Microwave Assisted Synthesis of Porous Organic Cages CC3 and CC2

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Supporting Information

1.1. Materials

1, 3, 5- triformylbenzene (ACROS Organics, 98%) was used in the synthesis of both CC2, and CC3. (±)-*trans*-1,2-diaminocylcohexane (99%), and 1,2-diaminopropane (99%) were purchased from Sigma Aldrich. Dichloromethane (ACS certified, stabilized, Fisher Scientific), and acetonitrile (ACS certified, Fisher Scientific) were used as solvents. Trifluoroacetic acid (Alfa Aesar, 99%) was used as acid catalyst. All chemicals were used as received.

1.2. CC3 and CC2 Synthesis

Synthesis of CC3 crystals via microwave

For synthesis of CC3, in a Teflon liner, 25 mL of dichloromethane was slowly added to 100 mg of 1, 3, 5-triformylbenzene, followed by 100 µL of trifluoroacetic acid for the catalysis of the formation of the imine bond. A separate solution, was prepared by the addition of 102 mg of (±)-*trans*-1, 2-diaminocylcohexane in 25 mL of dichloromethane. The diamine solution was added slowly to the aldehyde solution in the Teflon liner, and sealed with a XP1500 vessel. The vessel was placed in a CEM Mars 5 microwave, a thermocouple was inserted into the vessel for temperature control. The selected program ramped the temperature over a course of 5 minutes to a hold temperature of 100°C, by supplying 100% of 400w of power. The max temperature was held for 5, 15, 30, and 60 minutes. The vessel was allowed to cool to room temperature before removal. The resulting solution was opaque with many white precipitates visible. Ethanol was added to the solution in a 60/40 ratio (EtOH/DCM), before centrifugation to afford a white product. The powder was washed 2X with clean ethanol, and allowed to dry in an oven at 80°C.

Synthesis of CC2 crystals via microwave

In a typical synthesis, acetonitrile (20 mL) was added to 1,3,5-triformylbenzene (83 mg) in a Teflon liner at room temperature. In a separate glass beaker, acetonitrile (10 ml) was added to 1,2-diaminopropane (58 mg). After 5 minutes, the diamine solution was slowly added to the Teflon liner. Acetonitrile (20 mL) was added to reach a total volume of 50 mL. Teflon liner was sealed, and placed in the microwave (CEM Mars 5). The temperature was ramped to 50°C over a course of 5 minutes, and held for 8 hours. The power was set to 100% of 400w. The solution was then transferred to a glass beaker, covered with parafilm, and allowed to sit under ambient conditions. The resultant solution was filtered through a Whatman filter (Cat. No. 1001-070), and dried at 80°C.

1.3. Characterization

Powder X-Ray Diffraction

All samples were analyzed using a Siemens Kristalloflex800, operated at 25 mA, 30 kV, Cu Kα radiation. Two theta ranges were from $2\theta° = 5°- 35°$.

Scanning Electron Microscopy

FE-SEM images were collected on a JEOL ISM-7000F with an accelerating voltage of 2.0 – 5.0 kV. Before imaging, all samples were gold sputter coated using a Hummer IV Sputtering System (Au/C coater).

Surface Area Analysis

BET surface areas, external surface areas, and porosity information, was extracted from nitrogen isotherm data collected at 77 K, on a Micromeritics, ASAP 2020 porosity analyzer. Prior to BET analysis, samples were degassed at 180 °C, under vacuum for 6 hours.

Fourier Transform Infrared Spectroscopy

FTIR data was collected on a ThermoFisher, Nicolet iS50, equipped with a built in diamond ATR. All samples were analyzed as powders.

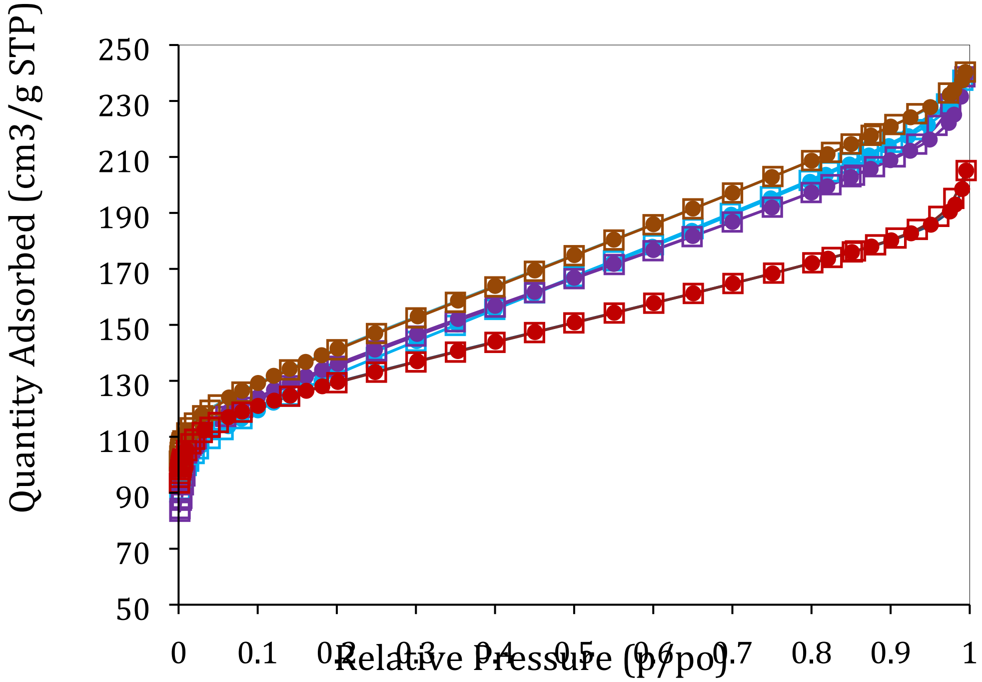

Figure S1. N_2 adsorption (filled circles) / desorption (open squares) isotherms @ 77 K, for CC3 synthesized via microwave for 5 min (🟪), 15 min (🟦), 30 min (🟥), 60 min (🟩).

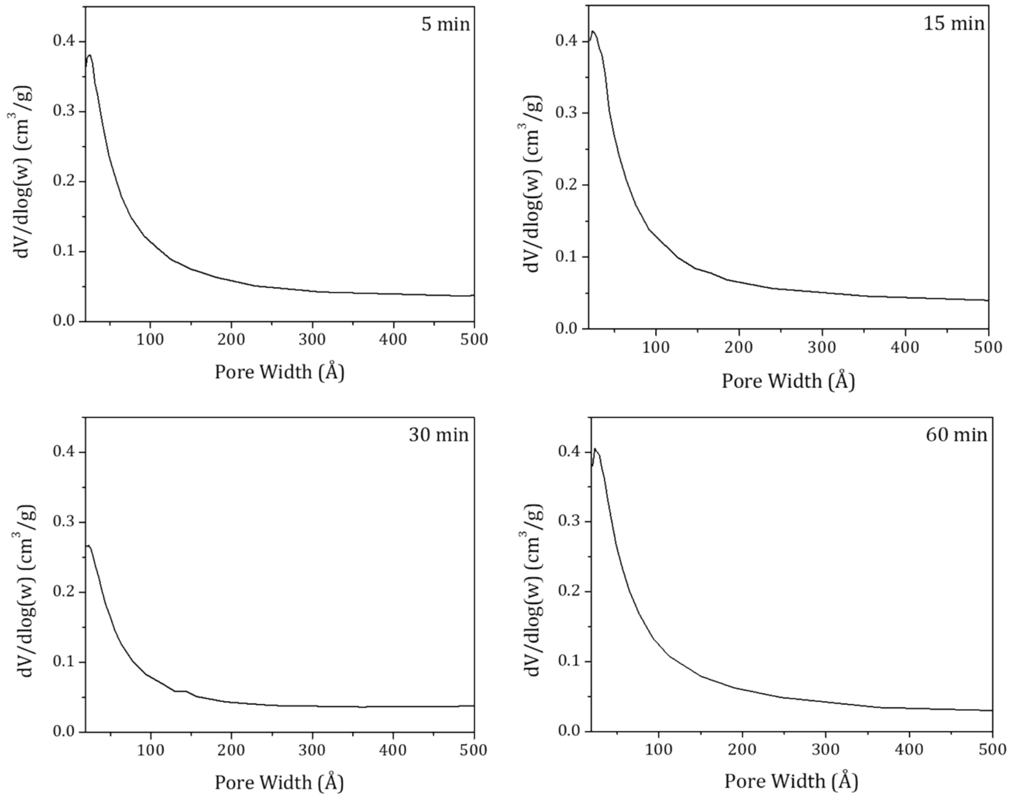

Figure S2. Pore distributions for CC3 synthesized via microwave.

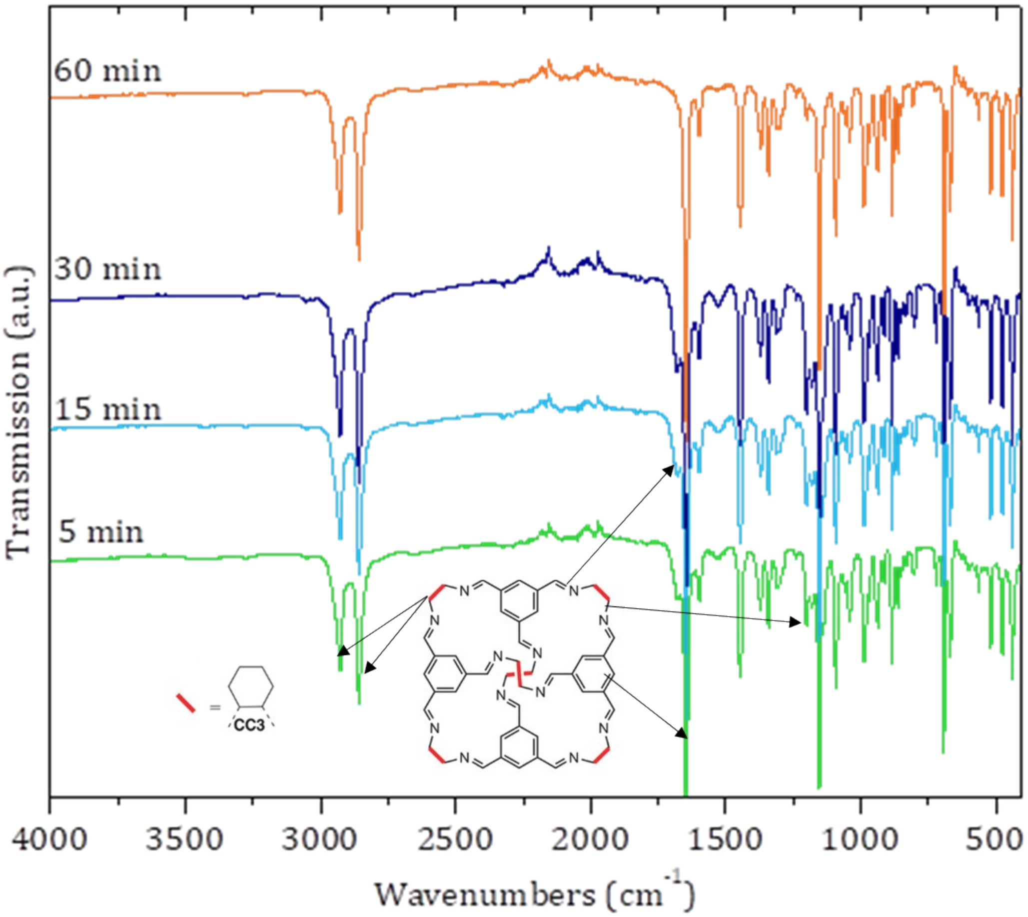

Figure S3. Fourier Transform Infrared Spectroscopy of microwave synthesized CC3α. CC3 molecule depiction was taken from Song *et al.*[1]

We can confirm peaks from an alkane C-H stretch appearing at 3000-2840 cm^{-1}, C-N stretches at 1250-1020 cm^{-1}, a conjugated alkene stretch at 1650-1600 cm^{-1}, and the imine C=N stretch is visible from 1690-1640 cm^{-1}, These are the main stretches which indicate bonding within the cage molecule.

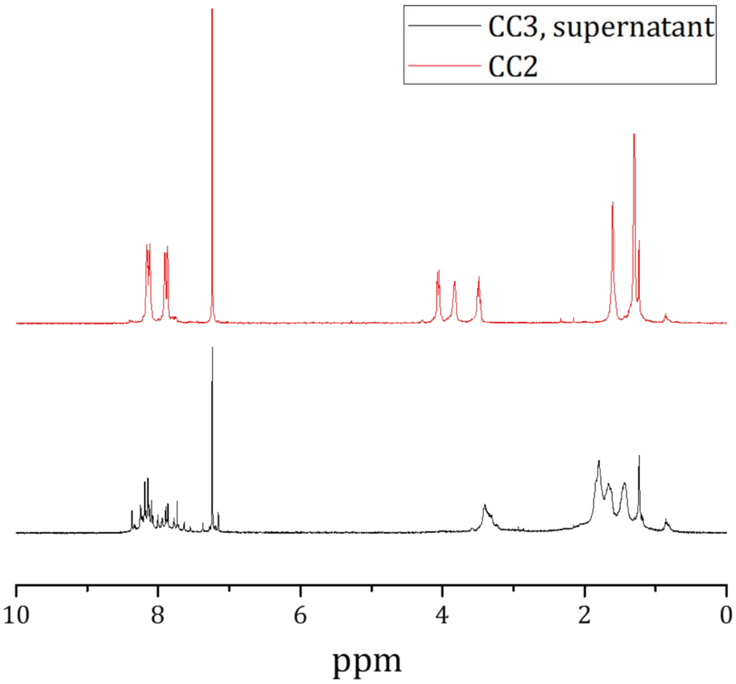

Figure S4. 1-D ^{1}H NMR spectra ($CDCl_3$) of microwave synthesized CC3, and CC2. Since the precipitate of CC3 has very low solubility in most solvents,[2] the supernatant was dried from DCM and re-dissolved in $CDCl_3$. The NMR spectra for the CC3 supernatant is comparable to the NMR spectra of the soluble dissymmetric cage CC3-RS/CC3-SR which remains dissolved in solution.[3]

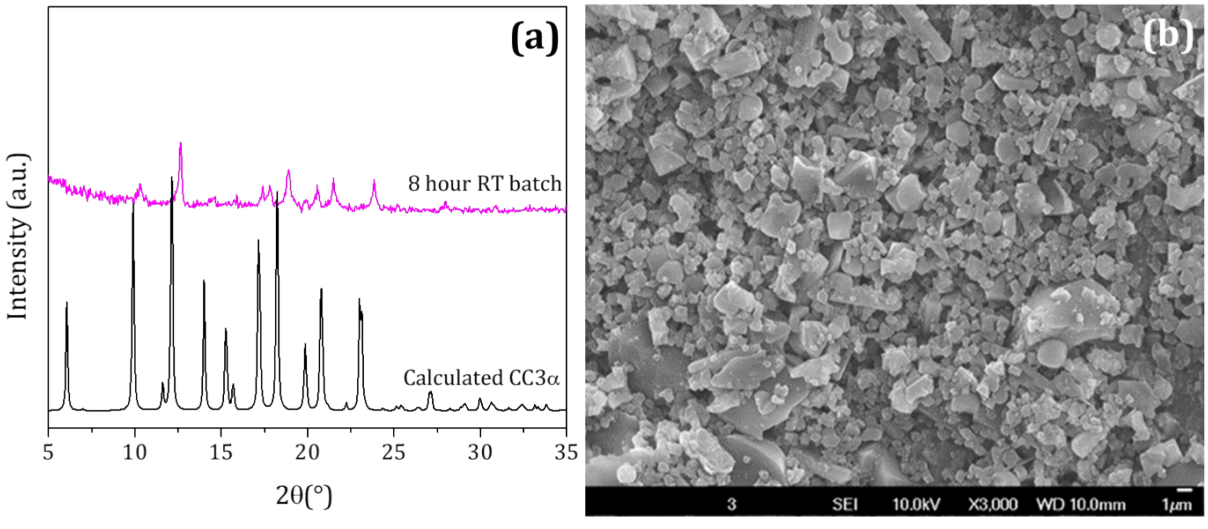

Figure S5. (a) PXRD pattern of CC3a synthesized at room temperature in a batch synthesis for 8 hours, compared with the calculated CC3 pattern. (b) SEM image of irregularly shaped CC3 crystals.[4]

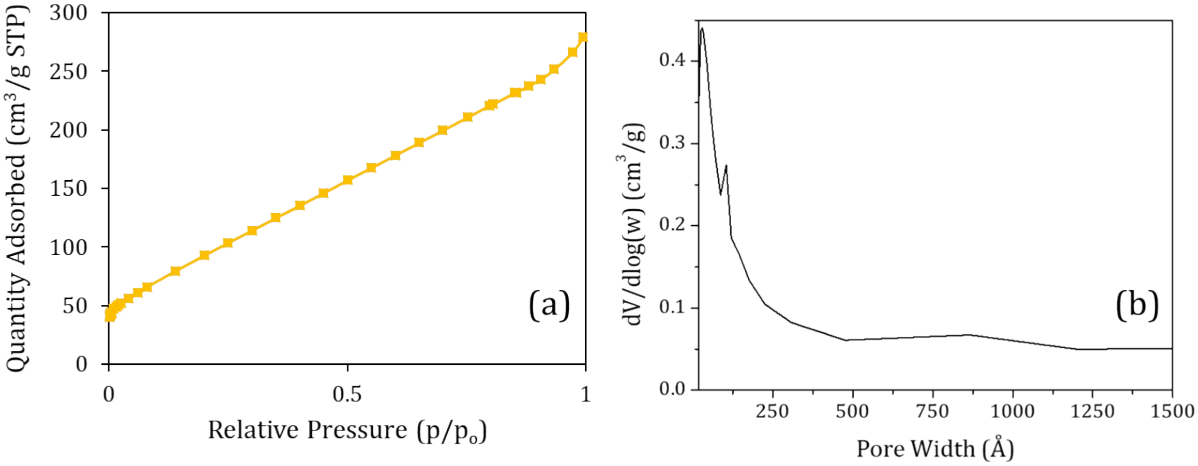

Figure S6. (a) N_2 isotherm @ 77 K of microwave synthesized CC2. (b) Pore distribution for CC2.

References

1. Q. L. Song, S. Jiang, T. Hasell, M. Liu, S. J. Sun, A. K. Cheetham, E. Sivaniah and A. I. Cooper, *Advanced Materials*, 2016, **28**, 2629-+.
2. T. Hasell, S. Y. Chong, K. E. Jelfs, D. J. Adams and A. I. Cooper, *Journal of the American Chemical Society*, 2012, **134**, 588-598.
3. A. G. Slater, M. A. Little, M. E. Briggs, K. E. Jelfs and A. I. Cooper, *Molecular Systems Design & Engineering*, 2018, **3**, 223-227.
4. J. Lucero, S. K. Elsaidi, R. Anderson, T. Wu, D. A. Gomez-Gualdron, P. K. Thallapally and M. A. Carreon, *Crystal Growth & Design*, 2018, **18**, 921-927.