Electronic Supplementary Material (ESI) for Chemical Communications.

ESI: Toward sustainable syntheses of Ca-based MOFs

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A data repository containing all necessary data sets and images for this work can be found at https://doi.org/10.5258/SOTON/D1926.

Experimental Procedures

Ball-milling experiments were conducted on a Fritsch Pulverisette 23 mini-mill. A 10 mL Teflon-lined reaction vessel and ZrO_2 5 mm diameter balls were used.

Powder X-Ray Diffraction (PXRD) was conducted on a Bruker D2 diffractometer in theta-theta geometry using Cu ($K\alpha1/K\alpha2$) radiation and a Ni $K\beta$ filter (detector side). Additional beam optics and settings include primary and secondary axial soller slits (2.5°), fixed 0.6mm divergence slit and 1mm anti-scatter-screen. A 1D LYNXEYE detector with a 5° window was used.

Thermogravimetric analysis (TGA) was conducted on a Netzsch TG 209 F1 Libra. The sample was loaded into an Al_2O_3 crucible and heated from 30 to 900 °C at a rate of 10 °C min^{-1}. All experiments were conducted in an air atmosphere with a gas flow rate of 50 ml min^{-1}.

Scanning electron microscopy (SEM) was conducted on three different instruments due to instrument availability. All samples were sputter coated with gold to a thickness of 5 nm prior to characterisation to improve conductivity.

CO_2 adsorption measurements were carried out on a Micromeritics ASAP 2050 sorption analyser equipped with a recirculating dewar and a Julabo circulator. CO_2 was N4.0 grade from BOC. The samples were loaded into glass measurement tubes, weighed then heated to 100 °C under dynamic vacuum for 900 minutes on the instrument degas ports. The samples were then reweighed and transferred to the analysis port for the analysis.

^1H Nuclear magnetic resonance (NMR) was conducted on a Bruker AVII400 FT-NMR Spectrometer with an operating frequency of 400MHz. Samples were dissolved into d6-DMSO prior to analysis.

Calcium carbonate, squaric acid (H_2SQ), ethylene glycol and dimethylformamide (DMF) were purchased from Alfa Aesar. Fumaric acid (H_2FU), disodium fumarate and terephthalic acid (H_2BDC) were purchased from Sigma Aldrich. Chicken eggshells and PET bottles were recycled from lab members' homes. All recycled materials were thoroughly washed with deionised water prior to use. Bottle caps and labels were removed and appropriately recycled. The interior organic membrane of the eggshells were removed by immersing in deionised water to moisten the membrane followed by gentle mechanical exfoliation and air drying.

Reclaimed H_2BDC was synthesised from PET bottles following the procedure described by Ren *et al.*[1]

$Ca(BDC)(H_2O)_3$ bulk reference sample was synthesised following the procedure described by Sumida *et al.*[2]

$Ca(SQ)(H_2O)$ room temperature synthesis

H_2SQ (0.172 g, 1.52 mmol) was dissolved in deionised water (20 mL). Commercially bought $CaCO_3$ (0.152 g, 1.52 mmol) was added to the solution and stirred at room temperature for 24 hours. Pierced parafilm covered the reaction vessel to stop pressurisation from occurring due to gas evolution. The resulting white precipitate was washed with water and centrifugation cycles thrice. The white powder was left to air dry at room temperature. Yield = 0.1522 g (61%).

$Ca(SQ)(H_2O)$ from egg shell

H_2SQ (0.230 g, 2 mmol) was dissolved in deionised water (10 mL). An eggshell fragment (0.198 g, 2 mmol) was added to the squaric acid solution and left for 7 days. The resulting material was removed from solution, dried and ground to a powder for subsequent analysis. Yield = 0.117 g (50%).

$Ca(SQ)(H_2O)$ mechanochemical synthesis

Commercially bought $CaCO_3$ (0.153 g, 1.5 mmol) and H_2SQ (0.229 g, 2 mmol) were combined in a 10 mL Teflon ball-mill vessel with several ZrO_2 balls and deionised water (50 µL). The vessel was sealed and shaken for 20 minutes at 50Hz. The resulting purple powder was washed with water and centrifugation cycles thrice and dried at room temperature. Yield = 0.1544 g (60%).

$Ca(FU)(H_2O)_3$ Hydrothermal synthesis

H_2FU (0.381 g, 3 mmol) was partially dissolved in deionised water (15 mL) by sonicating for 15 minutes. Commercially bought calcium carbonate (0.276 g, 2.8 mmol) was added to the mixture and sealed in a scintillation vial before being heated to 100 °C for 24 hours. The resulting clear solution was left at room temperature overnight resulting in the formation of large, clear crystals. Yield = 0.3052 g (52%).

$Ca(FU)(H_2O)_3$ mechanochemical synthesis

Eggshells or calcium carbonate (0.0600 g, 0.6 mmol) and fumaric acid (0.0700g, 0.6 mmol) were loaded into a 10 mL Teflon ball-mill vessel with several ZrO_2 balls. The vessel was sealed and shaken for 5 minutes at 50Hz. The vessel was open, 40 µL deionised water added and resealed. The vessel was shaken again at 50Hz for 20 minutes. Yield = 0.0923 g (75%).

$Ca(BDC)(H_2O)_3$ from egg shells and PET plastic

Ball-milled eggshells (0.244 g, 2.4 mmol) and PET plastic pieces (0.503 g, approximate terephthalate content of 2.6 mmol) were combined in a Teflon-lined steel autoclave with deionised water (15 mL) and ethylene glycol (1.5 mL), sealed and heated to 210 °C for 15 hours. The resulting material was washed with DMF and centrifugation cycles thrice followed by methanol and centrifugation cycled twice. The powder was dried at room temperature overnight. Yield = 0.330 g (55%).

$Ca(BDC)(H_2O)_3$ mechanochemical synthesis

Ball-milled eggshells (0.030 g, 0.3 mmol) and reclaimed H_2BDC (0.109 g, 0.6 mmol) were combined in a Teflon vessel along with several ZrO_2 balls and deionised water (40 µL). The vessel was sealed and shaken at 50Hz for 20 minutes. The resulting solid was washed with DMF and centrifugation cycles thrice followed by methanol and centrifugation cycled twice. The powder was dried at room temperature overnight. Yield = 0.130 g (83%).

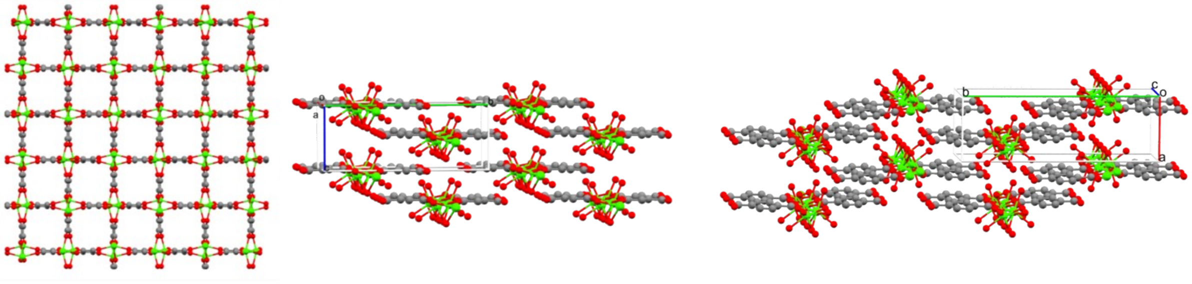

Figure S1. Crystal structures of (left to right) Ca(SQ)(H_2O); Ca(FU)(H_2O)$_3$ and Ca(BDC)(H_2O)$_3$.

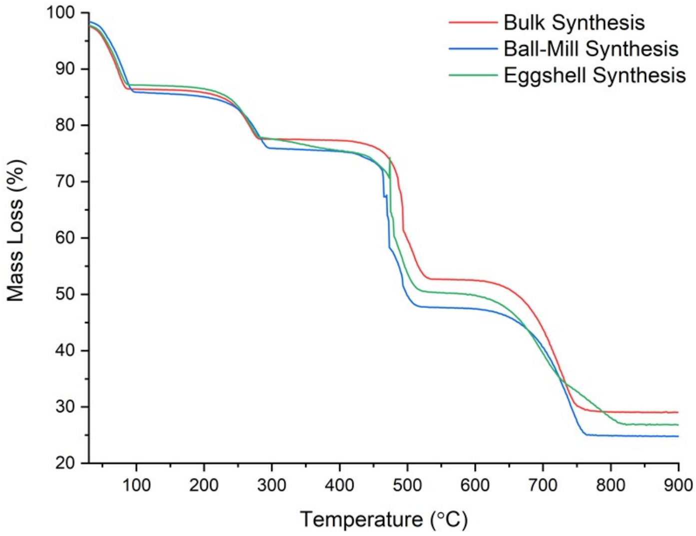

Figure S2. TGA comparison of Ca(SQ)(H_2O) synthesised from various calcite precursors. Expected mass losses calculated from the chemical formula of Ca(SQ)(H_2O) are 10%, 57% and 33% which correspond to solvent loss at 100 °C, organic loss between 250 – 800 °C and the residual mass at 800 °C respectively. The weight loss profiles match well but suggest slightly higher organic contents for the ball-milled and eggshell samples.

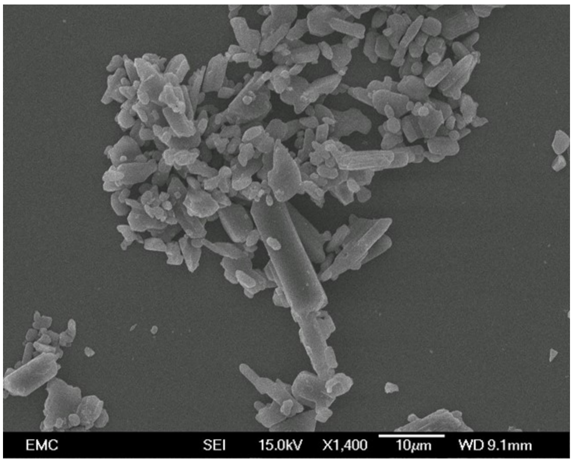

Figure S3. SEM image of Ca(SQ)(H_2O) synthesised from calcite.

Figure S4. Image of the colourless crystals produced from the hydrothermal synthesis of Ca(FU)(H_2O)$_3$.

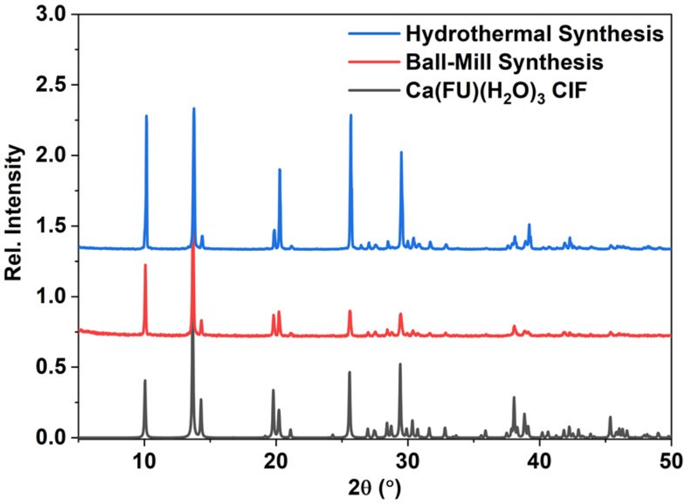

Figure S5. PXRD comparison of Ca(FU)(H_2O)$_3$ synthesised via ball-milling or hydrothermal methods from eggshells and calcite respectively.

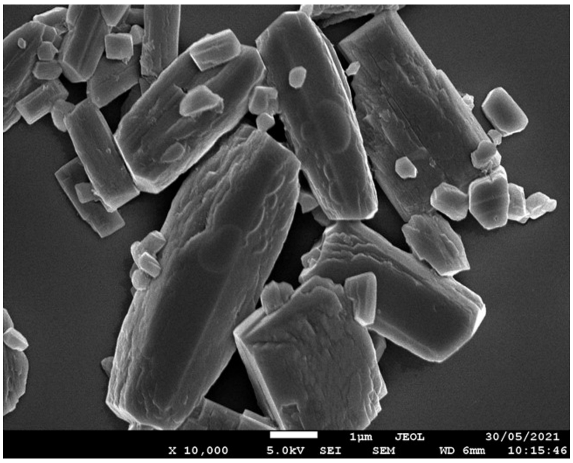

Figure S6. SEM image of $Ca(FU)(H_2O)_3$ synthesised via ball-milling.

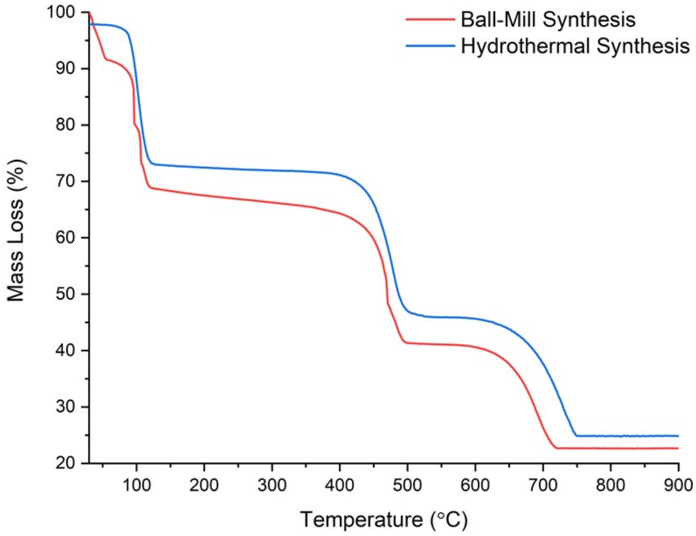

Figure S7. TGA comparison of $Ca(FU)(H_2O)_3$ synthesised via hydrothermal and ball-milling techniques. Expected mass losses calculated from the chemical formula of $Ca(FU)(H_2O)_3$ are 26%, 48% and 27% which correspond to solvent loss at 100 °C, organic loss between 400 – 750 °C and the residual mass at 750 °C respectively. Experimental values align well to the expected values. The decrease in mass of the ball-milled sample between 30 – 50 °C is likely due to residual solvent on the sample surface.

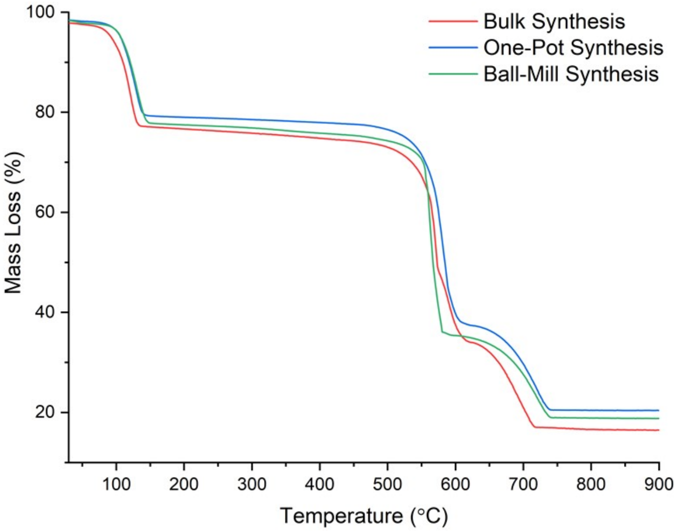

Figure S8. TGA comparison of Ca(BDC)(H_2O)$_3$ synthesised via various techniques. Expected masses loss calculated from the chemical formula of Ca(BDC)(H_2O)$_3$ are 20.9%, 57.4% and 21.7% corresponding to solvent loss at 100 °C, organic loss between 500 – 800 °C and the residual mass at 800 °C respectively. Our one-pot solvothermal synthesis of Ca(BDC)(H_2O)$_3$ from eggshells and PET plastic aligns very well to these values. The ball-milled and reference products display slightly lower than expected residual masses.

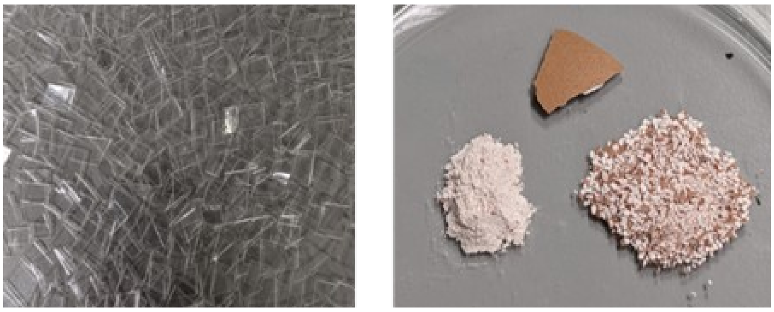

Figure S9. (Left) PET plastic bottles cut into small pieces. (Right, clockwise) eggshell fragment, ground eggshell and ball-milled eggshell.

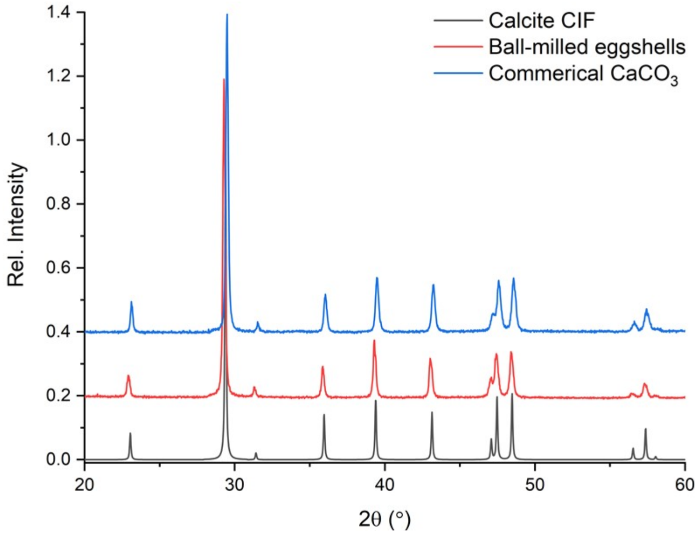

Figure S10. PXRD pattern comparison of ball-milled eggshells and commercial $CaCO_3$ to calcite CIF (CCDC deposition 1423724).[6]

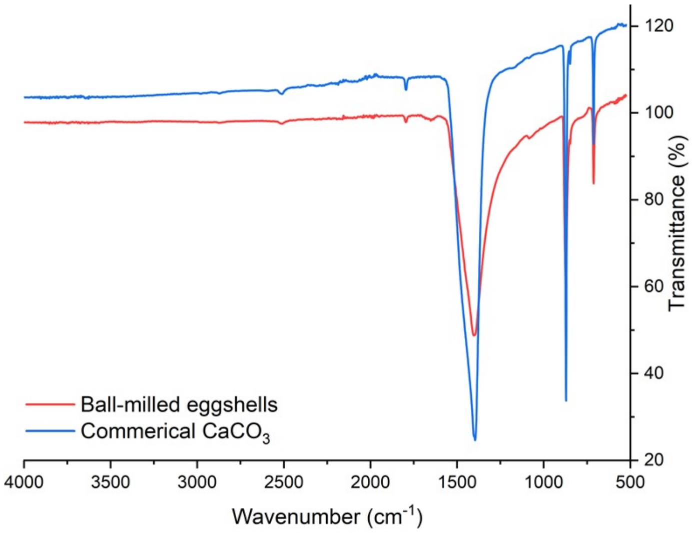

Figure S11. FTIR spectra of ball-milled eggshells with membrane removed and commercial $CaCO_3$.

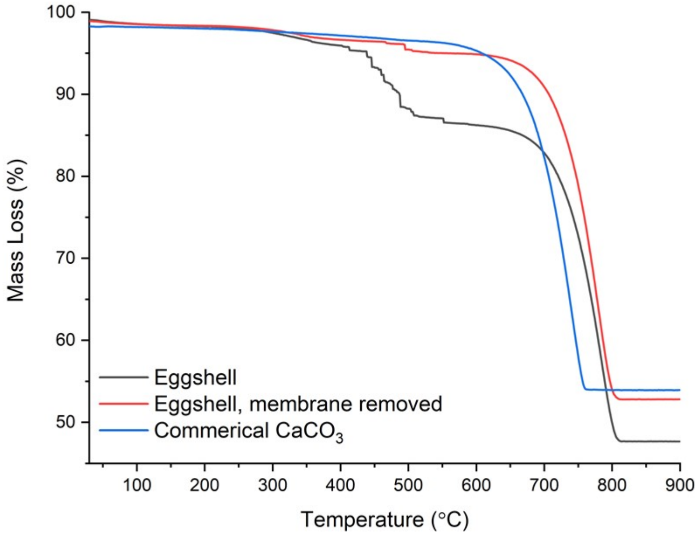

Figure S12. TGA of eggshells with and without the interior organic membrane compared to commercial $CaCO_3$. Thermal decomposition of $CaCO_3$ in all three samples occurs between 600 – 850 °C. The mass losses that occur between 400 – 600 °C in the eggshell samples correspond to organic loss from either residual organics or the organic membrane. The similar residual masses of the membrane removed eggshell and commercial $CaCO_3$ confirm that most organics are removed via exfoliation.

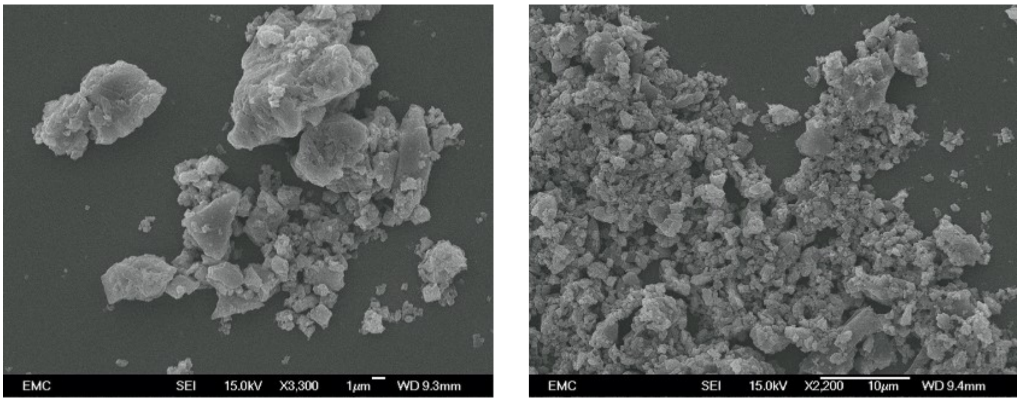

Figure S13. SEM images of ground eggshells, membrane removed. Scale bars = (left) 1 µm and (right) 10 µm.

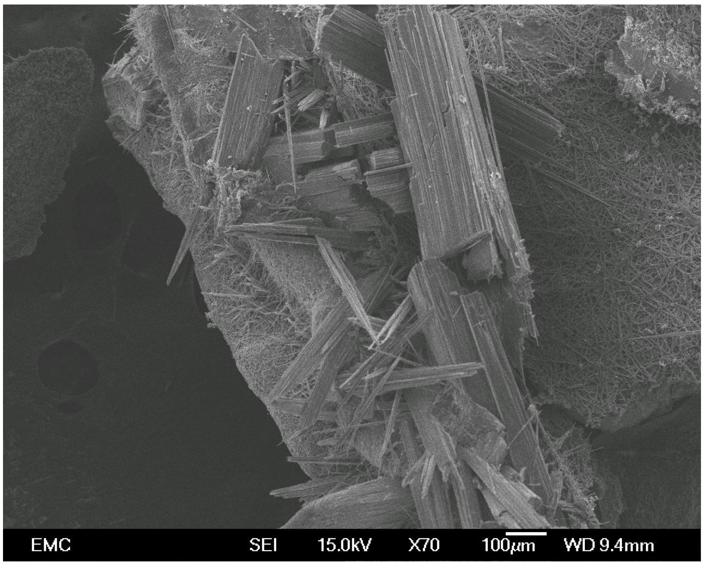

Figure S14. SEM image of initial Ca(SQ)(H_2O) crystal growth on the surface of an eggshell (scale bar = 100 µm).

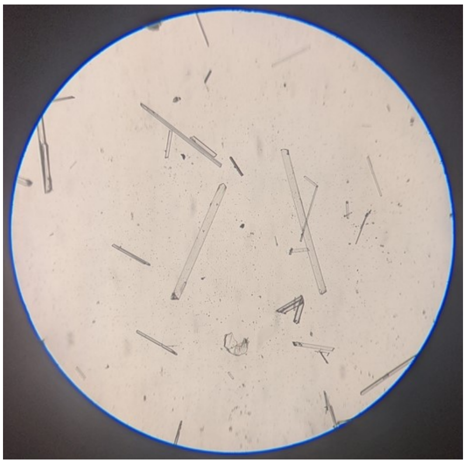

Figure S15. Optical microscope image of Ca(SQ)(H_2O) crystals grown from eggshell. Magnification = x80.

Figure S16. Image of $Ca(SQ)(H_2O)$ grown on the membrane intact internal surface of an eggshell.

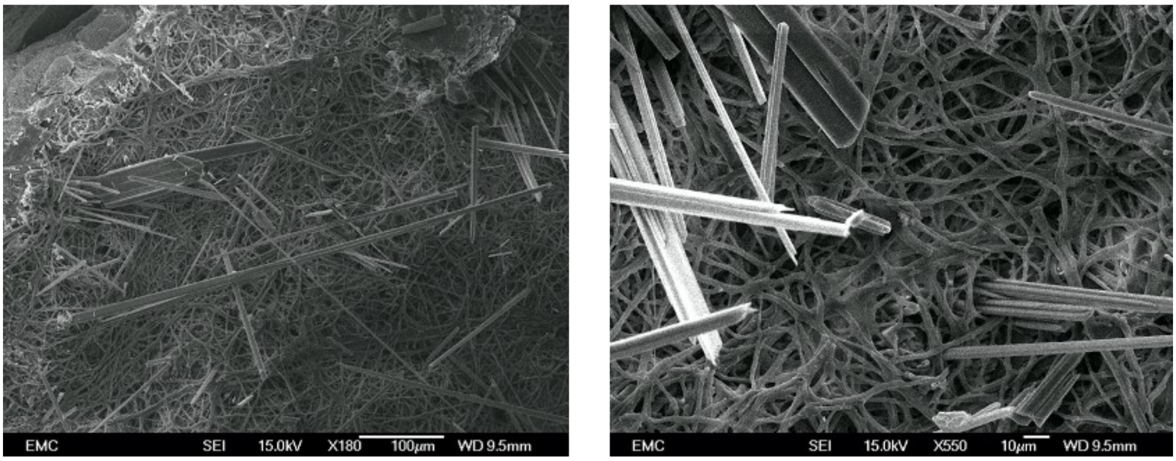

Figure S17. SEM images of $Ca(SQ)(H_2O)$ microcrystals on the inner surface of an eggshell with the membrane intact. Scale bar = (Left) 100 µm and (right) 10 µm.

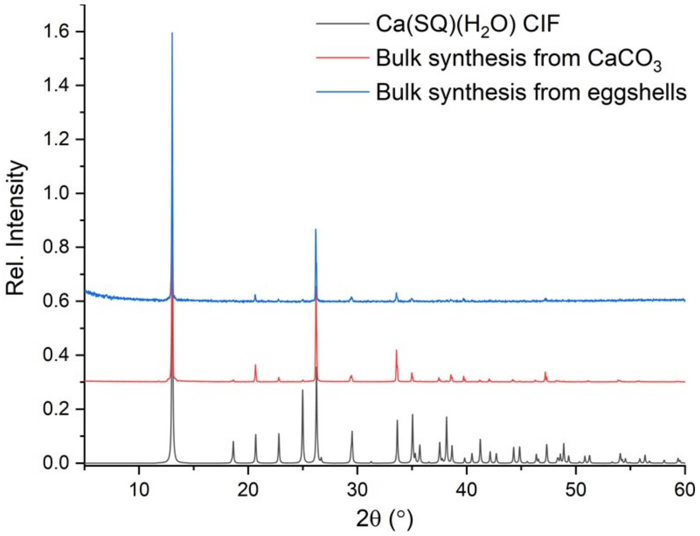

Figure S18. PXRD pattern comparison of Ca(SQ)(H_2O) synthesised from commercial $CaCO_3$ and eggshells in water.

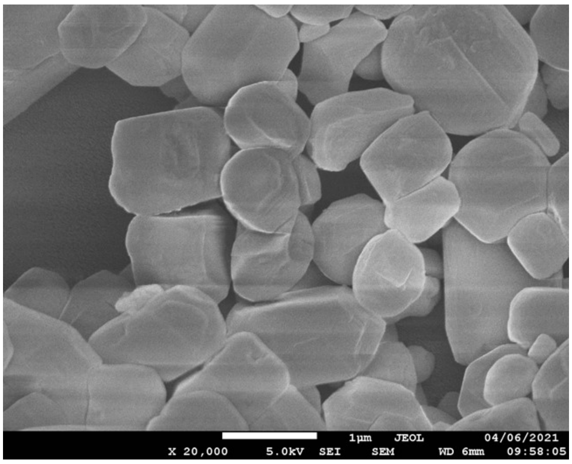

Figure S19. SEM image of ball-milled synthesised Ca(SQ)(H_2O). Scale bar = 1 μm.

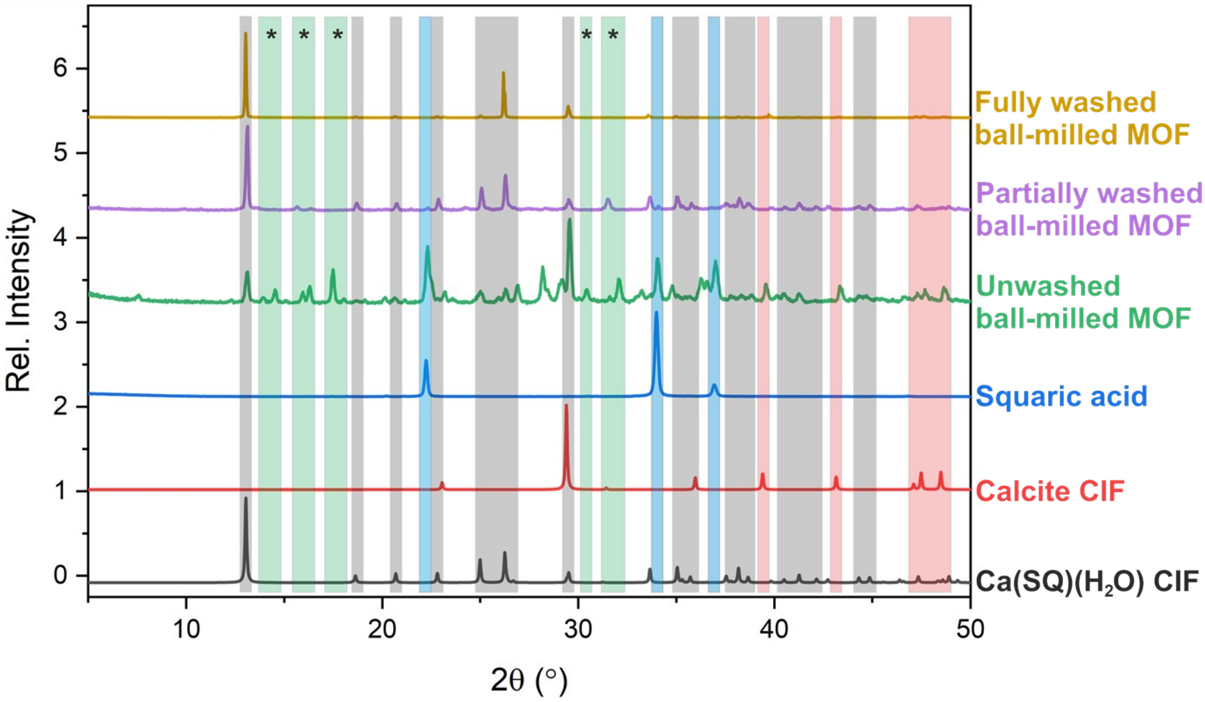

Figure S20. PXRD comparison of mechanochemically synthesised Ca(SQ)(H_2O) against its precursors. The unwashed product pattern consists of an overlap of peaks from the precursors, Ca(SQ)(H_2O) and an unknown phase (highlighted in green and *). The fully washed product (gold pattern, top) shows Ca(SQ)(H_2O) and a very small amount of residual calcite, indicated by the small peaks at 2θ = 23.2, 47.3, 47.6 and 48.5 °, strongly suggesting further conversion to the MOF has occurred during the washing step. It is clear from the partial and fully washed samples that the unknown phase is water soluble and can be removed via washing.

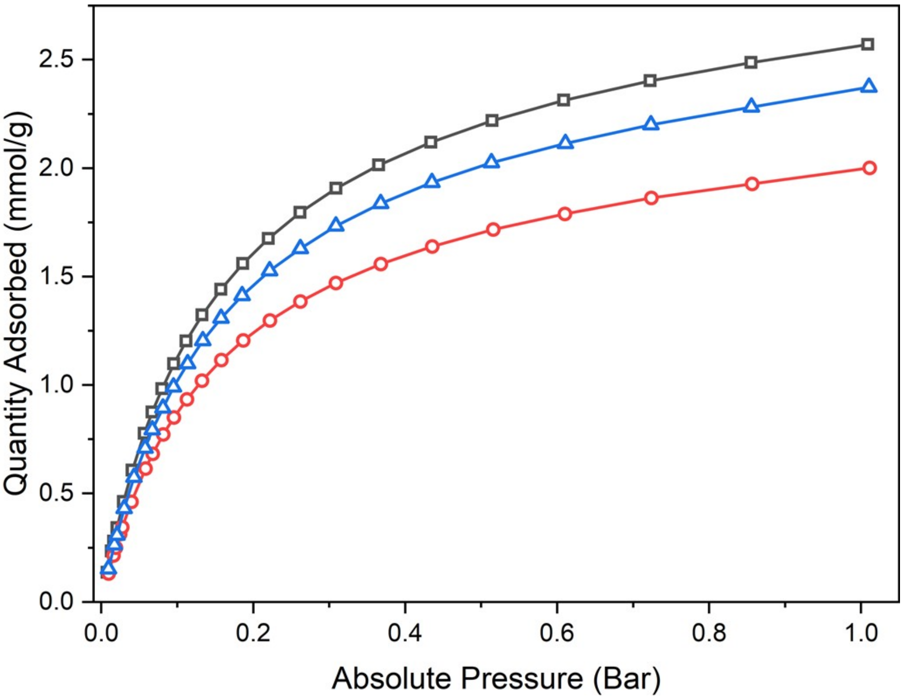

Figure S21. CO_2 adsorption isotherms of Ca(SQ)(H_2O) determined at 298 K: reference sample prepared according to *Energy Fuels*, 2021, **35**, 13900 (black squares); sample prepared mechanochemically from calcite (blue triangles) and a sample grown onto the eggshell surface under aqueous conditions (red circles). Uptakes at 1 bar are in good agreement for the reference sample (2.57 mmol/g) and the mechanochemically synthesised product (2.37 mmol/g). The material derived from eggshells while porous has a lower uptake of 2.00 mmol/g. The origin of this reduced uptake capacity is unknown, but may suggest that some additional organic material from the biomineral precursor may have been incorporated into the Ca(SQ)(H_2O) product which is consistent with the TGA data of the eggshells themselves even after inner membrane removal.

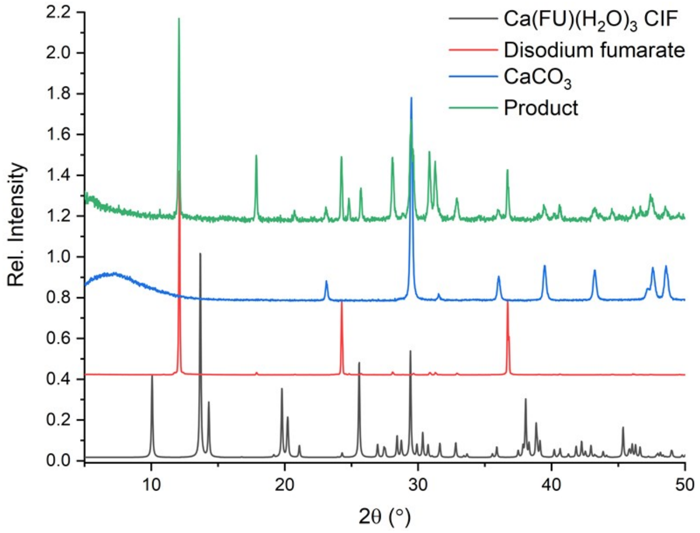

Figure S22. PXRD comparison of product from the attempted mechanochemical synthesis of Ca(FU)$(H_2O)_3$ from the disodium linker salt to its precursors. The product pattern consists of overlapping $CaCO_3$ and Na_2FU peaks.

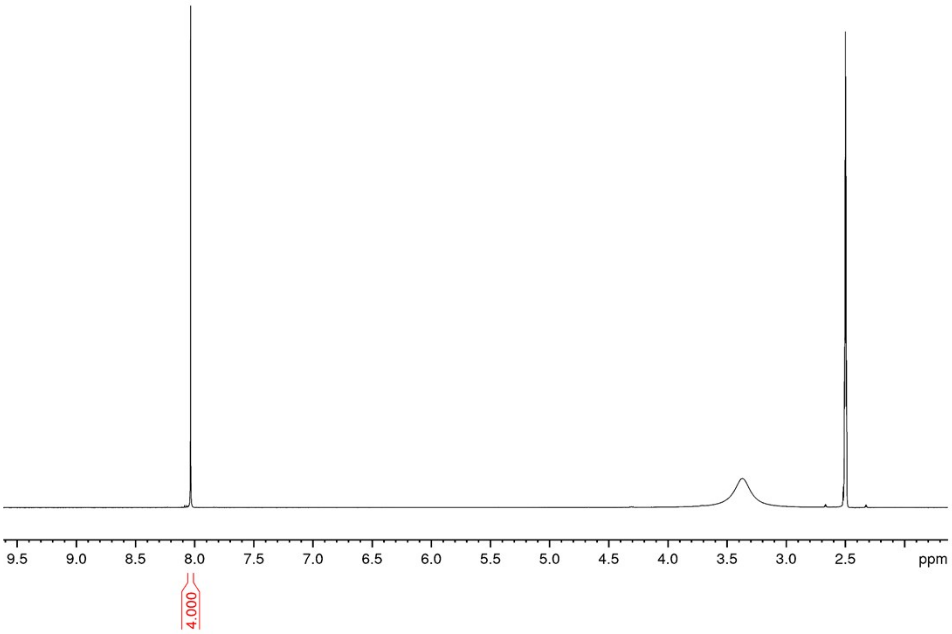

Figure S23. ^{1}H NMR spectrum of hydrolysed PET. Peak at 2.48 ppm corresponds to DMSO solvent and the broad peak at 3.4 ppm to residual water.

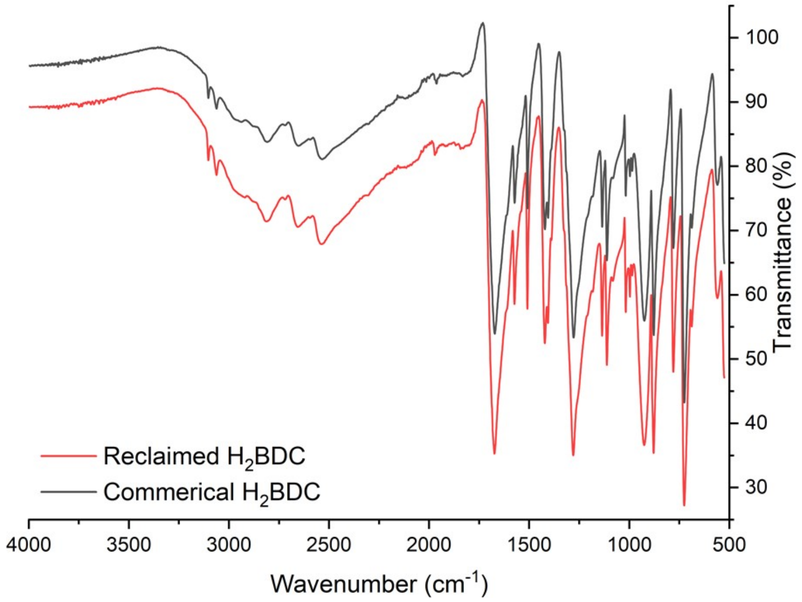

Figure S24. FTIR spectra of H_2BDC reclaimed from PET plastic and commercially bought H_2BDC.

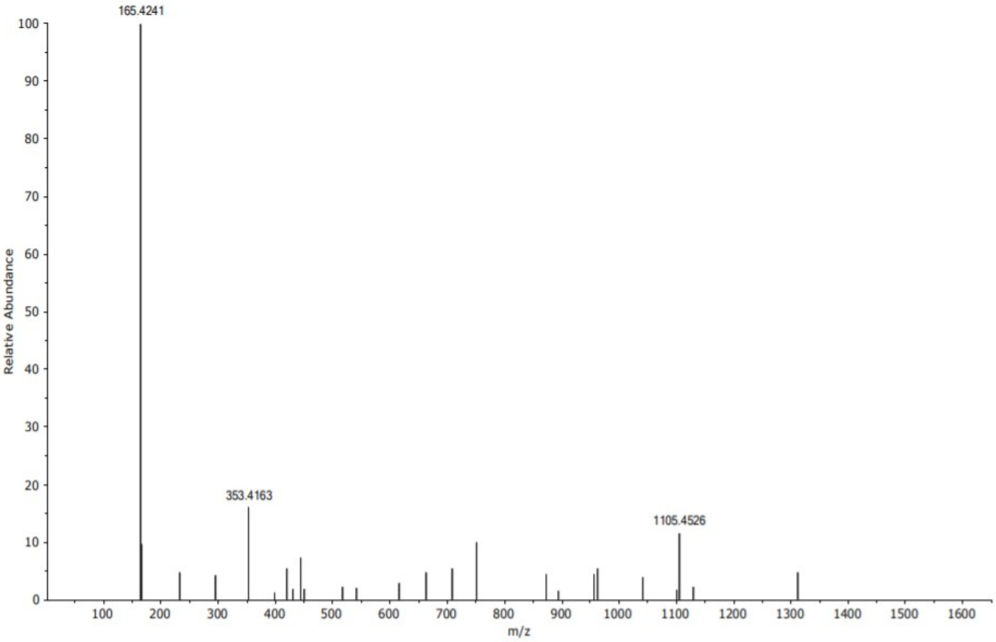

Figure S25. RP UHPLC MS via negative electrospray ionisation of H_2BDC from hydrolysed PET bottles. The high intensity peak at 165.4 m/z corresponds to $HBDC^-$.

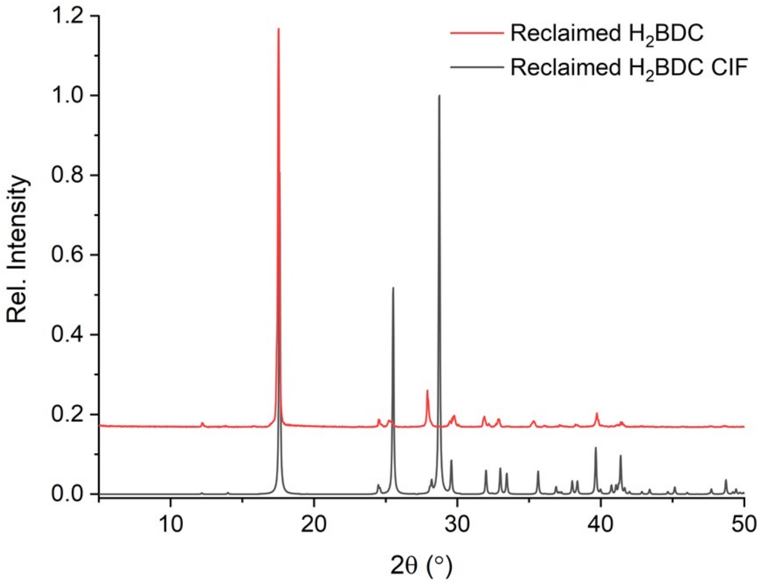

Figure S26. PXRD pattern comparison of H_2BDC reclaimed from PET plastic to the crystal structure pattern.

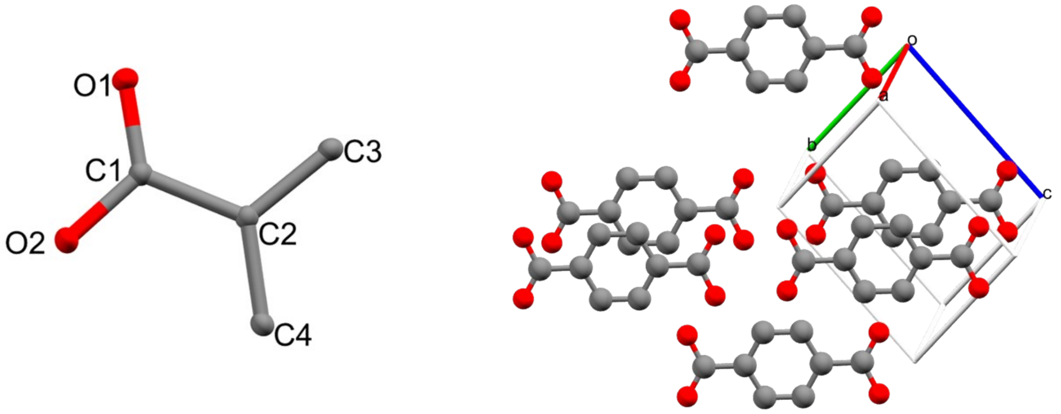

Figure S27. (Left) Asymmetric unit of terephthalic acid from hydrolysed PET plastic bottles. Thermal ellipsoids are set to 40% probability. (Right) Crystal packing of H_2BDC. Red = oxygen and grey = carbon. Hydrogen atoms have been omitted for clarity.

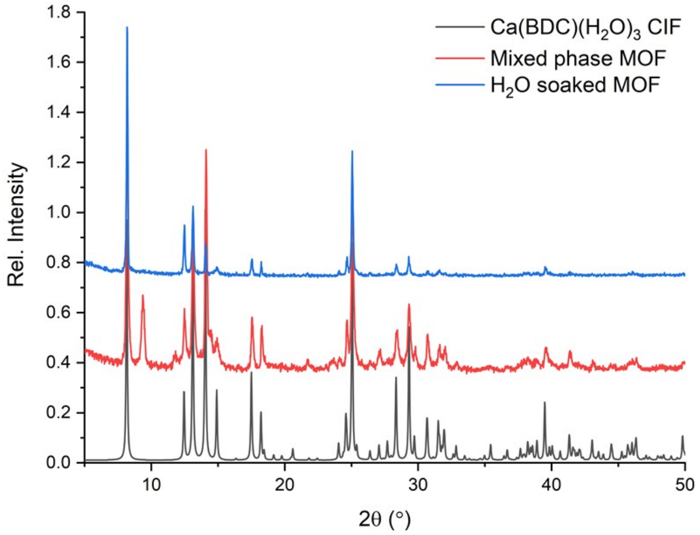

Figure S28. PXRD comparison of mixed phase Ca(BDC) MOF to sample that has been immersed in deionised water to recover Ca(BDC)(H_2O)$_3$. The presence of a peak at 9.4 ° corresponds to the dehydrated phase in the mixed phase sample.

Table S1. pKa values of utilised organic linkers for the formation of Ca-MOFs.

Organic linker	**pKa values (at 25 °C)**
Squaric acid[3]	pK_1 = 0.5 – 1.2 pK_2 = 2.2 – 3.5
Fumaric acid[4]	pK_1 = 2.9 pK_2 = 4.3
Terephthalic acid[5]	pK_1 = 3.5 pK_2 = 4.8

Table S2. Crystal data and structure refinement information for H_2BDC from PET plastic hydrolysis.

Empirical Formula	$C_4H_3O_2$
Formula Weight	83.06
Temperature/K	100
Crystal System	triclinic
Space Group	P-1 (2)
a/Å	3.6762(4)
b/Å	6.3654(8)
c/Å	7.4242(11)
α/°	83.688(11)
β/°	79.779(12)
γ/°	87.413(10)
Volume/Å^3	169.88(4)
Z	2
ρ_{calc}g/cm^3	1.624
μ/mm^{-1}	0.133
Crystal size/mm^3	0.20×0.02×0.02
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	2.803 to 31.988
Reflections collected	1891
Independent reflections	969 [R_{int}=0.0298]
Data/restraints/parameters	969/0/59
Final R indexes [all data]	R_1= 0.0677, wR_2=0.1474
Final R indexes [I>=2σ (I)]	R_1= 0.0537, wR_2 = 0.1477

Table S3. Unit cell parameter comparison between the collected and reported H_2BDC crystal structure.

	H_2BDC from hydrolysed PET	**H_2BDC from CCDC deposition 2042484.**[7]
Space group	P-1 (2)	P-1 (2)
a / Å	3.6762(4)	3.744(2)
b / Å	6.3654(8)	6.441(4)
c / Å	7.4242(11)	7.398(5)
α / °	83.688(11)	83.214(17)
β / °	79.779(12)	80.642(17)
γ / °	87.413(10)	88.464(15)

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