# Microwave-Assisted Syntheses of Highly $CO_2$-Selective Organic Cage Frameworks (OCFs)

Yinghua Jin,[a] Bret A. Voss,[b] Ryan McCaffrey,[a] Clyde T. Baggett,[a] Richard D. Noble,[b] Wei Zhang*[a]

[a]Department of Chemistry and Biochemistry and [b]Department of Chemical and Biological Engineering, University of Colorado, Boulder, Colorado 80309, USA

SUPPORTING INFORMATION

List of Contents

## *1. Materials and general methods*

Reagents and solvents were purchased from commercial suppliers and used without further purification, unless otherwise indicated. Tetrahydrofuran is purified by MBRAUN solvent purification systems. Linkers L1, L2, and L3 are prepared as reported in the literature.[1,2,3]

All microwave reactions were conducted under dry nitrogen in oven-dried glass tube using Discover SP microwave from CEM.

Solid state $^{13}C$ NMR spectra were taken on Inova 400 spectrometers.

For TGA analyses, samples were run on a TA Instruments Q-500 series thermal gravimetric analyzer with samples held in a platinum pan under nitrogen atmosphere, and a 10 K $min^{-1}$ ramp rate was used.

Powder X-ray-diffraction (XRD) profiles were obtained with an Inel CPS 120 diffraction system, using monochromated Cu K(alpha) radiation. All XRD spectra were calibrated against silver behenate as a diffraction standard (d100 = 58 Å), so the accuracy is within 1 Å up to the value of the d-spacings. XRD measurements were all performed at ambient temperature (21 ± 1 °C).

SEM images were recorded using a JSM-6480LV (LVSEM) at 5.0 kV. Sample was sputter-coated with gold prior to analysis.

## *2. Procedures*

**Cage framework F1**: To a glass tube were added $Pd(PPh_3)_2Cl_2$ (5 mg, 0.007 mmol), CuI (0.5 mg, 0.002 mmol), a solution of cage **1** (125 mg, 0.038 mmol) and 1,4-diethynylbenzene (14 mg, 0.114 mmol) in THF (2 mL), and piperidine (1 mL). The mixture was degassed by evacuating and refilling with nitrogen three times. The yellow solution was then heated at 100 $^oC$ for 1 h using microwave irradiation. The mixture was cooled to 60 $^oC$ and the red gel-like material was separated from yellow suspension by decantation. The red-gel was crushed into small pieces, and THF (10 mL) was added. After irradiation at 85 $^oC$ with microwave for 10 min, the solid material was filtered. The above procedure was repeated (~6 times) to wash the red-gel-like materials until the solution phase became colorless. The product was dried under high vacuum to obtain a red solid (121 mg, 90 %).

**Cage framework F2**: The above microwave assisted synthetic procedure for framework **F1** was followed. Using $Pd(PPh_3)_2Cl_2$ (4.5 mg, 0.006 mmol), CuI (0.4 mg, 0.002 mmol), cage **1** (118 mg, 0.036 mmol), linker **L2** (24 mg, 0.107 mmol), THF (2 mL), and piperidine (1 mL), the framework **F2** (110 mg, 74 %) was obtained as a red solid.

**Cage framework F3**: The above microwave assisted synthetic procedure for framework **F1** was followed. Using $Pd(PPh_3)_2Cl_2$ (5 mg, 0.007 mmol), CuI (0.4 mg, 0.002 mmol), cage **1** (125 mg,

[1] Demessence, A.; Long, J. R. *Chem. Eur. J.* **2010**, *16*, 5902-5908.
[2] Simpson, C. D.; Brand, J. D.; Berresheim, A. J.; Przybilla, L.; Räder, H. J.; Müllen, K. *Chem. Eur. J.* **2002**, *8*, 1424-1429.
[3] Lee, K.; Cho, J. C.; DeHeck, J.; Kim, J. *Chem. Commun.* **2006**, 1983-1985.

0.038 mmol), linker **L2** (51 mg, 0.113 mmol), THF (2 mL), and piperidine (1 mL), the framework **F3** (141 mg, 67 %) was obtained as a red solid.

**Cage framework F1'** (conventional heating method): To a Schlenk tube were added $Pd(PPh_3)_2Cl_2$ (8 mg, 0.011 mmol), CuI (0.7 mg, 0.0036 mmol), a solution of cage **1** (200 mg, 0.06 mmol) and 1,4-diethynylbenzene (23 mg, 0.18 mmol) in THF (4 mL), and piperidine (2 mL). The mixture was degassed by evacuating and refilling with nitrogen three times. The yellow solution was then heated at 85 $^{o}$C for 20 h. The mixture was cooled to room temperature and the red gel-like material was separated by decantation. Methylene chloride (15 mL) was added and heated at 85 $^{o}$C for 1 h in a sealed tube. The solid material was filtered and the above washing process was repeated with $H_2O$ (10 mL), THF (15 mL), MeOH-$H_2O$ (1:1 v/v, 20 mL), and MeOH (10 mL). The product was dried under high vacuum to obtain a brown solid (192 mg, 90 %).

### *3. Thermal gravimetric analysis of compounds F1-F3 and F1'*

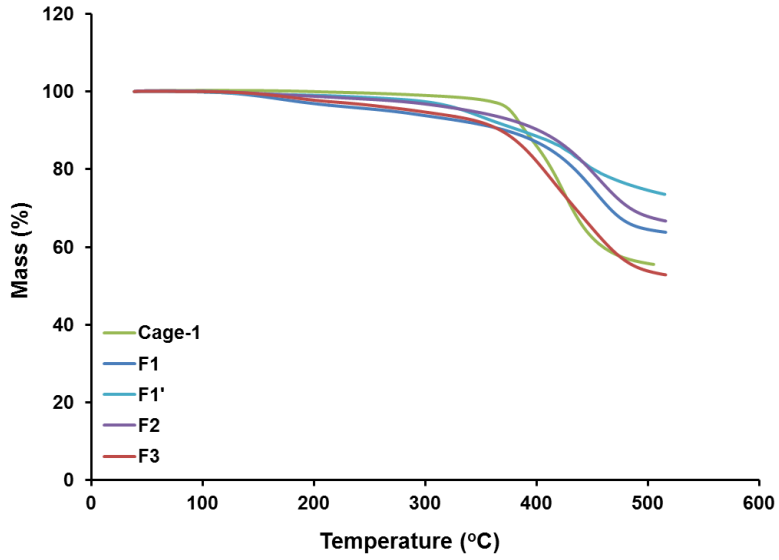



***Figure S1*:** TGA data of cage frameworks **F1-F3**, and **F1'**: Cage **1** shows about 5 % mass loss before the onset decomposition at 370 $^{o}$C; Framework **F1** shows about 14 % mass loss before the onset decomposition at 410 $^{o}$C; Framework **F2** shows about 12 % mass loss before the onset decomposition at 417 $^{o}$C; Framework **F3** shows about 12 % mass loss before the onset decomposition at 372 $^{o}$C; Framework **F1'** decomposes in two steps, with onset temperatures of 313 $^{o}$C and 417 $^{o}$C for the first and second step decomposition

### *4. Powder X-ray diffraction analysis of compound F1-F3 and F1'*

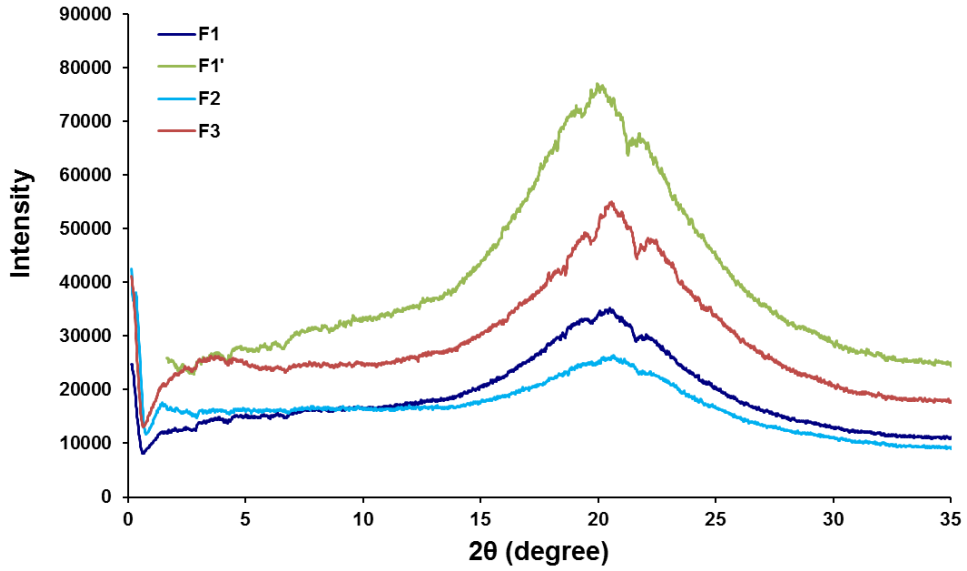



***Figure S2.*** PXRD patterns of cage frameworks **F1-F3** and **F1'**.

### *5. SEM images of frameworks F1-F3, and F1'*

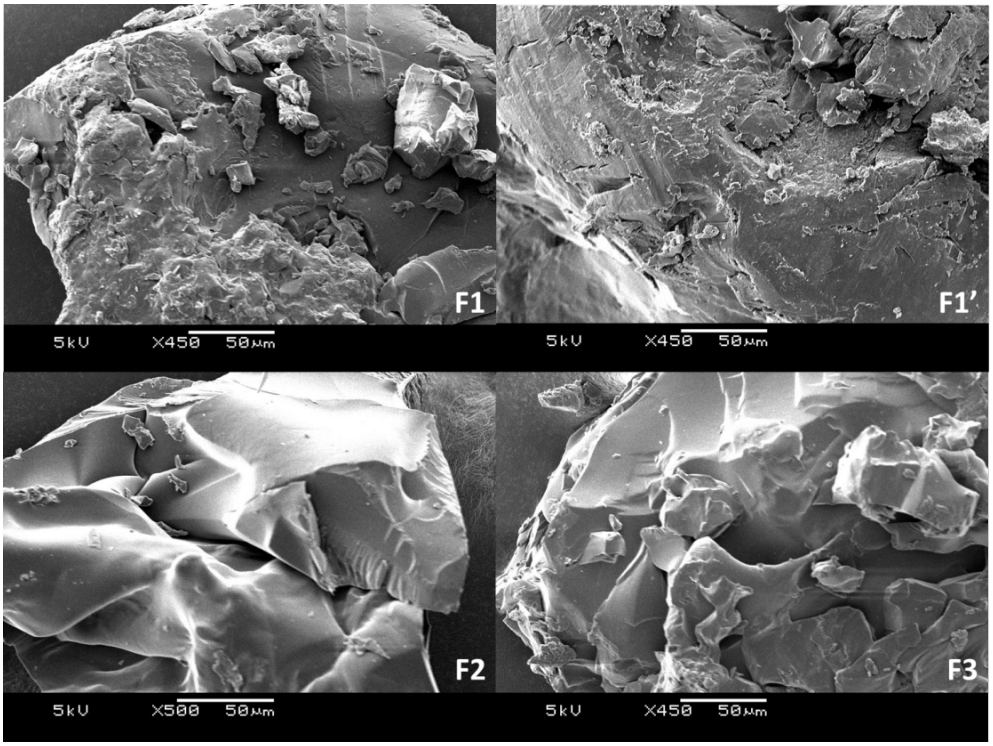



***Figure S3.*** SEM images of cage frameworks **F1-F3** and **F1'**.

### *6. Gas adsorption analyses of cage-1 and frameworks F1-F3*

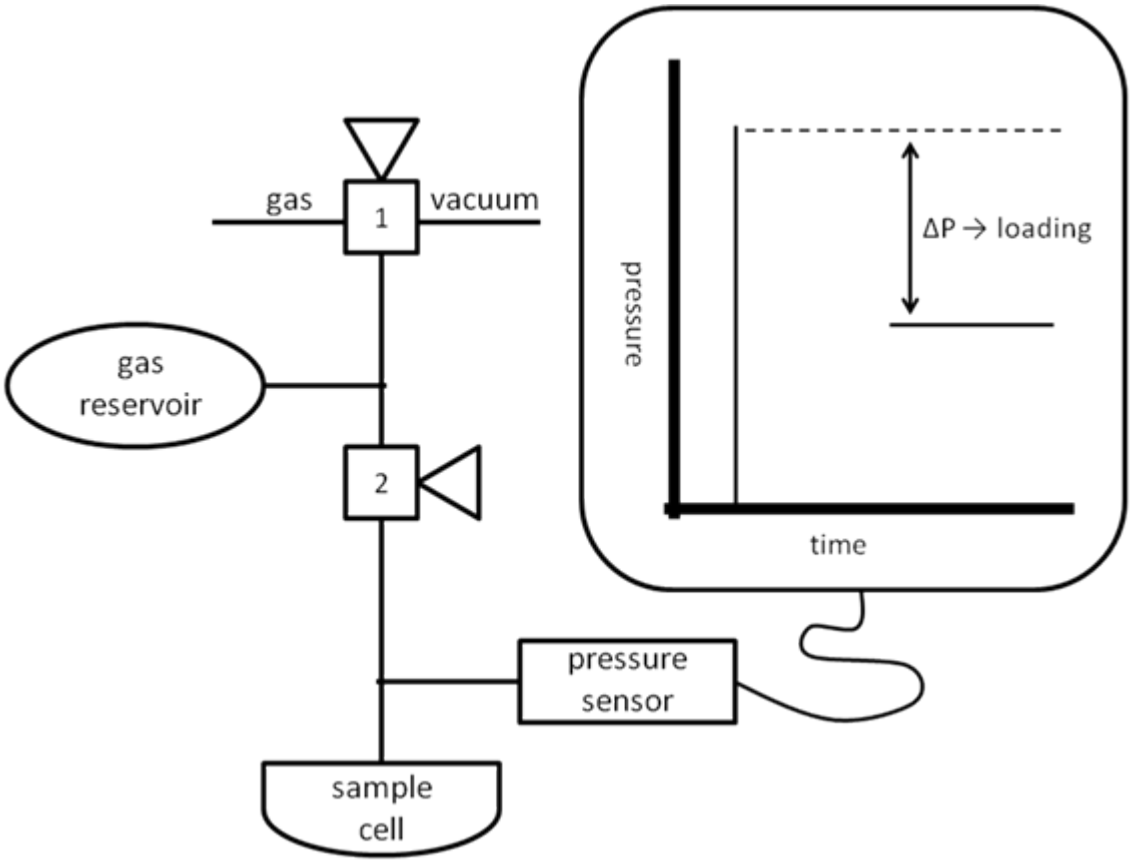
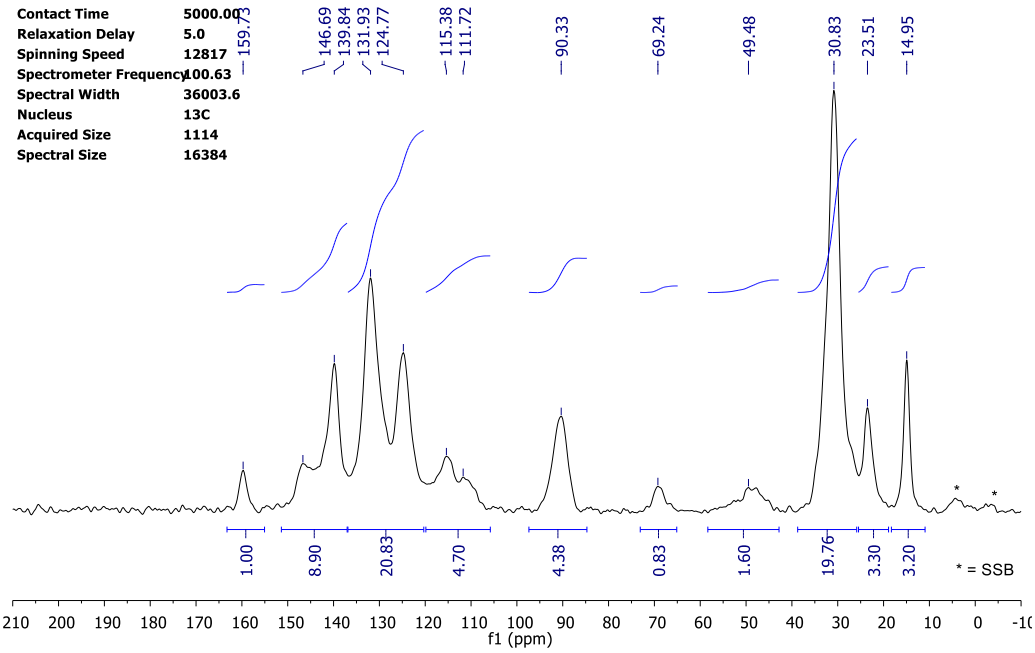


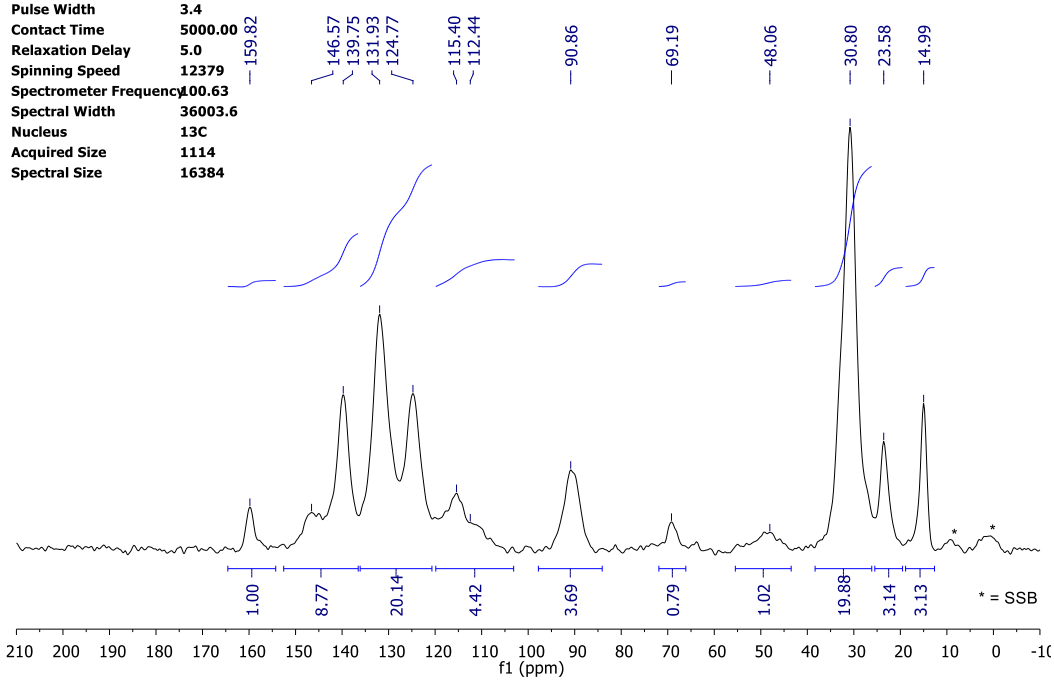

***Figure S4.*** Low-pressure gas adsorption apparatus was built specifically for small amount of samples with low gas adsorption capacity. The amount of gas adsorbed on the sample was measured for single component pure gas. The sample was loaded into a fine mesh envelope that was placed in the sample cell. The entire system was placed under vacuum overnight. Next, valve 2 was closed and valve 1 was opened to the gas line and closed once the gas reservoir was equilibrated. Then valve 2 was opened for 1 second and closed again. As the sample adsorbed the gas in the lower volume the pressure would drop until it reached equilibrium. The pressure drop was measured and recorded from the pressure sensor. The molar amount of gas adsorbed can be determined from the total change in pressure and the ideal gas equation. The gas adsorption was measured as a function of pressure. The reliability of the above method was confirmed with a standard sample of known MgO nano-particles tested for $N_2$ and $CO_2$ adsorption. The ideal adsorption selectivity between $CO_2$ and $N_2$ was calculated by interpolating the adsorption of the sample at 1 bar and taking the ratio.

## *7. Solid state $^{13}$C NMR Spectra for frameworks F1-F3, and F1'*

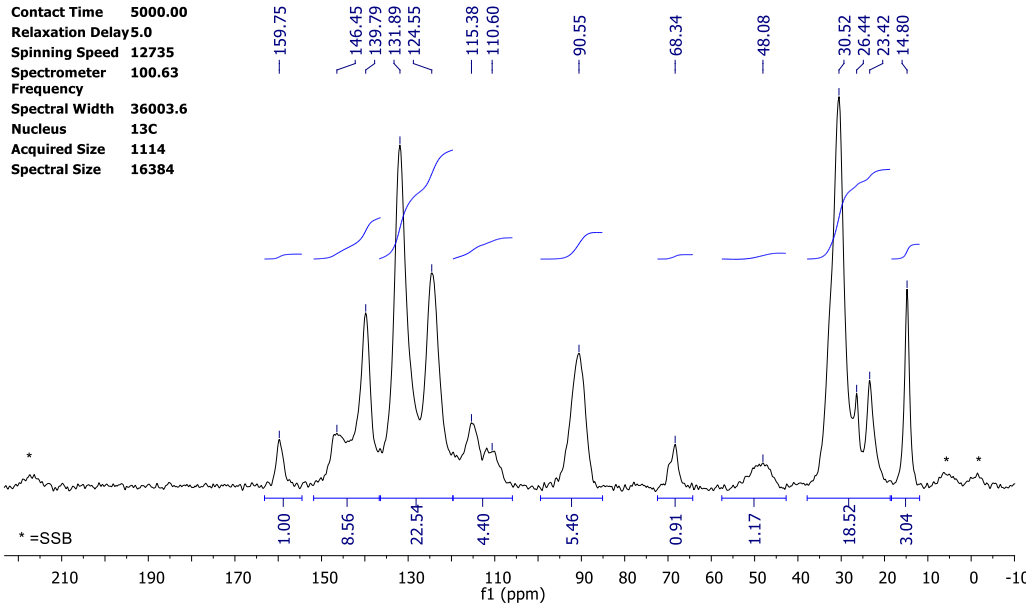
| | |
|---|---|
| Title | Framework F1 |
| Pulse Sequence | xpolvt1rho1 |
| Acquisition Date | 2011-08-11T10:00:28 |
| Temperature | 20.0 |
| Number of Scans | 568 |
| Pulse Width | 3.4 |
| Contact Time | 5000.00 |
| Relaxation Delay | 5.0 |
| Spinning Speed | 12817 |
| Spectrometer Frequency | 100.63 |
| Spectral Width | 36003.6 |
| Nucleus | 13C |
| Acquired Size | 1114 |
| Spectral Size | 16384 |




| | |
|---|---|
| Title | Framework F1' |
| Pulse Sequence | xpolvt1rho1 |
| Acquisition Date | 2011-08-11T12:29:17 |
| Temperature | 20.0 |
| Number of Scans | 1024 |
| Pulse Width | 3.4 |
| Contact Time | 5000.00 |
| Relaxation Delay | 5.0 |
| Spinning Speed | 12379 |
| Spectrometer Frequency | 100.63 |
| Spectral Width | 36003.6 |
| Nucleus | 13C |
| Acquired Size | 1114 |
| Spectral Size | 16384 |



| | |
|---|---|
| Title | Framework F2 |
| Pulse Sequence | xpolvt1rho1 |
| Acquisition Date | 2011-08-10T10:27:52 |
| Temperature | 20.0 |
| Number of Scans | 2016 |
| Pulse Width | 3.4 |
| Contact Time | 5000.00 |
| Relaxation Delay | 5.0 |
| Spinning Speed | 12735 |
| Spectrometer Frequency | 100.63 |
| Spectral Width | 36003.6 |
| Nucleus | 13C |
| Acquired Size | 1114 |
| Spectral Size | 16384 |




| | |
|---|---|
| Title | Framework F3 |
| Pulse Sequence | xpolvt1rho1 |
| Acquisition Date | 2011-08-11T08:15:00 |
| Temperature | 20.0 |
| Number of Scans | 1184 |
| Pulse Width | 3.4 |
| Contact Time | 5000.00 |
| Relaxation Delay | 5.0 |
| Spinning Speed | 12773 |
| Spectrometer Frequency | 100.63 |
| Spectral Width | 36003.6 |
| Nucleus | 13C |
| Acquired Size | 1114 |
| Spectral Size | 16384 |