

Supporting Information to the article: Synthesis and characterization of calcium dicarboxylates for thermochemical energy storage

## Synthesis

### Preparation of Calcium malonate dihydrate

To a solution of malonic acid (5.2 g, 50 mmol) in 250 ml deionized water, calcium carbonate (5 g, 50 mmol) was slowly added. The reaction was stirred until no further CO<sub>2</sub> formation could be observed, giving a white suspension which was then heated to 70 °C for 2 h. The suspension was allowed to cool to room temperature and left over night. The white precipitate was collected by filtration, washed with deionized water twice, and dried at 40 °C in vacuo. The product was obtained as a white solid (7 g, 49.25 mmol; 98.5 %)

### Preparation of Calcium glutarate monohydrate

Calcium glutarate was prepared by mechanochemical means. Glutaric acid (CAS 110-94-1) with a purity of 99 % from BLD Pharmatech was used without further purification. Commercially available calcium hydroxide (CAS 1305-62-0) was used as calcium source. CaOH was obtained from ThermoFisher Scientific and used as supplied.

Glutaric acid (0.64 g, 4.8 mmol) and calcium hydroxide (0.36 g, 4.8 mmol) were put in a ball mill, 130 µl deionized water were added and milled for 4 h. The product was obtained as light brown powder (0.75 g, 4.41 mmol, 91.8 %).

### Preparation of Calcium terephthalate trihydrate

Terephthalic acid (0.69 g, 4.15 mmol) and calcium hydroxide (0.31 g, 4.15 mmol) were put in a ball mill, 130 µl deionized water were added and milled for 4 h. The product was obtained as white powder (0.84 g, 4.11 mmol, 99.1 %).

### Preparation of 2-methyl calcium terephthalate hydrate

#### *Preparation of 2-methyl terephthalic acid*

To a solution of 2,5-dibromotoluene (4.23 ml, 30 mmol) in hexane (60 ml) 1.6 M n-butyllithium in hexane (70 ml, 841 mmol) was added. The mixture was heated to 60 °C for 20 h, cooled to rt and poured to a mixture of dry ice in 600 ml diethyl ether. After the mixture warmed up to room temperature, 3 N HCl was added until pH 1 was reached. The mixture was extracted with Et<sub>2</sub>O, washed with water, dried over MgSO<sub>4</sub>. Removing the solvent under reduced pressure yielded the product as a brown powder (3.9 g, 21.6 mmol). To remove hexane completely, the product was dried at 70 °C under vacuo.

#### *Preparation of 2-methyl calcium terephthalate*

*2-methyl terephthalic acid* (0.53 g, 6.49 mmol) and calcium hydroxide (0.21 g, 6.49 mmol) were filled into a ball mill, 130  $\mu$ l deionized water were added and milled for 4 h. The product was obtained as white powder (0.44 g, 1.98 mmol, 69.8 %).

### Preparation of 2-fluoro calcium terephthalate trihydrate

#### *Preparation of 2-fluoro terephthalic acid*

*3-fluoro-4-methylbenzoic acid* (2 g, 12.3 mmol) and  $\text{KMnO}_4$  (6.7 g, 42.4 mmol) were dissolved in an aqueous KOH solution (70 ml, 5 %). The solution was refluxed for 4 h, cooled to room temperature and stirred for 18 h. Afterwards the solution was filtered, and diluted with 50 ml distilled water. The filtrate was acidified by the addition of concentrated HCl until pH 1 was reached. The formation of a white precipitate could be observed, which was collected by filtration, washed with water three times, and dried in vacuo (50 °C). *2-fluoro terephthalic acid* was obtained as a white powder (1.79 g, 9.72 mmol).

$^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  7.97 (t, 1H), 7.83 (dd, 1H), 7.73 (dd, 1H).

#### *Preparation of 2-fluoro calcium terephthalate*

*2-fluoro terephthalic acid* (0.53 g, 6.49 mmol) and calcium hydroxide (0.21 g, 6.49 mmol) were filled into a ball mill, 130  $\mu$ l deionized water were added and milled for 4 h. The product was obtained as white powder (0.44 g, 1.98 mmol, 69.8 %).

### Preparation of 2-fluoro calcium terephthalate disodium salt

*2-fluoro terephthalic acid* (0.5 g, 2.72 mmol) was added to a solution of NaOH (0.22 g, 5.43 mmol) in 50 ml distilled water. After a complete dissolution was observed the mixture was stirred for 1 h and poured into cold acetone. The white precipitate was filtered, washed with  $\text{Et}_2\text{O}$  twice and dried in vacuo at 80 °C for 2 h. The product was isolated as a white/ slightly yellow solid (0.58 g, 2.54 mmol).

### Preparation of 2-chloro calcium terephthalate

#### *Preparation of 2-chloro terephthalic acid*

*3-chloro-4-methylbenzoic acid* (4 g, 23.2 mmol) and  $\text{KMnO}_4$  (12.23 g, 77.38 mmol) were dissolved in an aqueous KOH solution (130 ml, 5 %). The solution was refluxed for 4 h, cooled to room temperature and stirred for 18 h. Afterwards the solution was filtered, and diluted with 100 ml distilled water. The filtrate was acidified by the addition of concentrated HCl until pH 1 was reached. The formation of a white precipitate could be observed, which was collected by filtration, washed with water three times, and dried in vacuo (50 °C). *2-chloro terephthalic acid* was obtained as a white powder (3.75 g, 18.7 mmol, 80.59 %).

#### *Preparation of 2-chloro calcium terephthalate n-hydrate*

2-chloro terephthalic acid (0.8 g, 3.99 mmol) and calcium hydroxide (0.21 g, 3.99 mmol) were filled into a ball mill, 130  $\mu$ l deionized water were added and milled for 4 h. The product was obtained as white powder (0.9 g, 3.75 mmol, 93.99 %).

#### Preparation of Tetrafluoro calcium terephthalate tetrahydrate

Tetrafluoro terephthalic acid (0.76 g, 3.1 mmol) and calcium hydroxide (0.24 g, 3.1 mmol) were filled into a ball mill, 130  $\mu$ l deionized water were added and milled for 4 h. The product was obtained as white/light grey powder (0.76 g, 2.75 mmol, 86.27 %).

#### Preparation of Tetrachloro calcium terephthalate hydrate

Tetrachloro terephthalic acid (0.8 g, 2.5 mmol) and calcium hydroxide (0.2 g, 2.5 mmol) were filled into a ball mill, 130  $\mu$ l deionized water were added and milled for 4 h. The product was obtained as white powder (0.81 g, 2.37 mmol, 90.06 %).

## STA Data

Table S1: DSC and TG data for Figure 3–9

	DSC-onset (°C)	DSC-peak <sub>max</sub> (°C)	heat flow (J g <sup>-1</sup> )	mass-loss (%)
Ca-oxalate monohydrate	158	197	466	12.2
Ca-malonate dihydrate	127	154	637	17.9
Ca-succinate monohydrate	166	191	313	10.2
Ca-glutarate monohydrate	148	189	398	12.1
Ca-terephthalate trihydrate	103	125	695	20.1
2-fluoro Ca-terephthalate n-hydrate	126	157	483	15.6
2-methyl Ca-terephthalate n-hydrate	88	113	262	15.8
Tetrafluoro Ca-terephthalate tetrahydrate	99	126	657	19.0

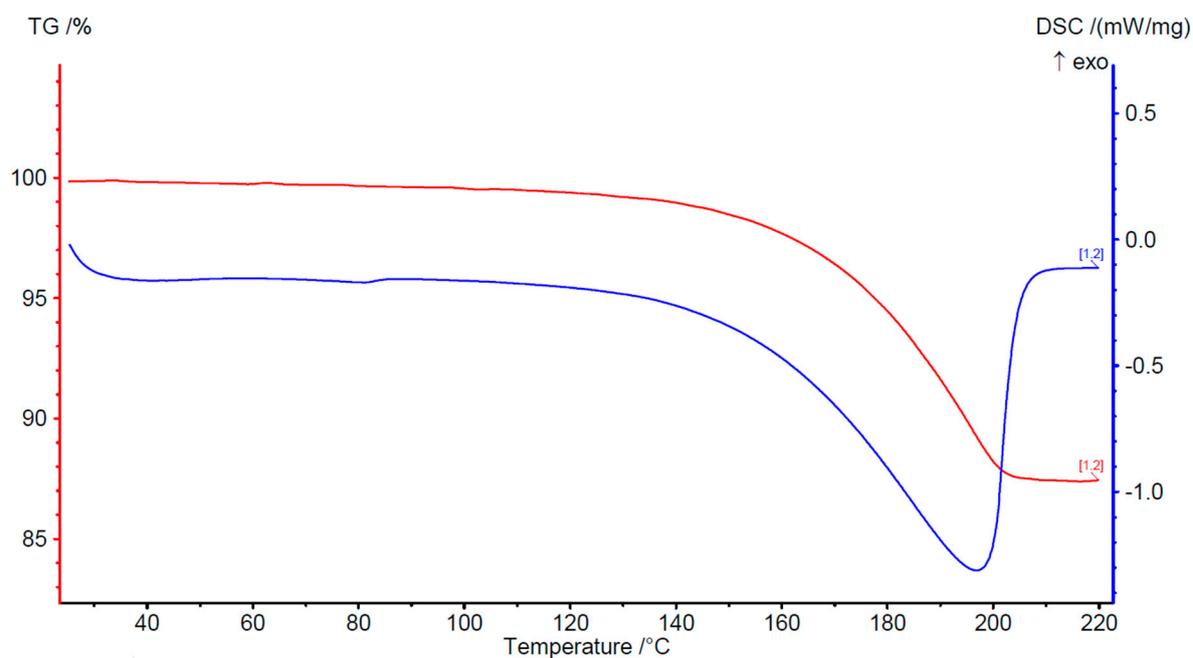


Figure S1: STA of Ca-oxalate monohydrate

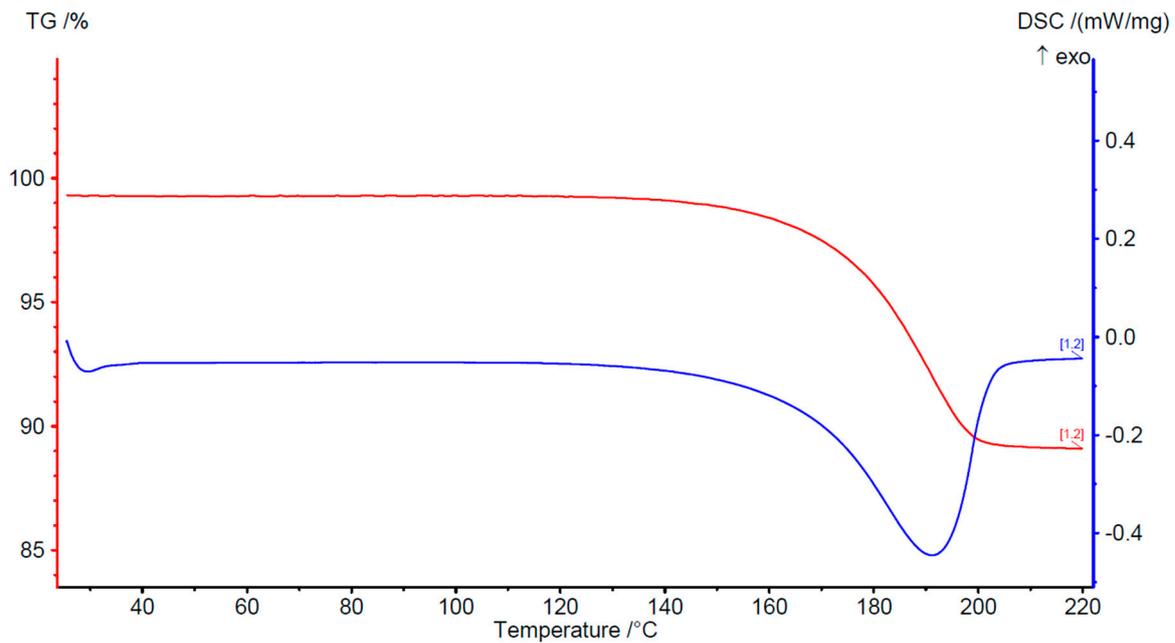


Figure S2: STA of Ca-succinate monohydrate

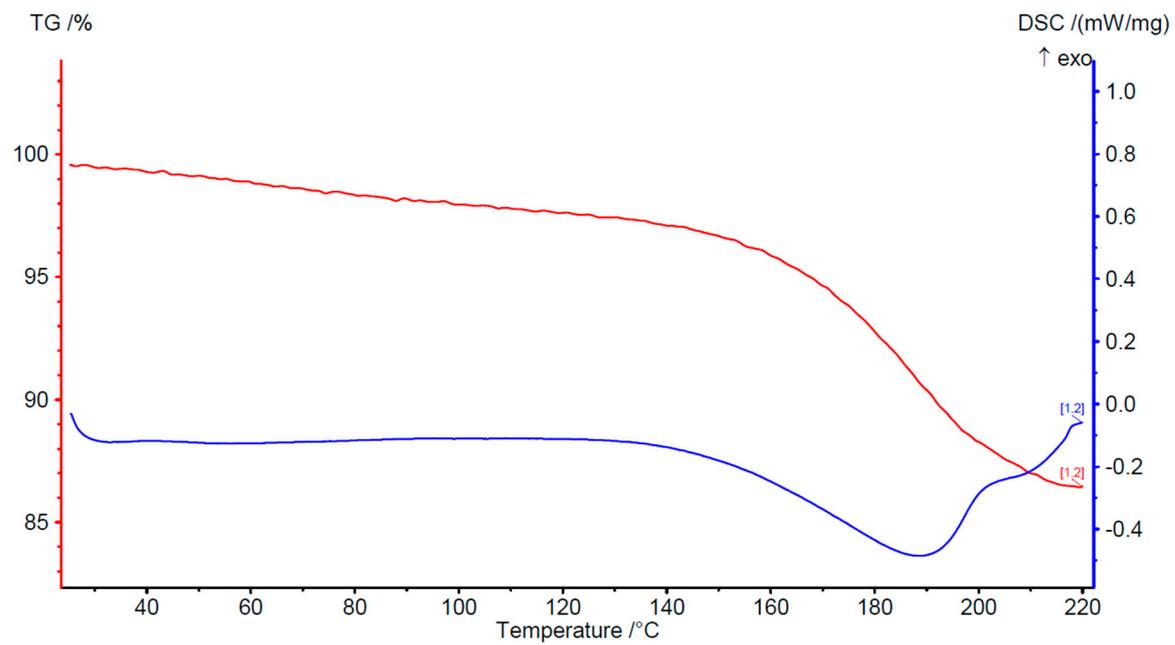


Figure S3: STA of Ca-glutarate monohydrate

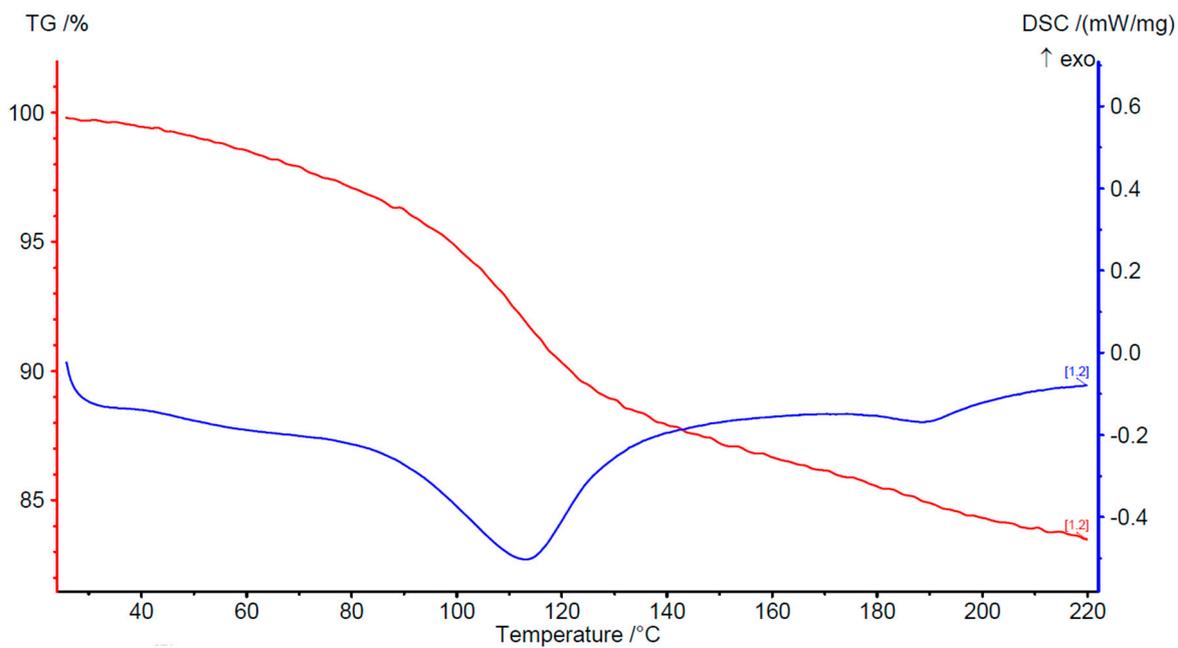


Figure S4: STA of 2-methyl Ca-terephthalate n-hydrate

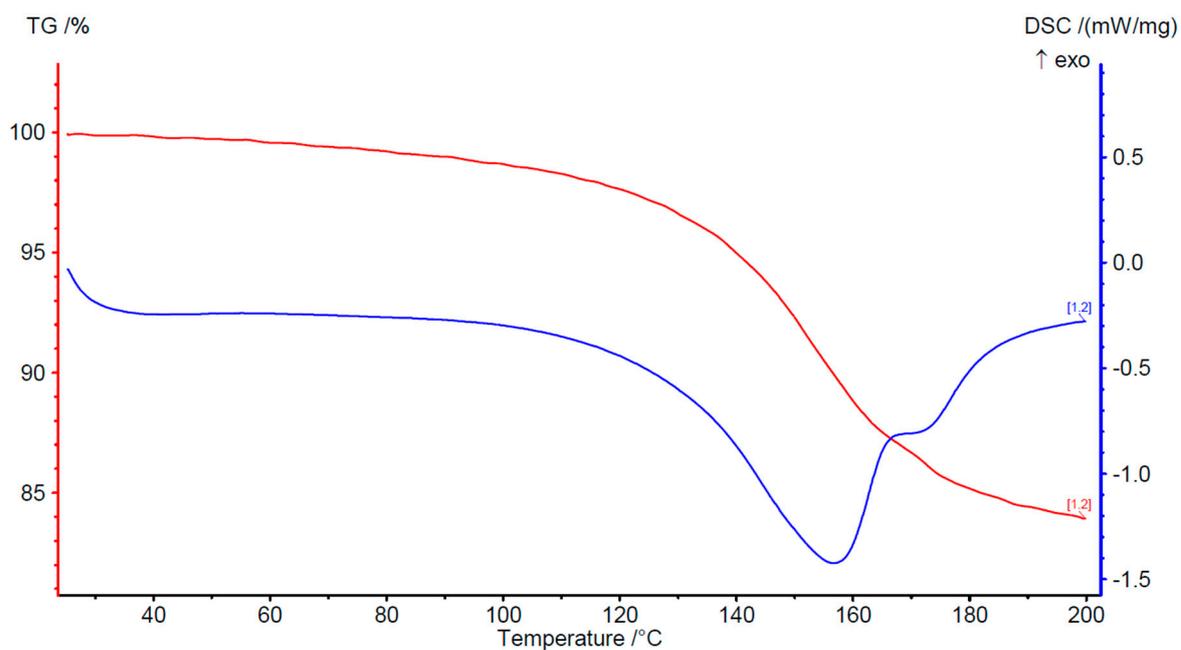


Figure S5: STA of 2-fluoro Ca-terephthalate trihydrate

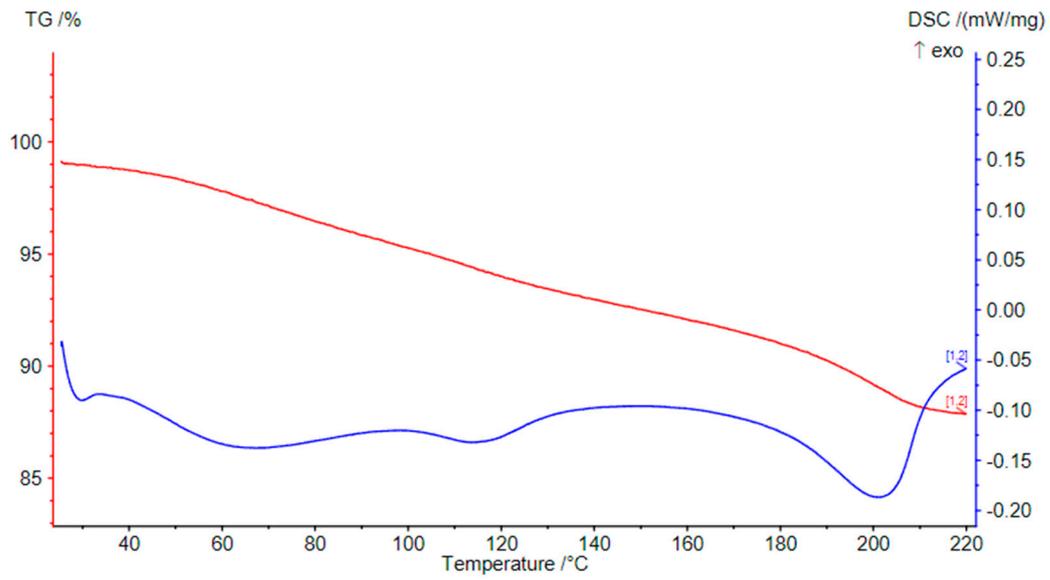


Figure S6: STA of 2-chloro Ca-terephthalate, measurement 1

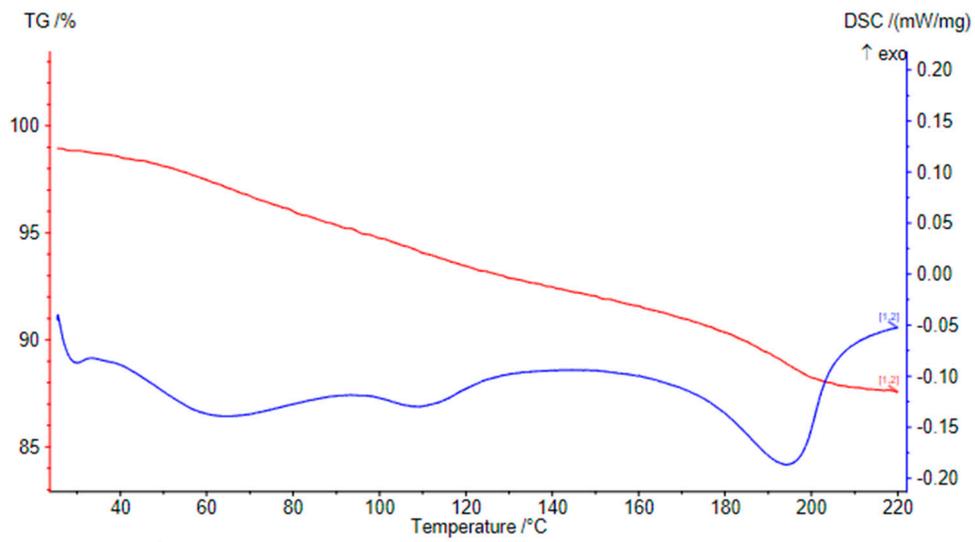


Figure S7: STA of 2-chloro Ca-terephthalate, measurement

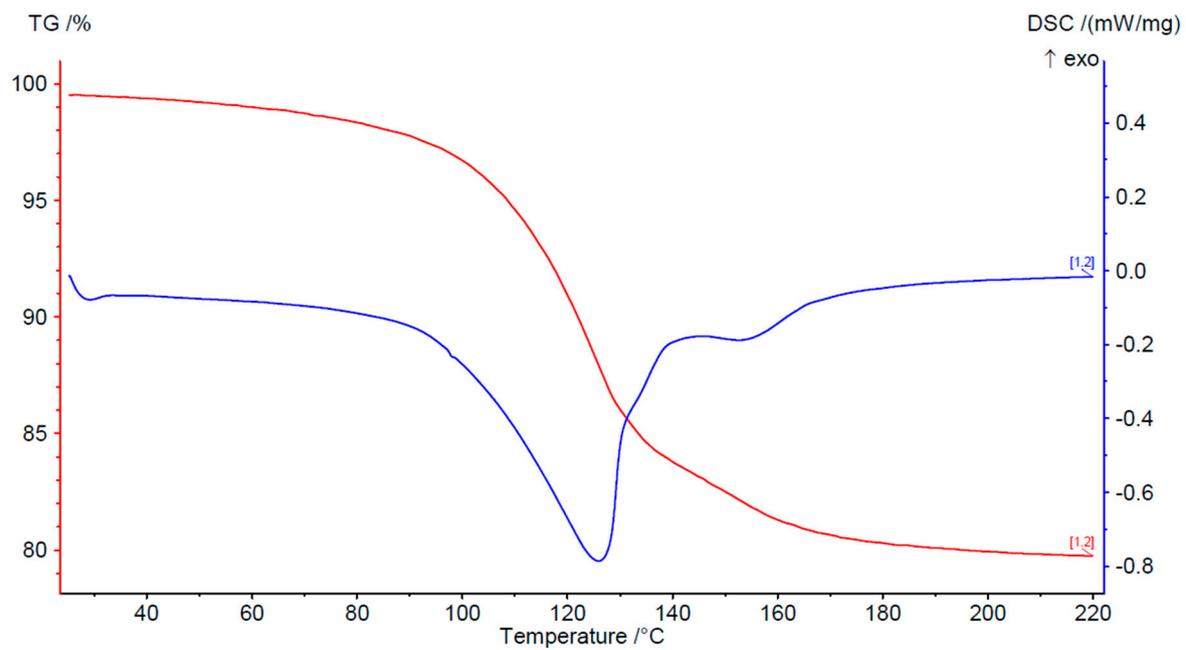


Figure S8: STA of Tetrafluoro Ca-terephthalate tetrahydrate

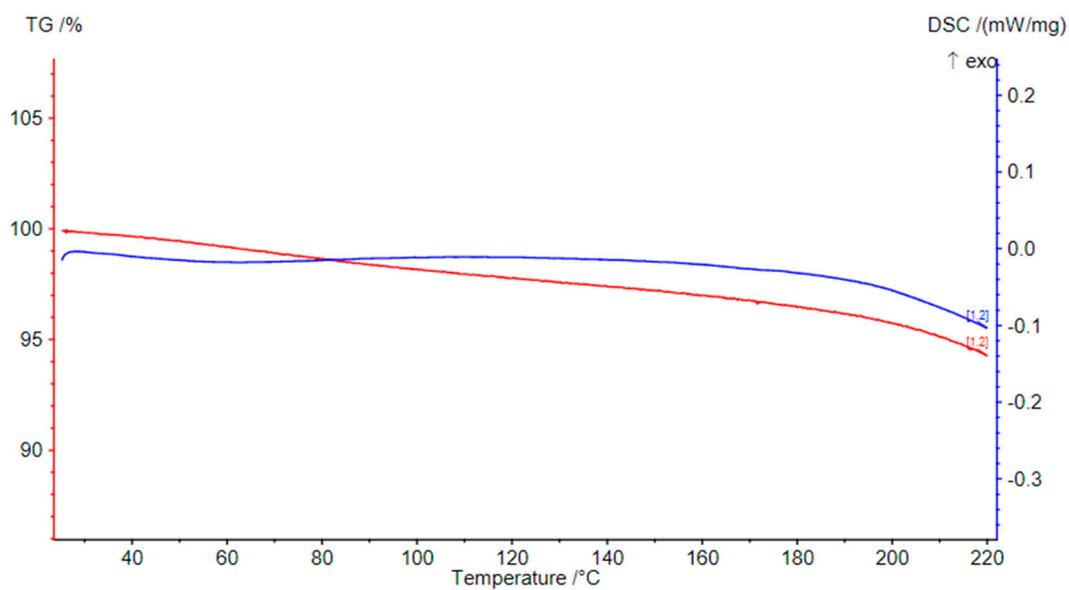


Figure S9: STA of Tetrachloro Ca-terephthalate n-hydrate

# Powder X-ray diffraction patterns

## Ca-oxalate

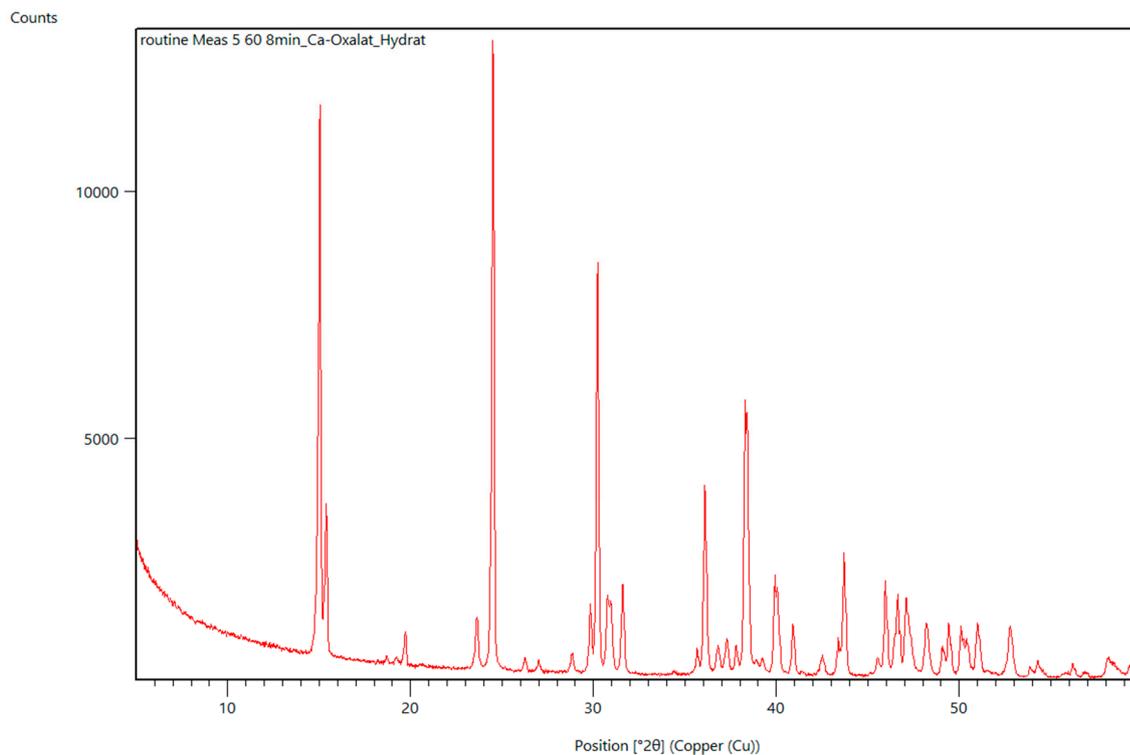


Figure S10: PXRD Ca-oxalate monohydrate

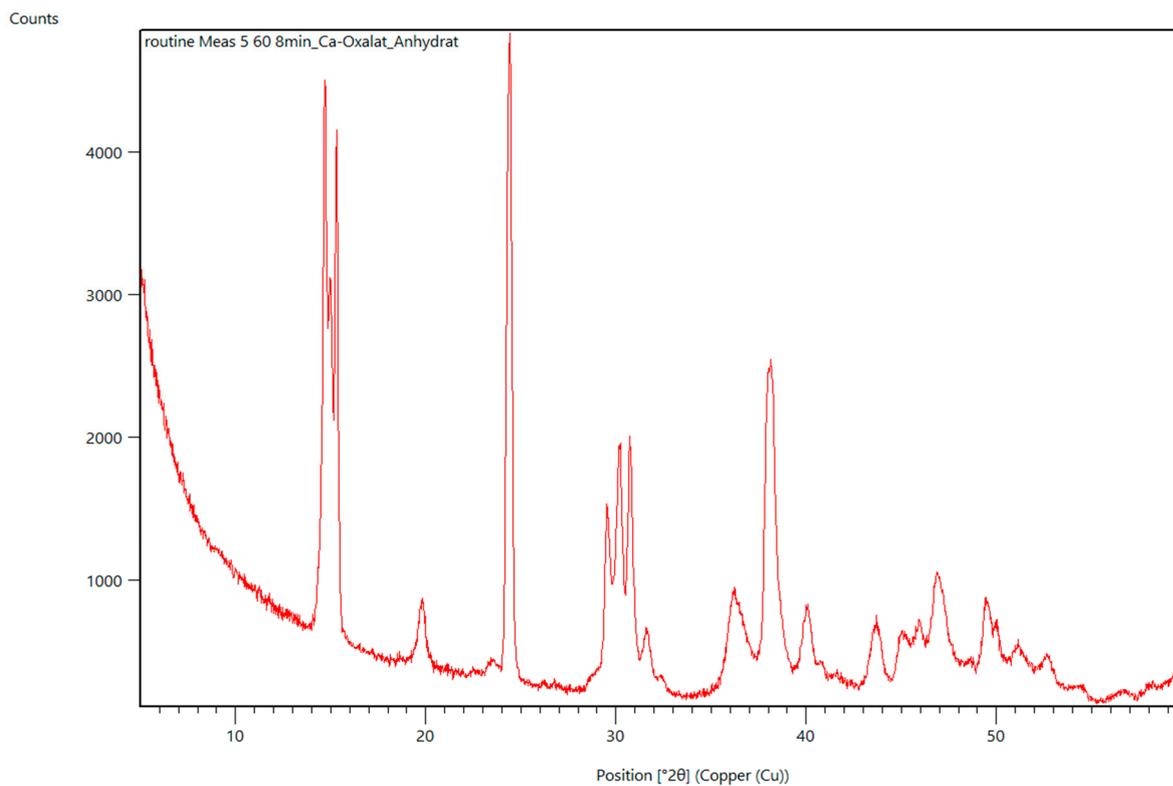


Figure S11: PXRD Ca-oxalate anhydrate

## Ca-malonate

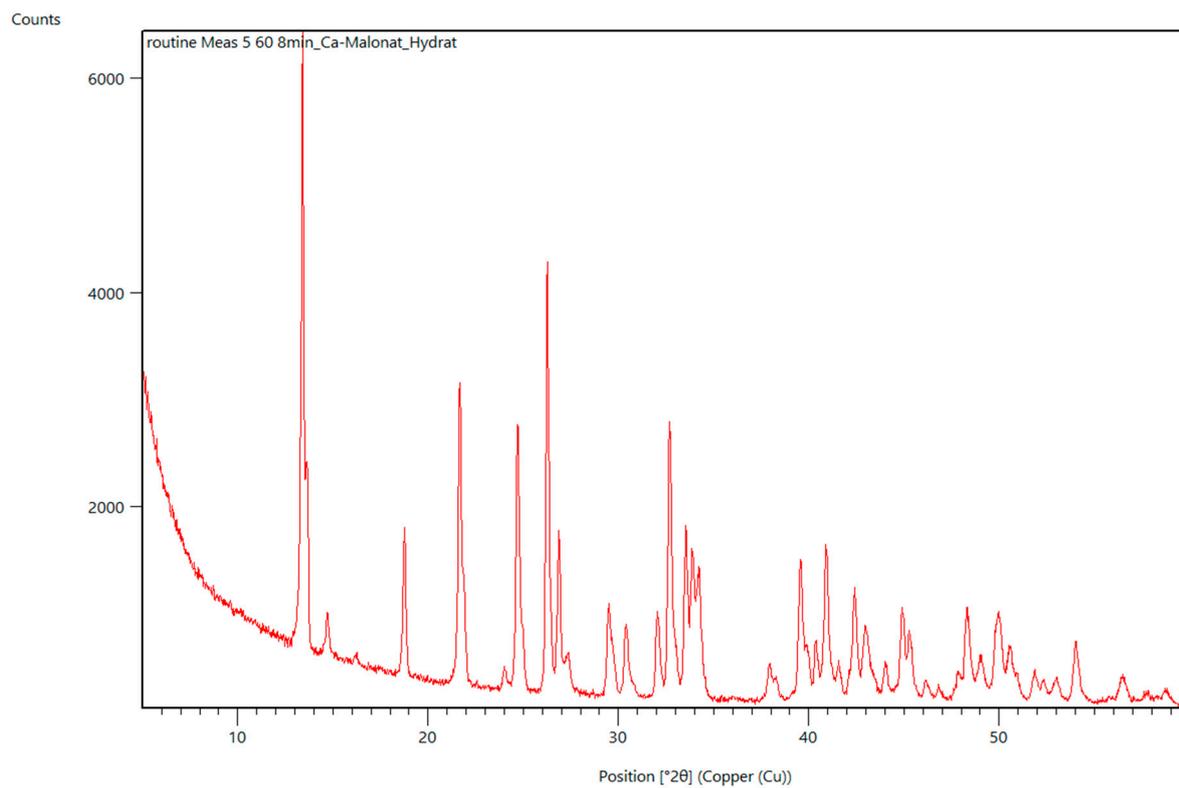


Figure S12: PXRD Ca-malonate dihydrate

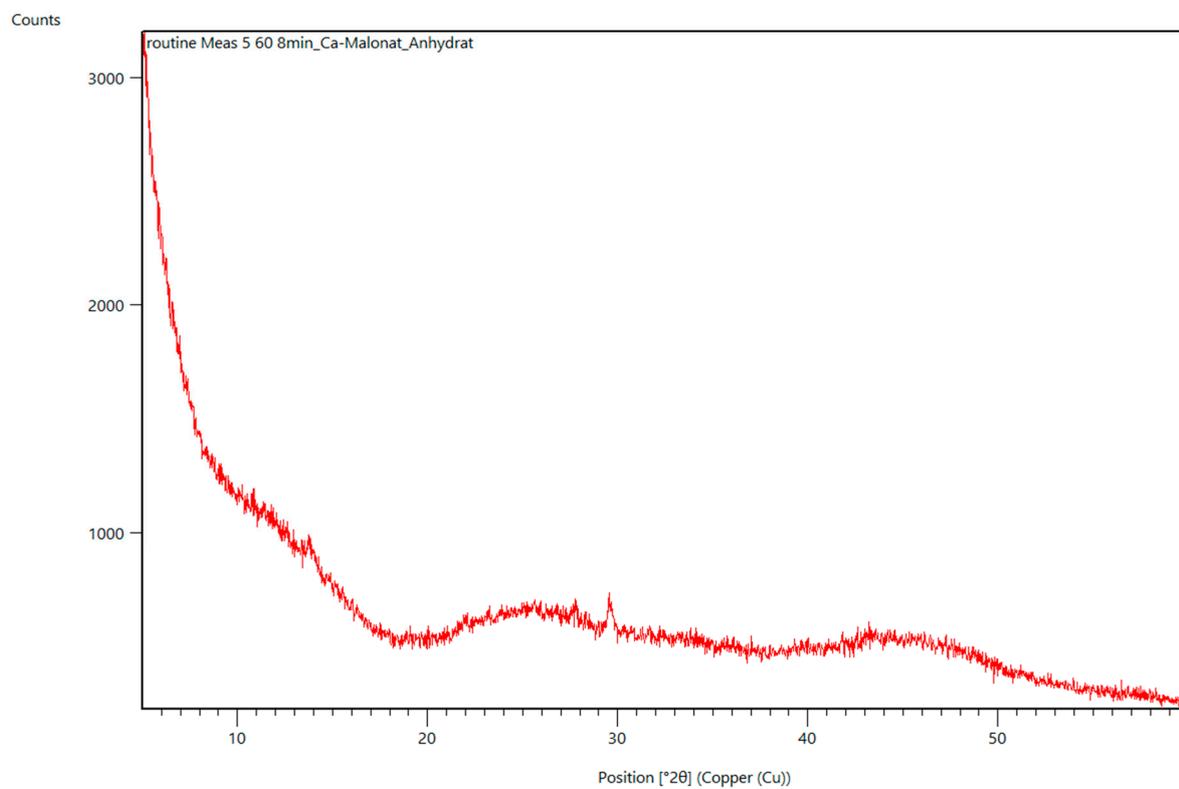


Figure S13: PXRD Ca-malonate anhydrate

## Ca-succinate

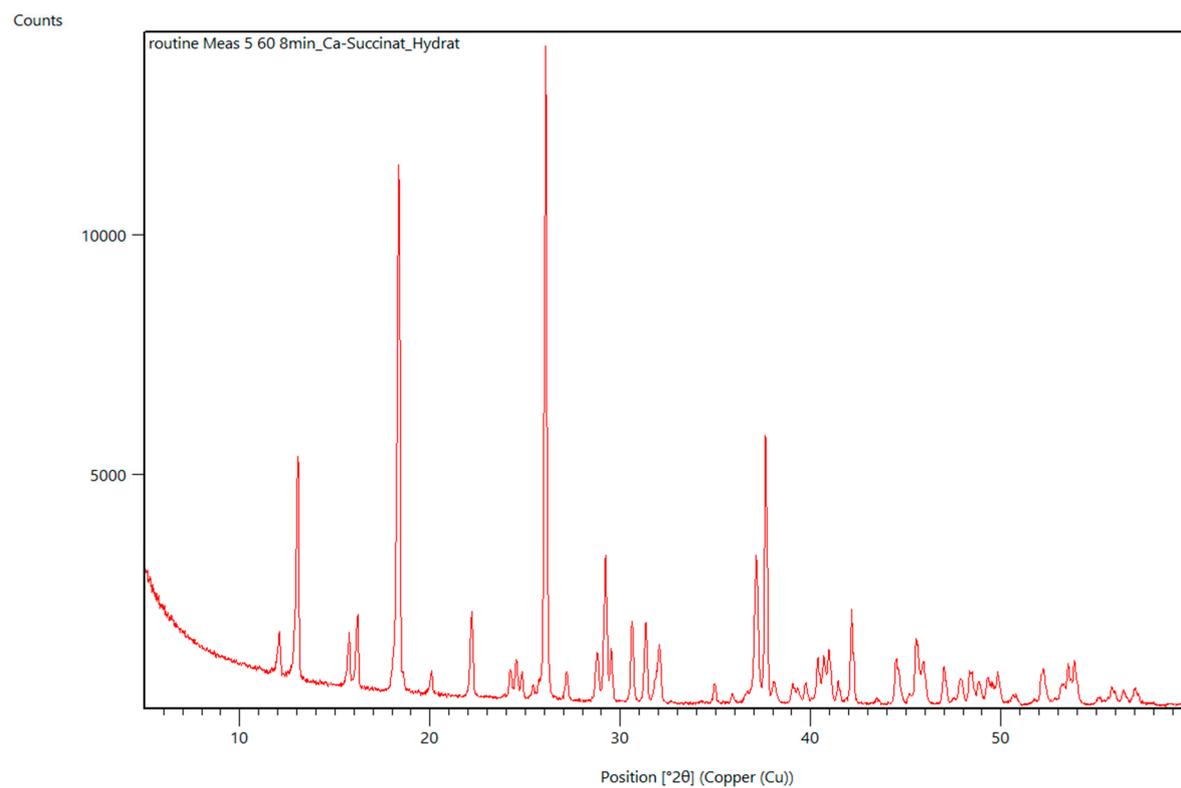


Figure S14: PXRD Ca-succinate monohydrate

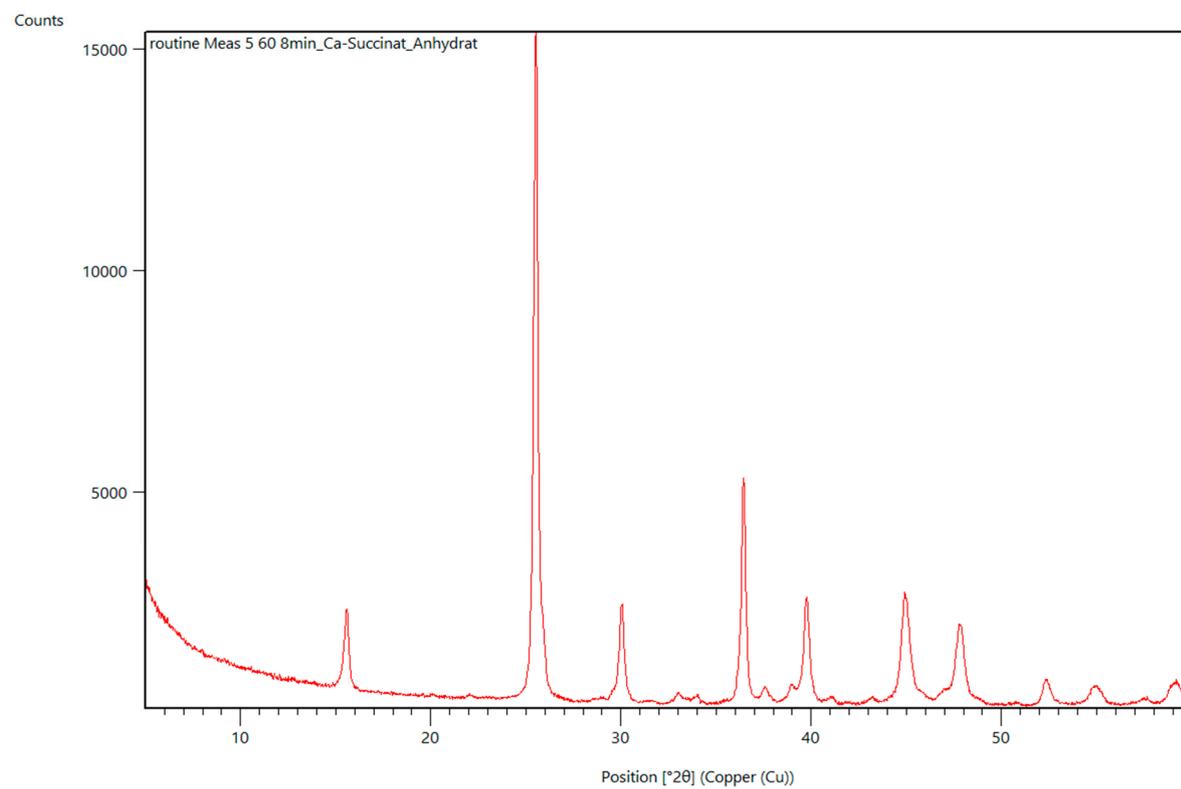


Figure S15: PXRD Ca-succinate anhydrate

## Ca-glutarate

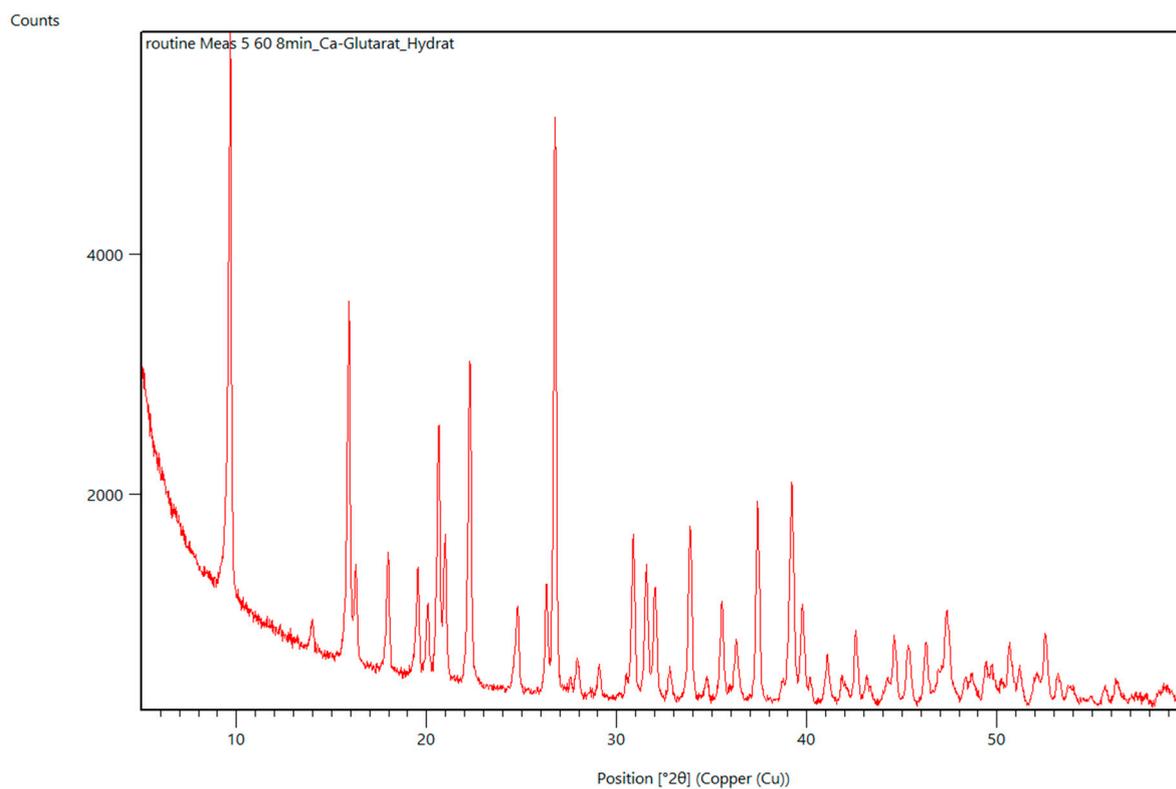


Figure S16: PXRD Ca-glutarate monohydrate

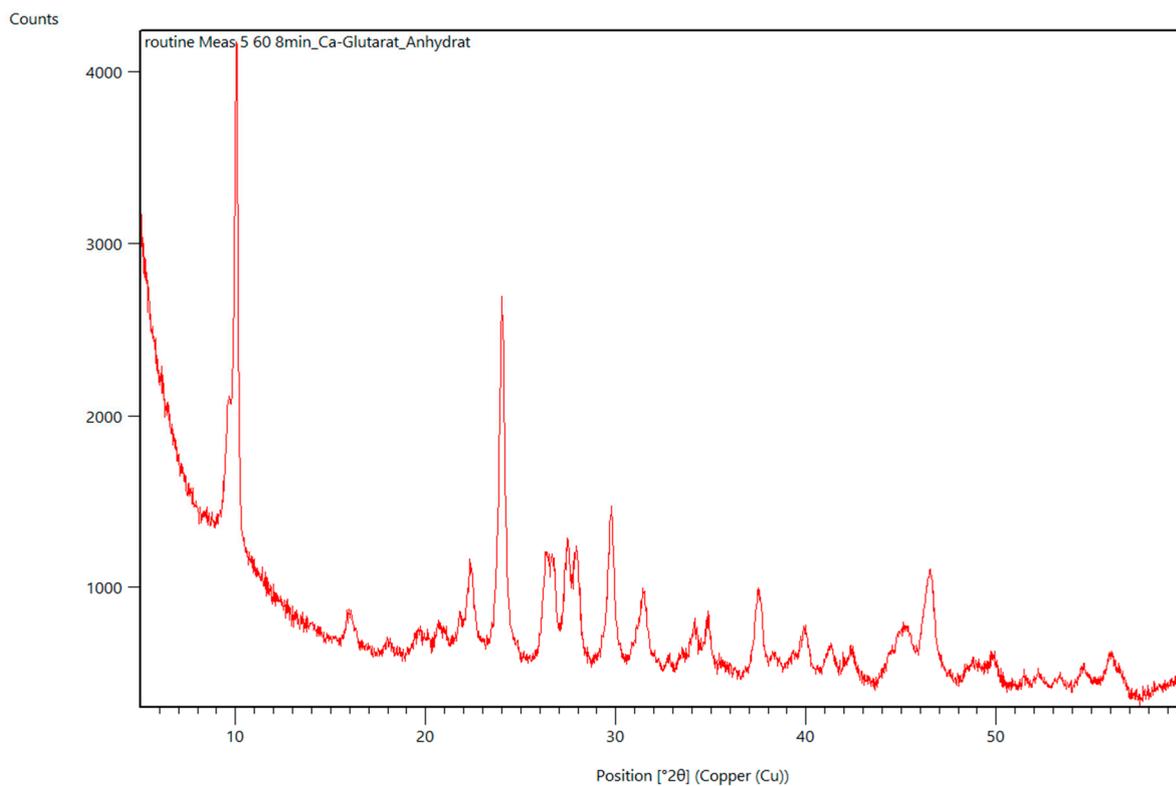


Figure S17: PXRD Ca-glutarate anhydrate

## Ca-terephthalate

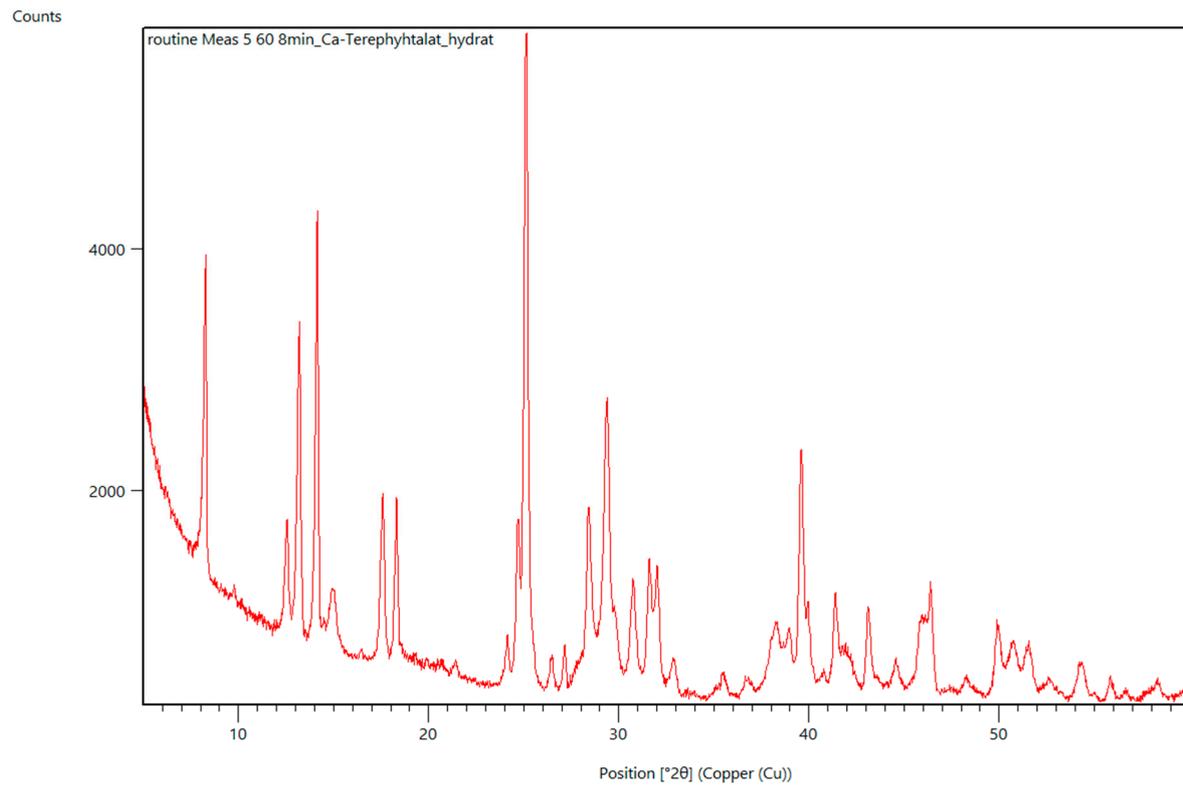


Figure S18: PXRD Ca-terephthalate trihydrate

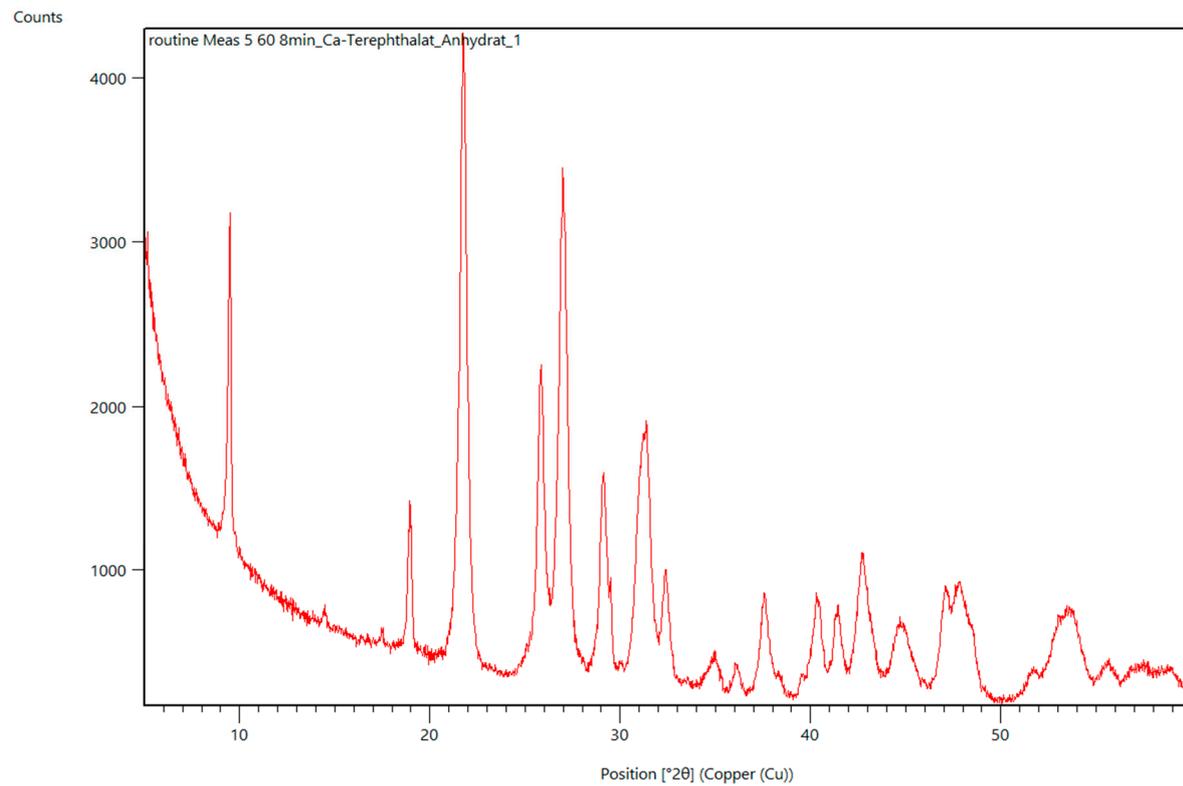


Figure S19: PXRD Ca-terephthalate anhydrate

## 2-fluoro Ca-terephthalate

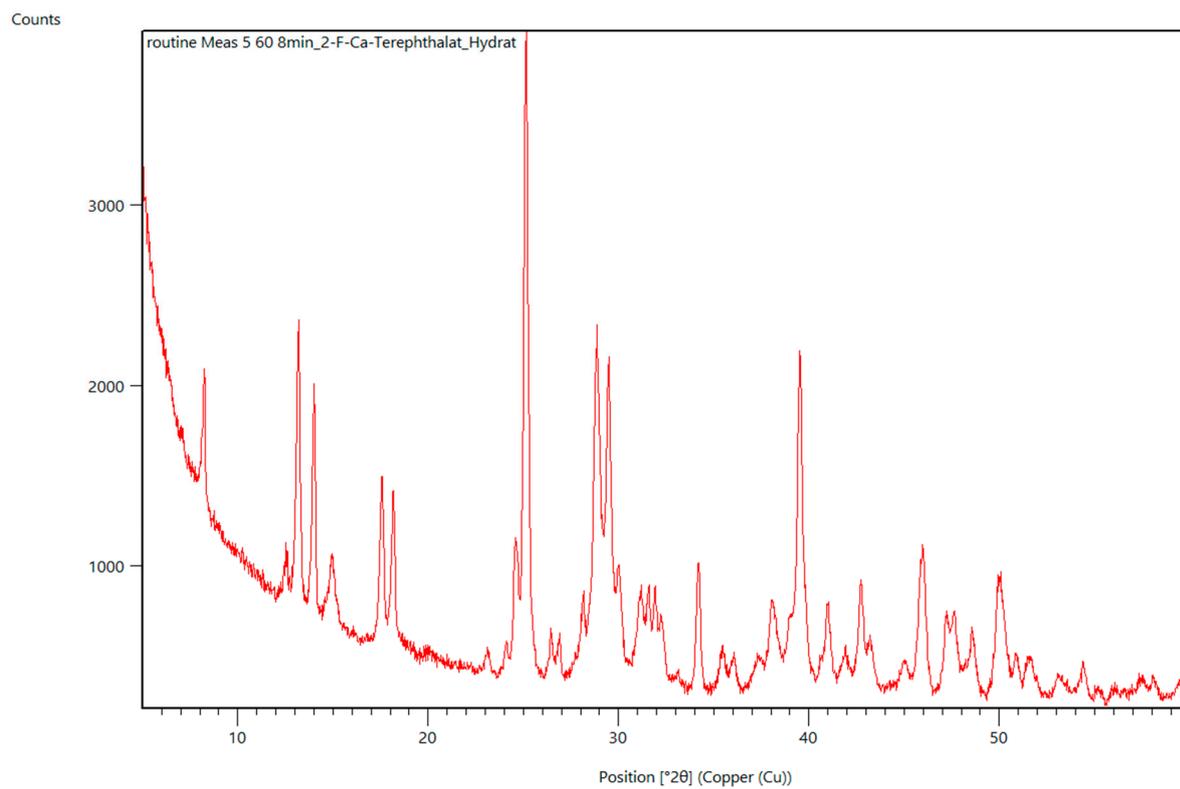


Figure S20: PXRD 2-fluoro Ca-terephthalate trihydrate

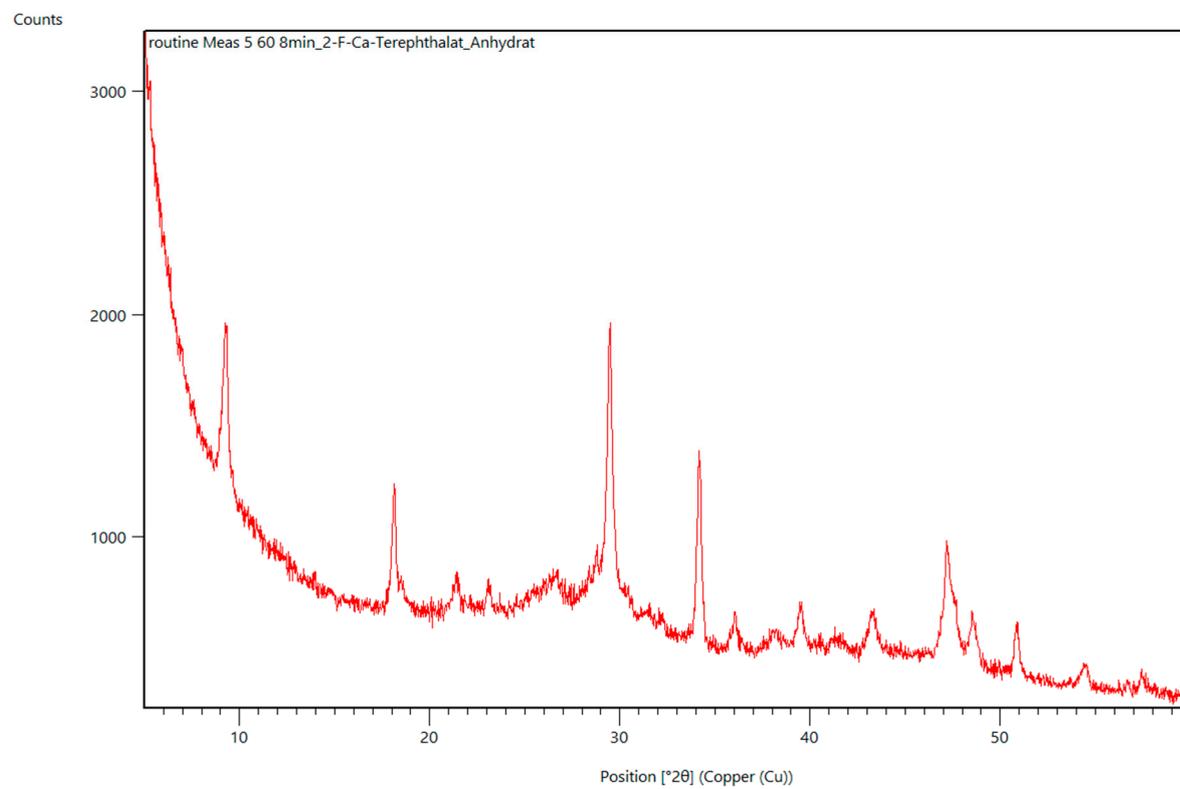


Figure S21: PXRD 2-fluoro Ca-terephthalate anhydrate

## 2-methyl Ca-terephthalate

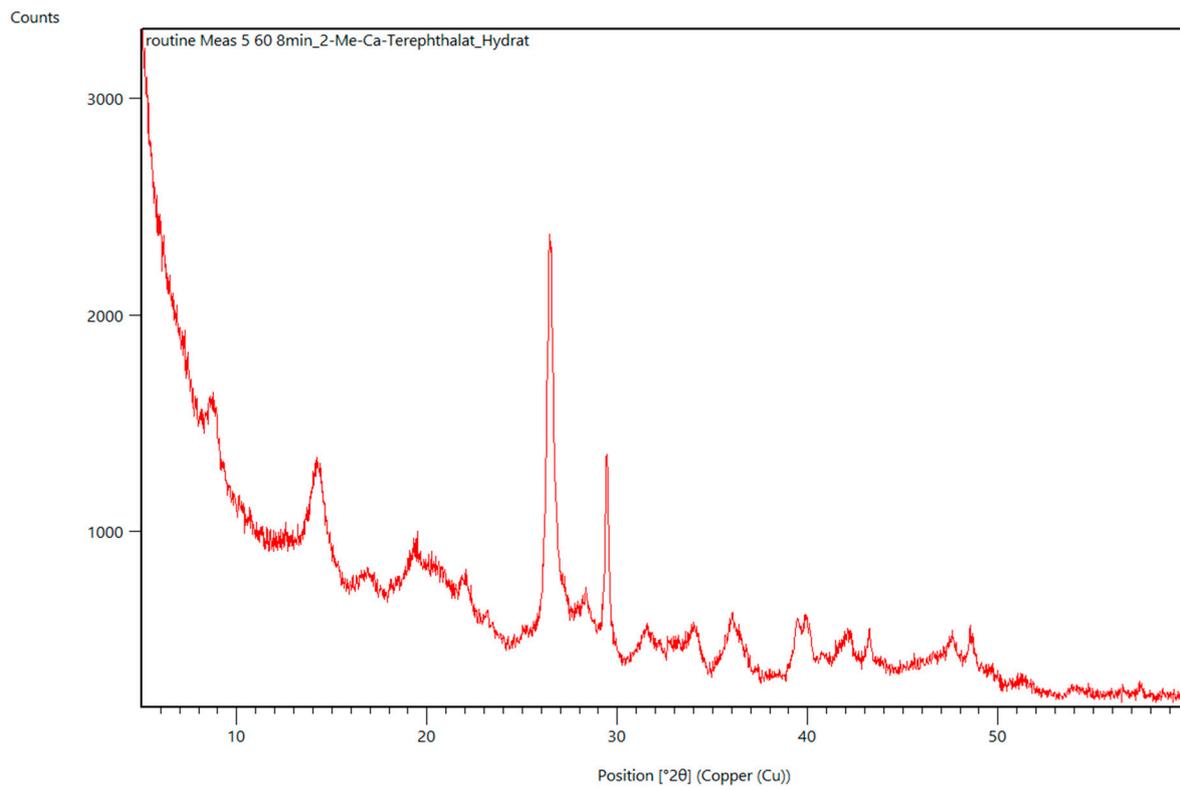


Figure S22: PXRD 2-methyl Ca-terephthalate n-hydrate

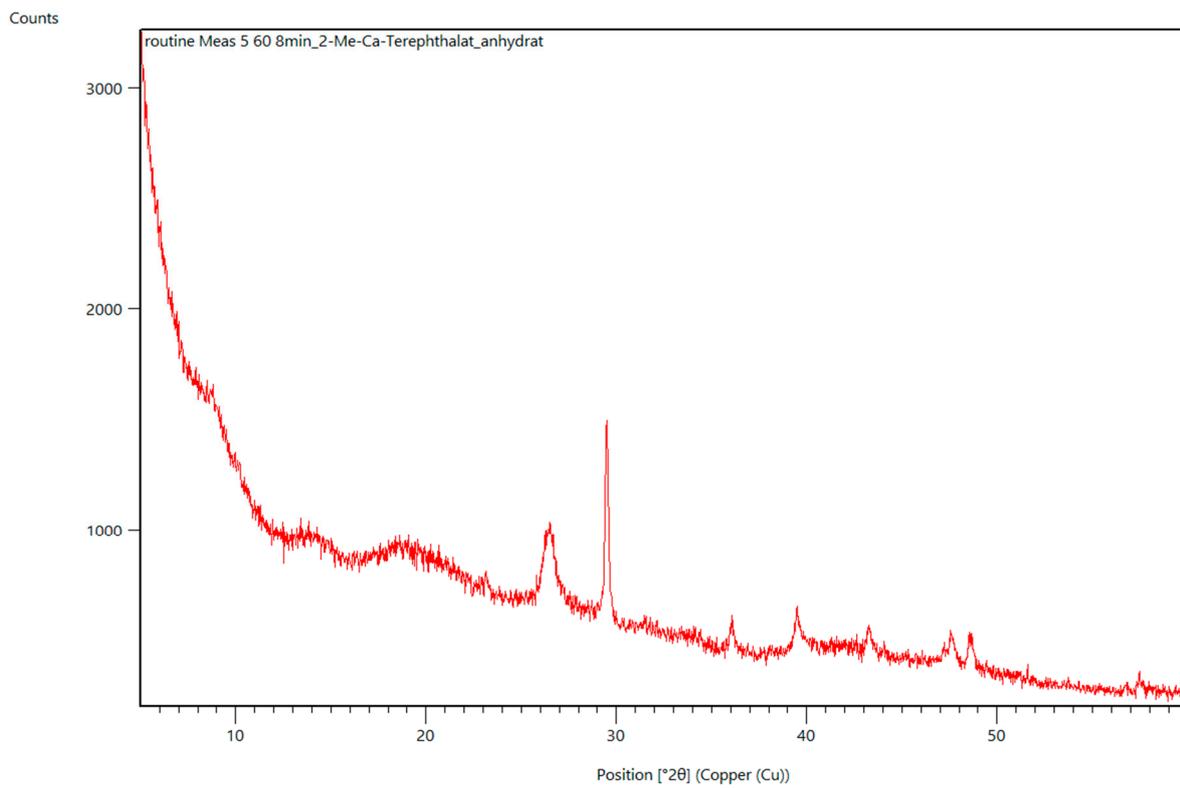


Figure S23: PXRD 2-methyl Ca-terephthalate anhydrate

## IR Spectra

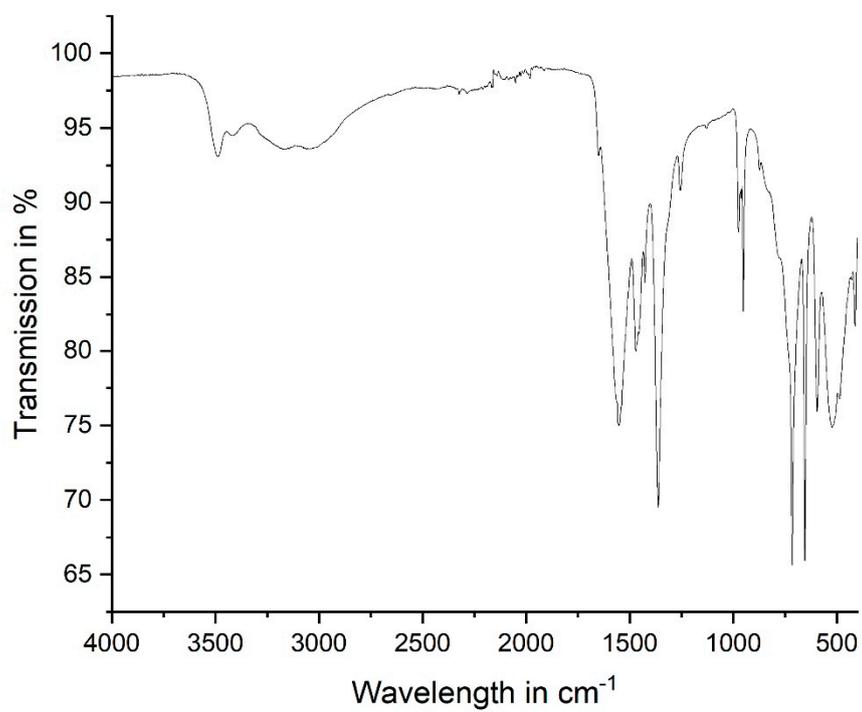


Figure S24: FTIR spectrum of Ca-malonate dihydrate

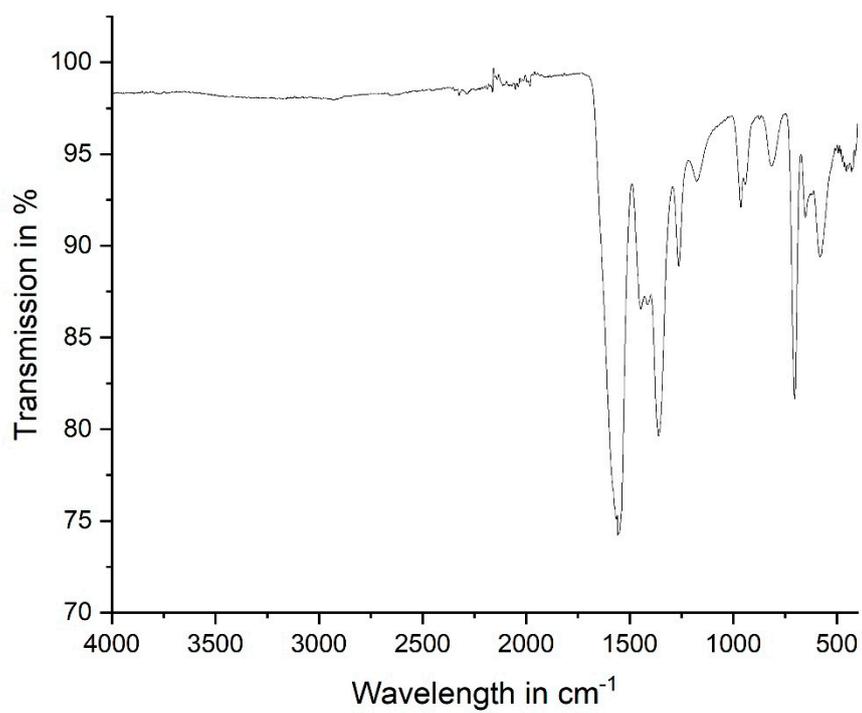


Figure S25: FTIR spectrum of Ca-malonate anhydrous

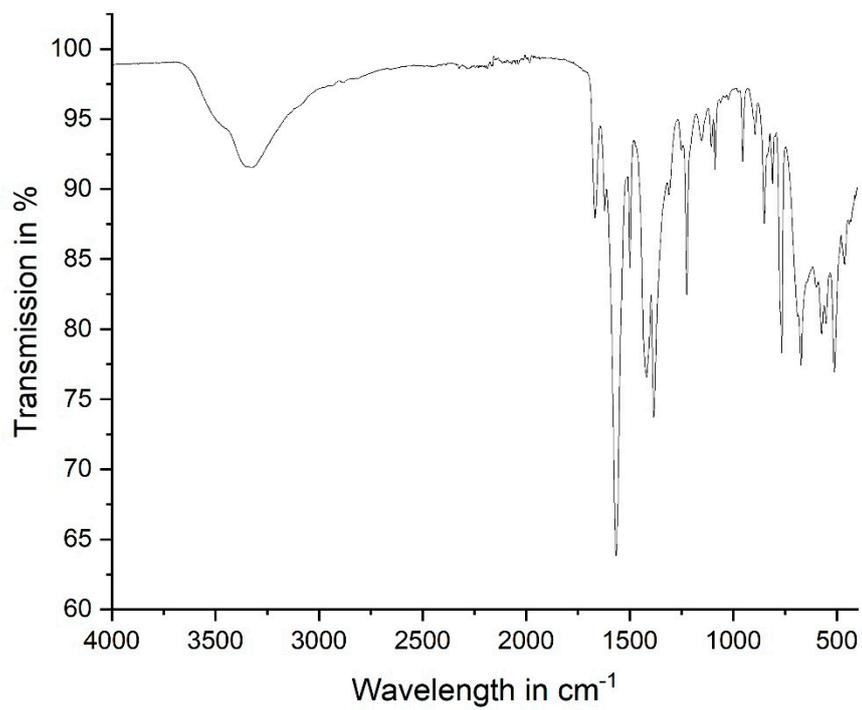


Figure S26: FTIR spectrum of 2-fluoro Ca-terephthalate trihydrate

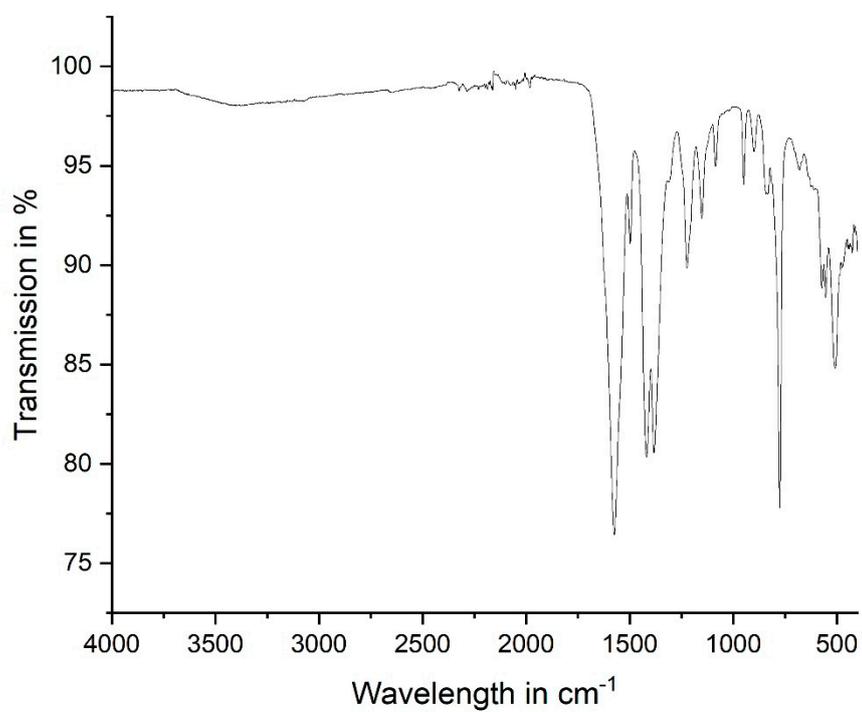


Figure S27: FTIR spectrum of 2-fluoro Ca-terephthalate anhydrate

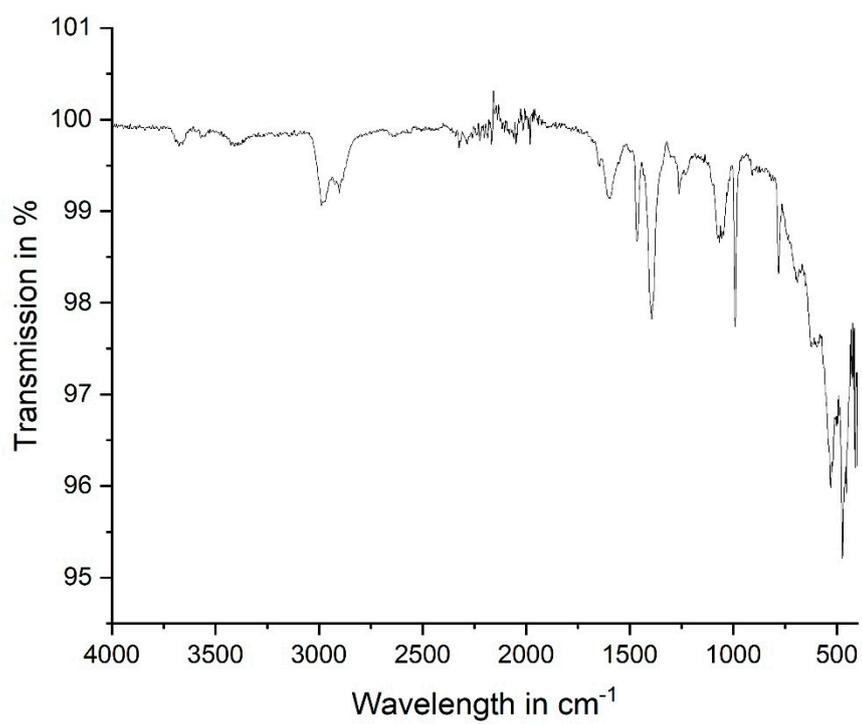


Figure S28: FTIR spectrum of tetrafluoro Ca-terephthalate tetrahydrate

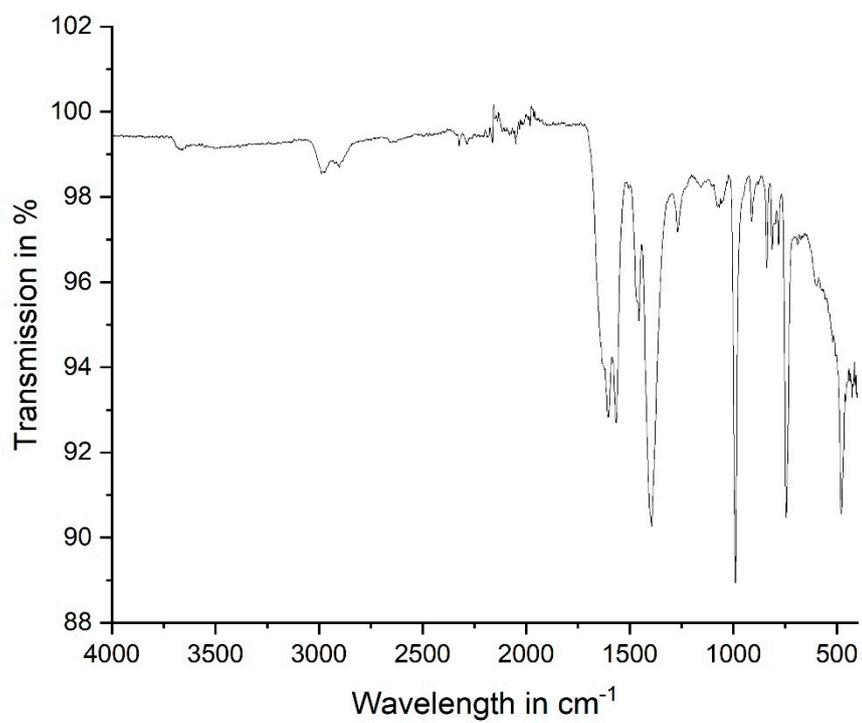


Figure S29: FTIR spectrum of tetrafluoro Ca-terephthalate anhydrate