Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

Calcium Cyclic Carboxylates as Structural Models for Calcium Carbonate Scale Inhibitors

Yuexian Hong,[a] Dmitry S. Yufit,[a] Nathalie Letzelter,[b] Jonathan W. Steed*[a]

(a) Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, United Kingdom
Email:jon.steed@durham.ac.uk
(b) Procter & Gamble Newcastle Innovation Centre, Longbenton, Whitley Road, Newcastle upon Tyne, NE12 9BZ, United Kingdom

Materials

All reagents were purchased commercially and used without further purification.

The PXRD, IR and TGA data for Crystals 2-4

The following figures are drawn by software Plot2.[1]

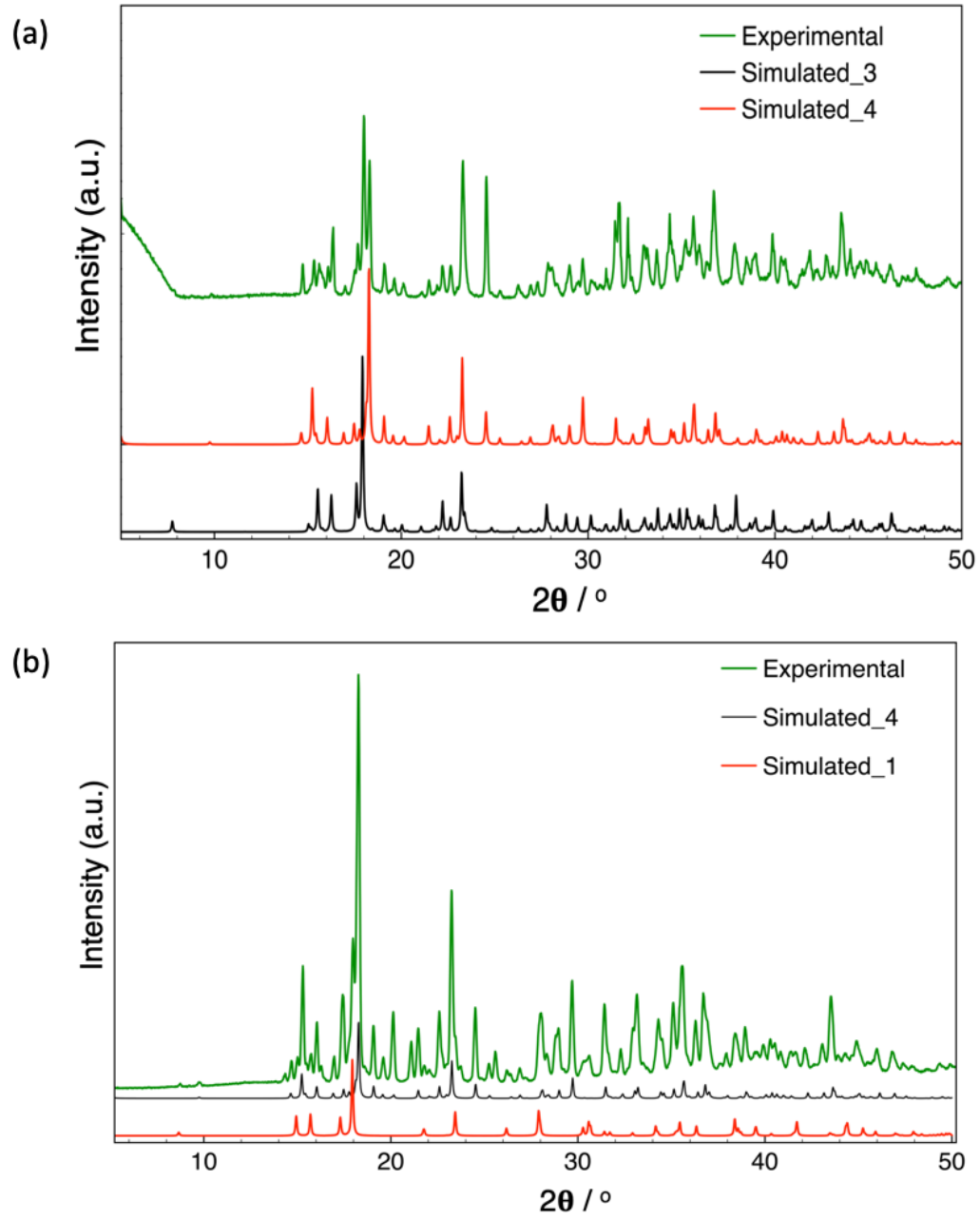

Figure S1. The XRPD patterns plot in a 2θ range of 5° to 50° for new complexes obtained from (a) reactions of $Ca(OH)_2$ with 1,2,3,4-cyclopentanetetracarboxylic acid (CPTCA, a mix of *trans*- and *cis*-), in 1 : 1 ratio, resulted in the crystallisation of $Ca(H_2O)_8][Ca(C_9H_8O_8)_2(H_2O)_4]$ (3), and $[Ca(C_9H_9O_8)_2(H_2O)_4]$ (4); (b) after four months later, this mixture transformed into a mix of $[Ca(\mu\text{-}C_9H_8O_8)(H_2O)_4]_n$ (1)[2] and 4. Experimental pattern and simulated pattern are shown in green, red and black, respectively.

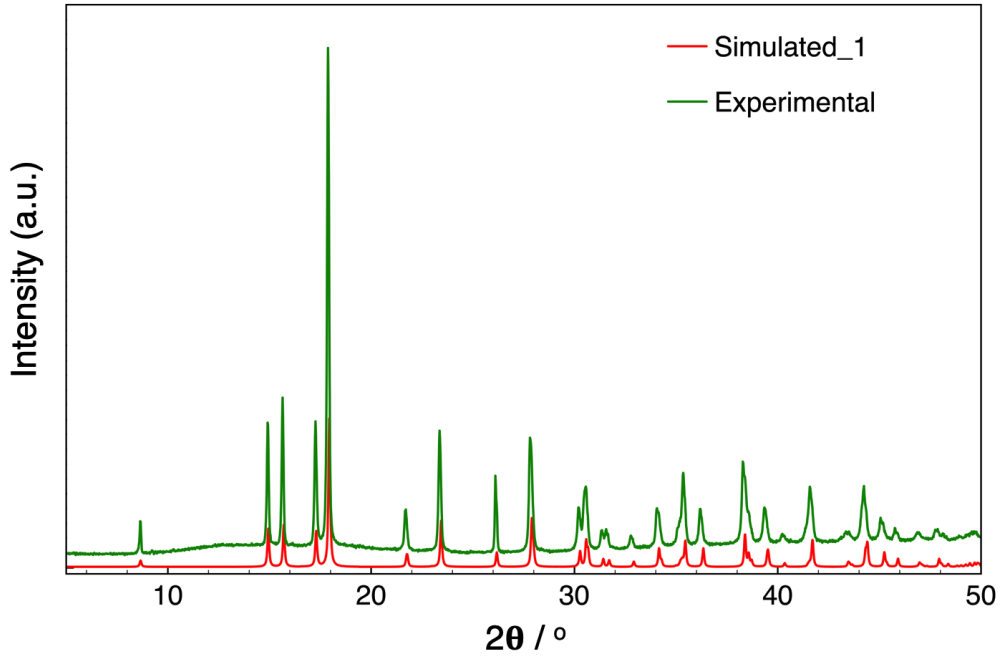

Figure S2. PXRD pattern plot in the 2θ range of 5° to 50° shows the bulk sample of compound $[Ca(H_2O)_8][Ca(C_9H_8O_8)_2(H_2O)_4]\cdot 2H_2O$ (2) transforms in to compound $[Ca(\mu\text{-}C_9H_8O_8)(H_2O)_4]$ (1) upon drying up. Experimental pattern and simulated pattern are shown in green and red, respectively.

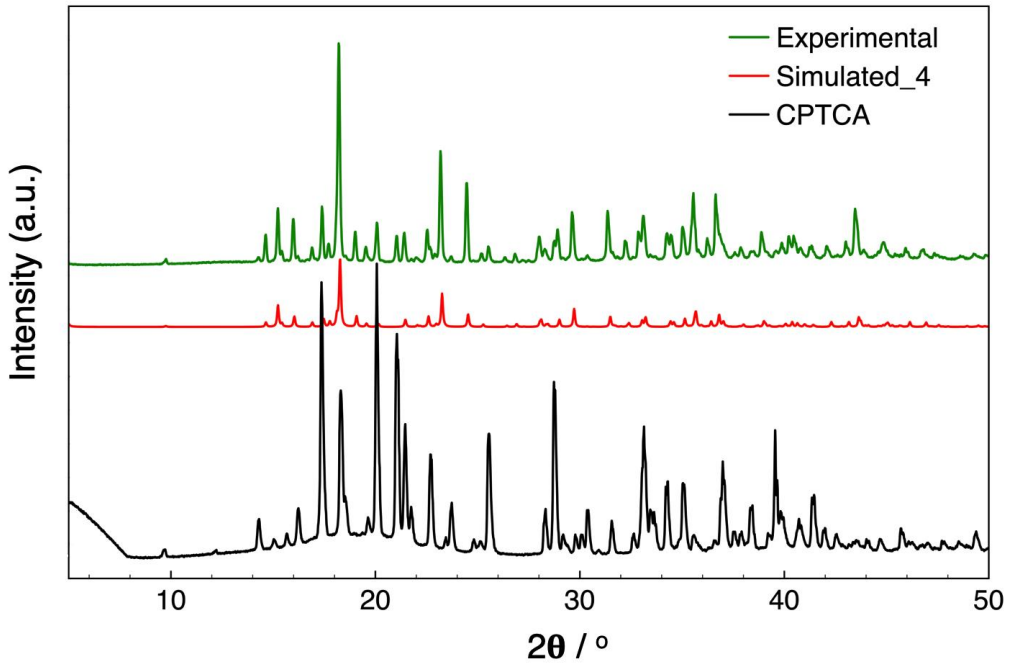

Figure S3. PXRD pattern plot in the 2θ range of 5° to 50° for compound $Ca(C_9H_9O_8)_2(H_2O)_4]$ (4). Experimental pattern and simulated pattern are shown in green and red, respectively; the pattern in black is the original material CPTCA (a mix of *cis*- and *trans*-). The peak positions correspond well with the results simulated from the single crystal data of compound (4). The unmatched peaks belong to CPTCA, which may belong to the unreacted *trans*-CPTCA.

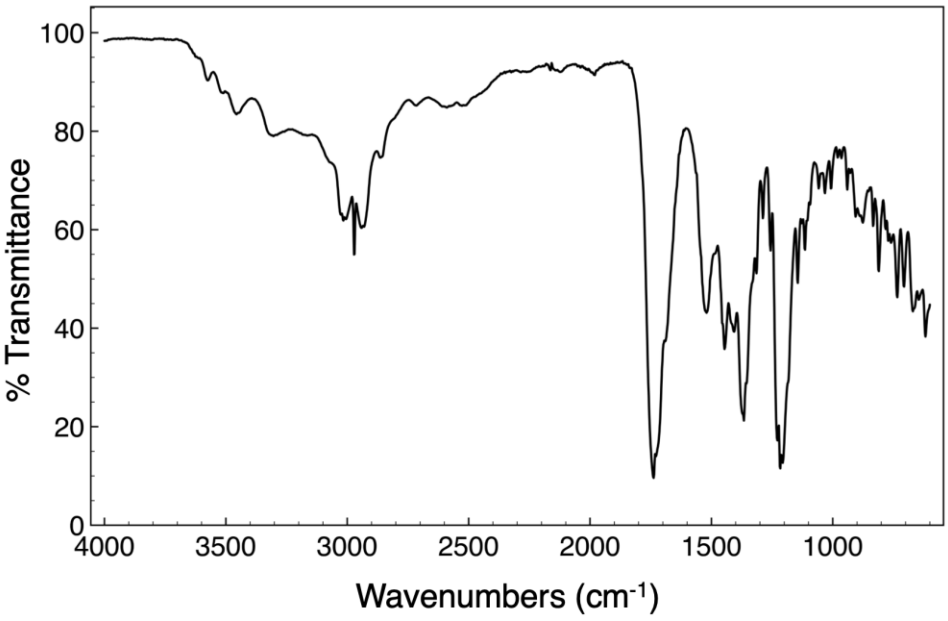

Figure S4. IR spectra for complex [Ca(C$_9$H$_9$O$_8$)$_2$(H$_2$O)$_4$] (4) in the range 4,000 to 400 cm^{-1}.

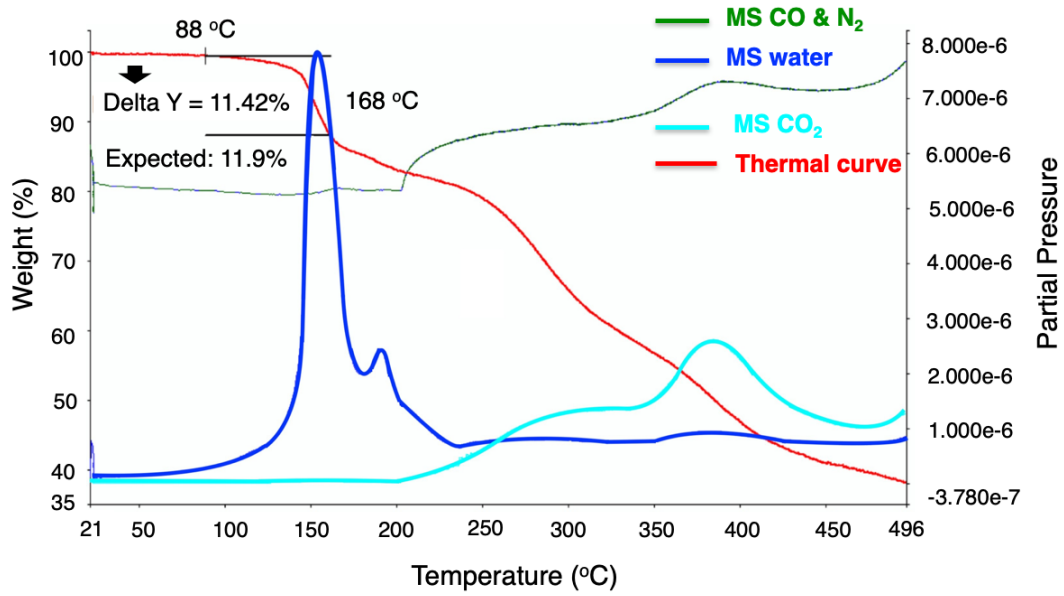

Figure S5. TGA with MS for compound 4. An obvious water loss is observed from 88 °C to 168 °C, followed by ligand decompostion of water, CO and CO$_2$. The water content is calculated from the first peaks, as the second water peak is correlaed with ligand decomposition. Green line for N$_2$ and CO. Blue curve and arctic curves are for water and CO$_2$, respectively. The red curve is for thermal curve and derivative curve, respectively.

The PXRD, IR and TGA data for Crystals 5-7

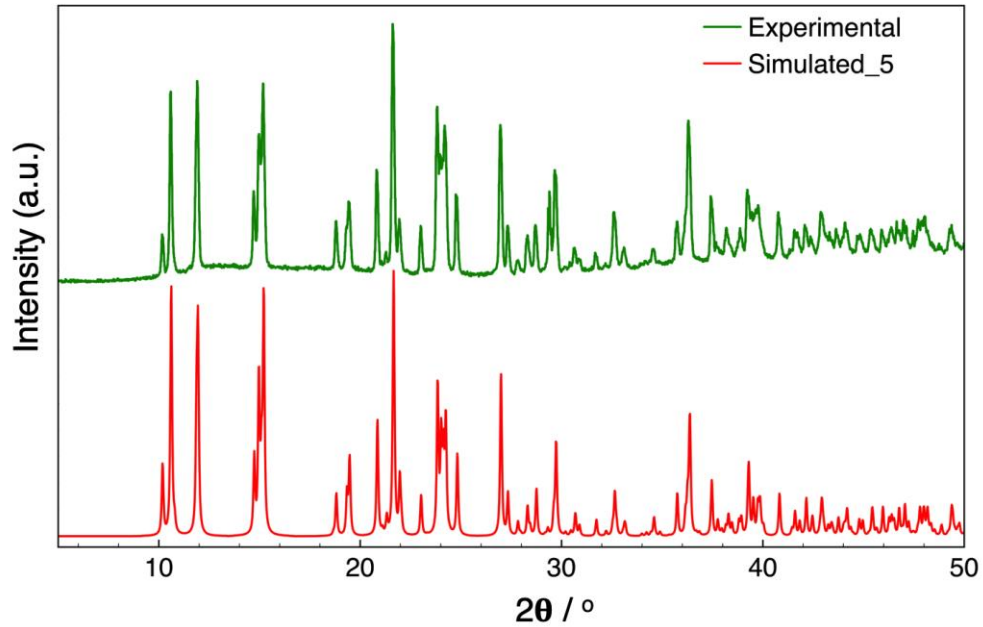

Figure S6. XRPD patterns plot in the 2θ range of 5° to 50° for compound $[Ca_3(C_9H_9O_6)_2(H_2O)_4]\cdot 3H_2O$ (5). The peak positions of the experimental pattern correspond well with simulated from the single crystal data of 5, indicating the purity of the synthesised sample. The experimental pattern and simulated patterns of 5 are shown in green and red, respectively.

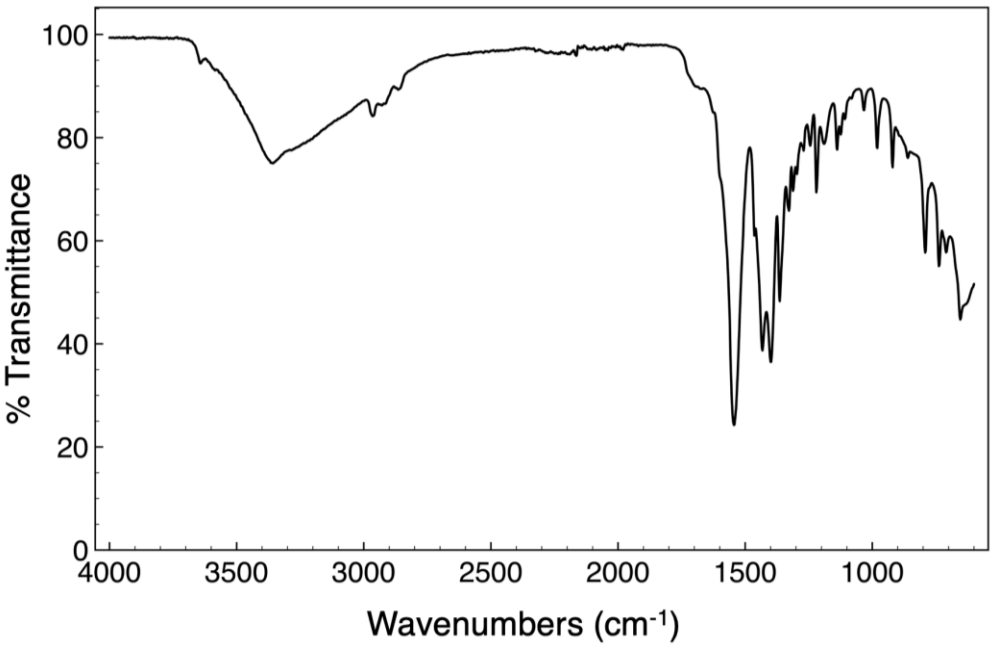

Figure S7. IR spectra for complex $[Ca_3(C_9H_9O_6)_2(H_2O)_4]\cdot 3H_2O$ (5) in the range 4,000 to 400 cm^{-1}.

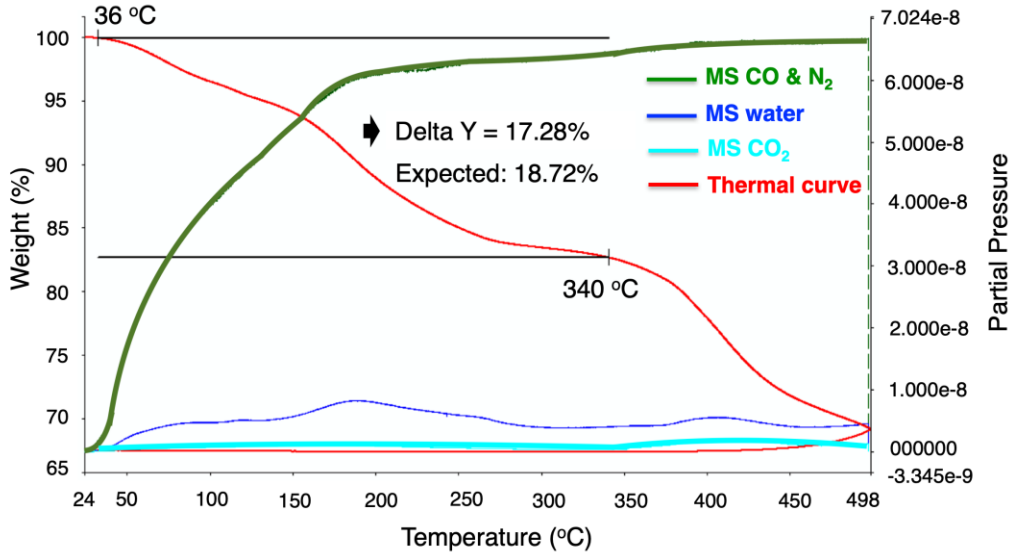

Figure S8. TGA with MS for compound 5. Green line for N_2 and CO. Blue curve and arctic curves are for water and CO_2, respectively. The red curve is for thermal curve and derivative curve, respectively. The water content is calculated from the first broad peaks from 36 °C to 340 °C. The water peak from 375 °C to 450 °C is correlaed with ligand decomposition where water, CO and CO_2 were released.

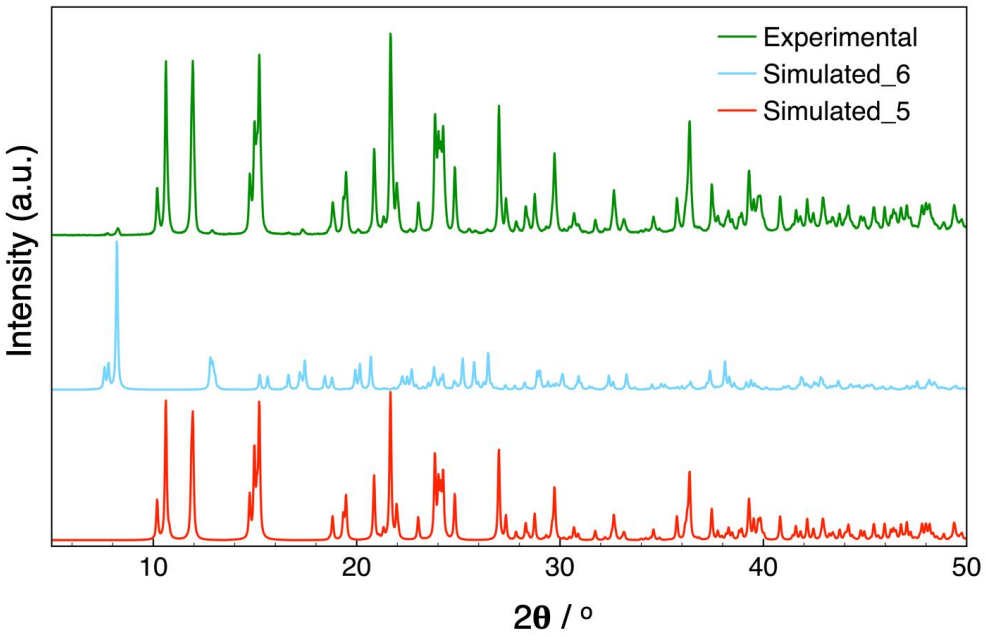

Figure S9. XRPD patterns plot in the 2θ range of 5° to 50° for a mix of 5 and 6 grown in the media of ethanol. The peak positions of the experimental pattern correspond well with simulated from the single crystal data, indicating the purity of the synthesized samples. The experimental pattern and simulated pattern are shown in green and red, respectively.

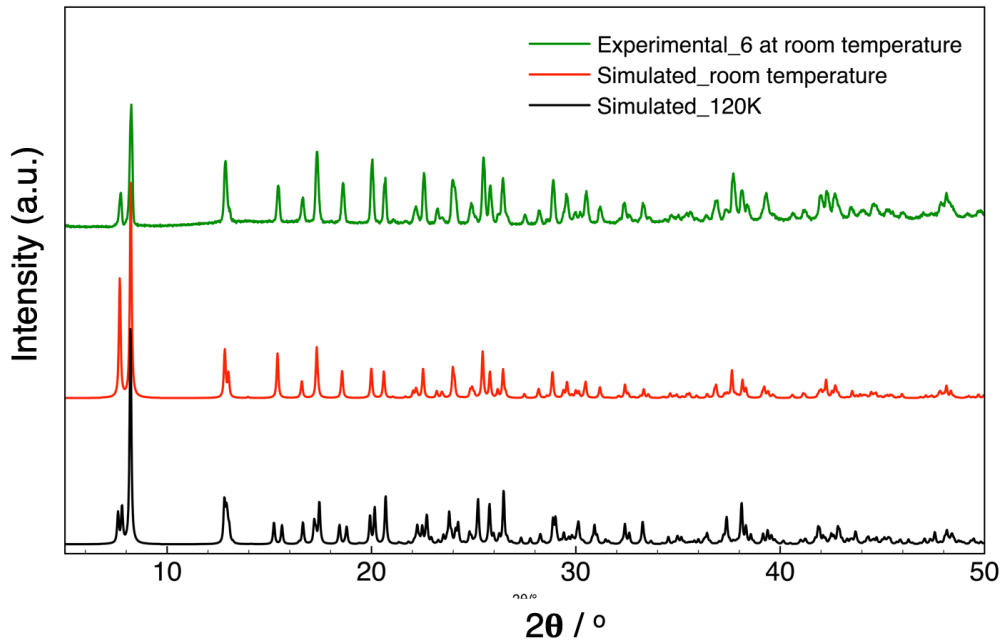

Figure S10. XRPD patterns plot in the 2θ range of 5° to 50° for [Ca($C_9H_{10}O_6$)(H_2O)$_2$]·H_2O (6). The peak positions of the experimental pattern correspond well with simulated from the single crystal data that collected at 290 K that with half a lattice water less. The variable temperature study shows that compound 6 can easily transform into 7 after 290 K. The experimental pattern and simulated pattern are shown in green, red and black, respectively.

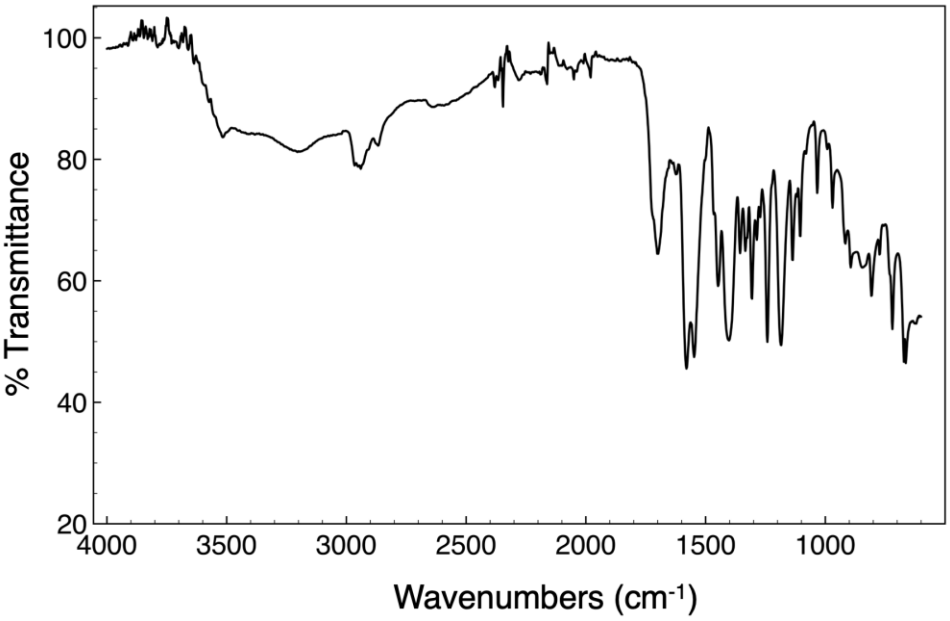

Figure S11. IR spectra for complex and [Ca($C_9H_{10}O_6$)(H_2O)$_2$]·H_2O (6) in the range 4,000 to 400 cm^{-1}.

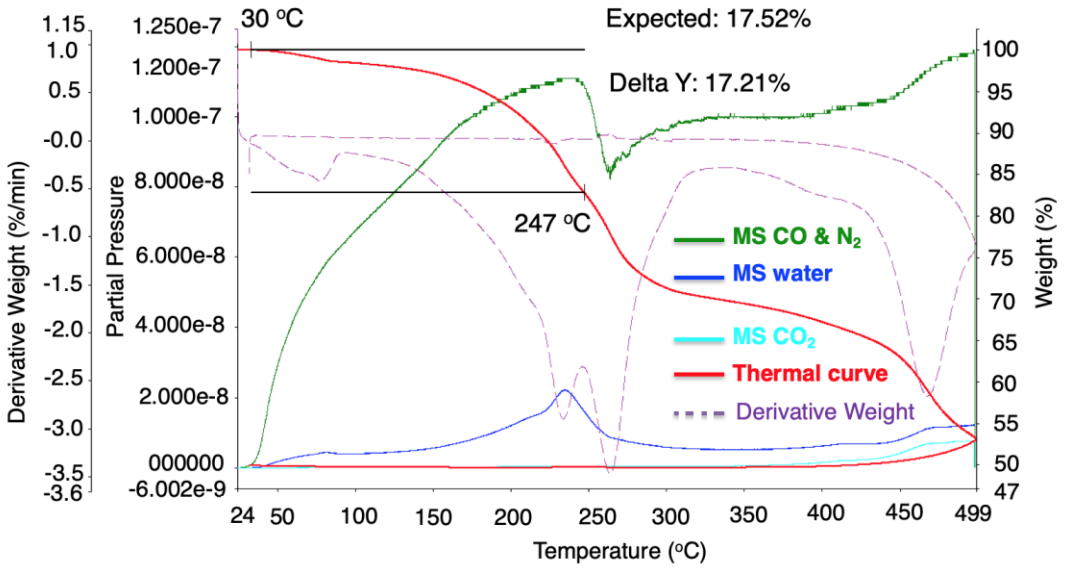

Figure S12. TGA with MS for compound 6. Green line for N_2 and CO. Blue curve and arctic curves are for water and CO_2, respectively. Red and dashed purple line are for thermal curve and derivative curve, respectively. The water content is calculated from the first derivative peak from 30 °C to 247 °C. The water peak after is correlaed with ligand decomposition where water, CO and CO_2 were released. The sudden drop of CO&N_2 (in green) is due to the shake of machine.

The PXRD, IR and TGA data for Crystals 8-10

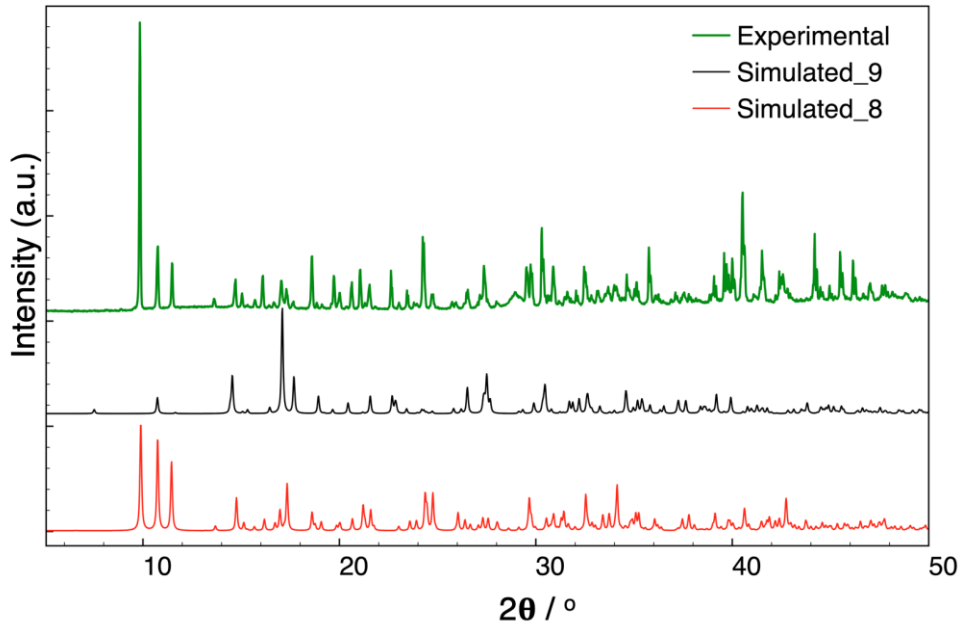

Figure S13. XRPD patterns plot in the 2θ range of 5° to 50° show the presence of compouds $[Ca_2(C_{10}H_8O_8)(H_2O)_7]\cdot 2H_2O$ (8) and $[Ca(C_{10}H_{10}O_8)(H_2O)_6]\cdot H_2O$ (9). The peak positions of the experimental pattern correspond well with simulated from the single crystal data of 8 and 9, indicating a mix of 8 and 9 with 8 as the majoy phase formed in the bulk sample. The experimental pattern and simulated patterns of 8 and 9 are shown in green, red and black, respectively.

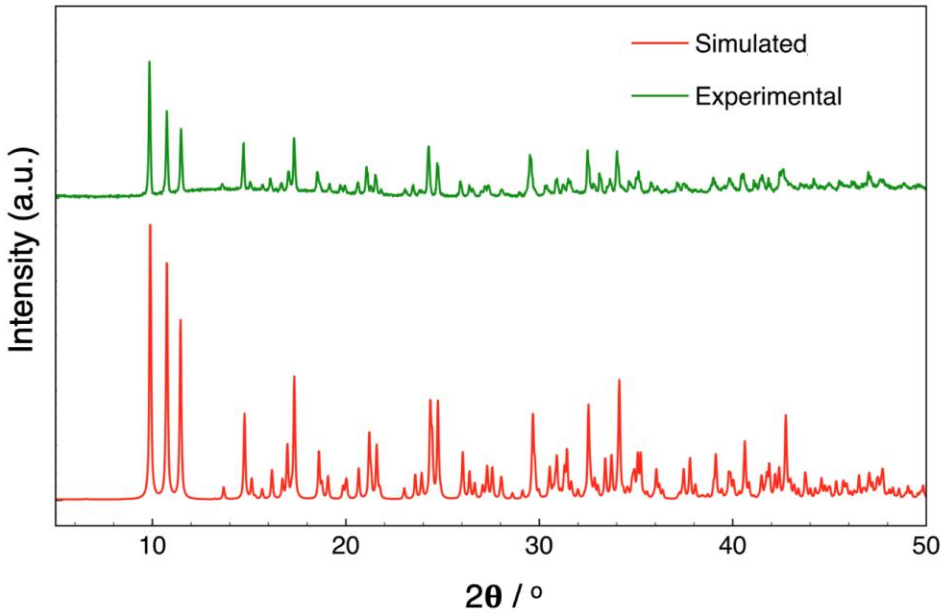

Figure S14. XRPD patterns plot in the 2θ range of 5° to 50° for compound $[Ca_2(C_{10}H_8O_8)(H_2O)_7]\cdot 2H_2O$ (8). The peak positions of the experimental pattern correspond well with simulated from the single crystal data, indicating the purity of the synthesized samples. The experimental pattern and simulated pattern are shown in green and red, respectively.

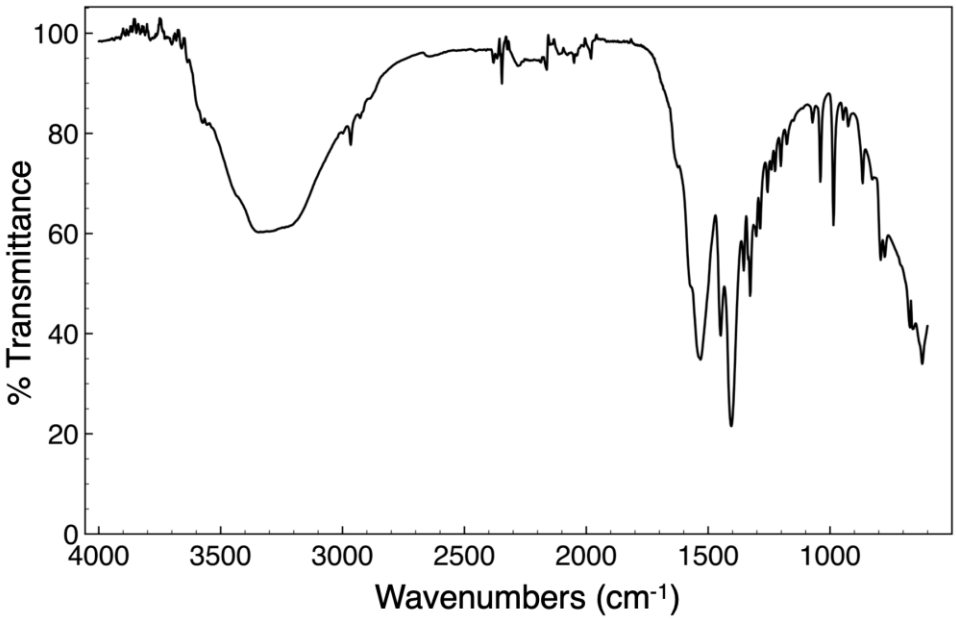

Figure S15. IR spectra for complex $[Ca_2(C_{10}H_8O_8)(H_2O)_7]\cdot 2H_2O$ (8) in the range 4,000 to 400 cm^{-1}.

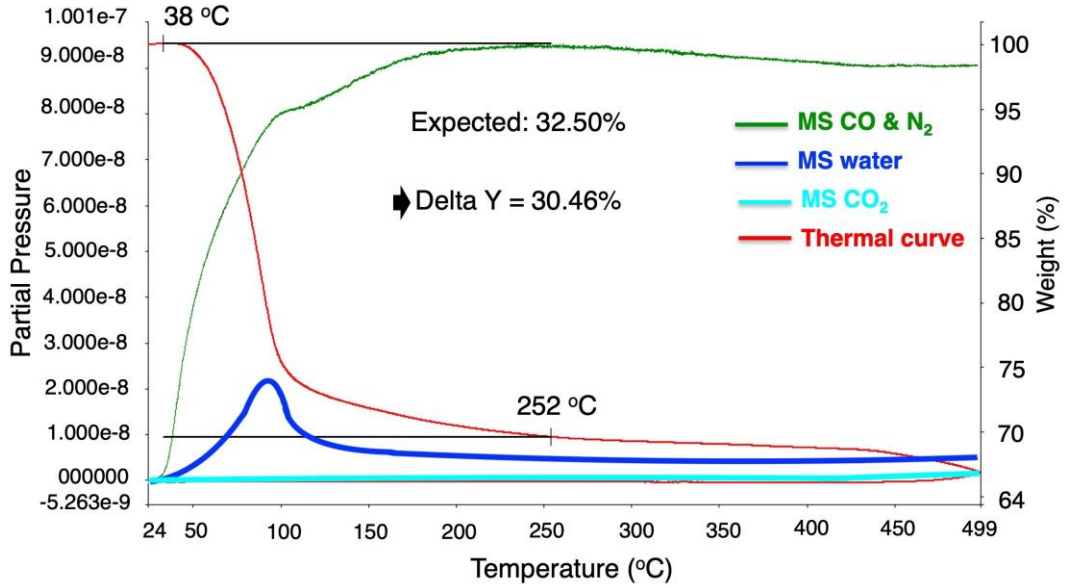

Figure S16. TGA with MS for compound 8. The thermal curve is shown in red; green line for N_2 and CO; blue curve and arctic curves are for water and CO_2, respectively; The difference in percentage may be due to the loss of free water. The water loss is observed from 38 °C to 252 °C. The strucure seems to be stable even after 400 °C.

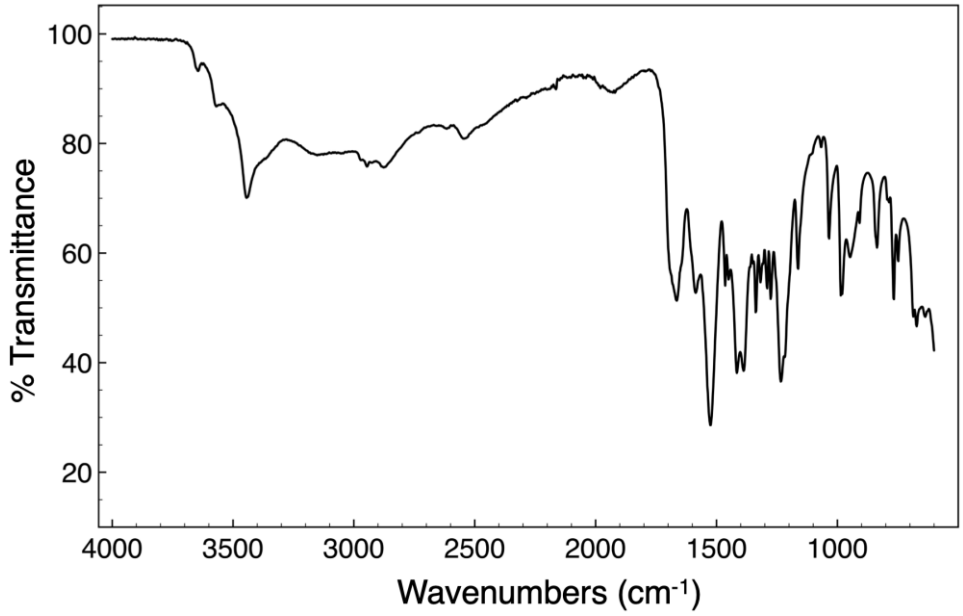

Figure S17. IR spectra for complex $[Ca(C_{10}H_{10}O_8)(H_2O)_6]\cdot H_2O$ (98) in the range 4,000 to 400 cm^{-1}.

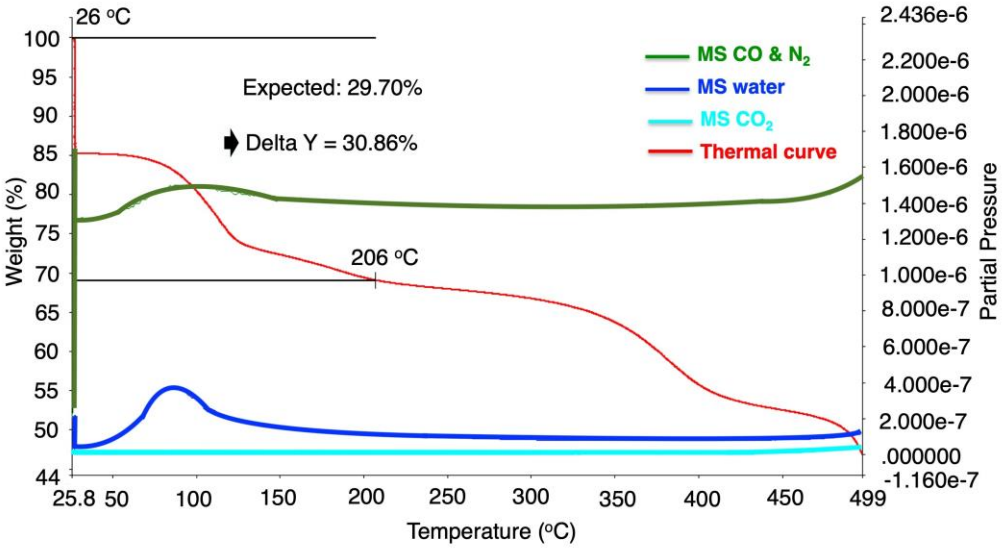

Figure S18. TGA with MS for compound 9. Green line for N_2 and CO. Blue curve and arctic curves are for water and CO_2, respectively. The red curve is for thermal curve and derivative curve, respectively. An obvious water loss is observed from the 30 °C to 206 °C. The CO and CO_2 from structure starts to combust from 350 °C.

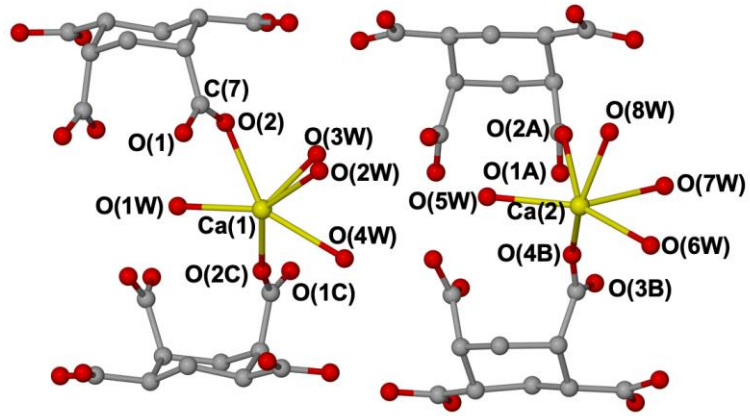

Figure S19. Low precision crystal structure of $[Ca(C_{10}H_{12}O_8)_2(H_2O)_4]_n$ (10). Crystal data for $[Ca(C_{10}H_{12}O_8)_2(H_2O)_4]_n$: M = 630.52, colorless, 0.31 × 0.22 × 0.03 mm^3, monoclinic *P21/c*, a = 23.544(5) Å, b = 16.359(3) Å, c = 13.049(3) Å, α = 90.00°, β = 90.05(3)°, γ = 90.00°, V = 5025.9(17) Å^3, Z = 8, D_c = 1.667 g/cm^3, F_{000} = 2640.0, Mo Kα radiation, λ = 0.71073 Å, T = 120 K, 2θmax = 54.0°, 46548 reflections collected, 10883 unique (R_{int} = 0.1089, R_{sigma} = 0.0910). Final GOF = 1.061, R_1 = 0.0915, wR_2 = 0.2595, R indices based on 10883 reflections with I >=2σ(I) (refinement on F^2), 358 parameters, 12 restraints, Max/min residual electron density 1.63/-0.83 Å^{-3}. Lp and absorption corrections applied, μ = 0.348 mm^{-1}.

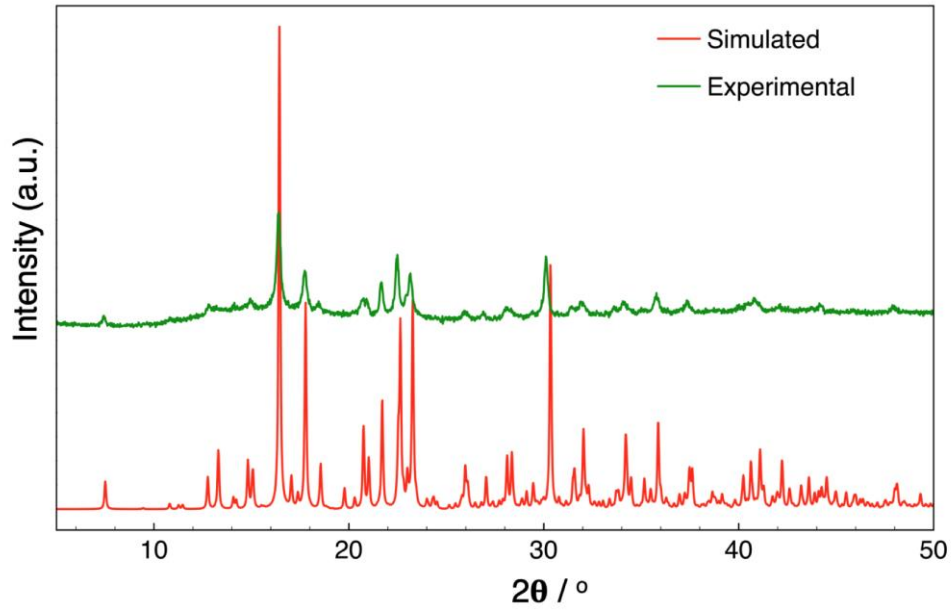

Figure S20. XRPD patterns plot in the 2θ range of 5° to 50° for compound $[Ca(C_{10}H_{12}O_8)_2(H_2O)_4]_n$ (10). The broadening of peaks show the poor crystallinity of the synthesised samples, however, the essentail peak positions of the experimental pattern correspond well with simulated pattern from the single crystal, indicating the reasonalbe unit cell parameter we get. The experimental pattern and simulated pattern are shown in green and red, respectively.

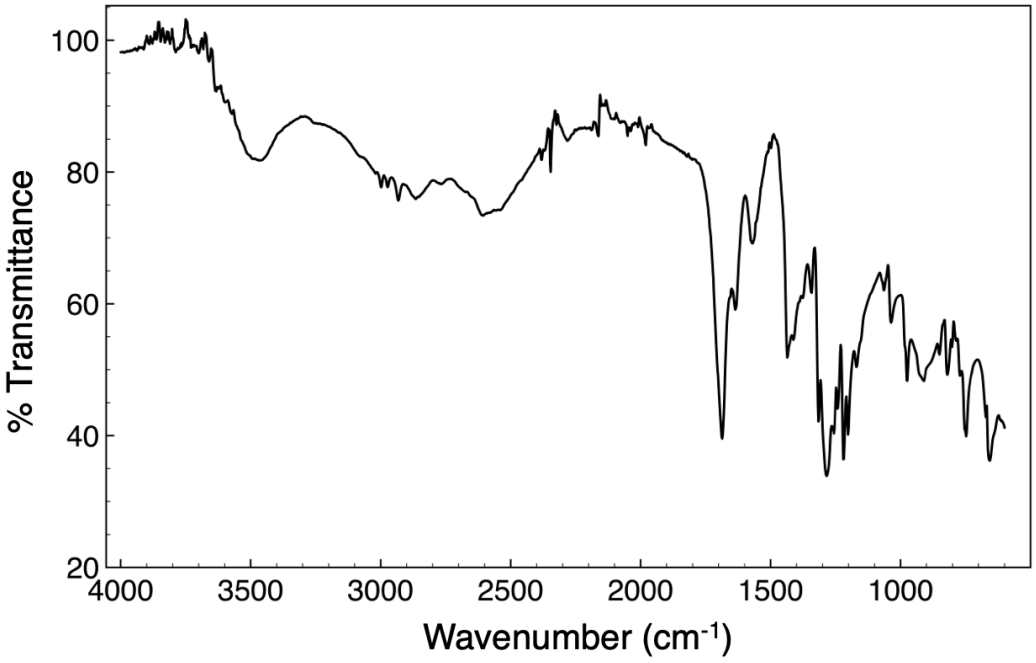

Figure S21. IR spectra for compound $[Ca(C_{10}H_{12}O_8)_2(H_2O)_4]_n$ (10) in the range 4,000 to 400 cm^{-1}. The absorption peaks around 3500 cm^{-1} indicates the stretching vibration of OH^- from water as we observed in other hydrated synthesised materials. Peaks at 1200-1700 cm^{-1} belongs to the CH_2 bending and the C-O stretching indicates the presence of carboxylate group.

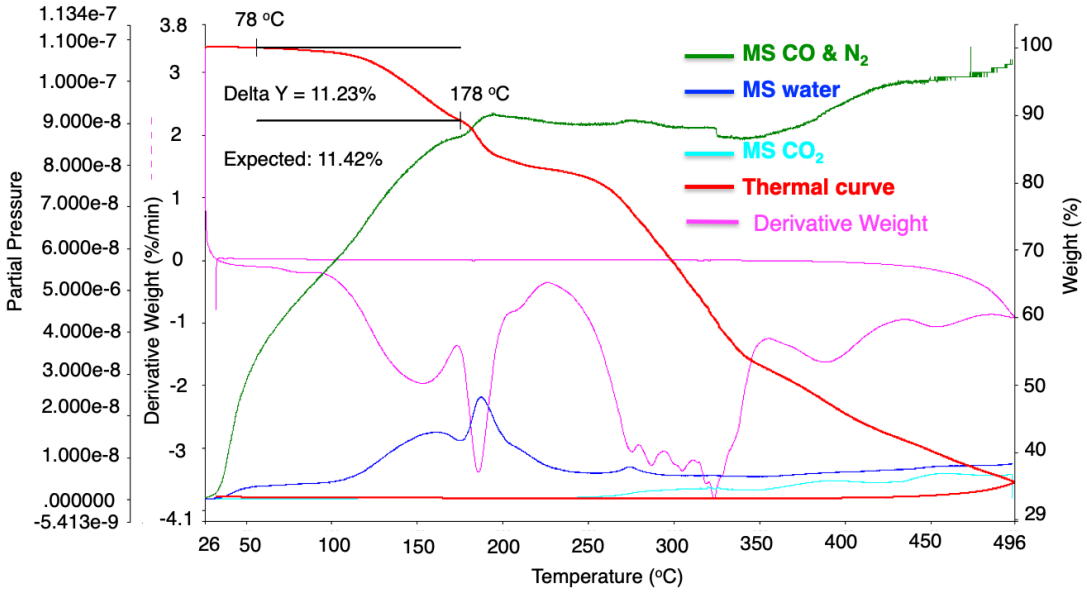

Figure S22. TGA with MS for compound $[Ca(C_{10}H_{12}O_8)_2(H_2O)_4]_n$ (10). Green line for N_2 and CO. Blue curve and arctic curves are for water and CO_2, respectively. Red and purple line are for thermal curve and derivative curve, respectively. The water content is calculated from the first derivative peak from 78 °C to 178 °C. The water peak after is correlaed with ligand decomposition where water, CO and CO_2 were released.

The PXRD, IR and TGA data for Crystal 13

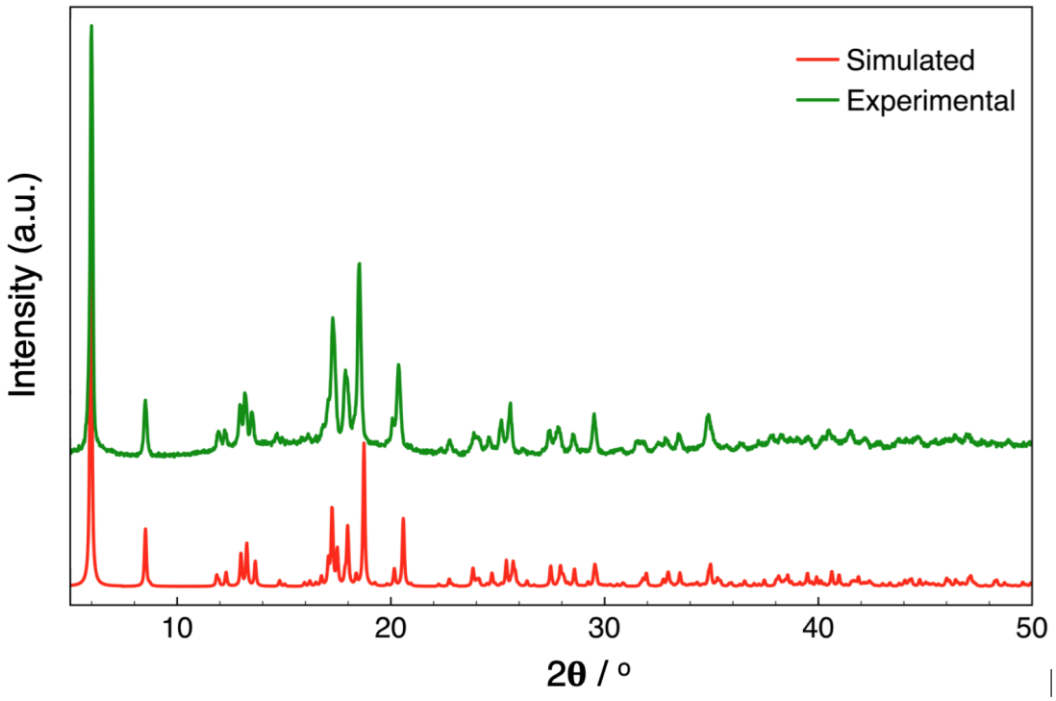

Figure S23. PXRD patterns plot in the 2θ range of 5° to 50° for compound $Ca(C_{10}H_{15}O_4)_2(H_2O)_2]_n$ (13). The peak positions of the experimental pattern correspond well with simulated from the single crystal data, indicating the purity of the synthesized samples. The experimental pattern and simulated pattern are shown in green and red, respectively.

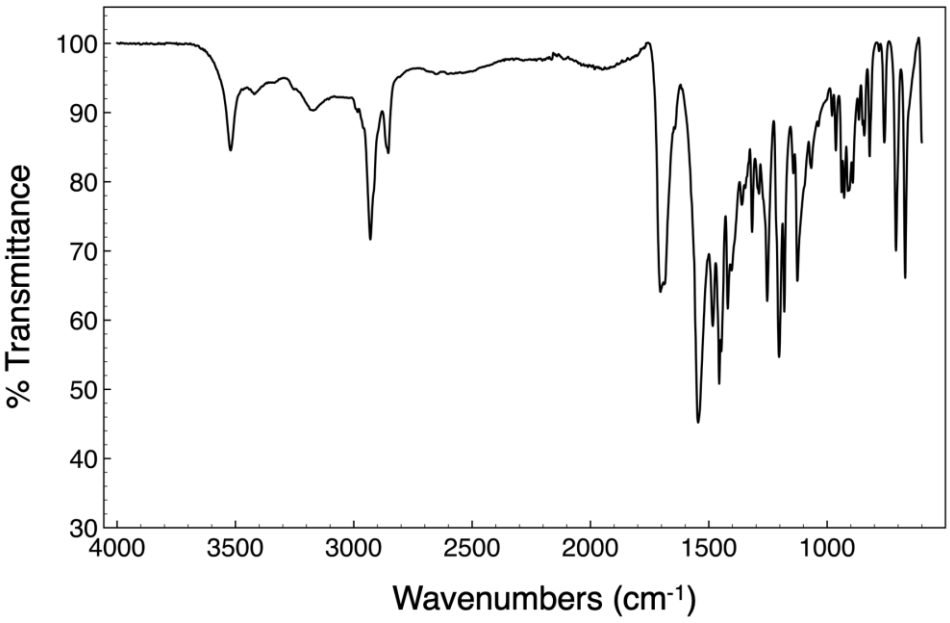

Figure S24. IR spectra for complex $Ca(C_{10}H_{15}O_4)_2(H_2O)_2]_n$ (13) in the range 4,000 to 400 cm^{-1}.

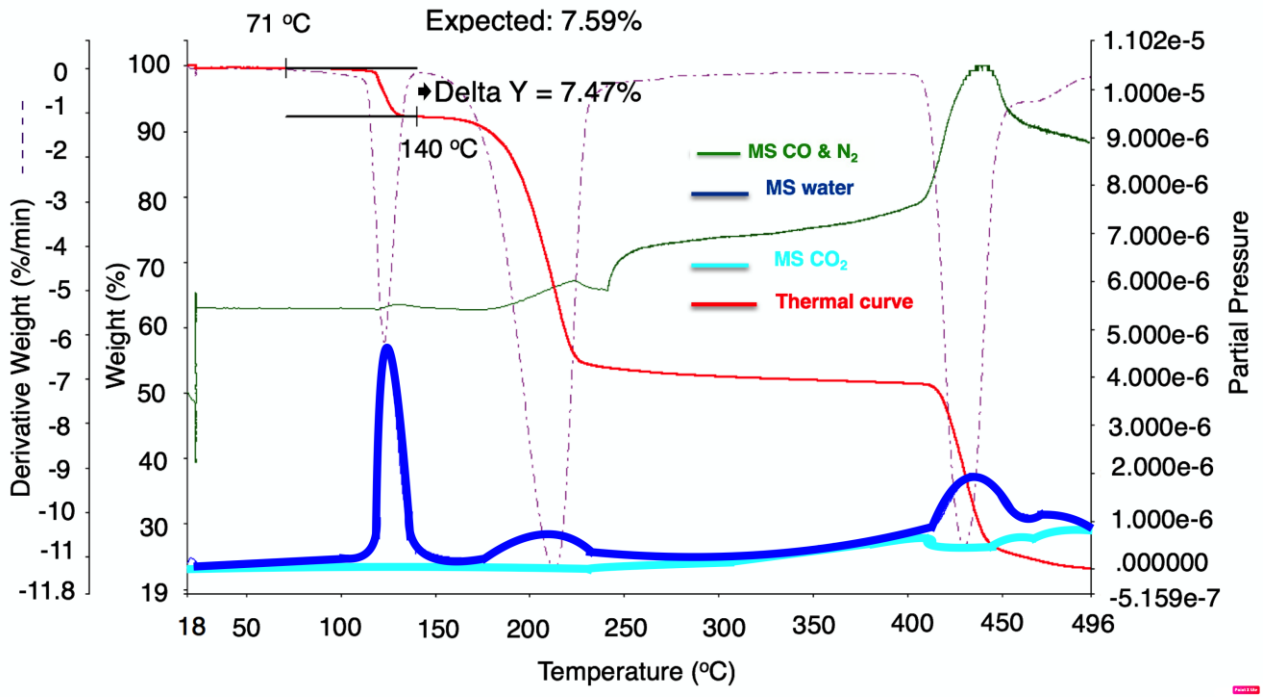

Figure S25. TGA with MS for compound $Ca(C_{10}H_{15}O_4)_2(H_2O)_2]_n$ (13). The amount of the coordinated water is calculated from the first derivative water peak from 71 ºC to 140 ºC, followed by the ligand decomposition of water, CO and CO_2. Green line for N_2 and CO. Blue curve and arctic curves are for water and CO_2, respectively. Red and dashed purple line are for thermal curve and derivative curve, respectively.

References:

1. Plot2: a scientific 2D plotting program for OS X, Version 2.6.5 (9969), 2018.
2. Y. Hong, N. Letzelter, J. S. O. Evans, D. S. Yufit and J. W. Steed, *Cryst. Growth Des.*, 2018, **18**, 1526–1538.
3. William E. Wallace, "Calcium hydroxide" in **NIST Chemistry WebBook, NIST Standard Reference Database Number 69**, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 4660, https://doi.org/10.18434/T4D303, (retrieved October 29, 2019).