# Solvothermal Synthesis of Porous Organic Cage CC3 in the Presence of Dimethylformamide as Solvent

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# Supplemental Information

## 1.1. Materials

1,3,5-Triformylbenzene (98%), and (±)-trans-1,2-diaminocyclohexane (98%), were purchased from ACROS Organics. Anhydrous N, N-dimethylformamide (99.8 %) , (DMF) was purchased from Sigma Aldrich. All chemicals were used as received.

## 1.2. Synthesis

Non-stirred experiments

The aldehyde solution was made by adding 0.150 g of 1,3,5-triformylbenzene to a glass beaker followed by the slow and careful addition of 12 mL of DMF. In a separate beaker, a molar excess amount (0.170 g) of (±)-trans-1,2-diaminocyclohexane was added to 12 mL of DMF. The diamine solution was very carefully layered onto the aldehyde solution to prevent mixing. The reaction was covered and allowed to sit at room temperature for 4 days. After 1 day of reacting, the solution turned from clear to neon yellow in color, and white precipitates were observed at the bottom of the beaker. After 4 days, the solution was centrifuged for 10 minutes at 4000 rpm to obtain the product, and washed with clean DMF 3X. The powder was then allowed to dry in a vacuum oven at 110°C overnight. (Yield 14%)

Stirred Experiments

The aldehyde solution was made by adding 0.150 g of 1,3,5-triformylbenzene to a glass beaker followed by the addition of 12 mL of DMF. In a separate beaker, a molar excess[1] amount (0.170 g) of (±)-trans-1,2-diaminocyclohexane was added to 12 mL of DMF. The two solutions were mixed together quickly, covered, and placed on a stir plate at 300 rpm, to stir for 4 days at room temperature. After 1 day of reacting, the solution turned from clear to turbid neon yellow in color, due to the precipitated mixed chiral cages in solution. After 4 days, the solution was centrifuged for 10 minutes

at 4000 rpm to obtain the product, and washed with clean DMF 3X. The powder was then allowed to dry in a vacuum oven at 110°C overnight. (Yield 14%)

Solvothermal Experiments (samples correspond to Figure 3 in manuscript)

The cage synthesis solution was made using the same procedure as the stirred experiments. After 3 days of stirring at room temperature, the reaction mixture was added to a Teflon lined stainless steel autoclave and placed in an oven for solvothermal treatment. A heating rate of 20°C/min to 100°C was used. Sample (c), (e), (f), and (g), were held at 100°C for 12-h, 16-h, 24-h, and 3-days respectively. After the holding temperature step was complete, the reaction decreased in temperature at a rate of 10°C/min to room temperature. Sample (d) followed the same heating rate to 100°C and was held for 12-h, it decreased in temperature at a the same rate as above to 50°C, where it was held at this lower temperature for an additional 12 hours. After 12 hours, the autoclave was set on the bench top to cool to room temperature. Samples (c), (d), (e), (f), and (g) were centrifuged at 4000 rpm for 5 minutes to afford the crystalline product, and washed 3X with clean DMF. The powered was allowed to dry in a vacuum oven at 110°C overnight. (Yield = 29.8%, 35.6%, 37.6%, 51.9%, 60% for samples e, d, c, f, and g respectively)

Testing for Presence of Soluble Heterochiral Cage

To prove that soluble heterochiral cages were being synthesized, we performed a small but efficient analysis. We repeated the 24 hour solvothermal treatment experiment, and instead of centrifuging the solution, we filtered the solution to ideally separate the co-crystal precipitates from the soluble cages in DMF. The precipitates were washed copiously with clean DMF to ensure most of the soluble cages were obtained in the filtrate. The filtrate was then dried from DMF under vacuum conditions. The dried filtrate powder was then analyzed by PXRD. The XRD pattern was then analyzed using Rietveld Refinement in the GSAS-II software.[2] Two crystal phases were refined; CC3α,[3] and the dissymmetric cage, (CC3-SR,RS).[4] Final refinement results: Number of function calls: 5. No. of observations: 601. No. of parameters: 28. User rejected: 0. Sp. gp. extinct: 0. Refinement time= 38.551s, 38.551/cycle, for 1 cycle. wR=12.96%, chi^2= 740.402, GOF = 1.14.

Elucidating the Effect of DMF as Solvent

Table S2 summarizes the experimental conditions used for these experiments. After each experiment, the resulting solution was centrifuged to afford a precipitate product, and a supernatant product. The precipitate was washed additionally, similar to the procedure above, and allowed to dry. The supernatant species was dried from solvent (DMF, DCM, or both), and redissolved in a small amount

of DCM (~3 mL), with stirring. About 10 mL of hexane, was added to the solution following Slater *et al*'s[4] procedure, in order to precipitate any dissymmetric cages left in the supernatant. Solids formed after adding hexane were filtered. The filtrate, and filtered products were further analyzed using XRD, and SEM. Additionally their final mass, and yields were quantitatively measured.

## 1.3. Characterization

**PXRD.** Powdered X-Ray Diffraction data was collected using a X'Pert PRO MPD X-ray Diffraction system operated at 30 kV and 25 mA with a Cu Kα1 radiation (λ=1.54059 Å).

**SEM.** Scanning electron microscopy was performed on a JEOL JSM-7000F operated at an accelerating voltage between 4-8 kV.

**Thermogravimetric Analysis**. TGA was performed on a TA Instruments (Q150), the samples were heated at a rate of 10°C/min from room temperature to 800°C.

**FTIR**. Fourier Transform Infrared Spectroscopy was performed using a DGTS detector on a Thermo Nicolet iS50 ATR FT-IR-Spectrometer using 15 scans, and 4 $cm^{-1}$ resolution.

**Surface Area Analysis**. BET areas, external surface areas, and pore volumes were extracted from collected nitrogen adsorption-desorption isotherms on a ASAP 2020 Porosimeter by Micromeritics. Prior to this analysis the samples were degassed at 180°C for 6 hours.

**Rietveld Refinement**. Refinement calculations on PXRD patterns were analyzed using GSAS-II software.[2]

**Nuclear Magnetic Resonance**. 1D $^{1}H$ NMR spectra were collected on a JEOL 500 MHZ liquid state NMR, in $CDCl_3$

## 1.4. Time Elapsed Photos

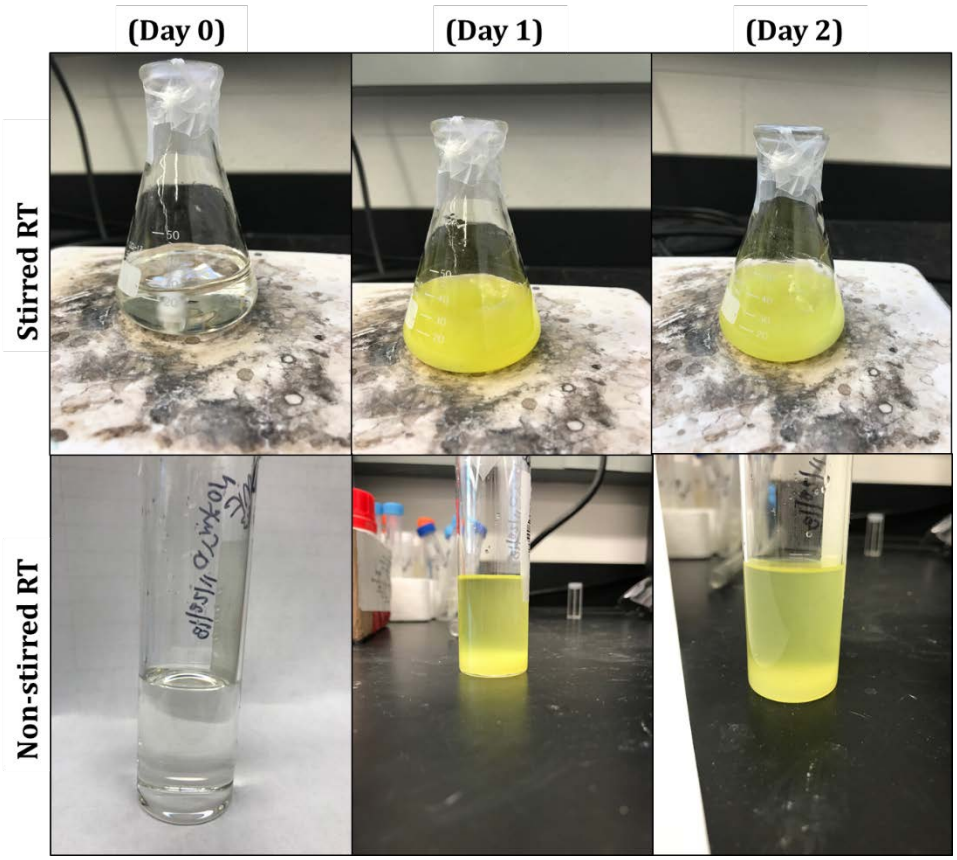
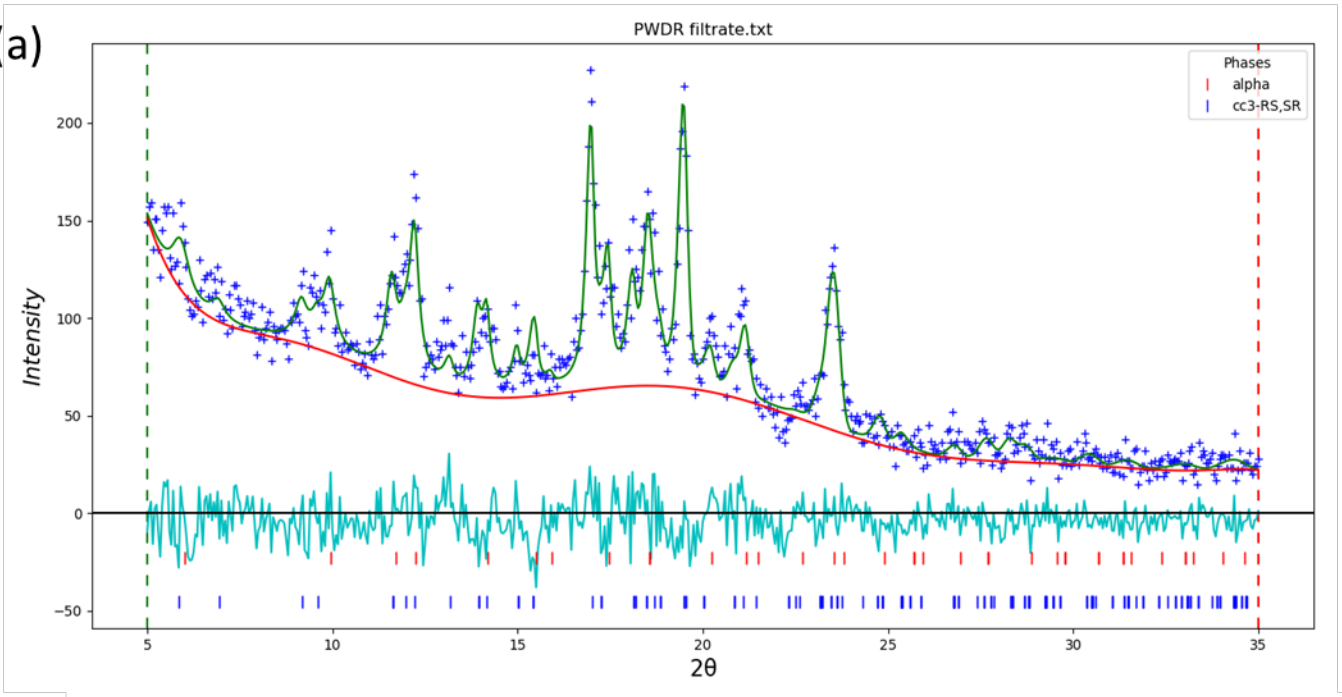



**Figure S1.** Time elapsed photos of stirred and non-stirred experiments. The third day is emitted due to little change in appearance from day 2.

### 1.5. Rietveld Refinement

(a)




(b)

```
Phase: cc3-RS,SR in histogram: PWDR filtrate.txt
================================================================================================================
Final refinement RF, RF^2 = 12.89%, 17.47% on 147 reflections
Durbin-Watson statistic = 1.616
Bragg intensity sum = 6.65e+03
Phase fraction  :    0.71323, sig    0.01503 Weight fraction  :  0.65100, sig    0.01372

Phase: alpha in histogram: PWDR filtrate.txt
================================================================================================================
Final refinement RF, RF^2 = 11.34%, 13.80% on 38 reflections
Durbin-Watson statistic = 1.616
Bragg intensity sum = 3.6e+03
Phase fraction  :    0.28677, sig    0.01503 Weight fraction  :  0.34900, sig    0.01830

Histogram: PWDR filtrate.txt histogram Id: 0
================================================================================================================
PWDR histogram weight factor = 1.000
Final refinement wR = 12.96% on 601 observations in this histogram
Other residuals: R = 10.11%, R-bkg = 10.39%, wR-bkg = 12.96% wRmin = 11.68%
Instrument type: Bragg-Brentano
```

**Figure S2.** Refinement plot (a), and data, (b), showing phase fractions of filtrate from 3 day RT stir + 24h@100°C solvothermal sample.

## 1.6.Thermogravimetric Analysis Profiles

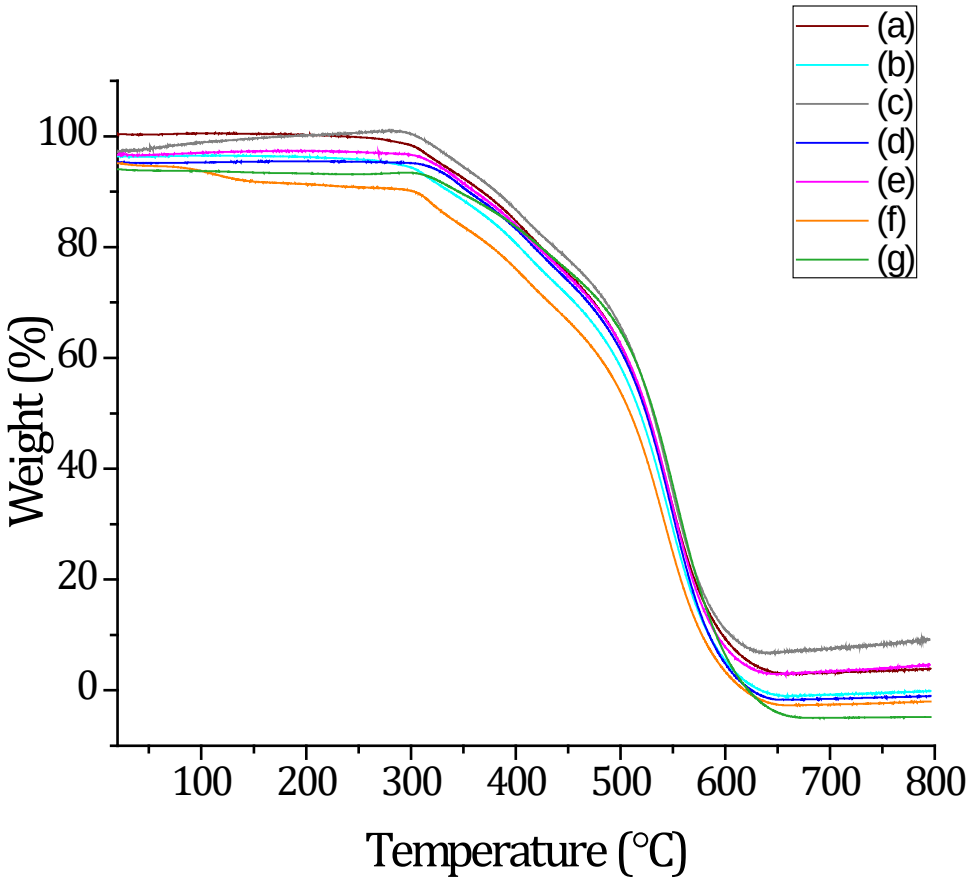



**Figure S3.** Thermogravimetric Analysis profiles for (a) 4 day RT non-stirred, (b) 4 day RT stir, (c) 3 day RT stir + 12h@100°C solvothermal, (d) 3 day RT stir + 12h@100°C +12h@50°C solvothermal, (e) 3 day RT stir + 16h@100°C solvothermal, (f) 3 day RT stir + 24h@100°C solvothermal, (g) 3 day RT stir + 3d@100°C solvothermal.

## 1.7.Fourier Transform Infrared Spectroscopy

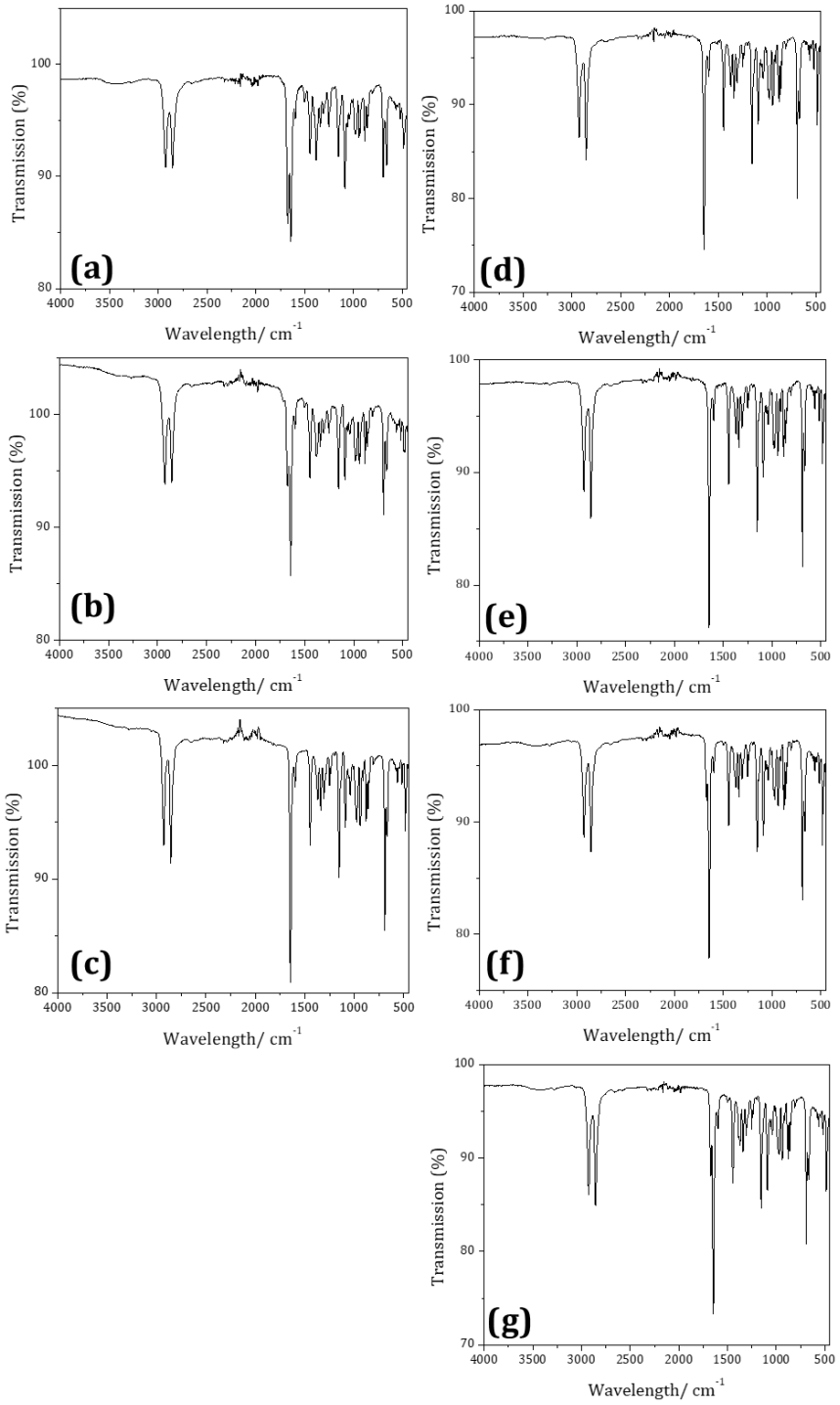



**Figure S4.** Fourier Transform Infrared Spectroscopy spectra for (a) 4 day RT non-stirred, (b) 4 day RT stir, (c) 3 day RT stir + 12h@100°C solvothermal, (d) 3 day RT stir + 12h@100°C +12h@50°C solvothermal, (e) 3 day RT stir + 16h@100°C solvothermal, (f) 3 day RT stir + 24h@100°C solvothermal, (g) 3 day RT stir + 3d@100°C solvothermal.

## 1.7. Additional Scanning Electron Microscopy Images

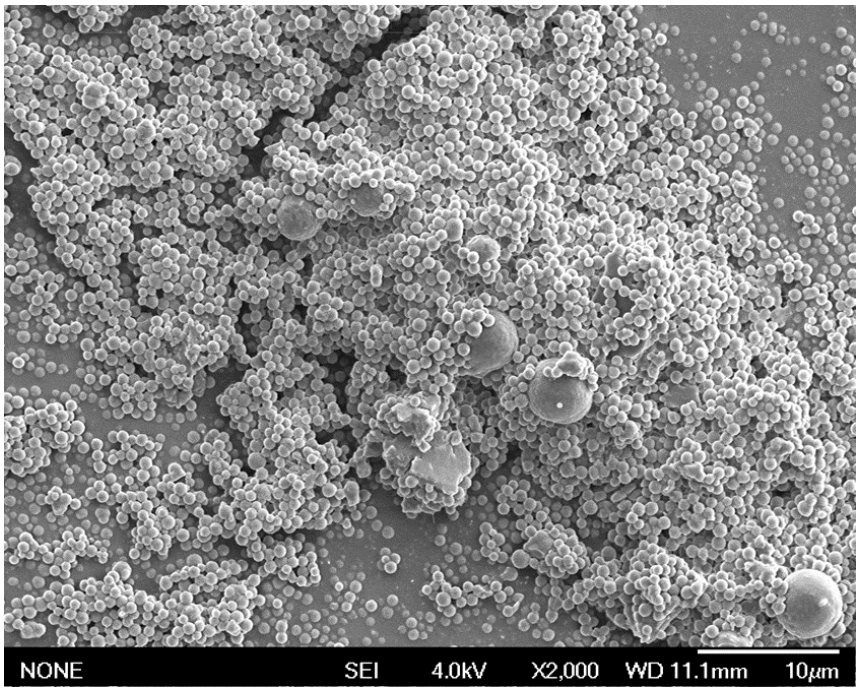



**Figure S5**. Scanning electron microscopy image of 4 day non-stirred room temperature sample.

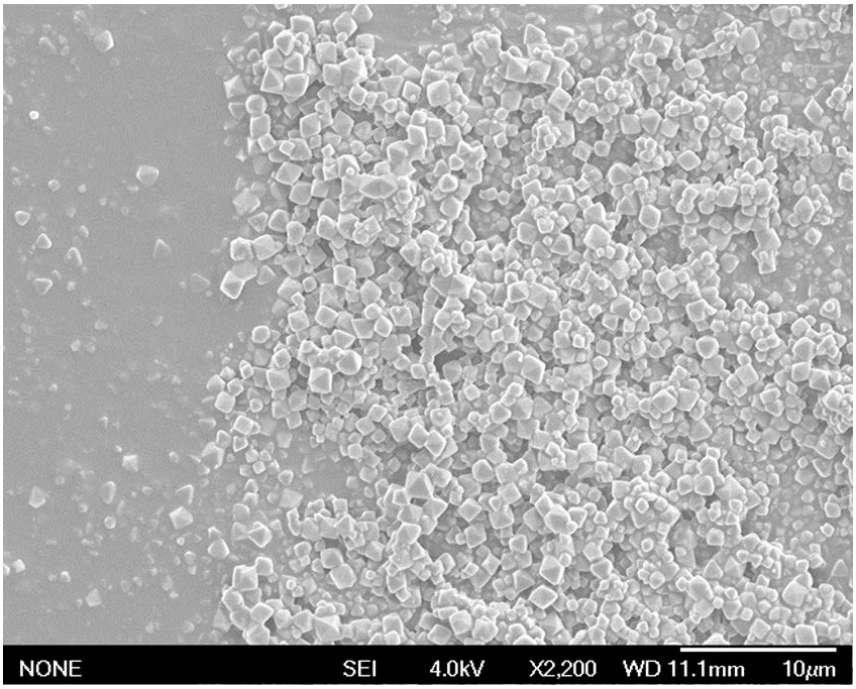



**Figure S6.** Scanning electron microscopy image of 4 day stirred room temperature sample.

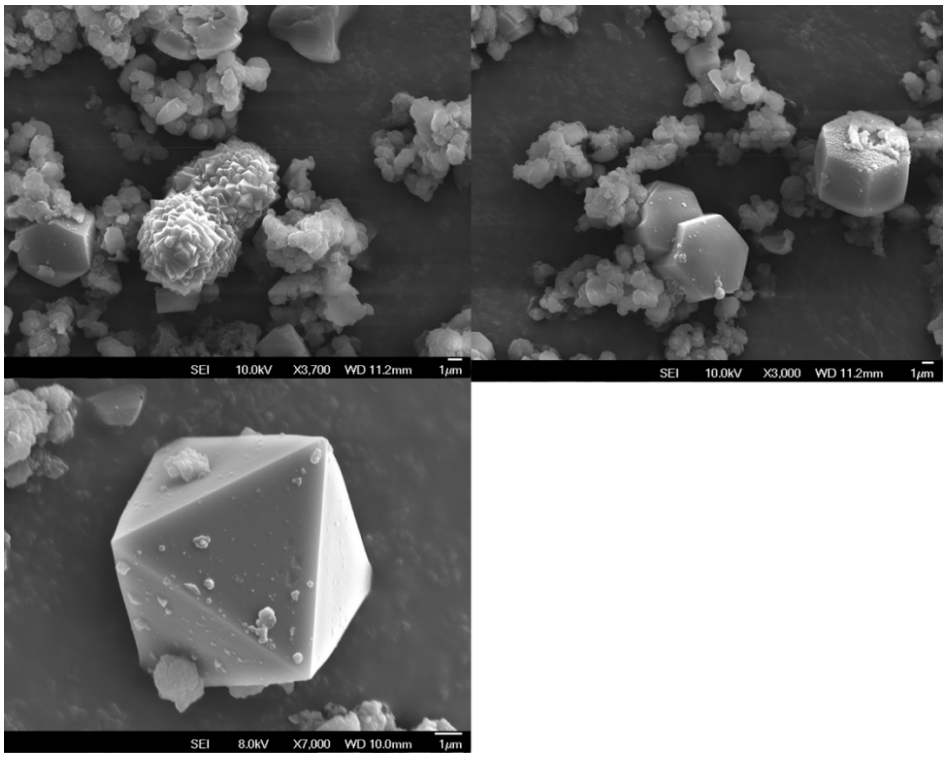



**Figure S7.** Scanning electron microscopy image of sample which was stirred at room temperature for 3 days, followed by 12 hours of solvothermal treatment.at 100°C.

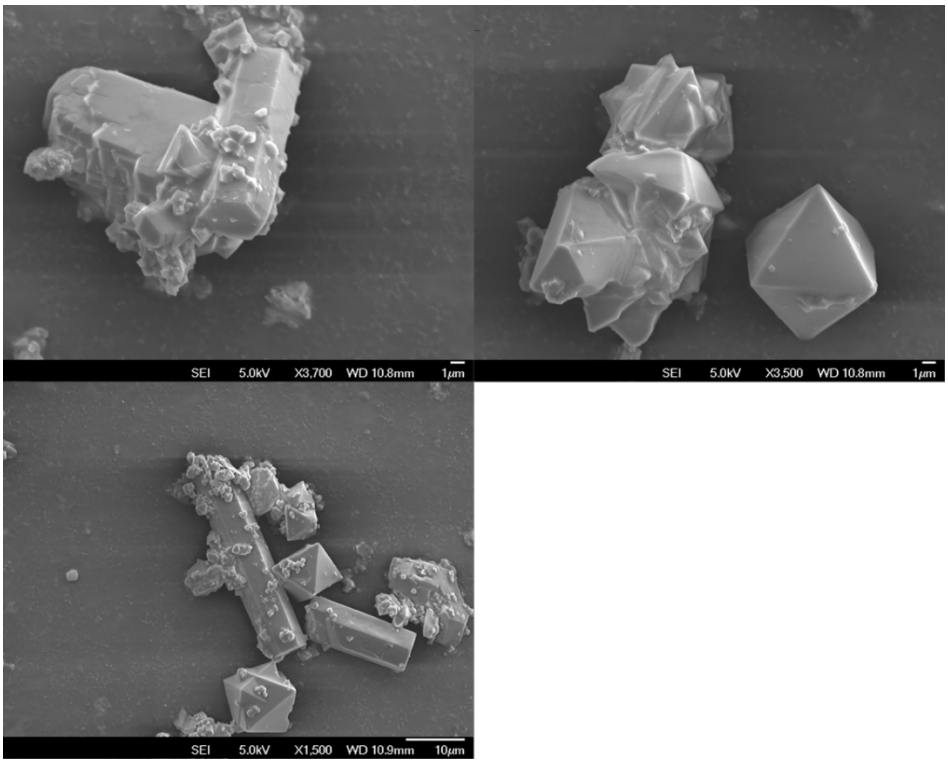



**Figure S8.** Scanning electron microscopy image of sample which was stirred at room temperature for 3 days, followed by 12 hours of solvothermal treatment at 100°C, and an additional 12 hours at 50°C.

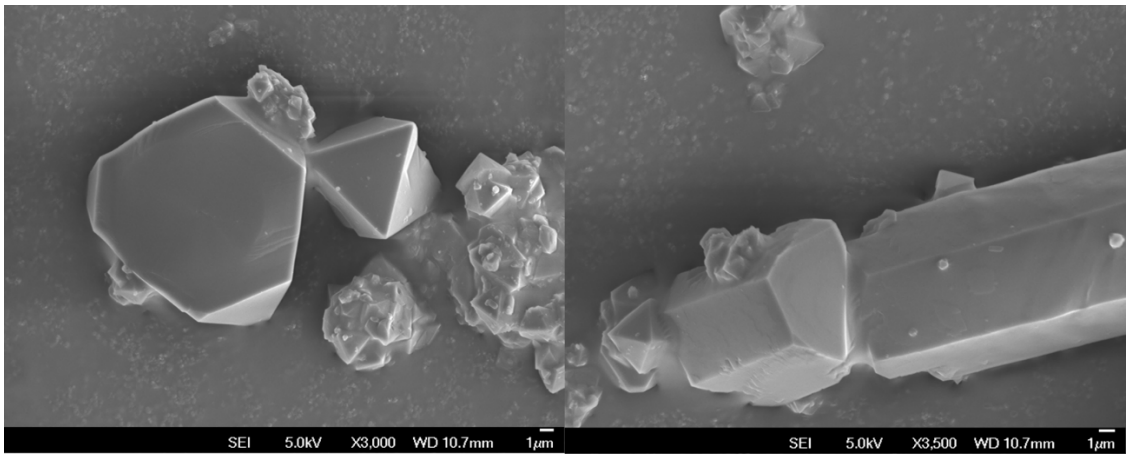



**Figure S9**. Scanning electron microscopy image of sample which was stirred at room temperature for 3 days, followed by 16 hours of solvothermal treatment at 100°C.

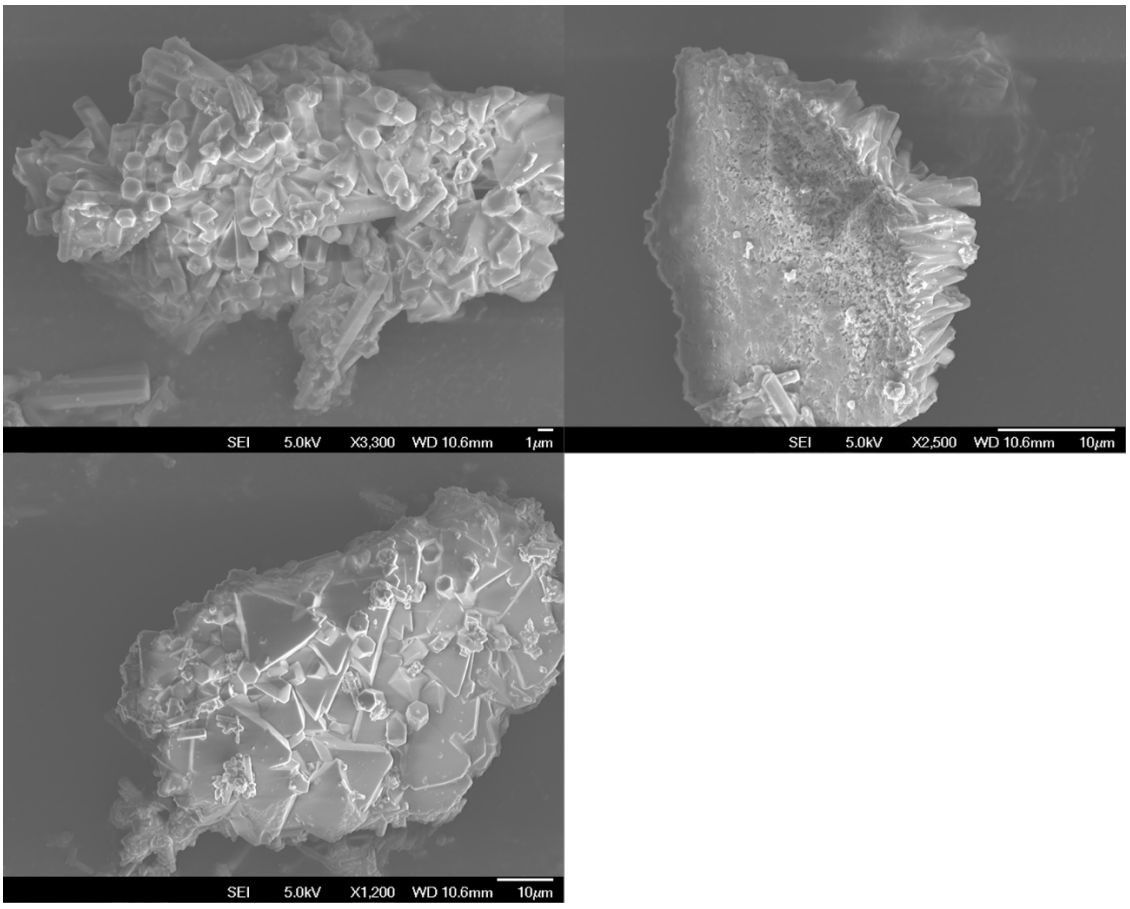



**Figure S10.** Scanning electron microscopy image of sample which was stirred at room temperature for 3 days, followed by 24 hours of solvothermal treatment at 100°C.

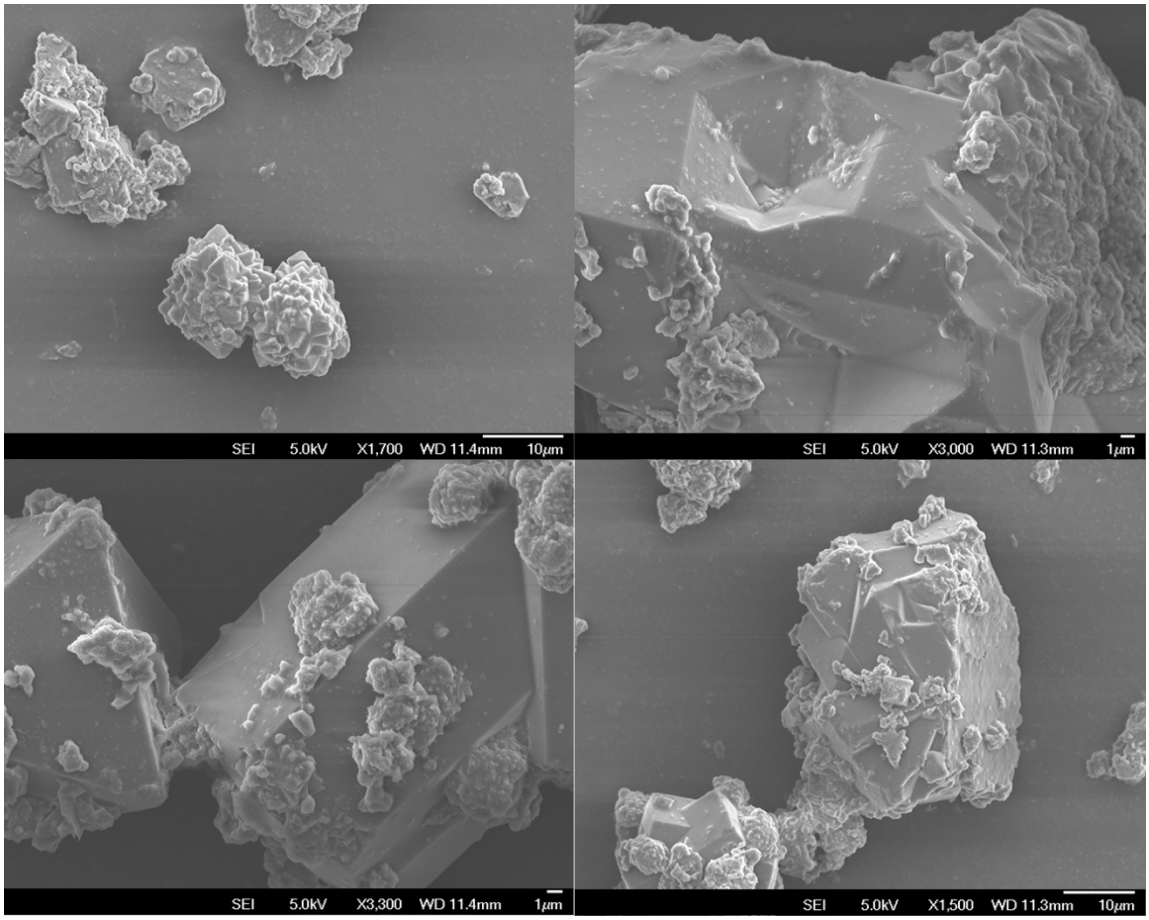



**Figure S11.** Scanning electron microscopy image of sample which was stirred at room temperature for 3 days, followed by 72 hours of solvothermal treatment at 100°C.

## 1.8.Adsorption/Desorption Isotherms and Surface Area data

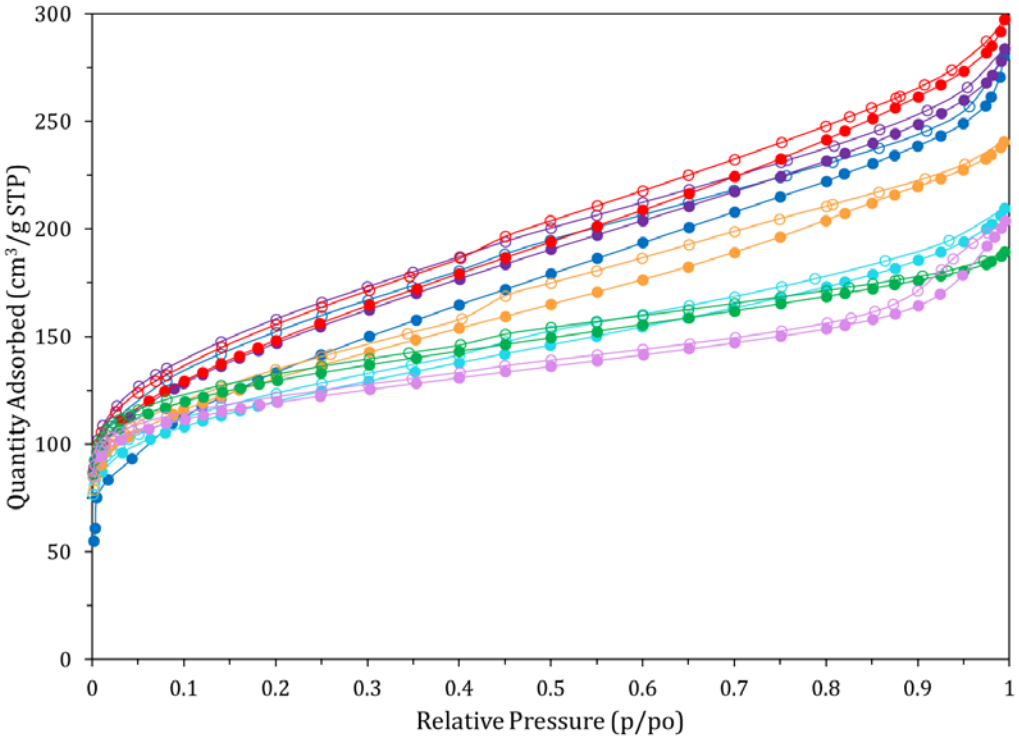



**Figure S12.** $N_2$ Adsorption and desorption isotherms @ 77 K. Filled circles indicate adsorption, while open circles indicate desorption. (●) 4 day RT non-stirred, (●) 4 day RT stir, (●) 3 day RT stir + 12h@100°C solvothermal, (●) 3 day RT stir + 12h@100°C +12h@50°C solvothermal, (●) 3 day RT stir + 16h@100°C solvothermal, (●) 3 day RT stir + 24h@100°C solvothermal, (●) 3 day RT stir + 3d@100°C solvothermal.

**Table S1**. Surface areas and Pore volumes of the CC3 synthesized samples.

| Sample | Surface Area $[m^2 \cdot g^{-1}]$ | | Pore volume $[cm^3 \cdot g^{-1}]$ | | | |
|---|---|---|---|---|---|---|
| | $S_{BET}$[a] | $S_{ext}$[b] | $V_{tot}$[c] | $V_{micro}$[b] | $V_{meso}$[d] | $V_{meso}$[e] |
| CC3 NO STIR | 462 | 338 | 0.40 | 0.06 | 0.34 | 0.34 |
| CC3 STIR RT | 511 | 321 | 0.41 | 0.09 | 0.33 | 0.32 |
| CC3 DMF 100C STIR 12 HR | 525 | 337 | 0.44 | 0.08 | 0.36 | 0.38 |
| CC3 DMF 100C&50C STIR 12 HR | 410 | 194 | 0.31 | 0.10 | 0.21 | 0.23 |
| CC3 DMF 100C STIR 16 HR | 452 | 254 | 0.36 | 0.09 | 0.27 | 0.28 |
| CC3 DMF 100C STIR 24 HR | 438 | 148 | 0.29 | 0.13 | 0.16 | 0.18 |
| CC3 DMF 100C STIR 72 HR | 401 | 125 | 0.30 | 0.13 | 0.17 | 0.20 |

[a] Specific surface area was calculated by BET method (positive c-value, R2>0.99), [b] external surface area and micropore volume were calculated by the t-plot method using the Kruk-Janoniec-Sayari Thickness, [c] total volume was calculated from the quantity adsorbed at P/Po=0.975, [d] mespore volume = total volume - micropore volume, [e] mesopore volume was calculated by BJH desportion method.

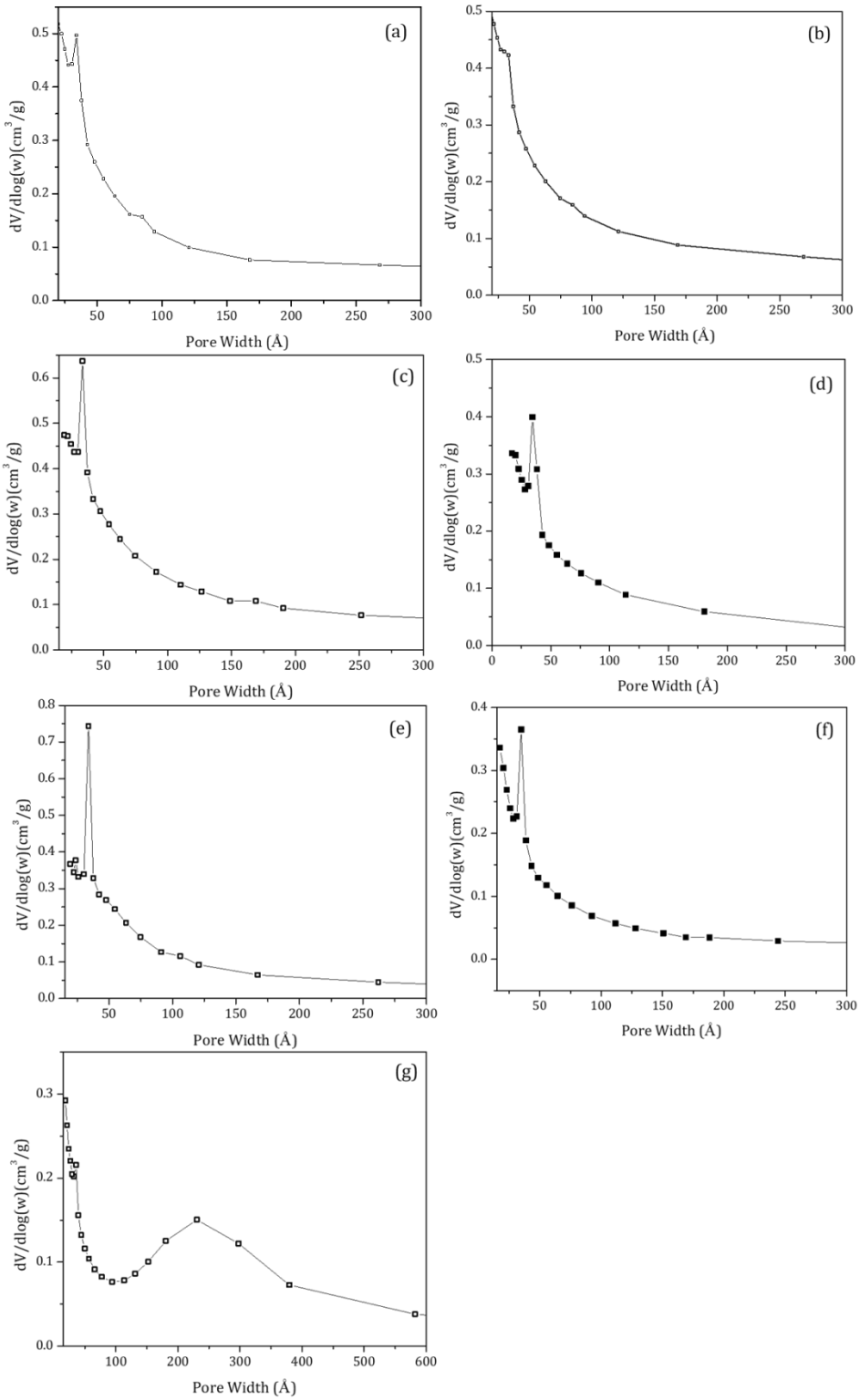



**Figure S13**. BJH pore distribution plots for (a) 4 day RT non-stirred, (b) 4 day RT stir, (c) 3 day RT stir + 12h@100°C solvothermal, (d) 3 day RT stir + 12h@100°C +12h@50°C solvothermal, (e) 3 day RT stir + 16h@100°C solvothermal, (f) 3 day RT stir + 24h@100°C solvothermal, (g) 3 day RT stir + 3d@100°C solvothermal.

**Table S2**. Summary of experiments to elucidate DMF effect on formation of cages. Mass amounts of each product component included.

| Sample | Solvothermal Condition | | | Solvent Composition | Actual Yield (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | 3D RT stir | Time (h) | Temp (°C) | | Precip | Filtered (F-ed) | Filtrate (F-ate) | Total |
| A | yes | 16 | 100 | 100% DCM | 25.01 | 29.57 | 0 | 54.58 |
| C | yes | 16 | 100 | 25% DMF/ 75% DCM | 44.52 | 5.00 | 0 | 49.52 |
| K | yes | 16 | 100 | 50% DMF/ 50% DCM | 22.01 | 7.00 | 5.00 | 34.01 |
| B | yes | 16 | 100 | 75% DMF/25% DCM | 2.50 | 11.50 | 12.50 | 26.51 |
| D | yes | 16 | 100 | 100% DMF | 2.00 | 45.02 | 4.00 | 51.02 |
| O | yes | 72 | 23 | 100% DMF | 14.00 | 25.01 | 10.00 | 49.02 |
| P | yes | 72 | 50 | 100% DMF | 17.00 | 6.00 | 0 | 23.01 |
| R | yes | 72 | 120 | 100% DMF | 6.00 | 12.00 | 5.00 | 23.01 |
| S | yes | 72 | 23 | 100% DCM | 54.02 | 29.01 | 8.00 | 91.04 |
| T | yes | 72 | 50 | 100% DCM | 40.01 | 3.00 | 0 | 43.02 |
| U | yes | 72 | 120 | 100% DCM | 75.03 | 23.01 | 0 | 98.04 |

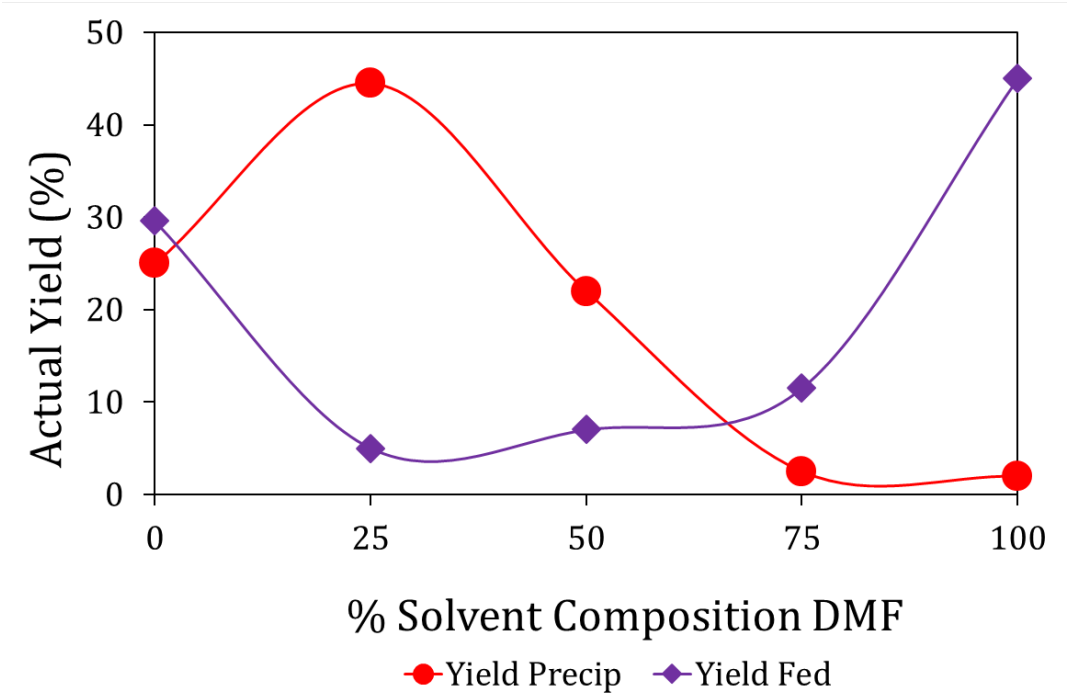



**Figure S14.** Actual yield of precipitate, and filtered product for samples A-D, and K, as a function of solvent composition. Balance solvent is DCM. Solvothermal temperature was constant at 100°C, and solvothermal time was constant at 16 hours.

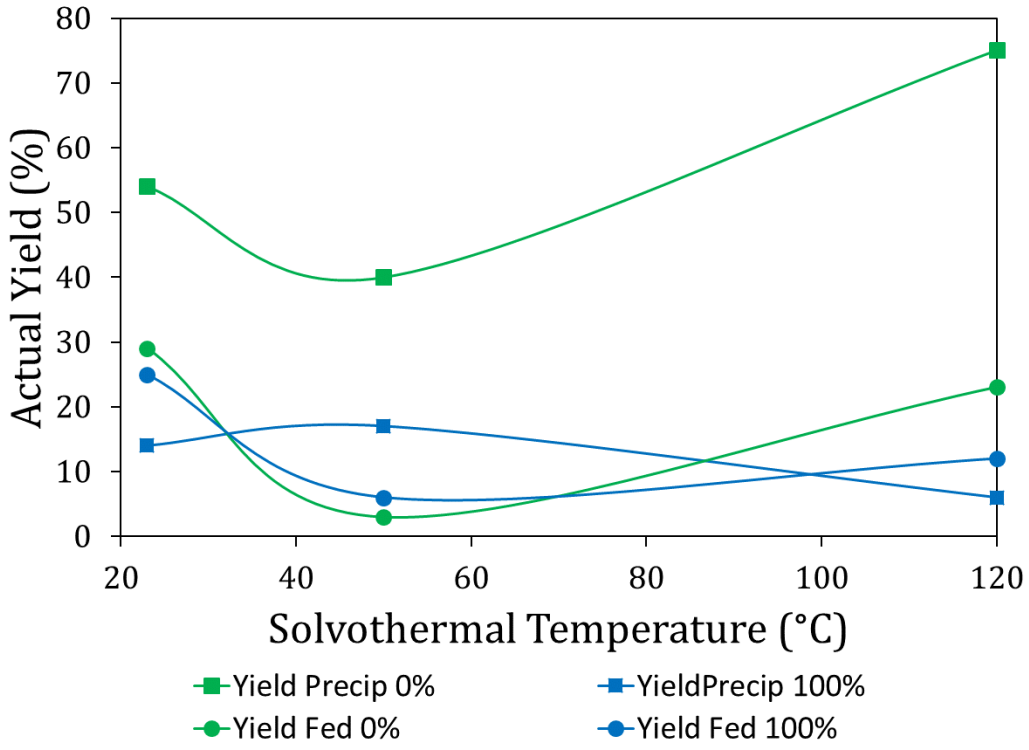



**Figure S15.** Actual yield of precipitate, and filtered products of samples O-U, as a function of solvothermal temperature. 0% corresponds to only DCM used as solvent, and 100% corresponds to 100% DMF. Solvothermal time was held constant at 72 hours for all experiments.

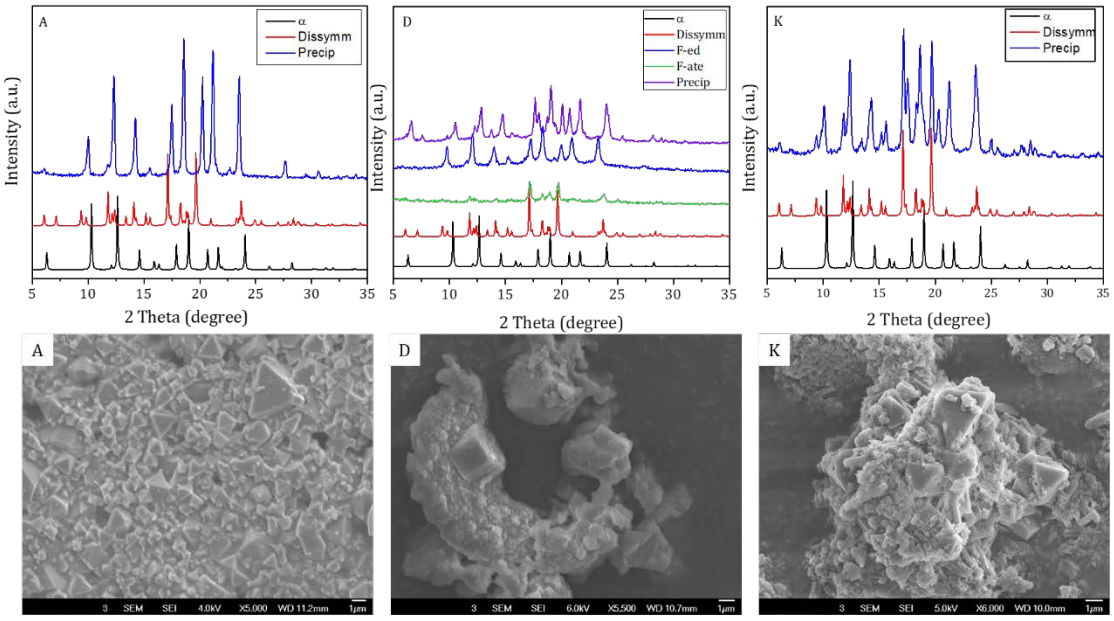



**Figure S16.** XRD patterns of samples A, D, and K separated by product. Lower panel shows SEM images of precipitate product. If a product component was omitted, there was not enough sample for XRD detection.

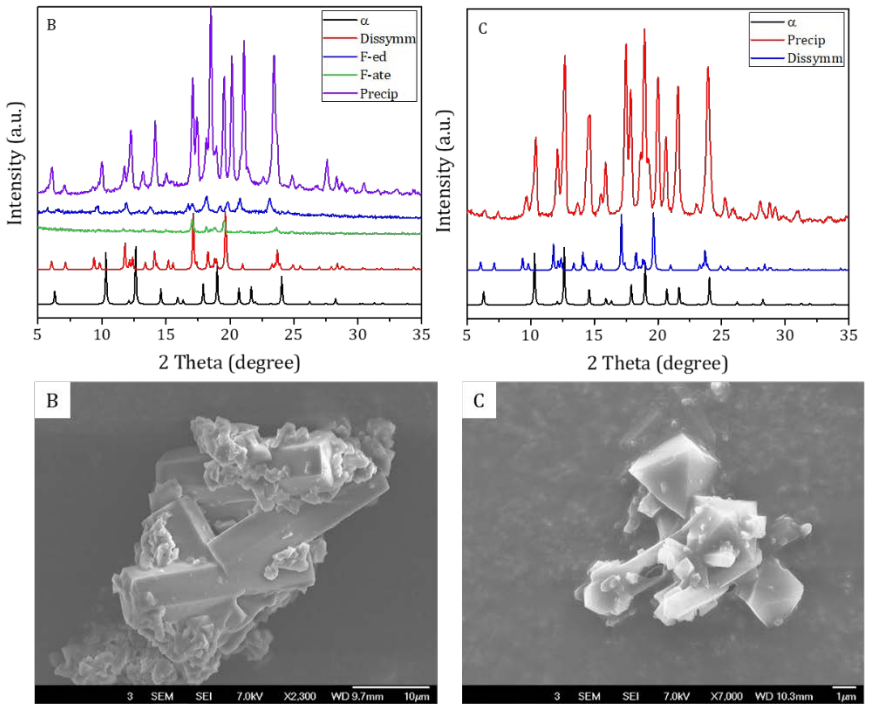



**Figure S17**. XRD patterns of samples B, and C separated by product. Lower panel shows SEM images of precipitate product. If a product component was omitted, there was not enough sample for XRD detection.

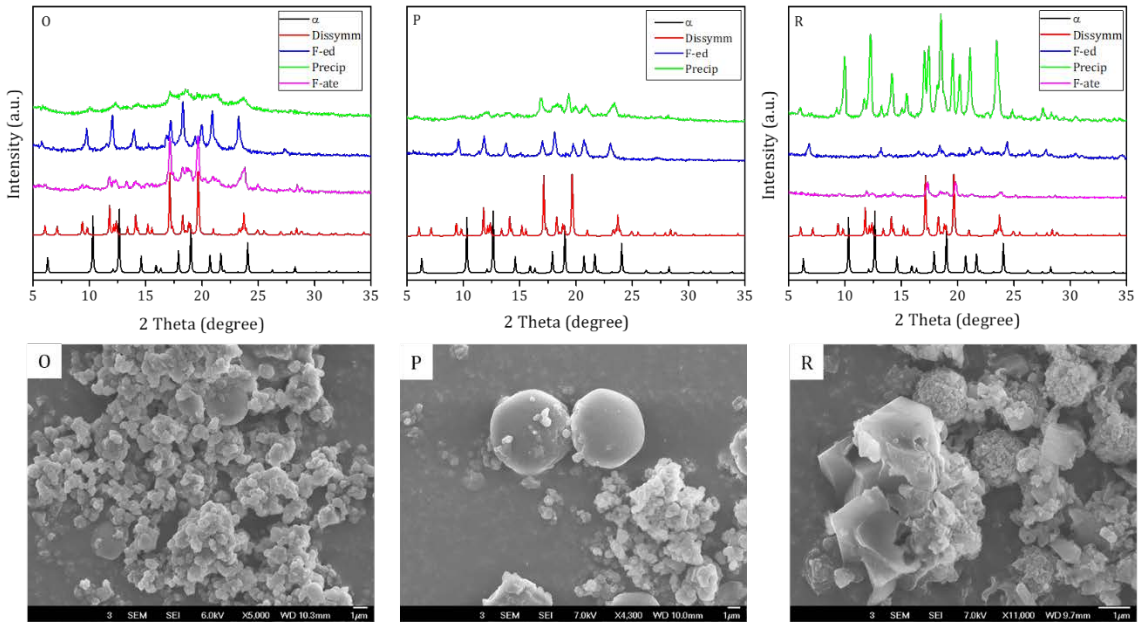



**Figure S18.** XRD patterns of samples O, P, and R separated by product. Lower panel shows SEM images of precipitate product. If a product component was omitted, there was not enough sample for XRD detection.

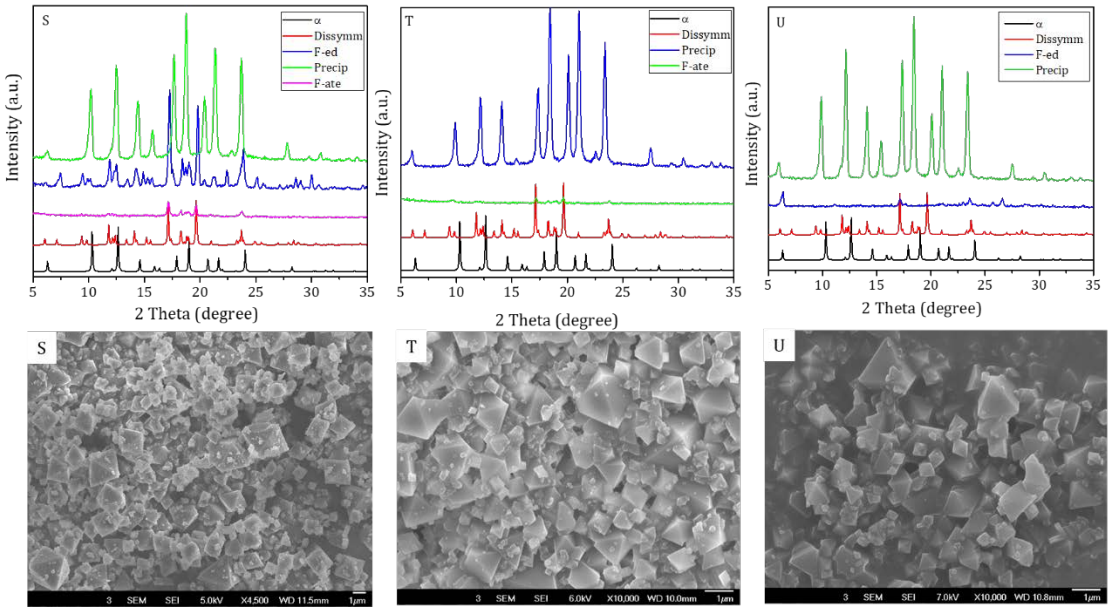



**Figure S19.** XRD patterns of samples S, T, and U separated by product. Lower panel shows SEM images of precipitate product. If a product component was omitted, there was not enough sample for XRD detection.

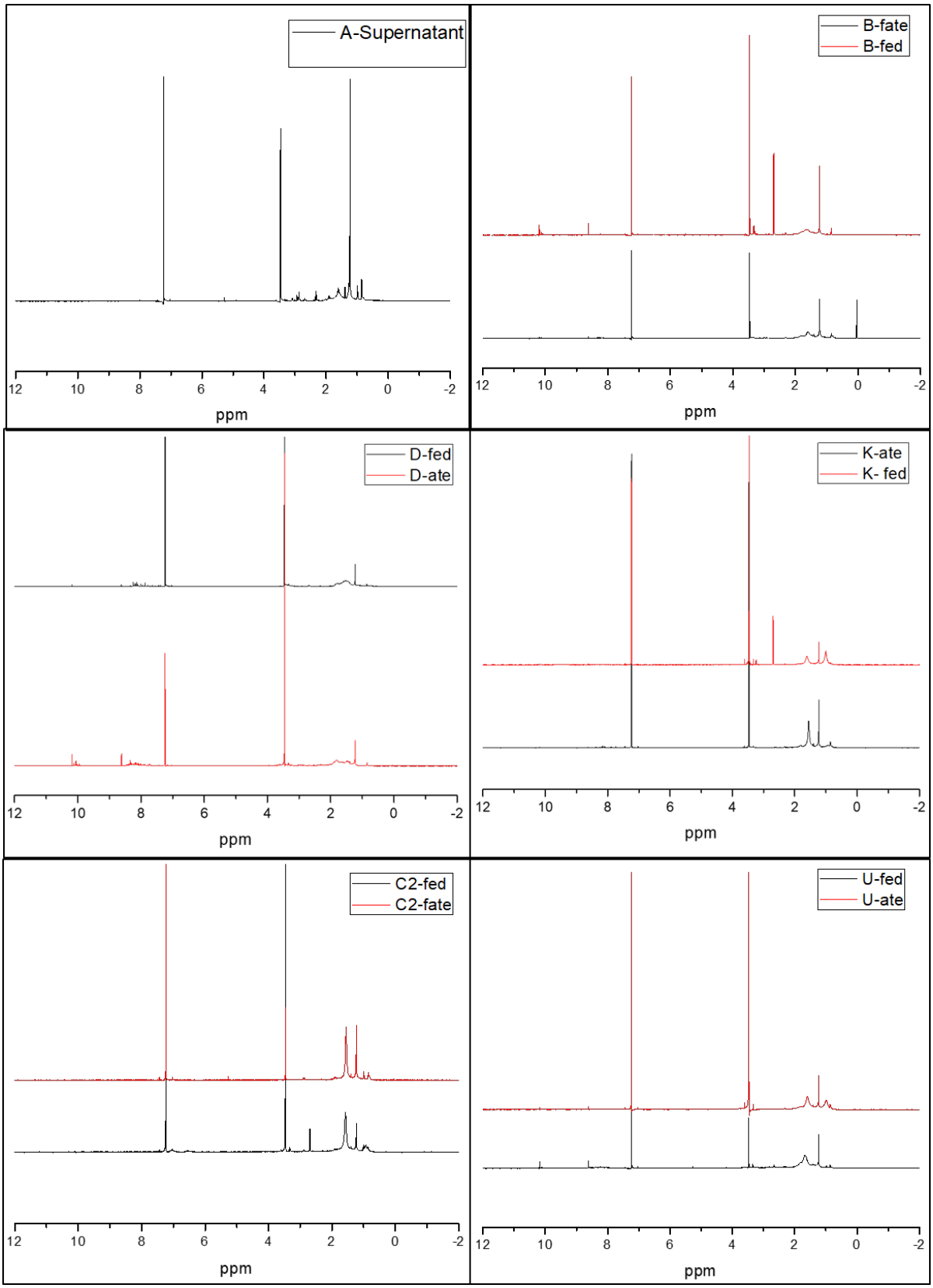



**Figure S20**. 1D $^{1}$H NMR spectra of filtrate and filtered products in $CDCl_3$ for samples shown in Table S2.

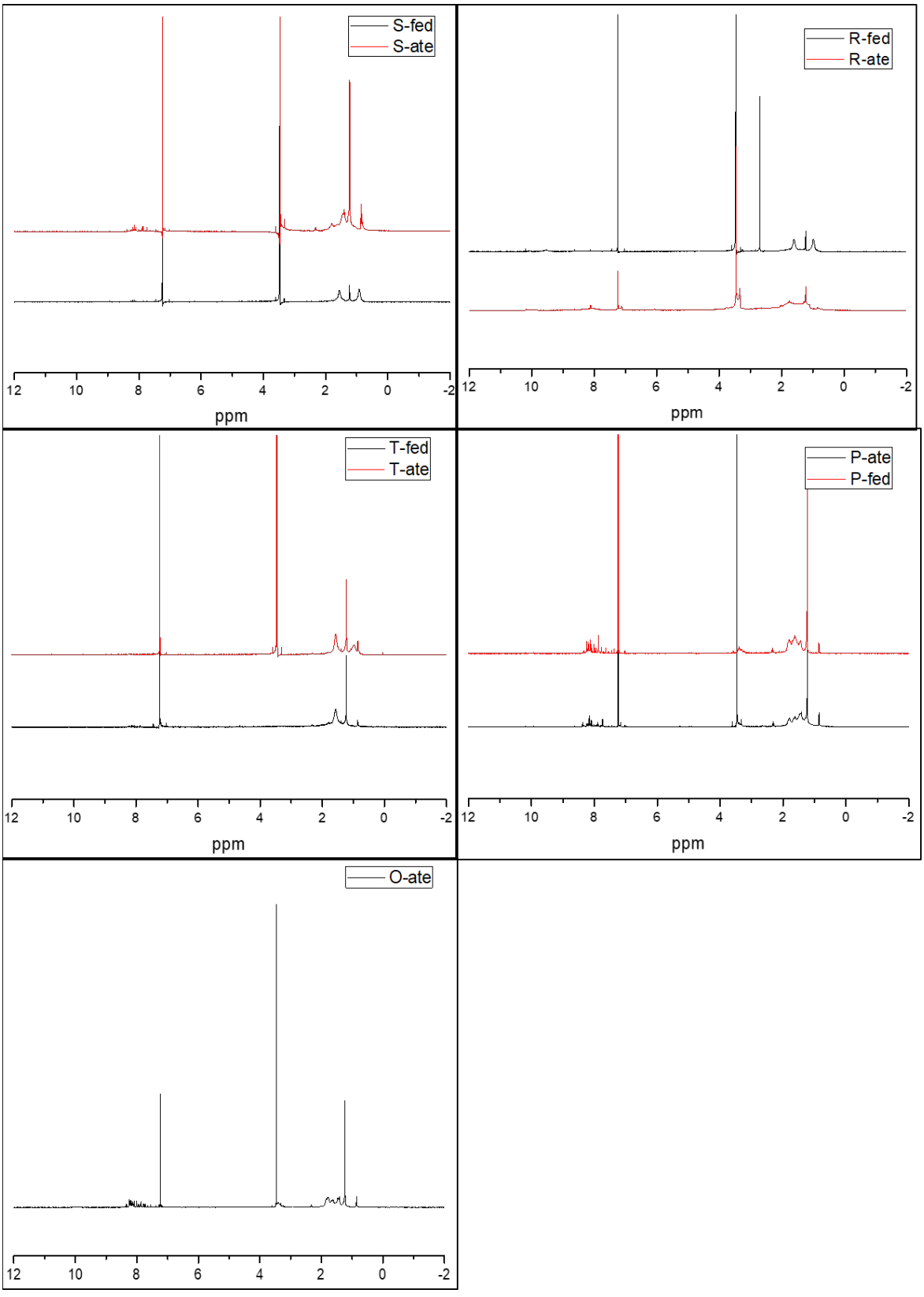



**Figure S21**. 1D $^{1}$H NMR spectra of filtrate and filtered products in $CDCl_3$ for samples shown in Table S2

References


1. M. E. Briggs and A. I. Cooper, *Chemistry of Materials*, 2017, **29**, 149-157.
2. B. H. Toby and R. B. V. Dreele, *Journal*, 2013, **46**, 544-549.
3. T. Tozawa, J. T. A. Jones, S. I. Swamy, S. Jiang, D. J. Adams, S. Shakespeare, R. Clowes, D. Bradshaw, T. Hasell, S. Y. Chong, C. Tang, S. Thompson, J. Parker, A. Trewin, J. Bacsa, A. M. Z. Slawin, A. Steiner and A. I. Cooper, *Nature Materials*, 2009, **8**, 973-978.
4. A. G. Slater, M. A. Little, M. E. Briggs, K. E. Jelfs and A. I. Cooper, *Molecular Systems Design & Engineering*, 2018, **3**, 223-227.