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Ab initio structure solution and thermal stability evaluation of a new Ca(II) 3D coordination polymer using synchrotron powder X-ray diffraction data

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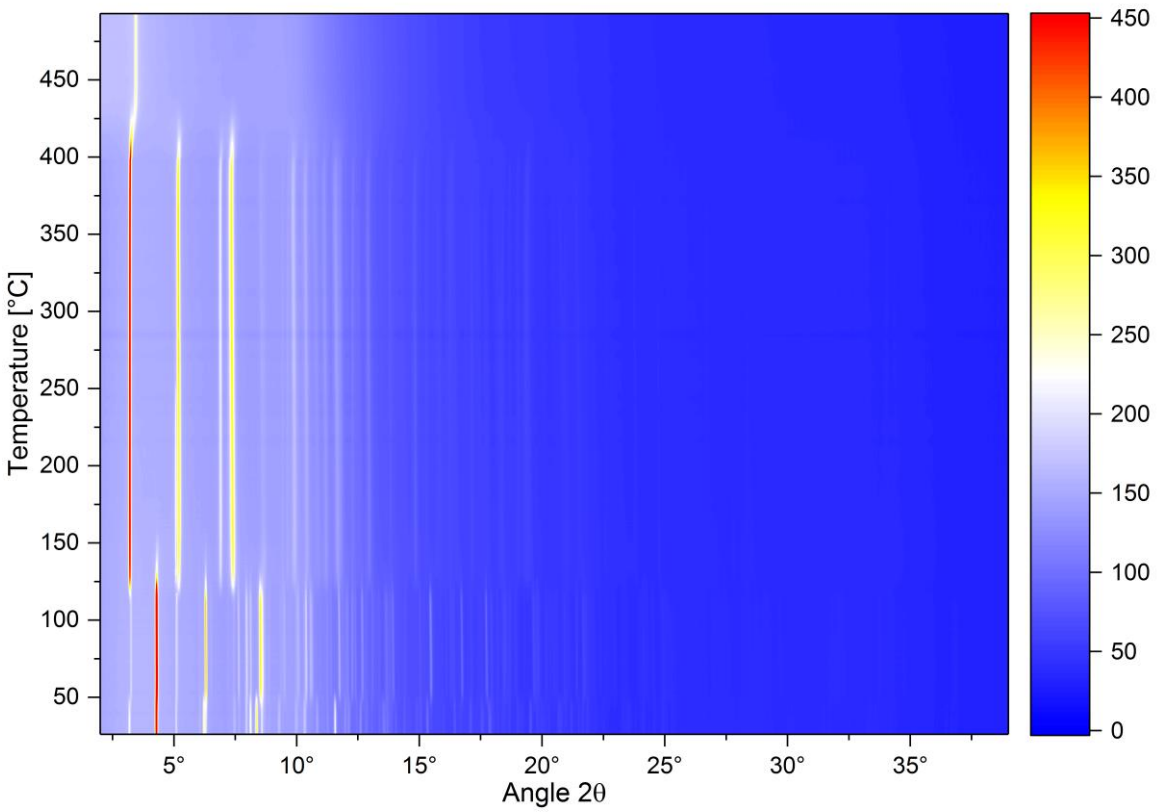

Figure S 1. The VT measurement of CPO-70-Ca (λ = 0.69396 Å).

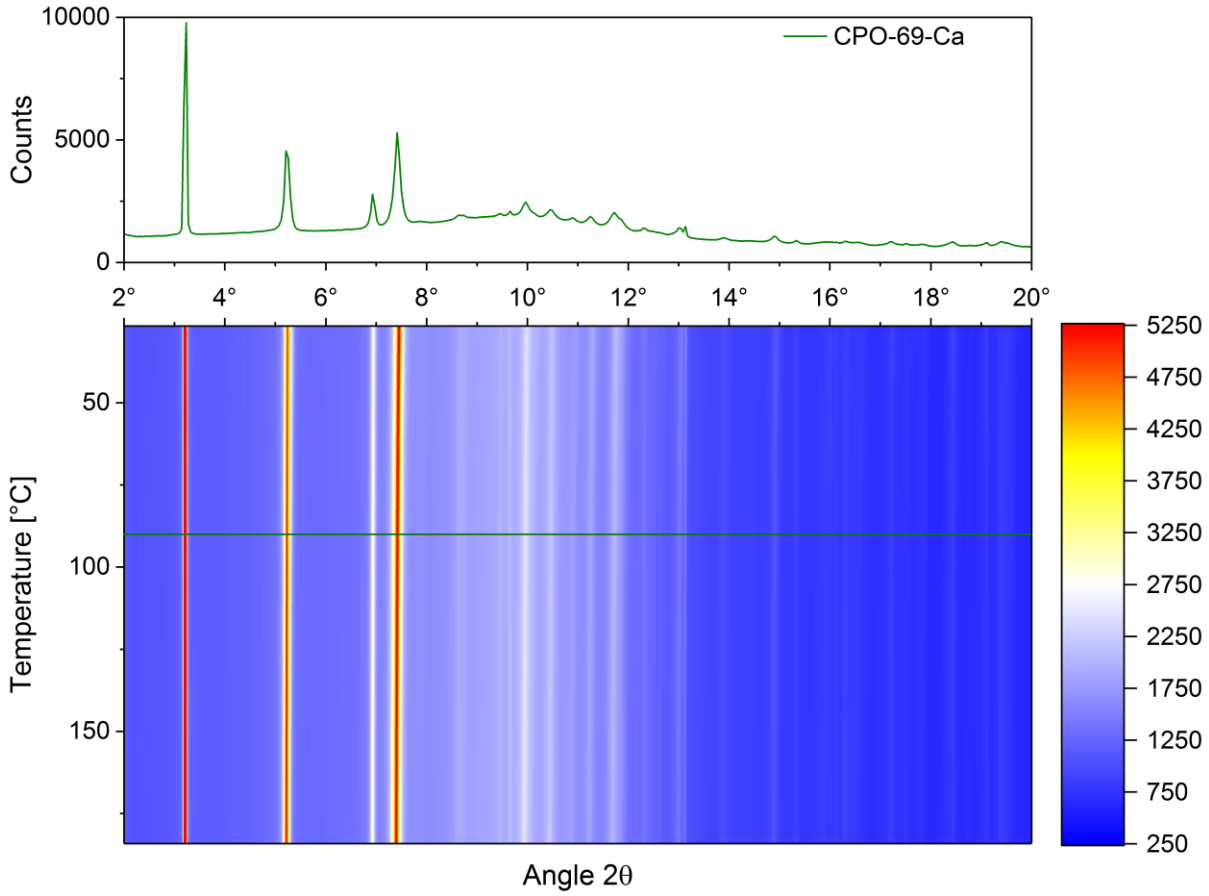

Figure S 2. Excerpt of the VT measurement of the transformed CPO-69-Ca during cooling down from 185 to 30 °C (λ = 0.69540 Å). A single PXRD pattern at 90 °C is included in green for reference.

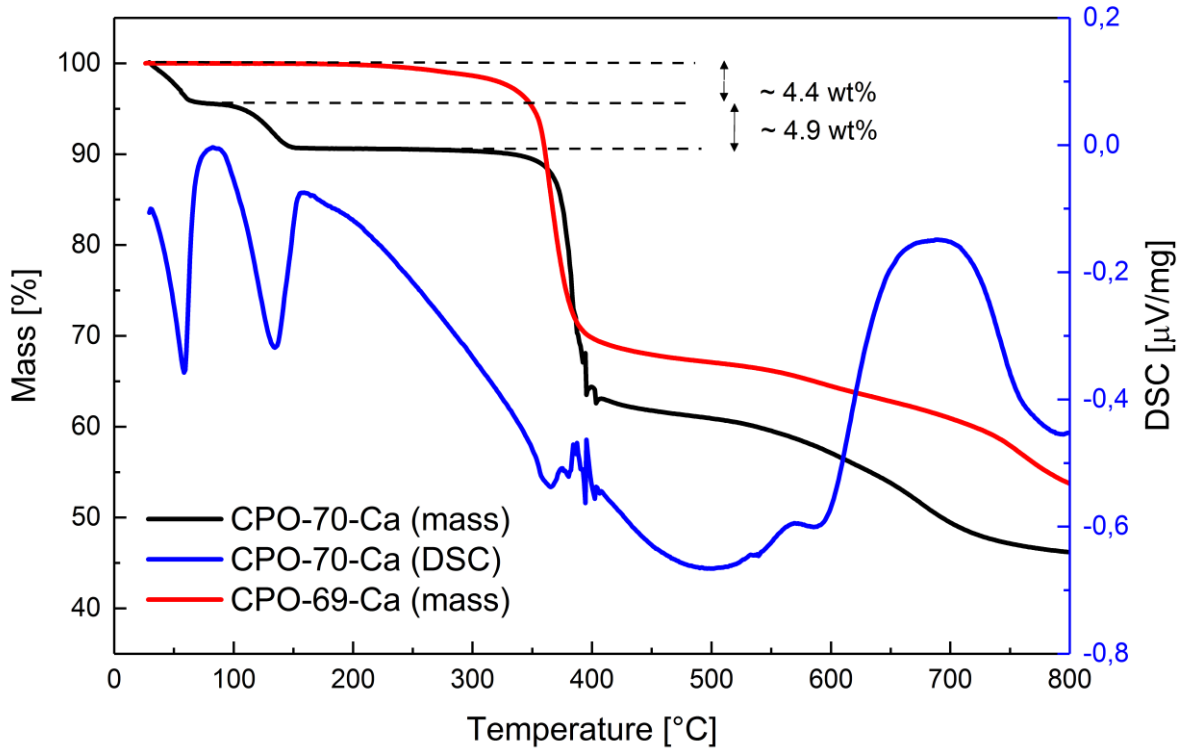

Figure S 3. Thermogravimetric analysis of CPO-69-Ca and CPO-70-Ca, as well as Differential Scanning Calorimetric analysis of CPO-70-Ca.

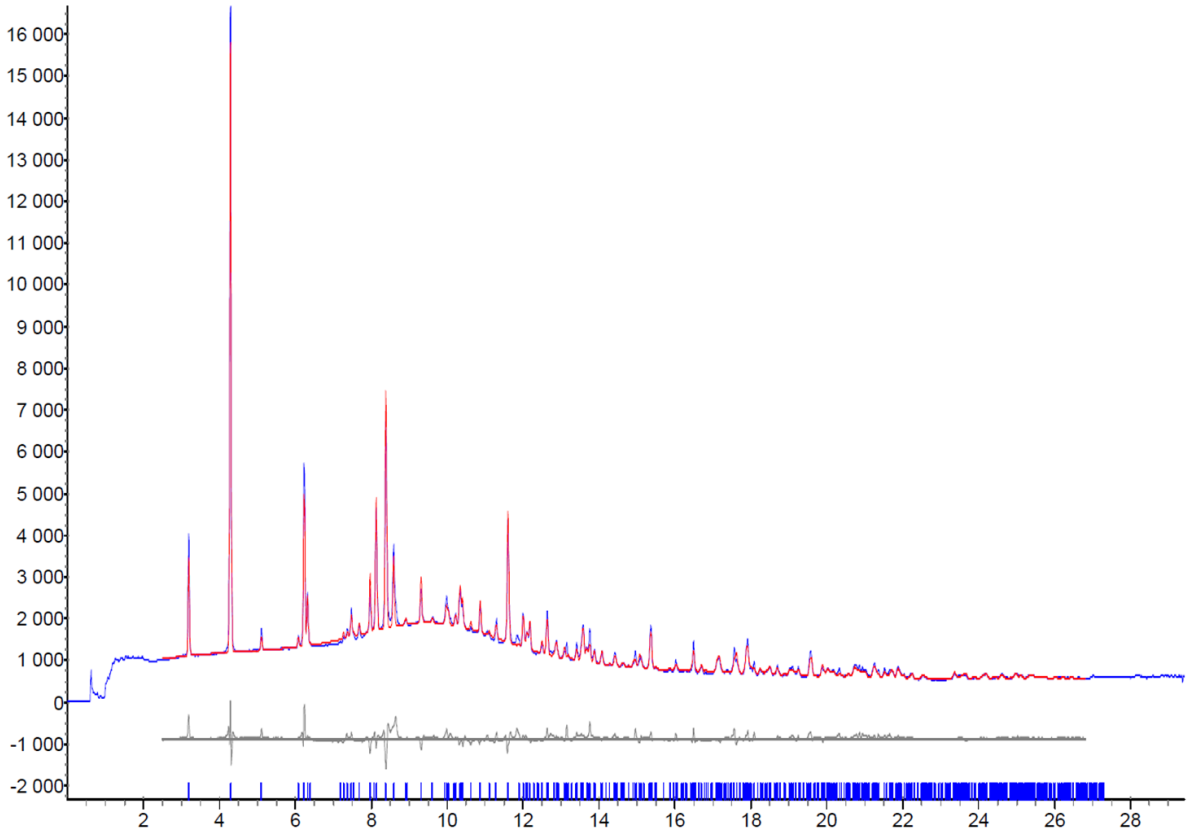

Figure S 4. Rietveld fit of CPO-70-Ca (AS). PXRD in blue, simulated pattern in red and difference in grey (λ = 0.69540 Å).

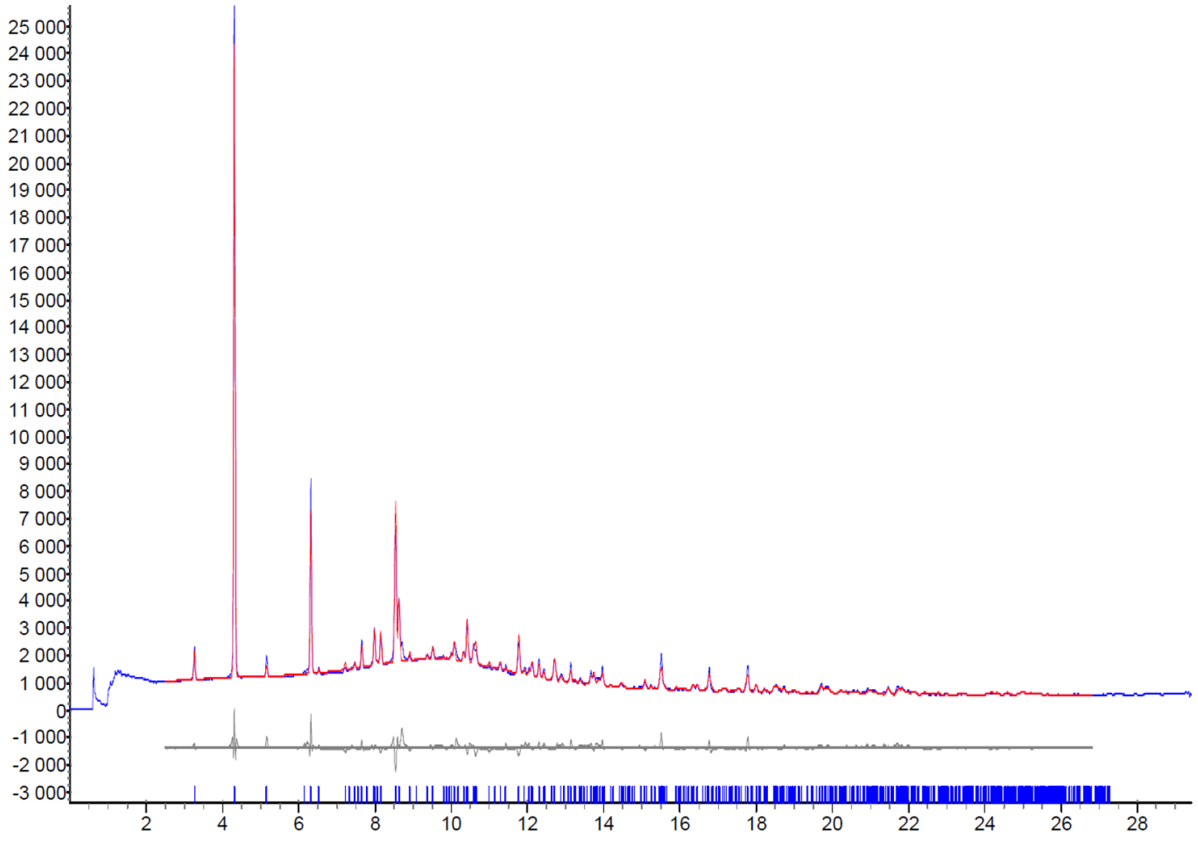

Figure S 5. Rietveld fit of CPO-70-Ca (NP). PXRD in blue, simulated pattern in red and difference in grey ($\lambda = 0.69540$ Å).

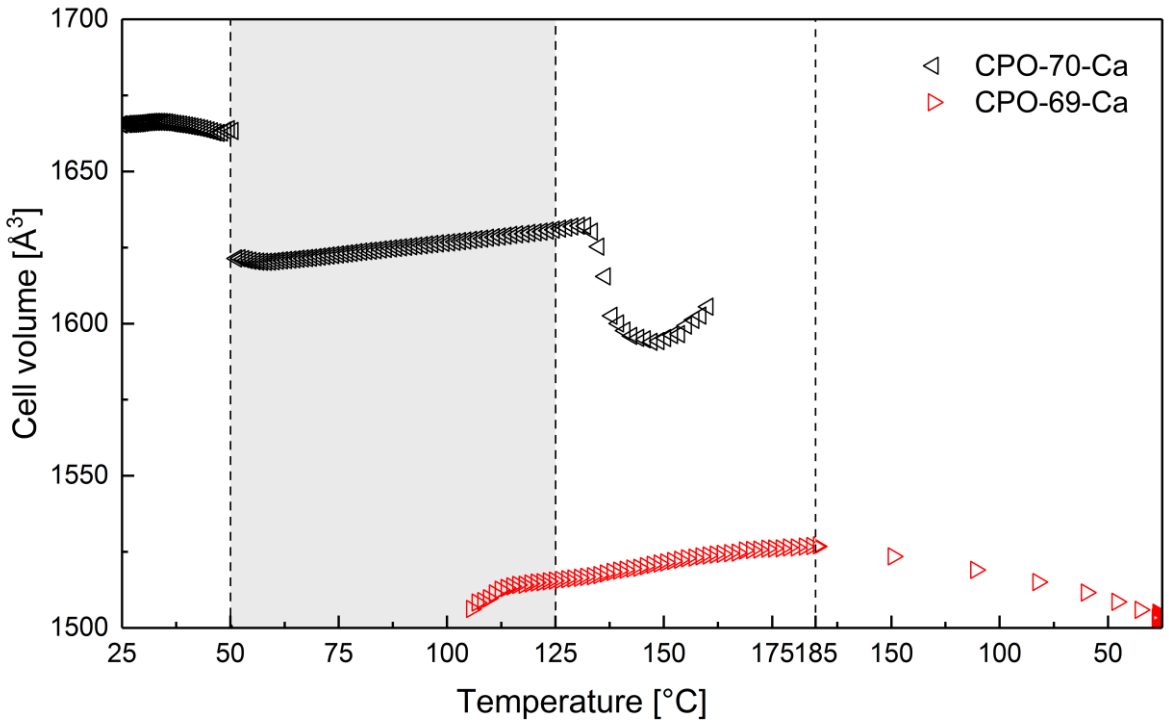

Figure S 6. The cell volumes of CPO-70-Ca (AS and NP) and CPO-69-Ca, plotted as function of temperature. The grey area indicates the temperature range where the NP form of CPO-70-Ca is dominant, and the dashed line at 185 °C indicates the maximum temperature of the experiment. The CPO-70-Ca and CPO-69-Ca datasets have been cut above 160 °C and below 100°C, respectively, due to low occupancy and refinement precision outside these temperature ranges.

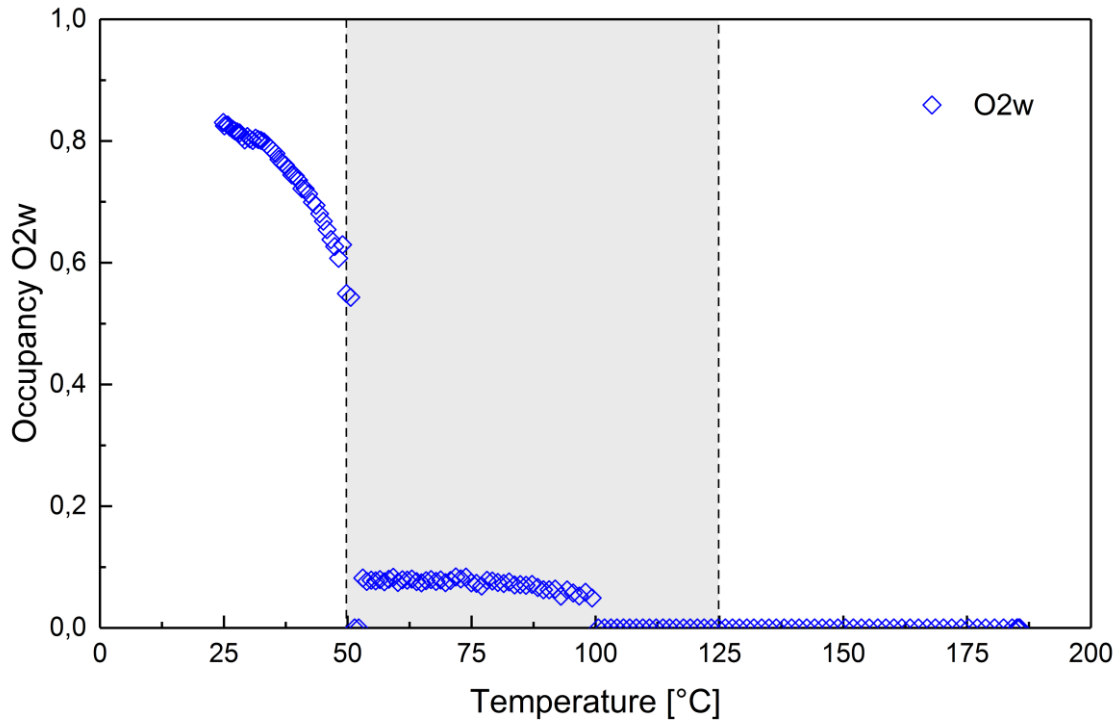

Figure S 7. The occupancy of the O2w water molecule located in the pores of CPO-70-Ca (AS), plotted as function of temperature. The grey area indicates the temperature range where CPO-70-Ca (NP) dominates.

Supplementary computational details

For the calculations presented in this work, we have used plane-wave cut-off energy of 600 eV which gave well converged results with respect to the basis set. The **k**-points were generated using the Monkhorst-Pack method with a grid size of 4 X 8 X 12, and 8 X 8 X 8 for CPO-70-Ca (AS/NP) and CPO-69-Ca respectively. Iterative relaxation of atomic positions was stopped when the change in total energy between successive steps was less than 1 meV/cell. With this criterion, the maximum forces generally acting on the atoms were found to be less than 10 meV/Å. In our theoretical simulation, we have relaxed the atomic positions and cell parameters globally using force-minimization technique fixed to experimental volume. Then the theoretical equilibrium volume is determined by varying the cell volume within ±10 % of the experimental volume. Finally, the calculated energy versus volume data are fitted into the universal-equation-of-state fit and the equilibrium cell parameters are extracted. The CPO-70-Ca (AS), CPO-70-Ca (NP) and CPO-69-Ca structures contain 2, 1, and 0 water molecules per formula unit, respectively. In order to compare the relative stability in the simulated structures we have normalized the water molecular total energy in the CPO-70-Ca (AS) and CPO-69-Ca structure. The total energy of the water molecule is calculated in the particle in a box approach with 1 X 1 X 1 **k**-points.

Table S 1. Comparison of the experimentally determined and calculated structural parameters of CPO-70-Ca (NP), CPO-70-Ca (AS) and CPO-69-Ca. The calculated values are given in parentheses.

Name	CPO-70-Ca (AS)	CPO-70-Ca (NP)	CPO-69-Ca
formula	$C_{16}H_{16}O_8Ca$	$C_{16}H_{14}O_7Ca$	$C_{16}H_{12}O_6Ca$
space group (#)	$P2_1/n$ (14)	$P2_1/n$ (14)	C2/c (15)
a (Å)	25.0265 (25.5188)	24.4632 (24.8848)	24.721 (25.0153)
b (Å)	10.0028 (10.0169)	9.9876 (10.0153)	8.000 (8.0923)
c (Å)	6.6715 (6.7812)	6.6405 (6.7653)	7.5253 (7.6354)
β (deg)	94.482 (94.82)	93.113 (93.10)	90.949 (91.02)

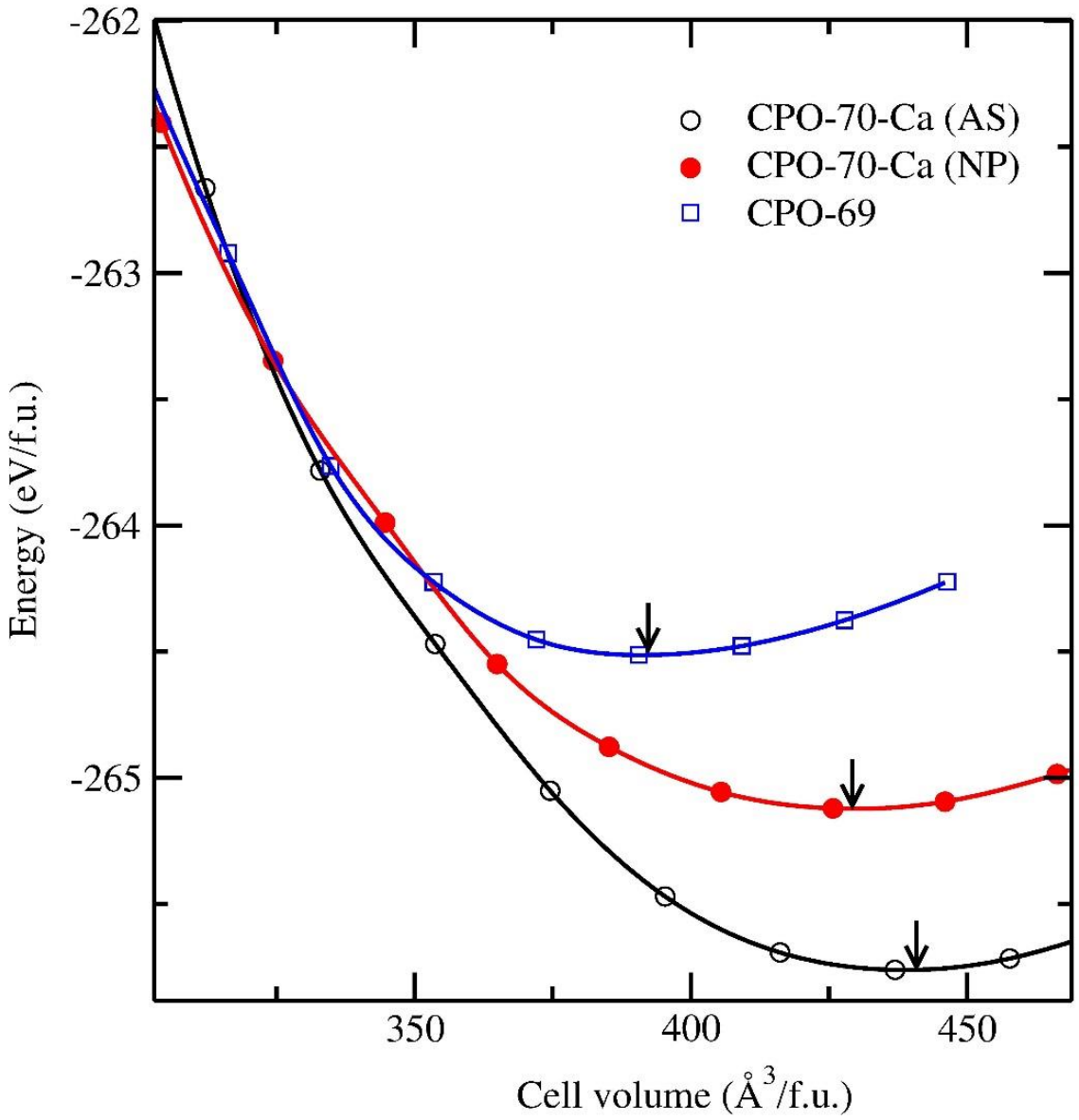

Figure S 8. Calculated unit cell volume vs. total energy (per formula unit; f.u.) for CPO-70-Ca(AS), CPO-70-Ca(NP), and CPO-69. The arrows indicate the theoretical equilibrium volume. To have the consistency in the total energy, the H_2O molecular total energy is normalized in the CPO-70-Ca (NP), and CPO-69-Ca phases, for more details see running text.

Example refinement input file for parametric refinement

'scan 1-90, CPO-70-Ca (AS/NP) dominant region
approximate_A
A_matrix_memory_allowed_in_Mbytes 2000
A_matrix_elements_tollerance 0.00001
conserve_memory

r_wp 5.06832162 r_exp 0.110396514 r_p 3.69410992 r_wp_dash 16.1203231 r_p_dash 14.9186379 r_exp_dash 0.351127576
weighted_Durbin_Watson 32.0885578 gof 45.9101598

iters 100000
chi2_convergence_criteria 0.001
'do_errors

xdd "FRL_M4242_400_80_0001p.xye"
bkg @ 858.804776` -367.894603` -23.2159444` 127.357726` -41.045667` 2.90574051`
start_X 2.5
finish_X 26.8
x_calculation_step = 0.001;
Zero_Error(ze, 0.00278`)
lam ymin_on_ymax 0.0001 la 1.0 lo 0.6954 lh 0.1
LP_Factor(90)

'capillary
xo_Is
phase_name "quartz cap"
xo x_glass 9.68893518` I @ 22.98197`
CS_G(csg_glass, 1.00025`)

str
phase_name "CPO-70-Ca"
a a_CPO70_0001 25.027804` max 25.1 min 24.4
b b_CPO70_0001 10.004142` max 10.1 min 9.95
c c_CPO70_0001 6.671921` max 6.75 min 6.55
be be_CPO70_0001 94.48173` max 94.6 min 93.0
volume V_CPO70_0001 1665.419`
space_group "p21/n"
prm boc_0001 4.60516` max 5.0 min 0.0
prm bh_0001 =1.5 boc_0001;
prm O2W_0000 1.00000`
prm O2W_0001 0.83032` max =O2W_0000+0.1; min 0.0

site C1	x 0.74557`	y 0.81777`	z -0.04792`	occ C 1	beq =boc_0001;
site C2	x 0.74962`	y 0.91759`	z -0.19087`	occ C 1	beq =boc_0001;
site H2	x 0.77883`	y 0.97532`	z -0.18167`	occ H 1	beq =bh_0001;
site C3	x 0.71001`	y 0.93110`	z -0.34757`	occ C 1	beq =boc_0001;
site H3	x 0.71272`	y 0.99789`	z -0.44321`	occ H 1	beq =bh_0001;
site C4	x 0.66635`	y 0.84481`	z -0.36132`	occ C 1	beq =boc_0001;
site C5	x 0.66230`	y 0.74500`	z -0.21837`	occ C 1	beq =boc_0001;
site C6	x 0.70191`	y 0.73148`	z -0.06167`	occ C 1	beq =boc_0001;
site H6	x 0.69920`	y 0.66470`	z 0.03397`	occ H 1	beq =bh_0001;
site C7	x 0.78774`	y 0.80338`	z 0.11892`	occ C 1	beq =boc_0001;
site O1	x 0.62731`	y 0.85813`	z -0.51577`	occ O 1	beq =boc_0001;
site C8	x 0.83850`	y 0.85619`	z 0.10064`	occ C 1	beq =boc_0001;
site H8	x 0.84596`	y 0.90057`	z -0.01644`	occ H 1	beq =bh_0001;
site C9	x 0.87811`	y 0.84267`	z 0.25734`	occ C 1	beq =boc_0001;
site C10	x 0.86696`	y 0.77634`	z 0.43232`	occ C 1	beq =boc_0001;
site C11	x 0.81620`	y 0.72353`	z 0.45061`	occ C 1	beq =boc_0001;
site H11	x 0.80874`	y 0.67915`	z 0.56768`	occ H 1	beq =bh_0001;
site C12	x 0.77659`	y 0.73705`	z 0.29391`	occ C 1	beq =boc_0001;
site H12	x 0.74263`	y 0.70172`	z 0.30614`	occ H 1	beq =bh_0001;
site O2	x 0.90600`	y 0.76302`	z 0.58677`	occ O 1	beq =boc_0001;
site C13	x 0.63859`	y 0.92673`	z -0.69395`	occ C 1	beq =boc_0001;
site H13a	x 0.61409`	y 0.89784`	z -0.80329`	occ H 1	beq =bh_0001;
site H13b	x 0.67191`	y 0.89519`	z -0.73835`	occ H 1	beq =bh_0001;
site H13c	x 0.62840`	y 1.01885`	z -0.68383`	occ H 1	beq =bh_0001;
site C14	x 0.90293`	y 0.65788`	z 0.72838`	occ C 1	beq =boc_0001;
site H14a	x 0.93833`	y 0.62560`	z 0.76763`	occ H 1	beq =bh_0001;
site H14b	x 0.88740`	y 0.58029`	z 0.66219`	occ H 1	beq =bh_0001;
site H14c	x 0.89297`	y 0.69372`	z 0.85363`	occ H 1	beq =bh_0001;
site C15	x 0.61581`	y 0.65311`	z -0.23302`	occ C 1	beq =boc_0001;

```
site O3     x 0.56783`      y 0.69967`      z -0.27684`     occ O 1             beq =boc_0001;
site O4     x 0.62297`      y 0.52585`      z -0.20205`     occ O 1             beq =boc_0001;
site C16    x 0.93216`      y 0.89890`      z 0.23787`      occ C 1             beq =boc_0001;
site O5     x 0.96265`      y 0.92971`      z 0.39789`      occ O 1             beq =boc_0001;
site O6     x 0.94913`      y 0.91747`      z 0.06075`      occ O 1             beq =boc_0001;
site Ca1    x 0.96451`      y 0.95847`      z 0.74407`      occ Ca 1            beq @ 0.00000` max 5 min 0
site O1w    x 1.02449`      y 0.77706`      z 0.80010`      occ O 1             beq @ 2.72137` max 5 min 0
site H1wa   x 1.01844`      y 0.73722`      z 0.91372`      occ H 1             beq =bh_0001;
site H1wb   x 1.04543`      y 0.77186`      z 0.70039`      occ H 1             beq =bh_0001;
site O2w    x 0.97473`      y 0.38221`      z 0.56353`      occ O =O2W_0001;    beq @ 0.00000` max 5 min 0
site H2wa   x 0.95882`      y 0.30574`      z 0.58548`      occ H =O2W_0001;    beq =bh_0001;
site H2wb   x 0.98003`      y 0.42650`      z 0.67731`      occ H =O2W_0001;    beq =bh_0001;

prm Torsion_0001 -21.16012`max -18 min -26
prm O3O4rot_0001 -43.27193`max 45 min -50
prm O5O6rot_0001 -24.39139`max -15 min -30
prm Merot1_0001 143.91529`max 150 min 130
prm Merot2_0001 156.90045`max 210 min 130
prm Metor1_0001 20.70769`max 25 min 0
prm Metor2_0001 23.58417`max 70 min 20

rigid
z_matrix C1
z_matrix C2 C1 1.39
z_matrix C6 C1 1.39         C2 120
z_matrix C7 C1 1.48         C2 120          C6 180
z_matrix C3 C2 1.39         C1 120          C7 180
z_matrix C5 C6 1.39         C1 120          C7 180
z_matrix C12 C7 1.39        C1 120          C6 =Torsion_0001;
z_matrix C8 C7 1.39         C1 120          C12 180
z_matrix C4 C3 1.39         C2 120          C1 0
z_matrix C15 C5 1.48        C6 120          C4 180
z_matrix C11 C12 1.39       C7 120          C8 0
z_matrix C9 C8 1.39         C7 120          C12 0
z_matrix O1 C4 1.37         C3 120          C5 180
z_matrix O3 C15 1.30        C5 120          C4 =O3O4rot_0001;
z_matrix O4 C15 1.30        C5 120          C6 =O3O4rot_0001;
z_matrix C10 C9 1.39        C8 120          C11 0
z_matrix C16 C9 1.48        C8 120          C10 180
z_matrix C13 O1 1.42        C4 120          C3 =Metor1_0001;
z_matrix O2 C10 1.37        C9 120          C11 180
z_matrix O5 C16 1.30        C9 120          C10 =O5O6rot_0001;
z_matrix O6 C16 1.30        C9 120          C8 =O5O6rot_0001;
z_matrix C14 O2 1.42        C10 120         C11 =Metor2_0001;
z_matrix H3 C3 0.93         C2 120          C1 180
z_matrix H2 C2 0.93         C1 120          C6 180
z_matrix H6 C6 0.93         C5 120          C4 180
z_matrix H8 C8 0.93         C9 120          C10 180
z_matrix H11 C11 0.93       C12 120         C7 180
z_matrix H12 C12 0.93       C7 120          C8 180
z_matrix H14a C14 0.96      O2 109.5        C10 =Merot1_0001;
z_matrix H14b C14 0.96      O2 109.5        C10 =Merot1_0001-109.5;
z_matrix H14c C14 0.96      O2 109.5        C10 =Merot1_0001+109.5;
z_matrix H13a C13 0.96      O1 109.5        C4 =Merot2_0001;
z_matrix H13b C13 0.96      O1 109.5        C4 =Merot2_0001-109.5;
z_matrix H13c C13 0.96      O1 109.5        C4 =Merot2_0001+109.5;

'rotate/translate linker
prm Linkrot1_0001 -140.84140` max -138 min -143
prm Linkrot2_0001 -28.09401` max -25 min -29
prm Linkrot3_0001 20.04755` max 22 min 18
prm Linktrans1_0001 0.74557` max 0.78 min 0.72
prm Linktrans2_0001 0.81777` max 0.85 min 0.77
prm Linktrans3_0001 -0.04792` max 0.01 min -0.07
rotate @ =Linkrot1_0001; qx 1
rotate @ =Linkrot2_0001; qy 1
rotate @ =Linkrot3_0001; qz 1
Translate( @ =Linktrans1_0001; , @ =Linktrans2_0001; , @ =Linktrans3_0001; )

rigid
z_matrix O1w
z_matrix Ca1 O1w @ 2.36626` max 2.4 min 2.2
z_matrix H1wa O1w 0.88      Ca1 109.5
z_matrix H1wb O1w 0.88      H1wa 109.5      Ca1 180
```

'rotate/translate coordinated water coordinated to Ca
prm O1Wrot1_0001 -107.69702` max -100 min -120
prm O1Wrot2_0001 58.79214` max 95 min 55
prm O1Wrot3_0001 23.77763` max 40 min 20
prm O1Wtrans1_0001 1.02449` max 1.05 min 0.95
prm O1Wtrans2_0001 0.77706` max 0.85 min 0.75
prm O1Wtrans3_0001 0.80010` max 0.81 min 0.72
rotate @ =O1Wrot1_0001; qx 1
rotate @ =O1Wrot2_0001; qy 1
rotate @ =O1Wrot3_0001; qz 1
Translate(@ =O1Wtrans1_0001; , @ =O1Wtrans2_0001; , @ =O1Wtrans3_0001;)

rigid
z_matrix O2w
z_matrix H2wa O2w 0.97
z_matrix H2wb O2w 0.97 H2wa 109.5

'rotate/translate water molecule in the interlayer
rotate @ 46.02881` qx 1 max 180 min -180
rotate @ 76.17717` qy 1 max 180 min -180
rotate @ -71.30406` qz 1 max 180 min -180
Translate(@ 0.97473` max 1.02 min 0.92, @ 0.38221` max 0.42 min 0.32, @ 0.56353` max 0.62 min 0.52)

scale @ 1.49943162e-005`
r_bragg @ 100
CS_G(csg_CPO70_0001, 97.19255`)
Strain_G(sg_CPO70_0001, 0.33592`_LIMIT_MIN_0.0001)
weight_percent 100.000`

'scan 91-135, transition region CPO-70-Ca to CPO-69-Ca
r_wp 5.4039603 r_exp 0.109818287 r_p 3.74747291 r_wp_dash 16.2490854 r_p_dash 14.5439577 r_exp_dash 0.330210924
weighted_Durbin_Watson 0.136147321 gof 49.2082005

iters 100000
chi2_convergence_criteria 0.001
'do_errors

xdd "FRL_M4242_400_80_0091p.xye"
bkg @ 848.391759` -380.839184` -10.5794137` 116.33329` -44.3793708` 6.69526946`
start_X 2.5
finish_X 26.8
x_calculation_step = 0.001;
Zero_Error(ze, 0.00278`)
lam ymin_on_ymax 0.0001 la 1.0 lo 0.6954 lh 0.1
LP_Factor(90)

'capillary
xo_Is
phase_name "quartz cap"
xo x_glass 9.68893518` I @ 22.62328`
CS_G(csg_glass, 1.00025`)

str
phase_name "CPO-70-Ca"
a a_CPO70_0091 24.536939` max 25.1 min 24.4
b b_CPO70_0091 10.007391` max 10.1 min 9.95
c c_CPO70_0091 6.636351` max 6.75 min 6.55
be be_CPO70_0091 93.28907` max 94.6 min 93.0
volume V_CPO70_0091 1626.877`
space_group "p21/n"
prm boc_0091 4.89062` max 5.0 min 0.0
prm bh_0091 =1.5 boc_0091;
prm !O2W_0091 0

site C1	x 0.75162`	y 0.80602`	z -0.01860`	occ C 1	beq =boc_0091;
site C2	x 0.75654`	y 0.90346`	z -0.16571`	occ C 1	beq =boc_0091;
site H2	x 0.78646`	y 0.96068`	z -0.15929`	occ H 1	beq =bh_0091;
site C3	x 0.71676`	y 0.91538`	z -0.32241`	occ C 1	beq =boc_0091;
site H3	x 0.72006`	y 0.98058`	z -0.42083`	occ H 1	beq =bh_0091;
site C4	x 0.67205`	y 0.82986`	z -0.33200`	occ C 1	beq =boc_0091;
site C5	x 0.66712`	y 0.73241`	z -0.18490`	occ C 1	beq =boc_0091;
site C6	x 0.70691`	y 0.72049`	z -0.02820`	occ C 1	beq =boc_0091;
site H6	x 0.70361`	y 0.65530`	z 0.07022`	occ H 1	beq =bh_0091;

```
site C7          x 0.79398`   y 0.79332`   z 0.14824`   occ C 1          beq =boc_0091;
site O1          x 0.63284`   y 0.84161`   z -0.48645`  occ O 1          beq =boc_0091;
site C8          x 0.84696`   y 0.83617`   z 0.12153`   occ C 1          beq =boc_0091;
site H8          x 0.85580`   y 0.87281`   z -0.00118`  occ H 1          beq =bh_0091;
site C9          x 0.88675`   y 0.82425`   z 0.27823`   occ C 1          beq =boc_0091;
site C10         x 0.87355`   y 0.76948`   z 0.46164`   occ C 1          beq =boc_0091;
site C11         x 0.82056`   y 0.72664`   z 0.48835`   occ C 1          beq =boc_0091;
site H11         x 0.81172`   y 0.69000`   z 0.61107`   occ H 1          beq =bh_0091;
site C12         x 0.78077`   y 0.73856`   z 0.33165`   occ C 1          beq =boc_0091;
site H12         x 0.74532`   y 0.70989`   z 0.34952`   occ H 1          beq =bh_0091;
site O2          x 0.91276`   y 0.75774`   z 0.61609`   occ O 1          beq =boc_0091;
site C13         x 0.63787`   y 0.94114`   z -0.63674`  occ C 1          beq =boc_0091;
site H13a        x 0.60284`   y 0.95721`   z -0.70429`  occ H 1          beq =bh_0091;
site H13b        x 0.65748`   y 0.90529`   z -0.74557`  occ H 1          beq =bh_0091;
site H13c        x 0.64469`   y 1.02619`   z -0.57328`  occ H 1          beq =bh_0091;
site C14         x 0.92745`   y 0.62954`   z 0.69319`   occ C 1          beq =boc_0091;
site H14a        x 0.96579`   y 0.62800`   z 0.73116`   occ H 1          beq =bh_0091;
site H14b        x 0.92575`   y 0.56561`   z 0.58517`   occ H 1          beq =bh_0091;
site H14c        x 0.91239`   y 0.61733`   z 0.82228`   occ H 1          beq =bh_0091;
site C15         x 0.61952`   y 0.64135`   z -0.19512`  occ C 1          beq =boc_0091;
site O3          x 0.60035`   y 0.59599`   z -0.36857`  occ O 1          beq =boc_0091;
site O4          x 0.59686`   y 0.60673`   z -0.03064`  occ O 1          beq =boc_0091;
site C16         x 0.94317`   y 0.86987`   z 0.24979`   occ C 1          beq =boc_0091;
site O5          x 0.97620`   y 0.89369`   z 0.40584`   occ O 1          beq =boc_0091;
site O6          x 0.95969`   y 0.88612`   z 0.06876`   occ O 1          beq =boc_0091;
site Ca1         x 0.96681`   y 0.94995`   z 0.74394`   occ Ca 1         beq @ 0.06562` max 5 min 0
site O1w         x 1.04036`   y 0.82099`   z 0.73282`   occ O 1          beq @ 4.99999` max 5 min 0
site H1wa        x 1.05451`   y 0.80780`   z 0.85607`   occ H 1          beq =bh_0091;
site H1wb        x 1.04565`   y 0.80010`   z 0.60662`   occ H 1          beq =bh_0091;
site O2w         x 0.92000`   y 0.32000`   z 0.55480`   occ O =O2W_0091; beq @ 0.00000` max 5 min 0
site H2wa        x 0.90322`   y 0.39775`   z 0.55069`   occ H =O2W_0091; beq =bh_0091;
site H2wb        x 0.93556`   y 0.30656`   z 0.44031`   occ H =O2W_0091; beq =bh_0091;

prm Torsion_0091 =Torsion_0090;
prm O3O4rot_0091 =O3O4rot_0090;
prm O5O6rot_0091 =O5O6rot_0090;
prm Merot1_0091 =Merot1_0090;
prm Merot2_0091 =Merot2_0090;
prm Metor1_0091 =Metor1_0090;
prm Metor2_0091 =Metor2_0090;

rigid
z_matrix C1
z_matrix C2 C1 1.39
z_matrix C6 C1 1.39          C2 120
z_matrix C7 C1 1.48          C2 120          C6 180
z_matrix C3 C2 1.39          C1 120          C7 180
z_matrix C5 C6 1.39          C1 120          C7 180
z_matrix C12 C7 1.39         C1 120          C6 =Torsion_0091;
z_matrix C8 C7 1.39          C1 120          C12 180
z_matrix C4 C3 1.39          C2 120          C1 0
z_matrix C15 C5 1.48         C6 120          C4 180
z_matrix C11 C12 1.39        C7 120          C8 0
z_matrix C9 C8 1.39          C7 120          C12 0
z_matrix O1 C4 1.37          C3 120          C5 180
z_matrix O3 C15 1.30         C5 120          C4 =O3O4rot_0091;
z_matrix O4 C15 1.30         C5 120          C6 =O3O4rot_0091;
z_matrix C10 C9 1.39         C8 120          C11 0
z_matrix C16 C9 1.48         C8 120          C10 180
z_matrix C13 O1 1.42         C4 120          C3 =Metor1_0091;
z_matrix O2 C10 1.37         C9 120          C11 180
z_matrix O5 C16 1.30         C9 120          C10 =O5O6rot_0091;
z_matrix O6 C16 1.30         C9 120          C8 =O5O6rot_0091;
z_matrix C14 O2 1.42         C10 120         C11 =Metor2_0091;
z_matrix H3 C3 0.93          C2 120          C1 180
z_matrix H2 C2 0.93          C1 120          C6 180
z_matrix H6 C6 0.93          C5 120          C4 180
z_matrix H8 C8 0.93          C9 120          C10 180
z_matrix H11 C11 0.93        C12 120         C7 180
z_matrix H12 C12 0.93        C7 120          C8 180
z_matrix H14a C14 0.96       O2 109.5        C10 =Merot1_0091;
z_matrix H14b C14 0.96       O2 109.5        C10 =Merot1_0091-109.5;
z_matrix H14c C14 0.96       O2 109.5        C10 =Merot1_0091+109.5;
z_matrix H13a C13 0.96       O1 109.5        C4 =Merot2_0091;
```

```
z_matrix H13b C13 0.96          O1 109.5            C4 =Merot2_0091-109.5;
z_matrix H13c C13 0.96          O1 109.5            C4 =Merot2_0091+109.5;

'rotate/translate linker
prm Linkrot1_0091 =Linkrot1_0090;
prm Linkrot2_0091 =Linkrot2_0090;
prm Linkrot3_0091 =Linkrot3_0090;
prm Linktrans1_0091 =Linktrans1_0090;
prm Linktrans2_0091 =Linktrans2_0090;
prm Linktrans3_0091 =Linktrans3_0090;
rotate =Linkrot1_0091; qx 1
rotate =Linkrot2_0091; qy 1
rotate =Linkrot3_0091; qz 1
Translate( =Linktrans1_0091; , =Linktrans2_0091; , =Linktrans3_0091; )

rigid
z_matrix O1w
z_matrix Ca1 O1w @ 2.22328` max 2.4 min 2.2
z_matrix H1wa O1w 0.88          Ca1 109.5
z_matrix H1wb O1w 0.88          H1wa 109.5          Ca1 180

'rotate/translate coordinated water coordinated to Ca
prm O1Wrot1_0091 =O1Wrot1_0090;
prm O1Wrot2_0091 =O1Wrot2_0090;
prm O1Wrot3_0091 =O1Wrot3_0090;
prm O1Wtrans1_0091 =O1Wtrans1_0090;
prm O1Wtrans2_0091 =O1Wtrans2_0090;
prm O1Wtrans3_0091 =O1Wtrans3_0090;
rotate =O1Wrot1_0091; qx 1
rotate =O1Wrot2_0091; qy 1
rotate =O1Wrot3_0091; qz 1
Translate( =O1Wtrans1_0091; , =O1Wtrans2_0091; , =O1Wtrans3_0091; )

rigid
z_matrix O2w
z_matrix H2wa O2w 0.97
z_matrix H2wb O2w 0.97          H2wa 109.5

'rotate/translate water molecule in the interlayer
rotate @ -85.31488` qx 1 max 180 min -180
rotate @ -112.27570` qy 1 max 180 min -180
rotate @ 23.46445` qz 1 max 180 min -180
Translate(@ 0.92000` max 1.02 min 0.92, @ 0.32000` max 0.42 min 0.32, @ 0.55480` max 0.62 min 0.52)

scale @ 1.48801448e-005`
r_bragg @ 100
CS_G(csg_CPO70_0091, 102.33110`)
Strain_G(sg_CPO70_0091, 0.38890`_LIMIT_MIN_0.0001)
weight_percent 99.772`

str
phase_name "CPO-69-Ca"
a a_CPO69_0091 24.827566` max 24.9 min 24.7
b b_CPO69_0091 8.099999` max 8.1 min 7.9
c c_CPO69_0091 7.434659` max 7.8 min 7.4
be be_CPO69_0091 90.80001` max 91.2 min 90.8
volume V_CPO69_0091 1494.989`
space_group "C2/c"

site C1     x -0.22327    y 0.7552    z 0.4569    occ C 1    beq 4.10575543
site C2     x -0.17650    y 0.7017    z 0.5427    occ C 1    beq 3.09510794
site H2     x -0.1792     y 0.6589    z 0.6571    occ H 1    beq 3.71097125
site C3     x -0.12603    y 0.7087    z 0.4674    occ C 1    beq 2.79507197
site C4     x -0.12141    y 0.7714    z 0.2960    occ C 1    beq 3.52937053
site C5     x -0.16748    y 0.8276    z 0.2094    occ C 1    beq 6.72712236
site H5     x -0.1649     y 0.8723    z 0.0958    occ H 1    beq 8.05359719
site C6     x -0.21696    y 0.8188    z 0.2874    occ C 1    beq 7.31140294
site H6     x -0.2473     y 0.8568    z 0.2247    occ H 1    beq 8.76420871
site C7     x -0.07930    y 0.6482    z 0.5791    occ C 1    beq 2.64505398
site C8     x -0.06576    y 0.8863    z 0.0712    occ C 1    beq 5.24273386
site H8A    x -0.0875     y 0.8477    z -0.0273   occ H 1    beq 7.89568352
site H8B    x -0.0285     y 0.8893    z 0.0376    occ H 1    beq 7.89568352
site H8C    x -0.0772     y 0.9965    z 0.1045    occ H 1    beq 7.89568352
site O1     x -0.08715    y 0.6087    z 0.7355    occ O 1    beq 4.4057914
```

site O2	x -0.03250	y 0.6410	z 0.5149	occ O 1	beq 3.06352521
site O3	x -0.07179	y 0.7762	z 0.2172	occ O 1	beq 4.03469428
site Ca1	x 0.0000	y 0.54205	z 0.2500	occ Ca 1	beq 2.57399283

scale @ 3.9035584e-008`_LIMIT_MIN_1e-015
r_bragg @ 100
CS_G(csg_CPO69_0091, 138.23728`_LIMIT_MIN_0.3)
Strain_G(sg_CPO69_0091, 0.03562`_LIMIT_MIN_0.0001)
weight_percent 0.228`

'scan 136-215, CPO-69-Ca dominant region
r_wp 4.64258695 r_exp 0.110926189 r_p 3.70420878 r_wp_dash 15.4315247 r_p_dash 15.4047524 r_exp_dash 0.368708275
weighted_Durbin_Watson 0.1709313 gof 41.8529382

iters 100000
chi2_convergence_criteria 0.001
'do_errors

xdd "FRL_M4242_400_80_0136p.xye"
bkg @ 858.316146` -389.929202` -3.40523492` 124.724868` -59.6349943` 13.6625756`
start_X 2.5
finish_X 26.8
x_calculation_step = 0.001;
Zero_Error(ze, 0.00278`)
lam ymin_on_ymax 0.0001 la 1.0 lo 0.6954 lh 0.1
LP_Factor(90)

'capillary
xo_Is
phase_name "quartz cap"
xo x_glass 9.68893518` I @ 22.22510`
CS_G(csg_glass, 1.00025`)

str
phase_name "CPO-70-Ca"
a a_CPO70_0136 24.400006`max 25.1 min 24.4
b b_CPO70_0136 9.950000` max 10.1 min 9.95
c c_CPO70_0136 6.550001` max 6.75 min 6.55
be be_CPO70_0136 93.00001`max 94.6 min 93.0
volume V_CPO70_0136 1588.030`
space_group "p21/n"
prm boc_0136 5.00000` max 5.0 min 0.0
prm bh_0136 =1.5 boc_0136;
prm !O2W_0136 0

site C1	x 0.75162`	y 0.80602`	z -0.01860`	occ C 1	beq =boc_0136;
site C2	x 0.75677`	y 0.90402`	z -0.16760`	occ C 1	beq =boc_0136;
site H2	x 0.78685`	y 0.96157`	z -0.16110`	occ H 1	beq =bh_0136;
site C3	x 0.71698`	y 0.91601`	z -0.32633`	occ C 1	beq =boc_0136;
site H3	x 0.72043`	y 0.98158`	z -0.42602`	occ H 1	beq =bh_0136;
site C4	x 0.67203`	y 0.82999`	z -0.33605`	occ C 1	beq =boc_0136;
site C5	x 0.66688`	y 0.73199`	z -0.18704`	occ C 1	beq =boc_0136;
site C6	x 0.70667`	y 0.72000`	z -0.02832`	occ C 1	beq =boc_0136;
site H6	x 0.70322`	y 0.65443`	z 0.07137`	occ H 1	beq =bh_0136;
site C7	x 0.79399`	y 0.79325`	z 0.15039`	occ C 1	beq =boc_0136;
site O1	x 0.63281`	y 0.84181`	z -0.49248`	occ O 1	beq =boc_0136;
site C8	x 0.84731`	y 0.83635`	z 0.12334`	occ C 1	beq =boc_0136;
site H8	x 0.85636`	y 0.87320`	z -0.00096`	occ H 1	beq =bh_0136;
site C9	x 0.88710`	y 0.82436`	z 0.28206`	occ C 1	beq =boc_0136;
site C10	x 0.87357`	y 0.76927`	z 0.46784`	occ C 1	beq =boc_0136;
site C11	x 0.82025`	y 0.72618`	z 0.49489`	occ C 1	beq =boc_0136;
site H11	x 0.81120`	y 0.68933`	z 0.61919`	occ H 1	beq =bh_0136;
site C12	x 0.78046`	y 0.73817`	z 0.33617`	occ C 1	beq =boc_0136;
site H12	x 0.74478`	y 0.70934`	z 0.35427`	occ H 1	beq =bh_0136;
site O2	x 0.91279`	y 0.75746`	z 0.62427`	occ O 1	beq =boc_0136;
site C13	x 0.63808`	y 0.94192`	z -0.64471`	occ C 1	beq =boc_0136;
site H13a	x 0.60295`	y 0.95808`	z -0.71314`	occ H 1	beq =bh_0136;
site H13b	x 0.65795`	y 0.90586`	z -0.75495`	occ H 1	beq =bh_0136;
site H13c	x 0.64485`	y 1.02746`	z -0.58044`	occ H 1	beq =bh_0136;
site C14	x 0.92746`	y 0.62852`	z 0.70237`	occ C 1	beq =boc_0136;
site H14a	x 0.96596`	y 0.62697`	z 0.74084`	occ H 1	beq =bh_0136;
site H14b	x 0.92590`	y 0.56422`	z 0.59296`	occ H 1	beq =bh_0136;
site H14c	x 0.91214`	y 0.61625`	z 0.83313`	occ H 1	beq =bh_0136;
site C15	x 0.61902`	y 0.64040`	z -0.19739`	occ C 1	beq =boc_0136;

```
site O3          x 0.59998`    y 0.59478`    z -0.37308`    occ O 1          beq =boc_0136;
site O4          x 0.59601`    y 0.60558`    z -0.03080`    occ O 1          beq =boc_0136;
site C16         x 0.94387`    y 0.87024`    z 0.25325`     occ C 1          beq =boc_0136;
site O5          x 0.97688`    y 0.89420`    z 0.41131`     occ O 1          beq =boc_0136;
site O6          x 0.96074`    y 0.88658`    z 0.06989`     occ O 1          beq =boc_0136;
site Ca1         x 0.96051`    y 0.96100`    z 0.74498`     occ Ca 1         beq @ 0.00167` max 5 min 0
site O1w         x 1.04036`    y 0.82099`    z 0.73282`     occ O 1          beq @ 0.00183` max 5 min 0
site H1wa        x 1.05442`    y 0.80772`    z 0.85766`     occ H 1          beq =bh_0136;
site H1wb        x 1.04585`    y 0.79998`    z 0.60499`     occ H 1          beq =bh_0136;
site O2w         x 0.92000`    y 0.32000`    z 0.55480`     occ O =O2W_0136;  beq @ 0.00000` max 5 min 0
site H2wa        x 0.90313`    y 0.39820`    z 0.55063`     occ H =O2W_0136;  beq =bh_0136;
site H2wb        x 0.93580`    y 0.30648`    z 0.43884`     occ H =O2W_0136;  beq =bh_0136;

prm Torsion_0136 =Torsion_0090;
prm O3O4rot_0136 =O3O4rot_0090;
prm O5O6rot_0136 =O5O6rot_0090;
prm Merot1_0136 =Merot1_0090;
prm Merot2_0136 =Merot2_0090;
prm Metor1_0136 =Metor1_0090;
prm Metor2_0136 =Metor2_0090;

rigid
z_matrix C1
z_matrix C2 C1 1.39
z_matrix C6 C1 1.39          C2 120
z_matrix C7 C1 1.48          C2 120          C6 180
z_matrix C3 C2 1.39          C1 120          C7 180
z_matrix C5 C6 1.39          C1 120          C7 180
z_matrix C12 C7 1.39         C1 120          C6 =Torsion_0136;
z_matrix C8 C7 1.39          C1 120          C12 180
z_matrix C4 C3 1.39          C2 120          C1 0
z_matrix C15 C5 1.48         C6 120          C4 180
z_matrix C11 C12 1.39        C7 120          C8 0
z_matrix C9 C8 1.39          C7 120          C12 0
z_matrix O1 C4 1.37          C3 120          C5 180
z_matrix O3 C15 1.30         C5 120          C4 =O3O4rot_0136;
z_matrix O4 C15 1.30         C5 120          C6 =O3O4rot_0136;
z_matrix C10 C9 1.39         C8 120          C11 0
z_matrix C16 C9 1.48         C8 120          C10 180
z_matrix C13 O1 1.42         C4 120          C3 =Metor1_0136;
z_matrix O2 C10 1.37         C9 120          C11 180
z_matrix O5 C16 1.30         C9 120          C10 =O5O6rot_0136;
z_matrix O6 C16 1.30         C9 120          C8 =O5O6rot_0136;
z_matrix C14 O2 1.42         C10 120         C11 =Metor2_0136;
z_matrix H3 C3 0.93          C2 120          C1 180
z_matrix H2 C2 0.93          C1 120          C6 180
z_matrix H6 C6 0.93          C5 120          C4 180
z_matrix H8 C8 0.93          C9 120          C10 180
z_matrix H11 C11 0.93        C12 120         C7 180
z_matrix H12 C12 0.93        C7 120          C8 180
z_matrix H14a C14 0.96       O2 109.5        C10 =Merot1_0136;
z_matrix H14b C14 0.96       O2 109.5        C10 =Merot1_0136-109.5;
z_matrix H14c C14 0.96       O2 109.5        C10 =Merot1_0136+109.5;
z_matrix H13a C13 0.96       O1 109.5        C4 =Merot2_0136;
z_matrix H13b C13 0.96       O1 109.5        C4 =Merot2_0136-109.5;
z_matrix H13c C13 0.96       O1 109.5        C4 =Merot2_0136+109.5;

'rotate/translate linker
prm Linkrot1_0136 =Linkrot1_0090;
prm Linkrot2_0136 =Linkrot2_0090;
prm Linkrot3_0136 =Linkrot3_0090;
prm Linktrans1_0136 =Linktrans1_0090;
prm Linktrans2_0136 =Linktrans2_0090;
prm Linktrans3_0136 =Linktrans3_0090;
rotate =Linkrot1_0136; qx 1
rotate =Linkrot2_0136; qy 1
rotate =Linkrot3_0136; qz 1
Translate( =Linktrans1_0136; , =Linktrans2_0136; , =Linktrans3_0136; )

rigid
z_matrix O1w
z_matrix Ca1 O1w @ 2.40000` max 2.4 min 2.2
z_matrix H1wa O1w 0.88       Ca1 109.5
z_matrix H1wb O1w 0.88       H1wa 109.5      Ca1 180
```

```
'rotate/translate coordinated water coordinated to Ca
prm O1Wrot1_0136 =O1Wrot1_0090;
prm O1Wrot2_0136 =O1Wrot2_0090;
prm O1Wrot3_0136 =O1Wrot3_0090;
prm O1Wtrans1_0136 =O1Wtrans1_0090;
prm O1Wtrans2_0136 =O1Wtrans2_0090;
prm O1Wtrans3_0136 =O1Wtrans3_0090;
rotate =O1Wrot1_0136; qx 1
rotate =O1Wrot2_0136; qy 1
rotate =O1Wrot3_0136; qz 1
Translate( =O1Wtrans1_0136; , =O1Wtrans2_0136; , =O1Wtrans3_0136; )

rigid
z_matrix O2w
z_matrix H2wa O2w 0.97
z_matrix H2wb O2w 0.97          H2wa 109.5

'rotate/translate water molecule in the interlayer
rotate @ -85.31488` qx 1 max 180 min -180
rotate @ -472.27570` qy 1 max 180 min -180
rotate @ 23.46445` qz 1 max 180 min -180
Translate(@ 0.92000` max 1.02 min 0.92, @ 0.32000` max 0.42 min 0.32, @ 0.55480` max 0.62 min 0.52)

scale @ 1.98389884e-007_LIMIT_MIN_1e-015
r_bragg @ 100
CS_G(csg_CPO70_0136, 1.49429`_LIMIT_MIN_0.3)
Strain_G(sg_CPO70_0136, 1.56866`_LIMIT_MIN_0.0001)
Known_Weight_Percent(0)
weight_percent 0.000`

str
phase_name "CPO-69-Ca"
a a_CPO69_0136 24.818057` max 24.9 min 24.7
b b_CPO69_0136 8.027959` max 8.1 min 7.9
c c_CPO69_0136 7.657704` max 7.8 min 7.4
be be_CPO69_0136 91.13338` max 91.2 min 90.8
volume V_CPO69_0136 1525.410`
space_group "C2/c"

site C1          x -0.22327      y 0.7552        z 0.4569   occ C 1        beq 4.10575543
site C2          x -0.17650      y 0.7017        z 0.5427   occ C 1        beq 3.09510794
site H2          x -0.1792       y 0.6589        z 0.6571   occ H 1        beq 3.71097125
site C3          x -0.12603      y 0.7087        z 0.4674   occ C 1        beq 2.79507197
site C4          x -0.12141      y 0.7714        z 0.2960   occ C 1        beq 3.52937053
site C5          x -0.16748      y 0.8276        z 0.2094   occ C 1        beq 6.72712236
site H5          x -0.1649       y 0.8723        z 0.0958   occ H 1        beq 8.05359719
site C6          x -0.21696      y 0.8188        z 0.2874   occ C 1        beq 7.31140294
site H6          x -0.2473       y 0.8568        z 0.2247   occ H 1        beq 8.76420871
site C7          x -0.07930      y 0.6482        z 0.5791   occ C 1        beq 2.64505398
site C8          x -0.06576      y 0.8863        z 0.0712   occ C 1        beq 5.24273386
site H8A         x -0.0875       y 0.8477        z -0.0273  occ H 1        beq 7.89568352
site H8B         x -0.0285       y 0.8893        z 0.0376   occ H 1        beq 7.89568352
site H8C         x -0.0772       y 0.9965        z 0.1045   occ H 1        beq 7.89568352
site O1          x -0.08715      y 0.6087        z 0.7355   occ O 1        beq 4.4057914
site O2          x -0.03250      y 0.6410        z 0.5149   occ O 1        beq 3.06352521
site O3          x -0.07179      y 0.7762        z 0.2172   occ O 1        beq 4.03469428
site Ca1         x 0.0000        y 0.54205       z 0.2500   occ Ca 1       beq 2.57399283

scale @ 1.44874527e-005`
r_bragg @ 100
CS_G(csg_CPO69_0136, 10000.00000`_LIMIT_MIN_0.3)
Strain_G(sg_CPO69_0136, 2.13403`)
weight_percent 100.000`
```