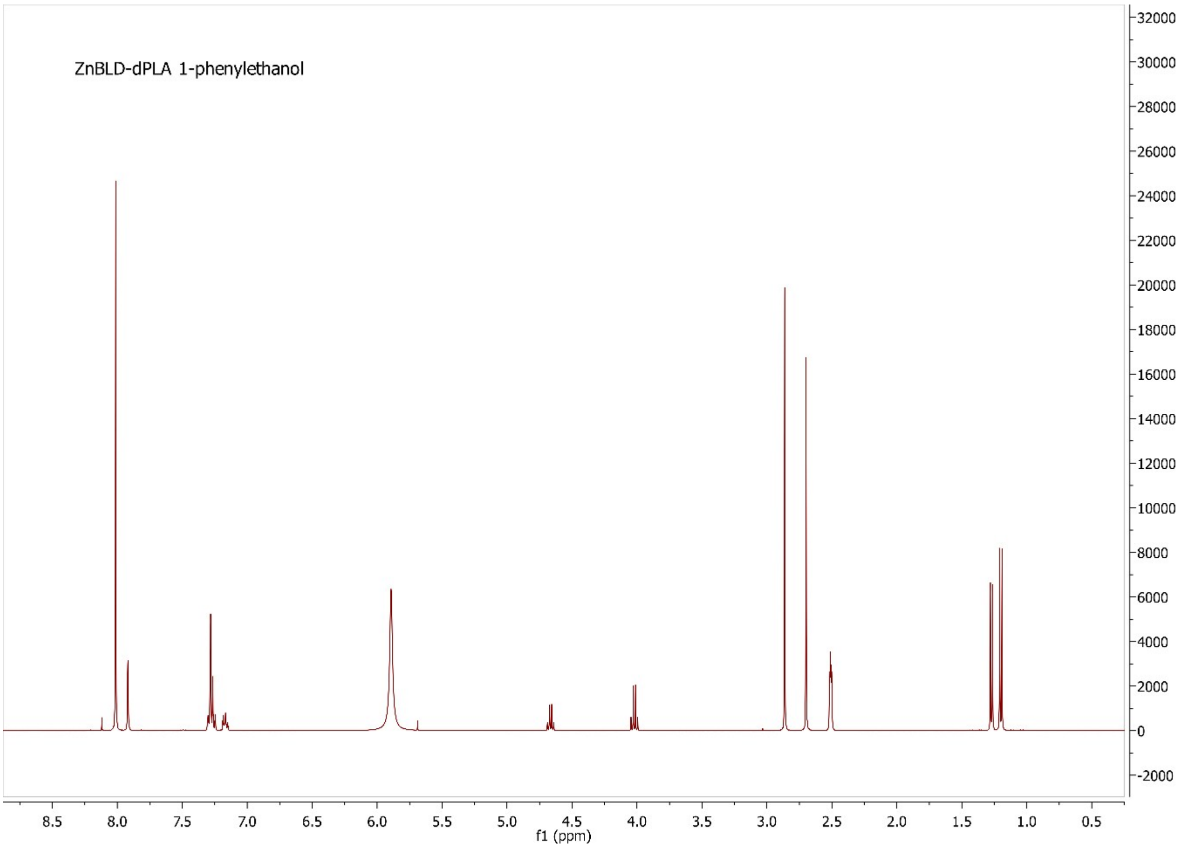


Figure S 16 NMR spectrum of digestedZnBLD-dPLA-1-phenylethanol

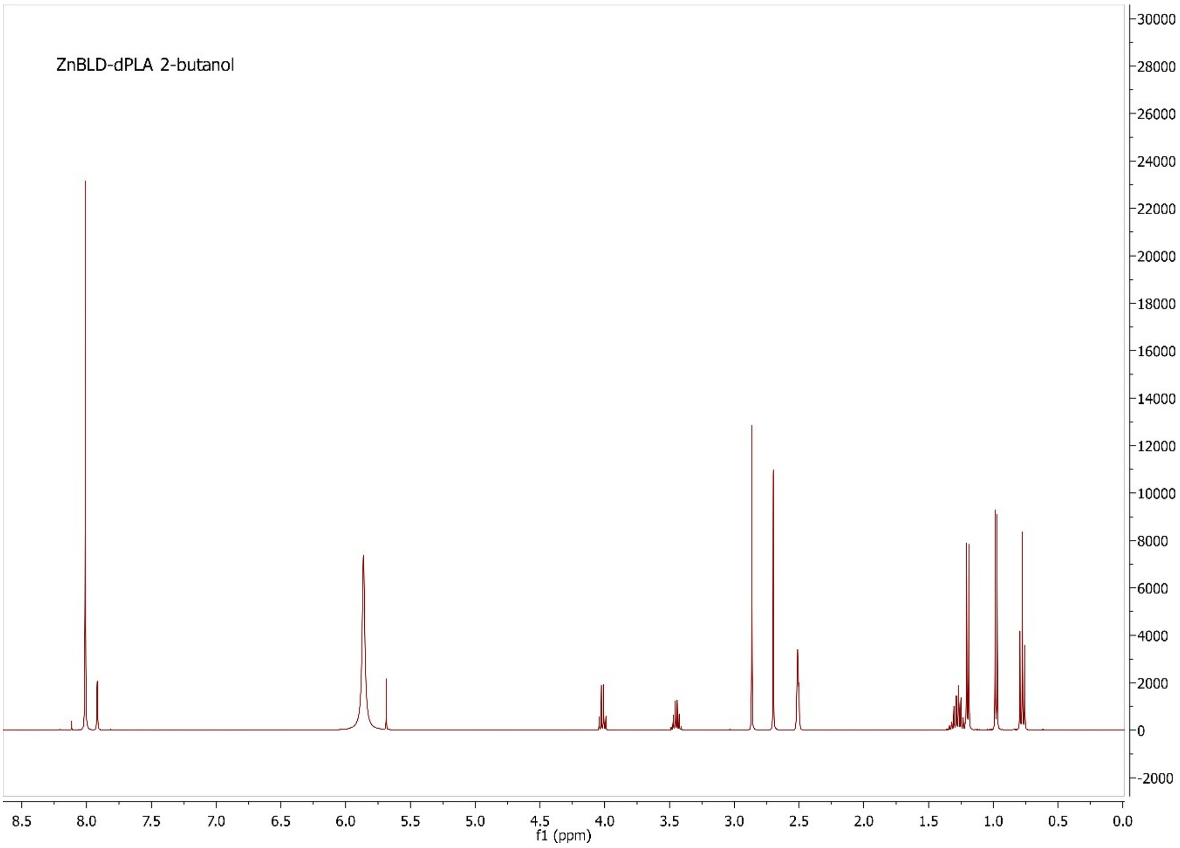


Figure S 17 NMR spectrum of digestedZnBLD-dPLA-2-butanol

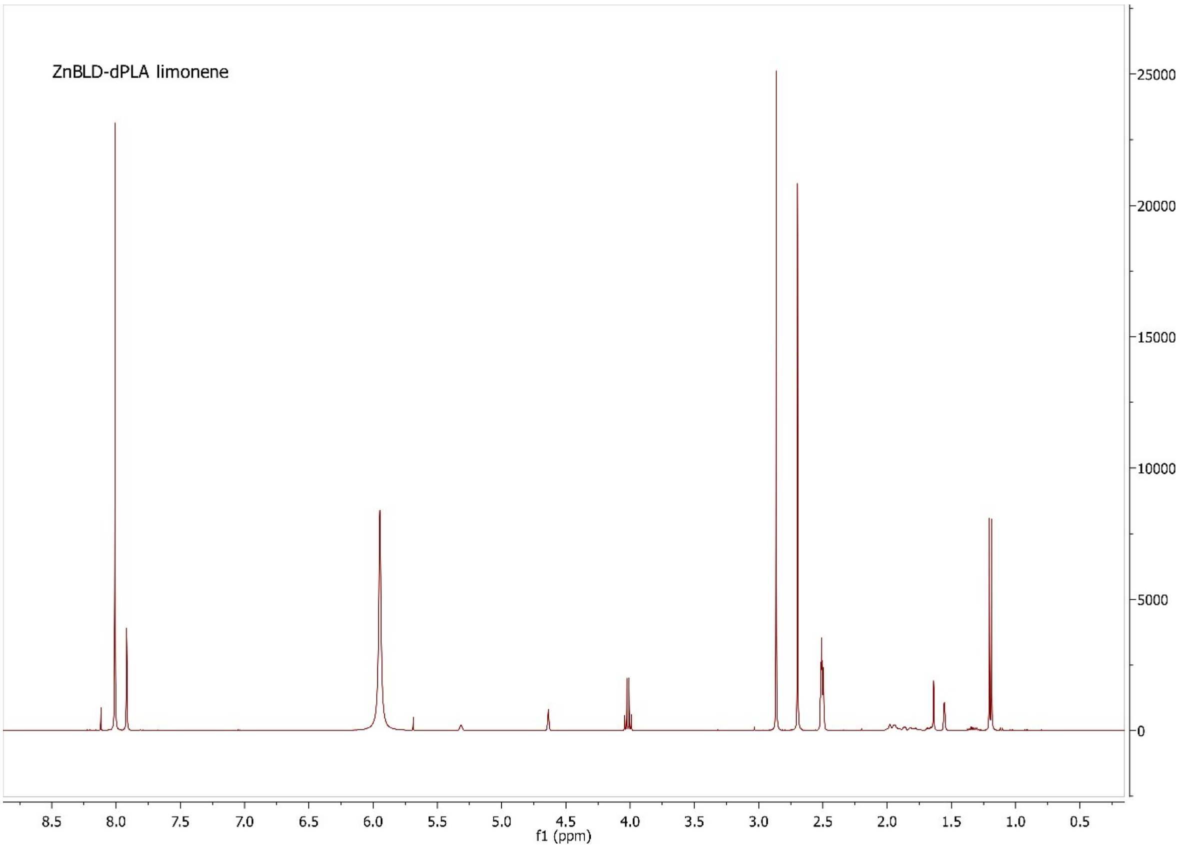


Figure S 18 NMR spectrum of digested ZnBLD-dPLA-limonene

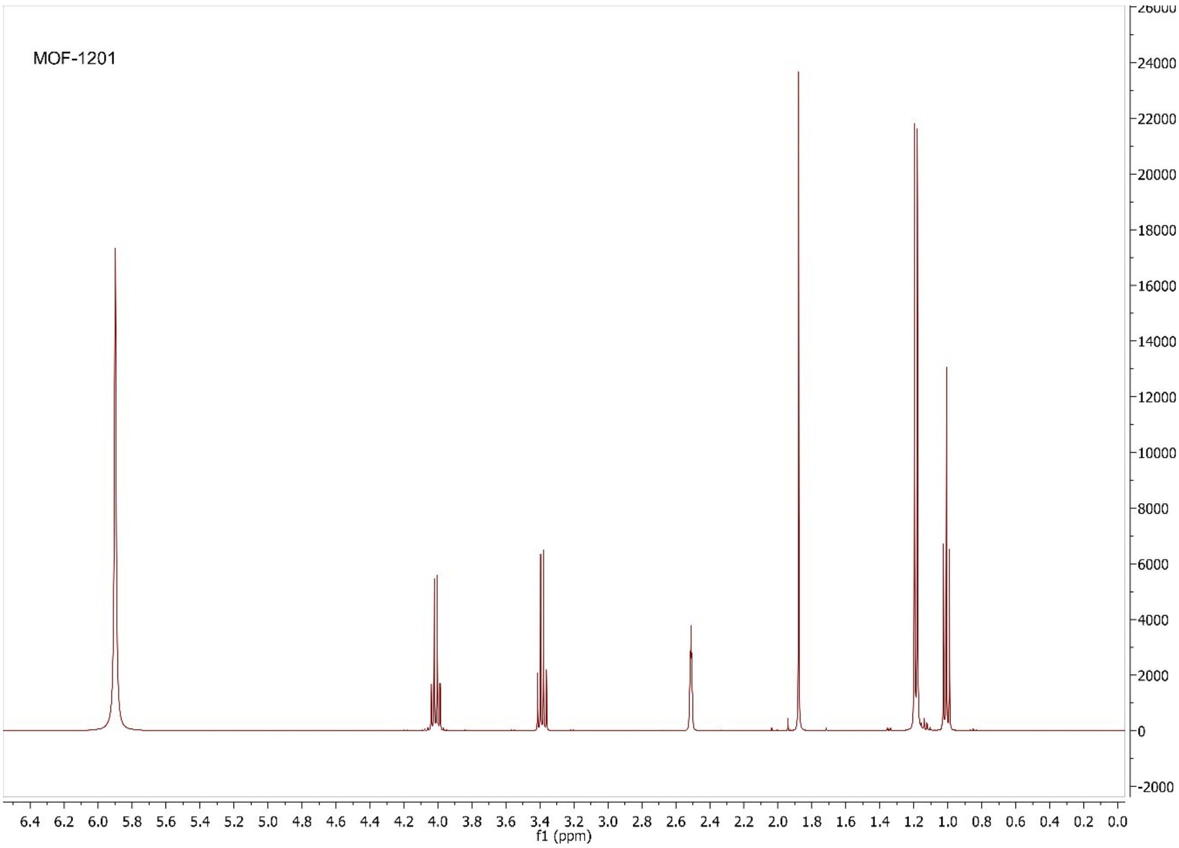


Figure S 19 NMR spectrum of digested MOF-1201

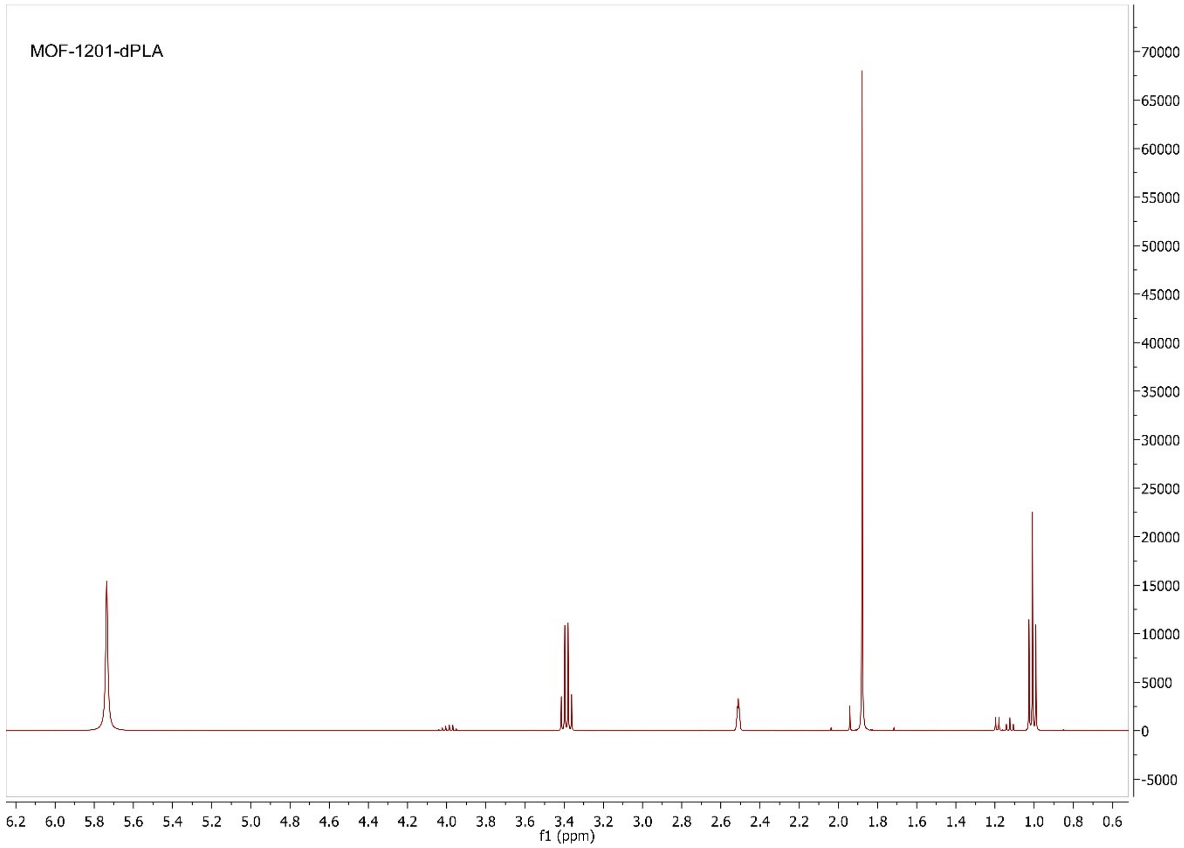


Figure S 20 NMR spectrum of digested MOF-1201-dPLA

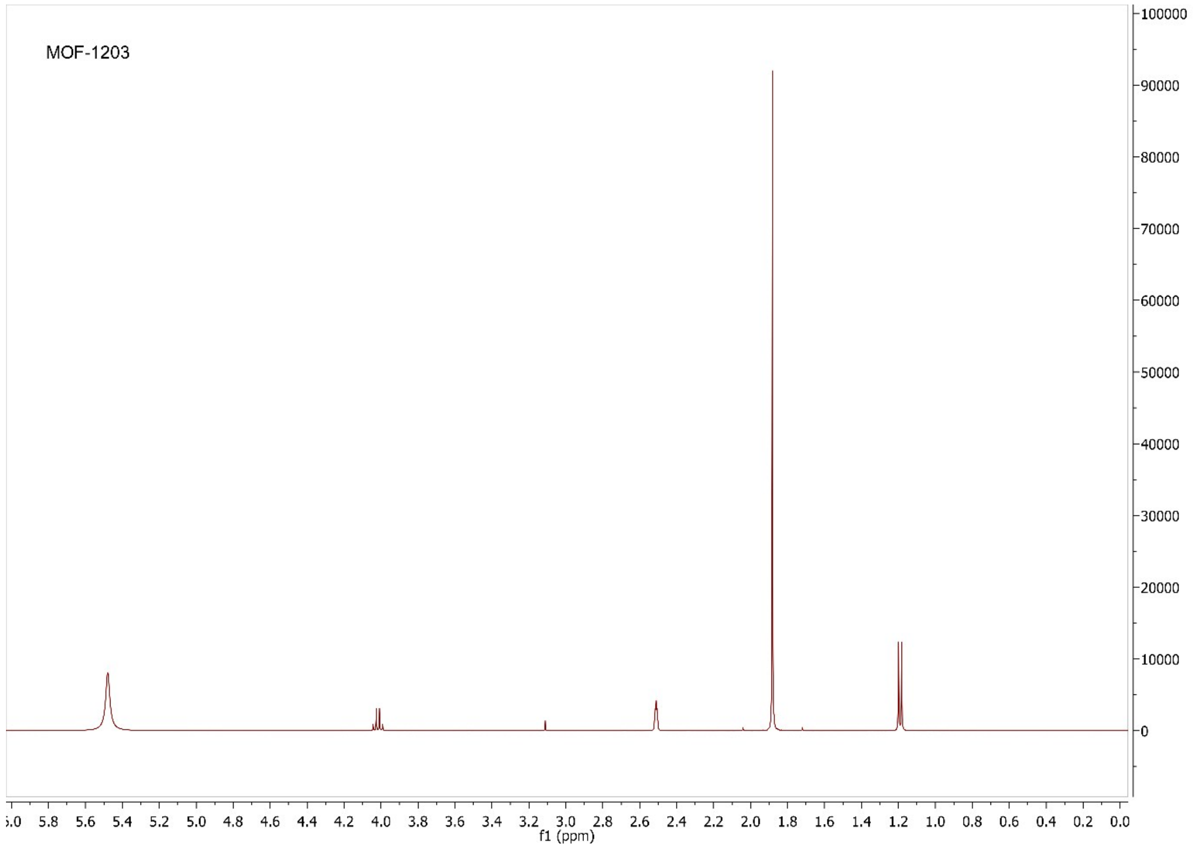


Figure S 21 NMR spectrum of digested MOF-1203

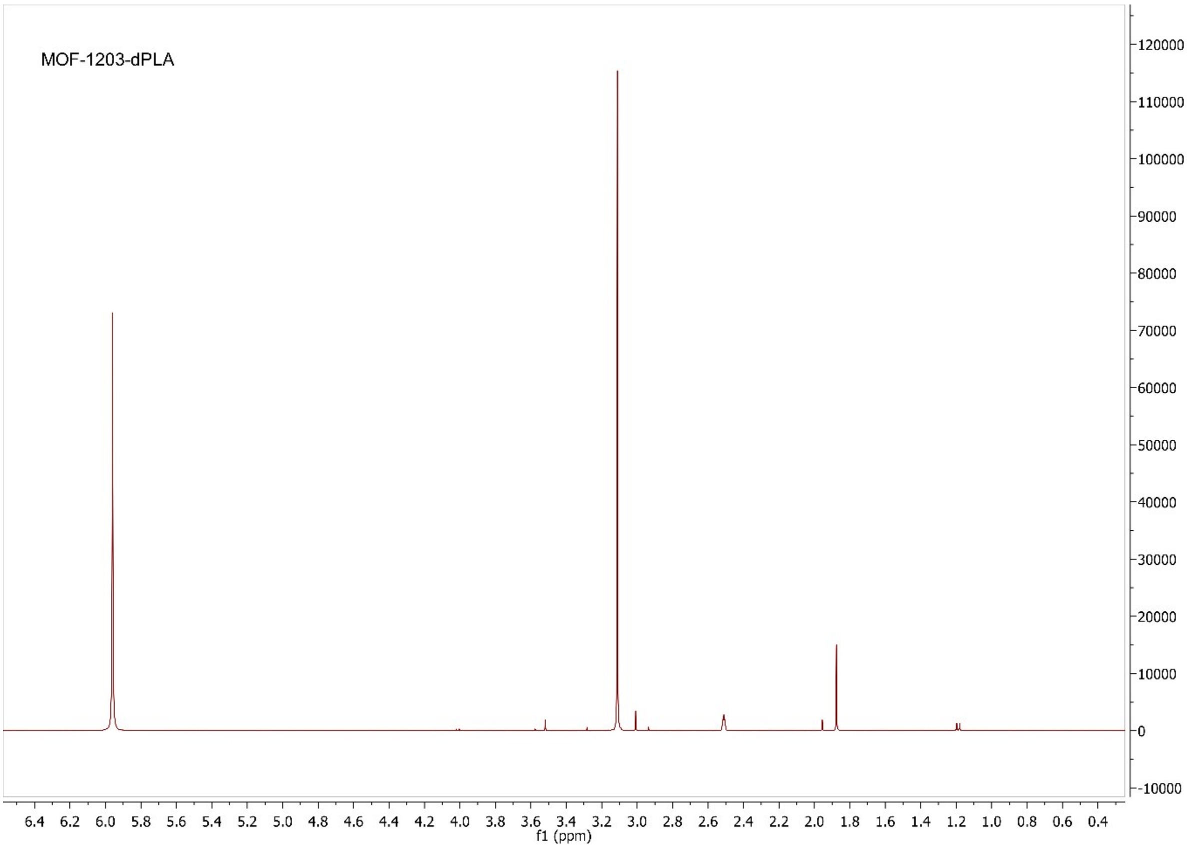


Figure S 22 NMR spectrum of digested MOF-1203-dPLA

Single Crystal X-ray Diffraction

Crystal data for **ZnBLD-dPLA**: $C_{14}H_{15}NO_8Zn_2\cdot1.5(C_3H_7NO)$, M = 565.65, orthorhombic, $P2_12_12_1$ (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,[3, 4] R_1(obs) = 0.0441, wR_2(all) = 0.1209, 4140 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to θ_{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.[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_3H_7NO, 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 $1.5(C_3H_7NO) = C_{4.5}H_{10.5}N_{1.5}O_{1.5}$ (and that for the unit cell low by $C_{18}H_{42}N_6O_6$) compared to what is actually presumed to be present. Figure S 22 depicts the asymmetric unit of ZnBLD-dPLA.

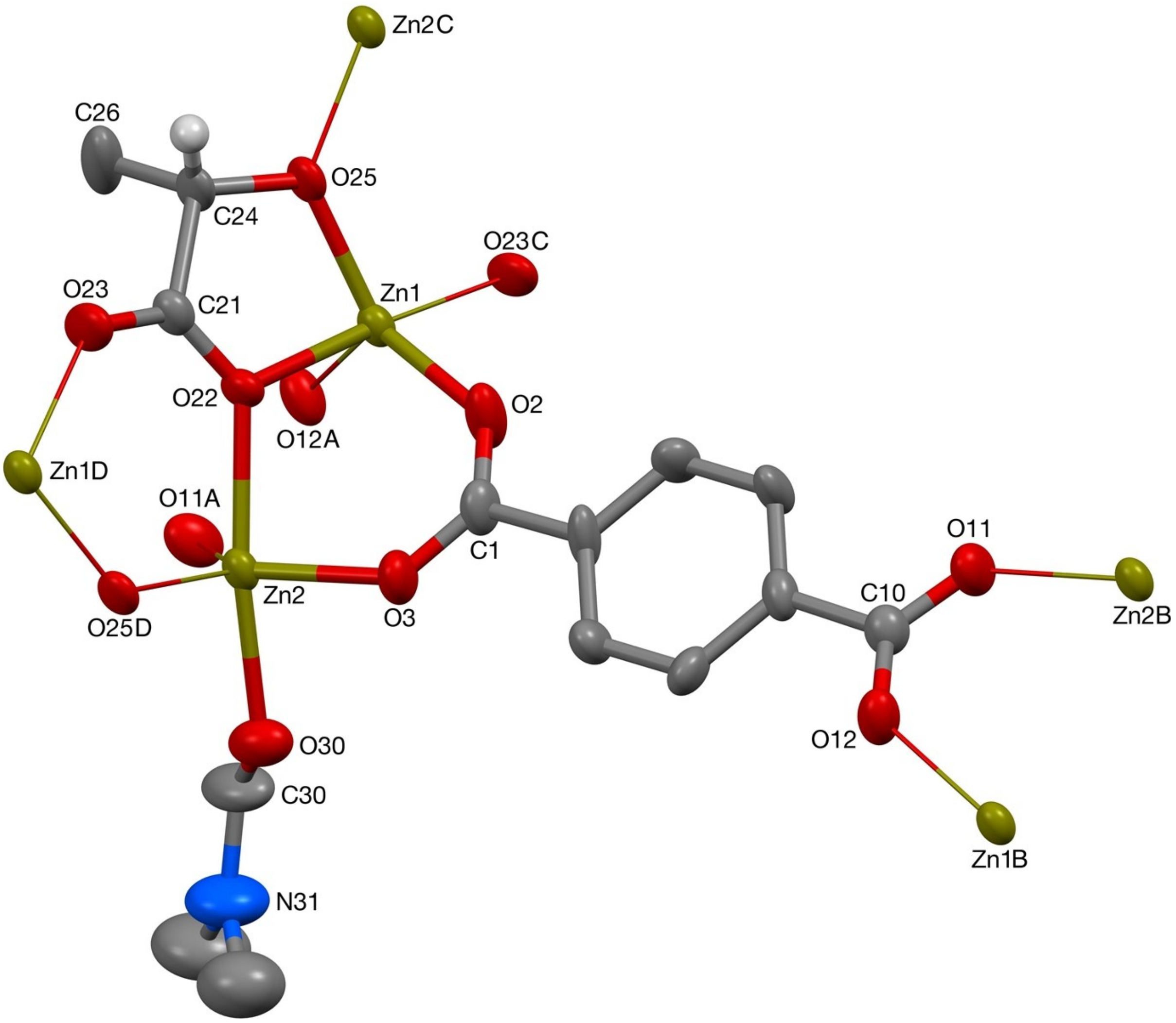


Figure S 23 The crystal structure of ZnBLD-dPLA showing the asymmetric unit and how it links to adjacent atoms (50% probability ellipsoids).

Photographs

Image S 1 Natureworks PLA plastic cups used as PLA source

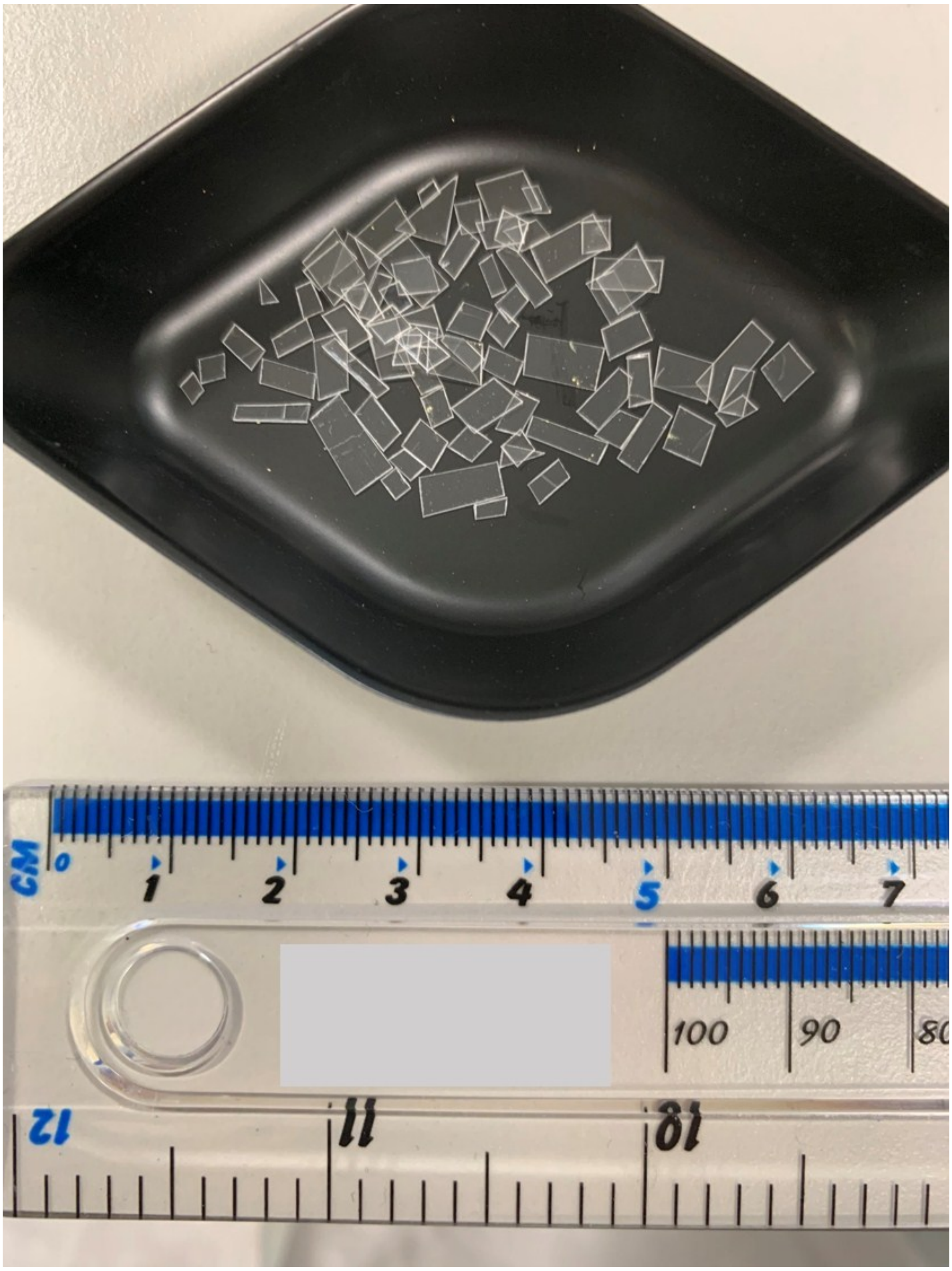


Image S 2 Example of size and shape of PET and PLA polymer flakes used

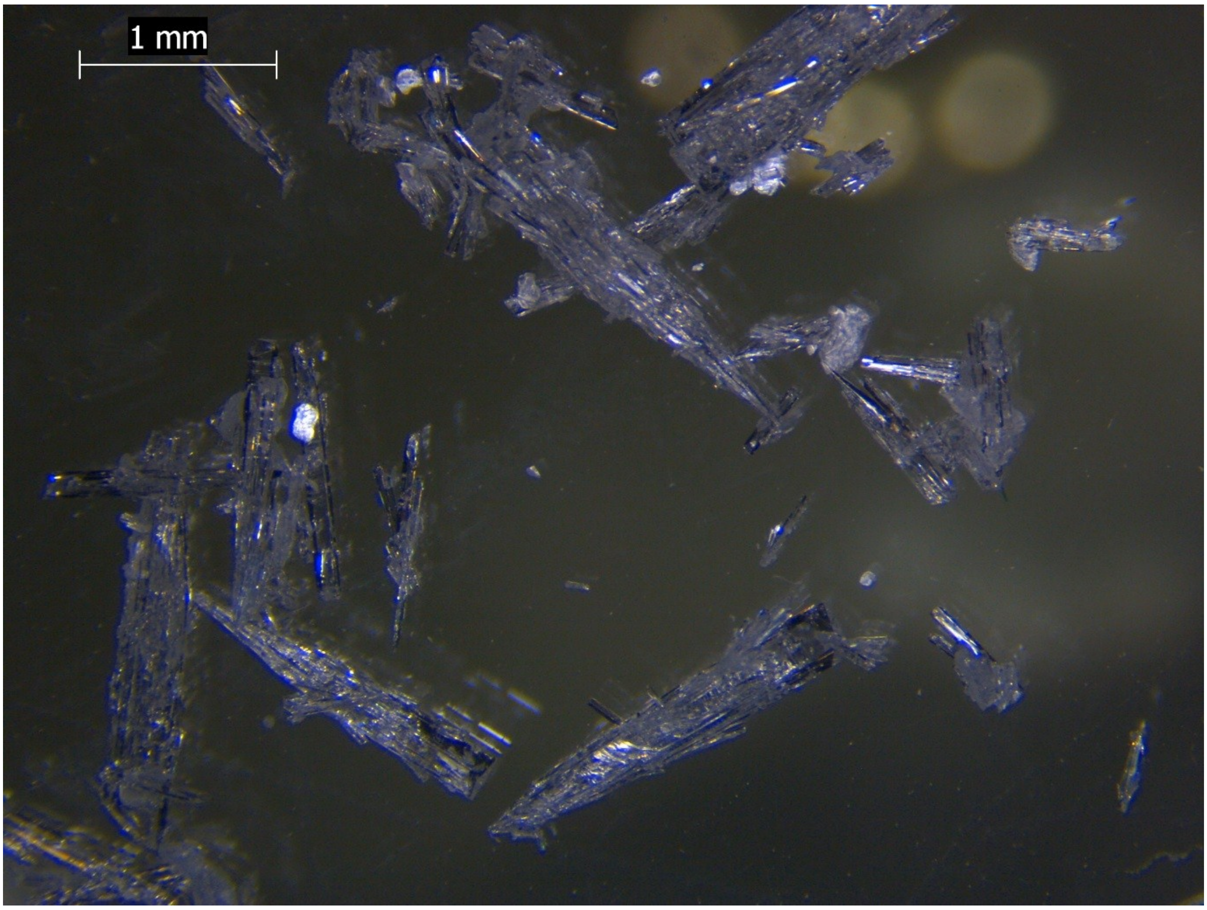


Image S 3 Optical microscope image of as-synthesised ZnBLD crystals

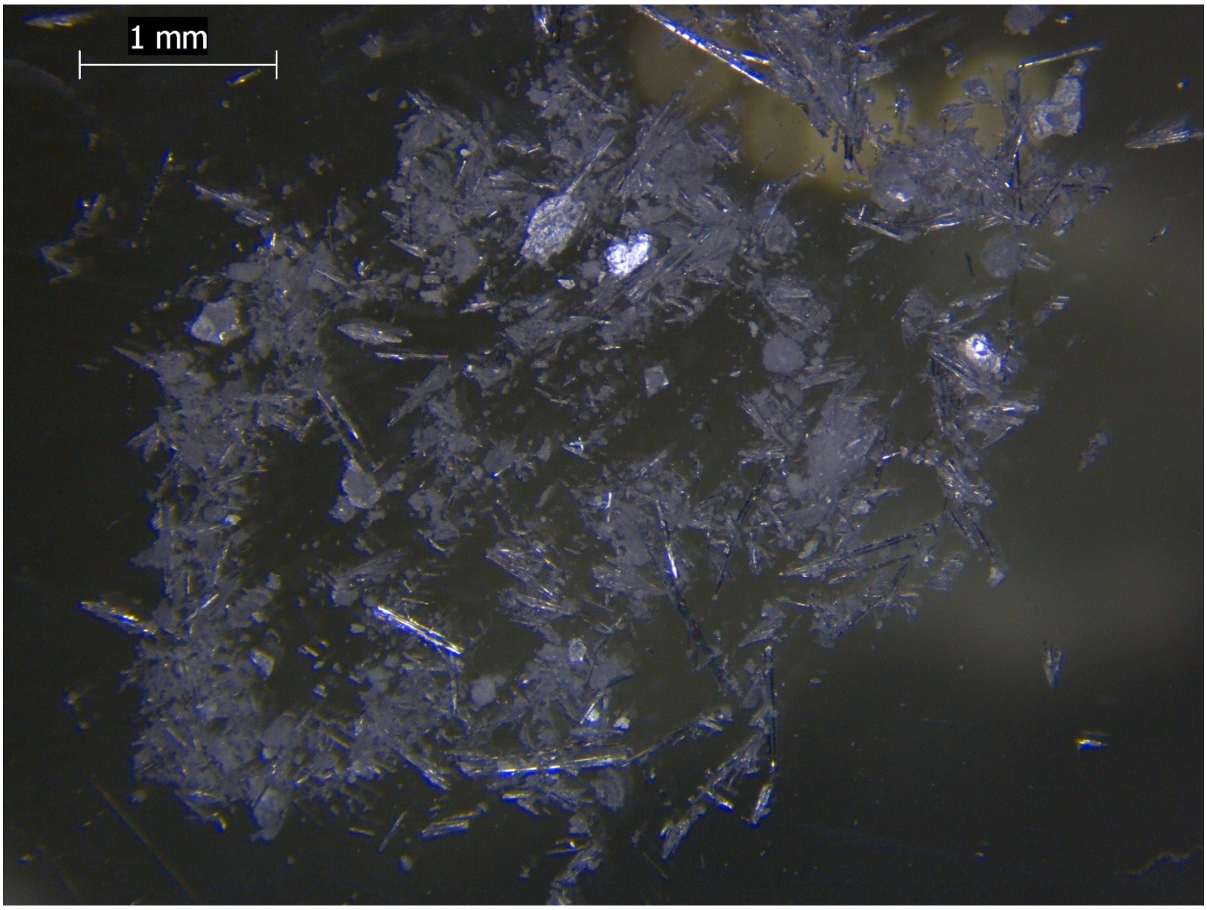


Image S 4 Optical microscope images of as-synthesised ZnBLD-dPLA crystals

References

1. D. N. Dybtsev, A. L. Nuzhdin, H. Chun, K. P. Bryliakov, E. P. Talsi, V. P. Fedin and K. Kim, *Angew. Chem. Int. Ed.*, 2006, **45**, 916-920.
2. J. Yang, C. A. Trickett, S. B. Alahmadi, A. S. Alshammari and O. M. Yaghi, *J. Am. Chem. Soc.*, 2017, **139**, 8118-8121.
3. SHELXTL v5.1, Bruker AXZ, Madison, WI, 1998.
4. G. Sheldrick, *Acta Crystallographica Section C*, 2015, **71**, 3-8.
5. A. Spek, *Acta Crystallographica Section C*, 2015, **71**, 9-18.