Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

A Microporous Metal-Organic Framework for Gas Chromatographic Separation of Alkanes

Banglin Chen, Chengdu Liang, June Yang, Damacio S. Contreras, Yvette L. Clancy, Emil B. Lobkovsky, Omar M. Yaghi and Sheng Dai

[†]*Department of Chemistry, University of Texas-Pan American, Edinburg, TX 78541-2999, USA. Fax: (+1) 956-384-5006, Email: banglin@utpa.edu*
[‡]*Chemical Sciences Divisions, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831. Fax: (+1) 865-576-5235, E-mail: dais@ornl.gov*
[§]*Materials Design and Discovery Group, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, USA.*
[⊥]*Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301*

Materials and Methods: All reagents and solvents employed were commercially available and used as supplied without further purification. TGA data were obtained on an TGA G500 V5.3 Build 171 instrument with a heating rate of 10 deg/min under N_2 atmosphere. The TGA plots of MOF-508a and MOF-508b are shown in Fig. S1. Powder XRD diffractograms were measured with a Siemens D5005 X-ray diffractometer with copper K_α line (λ = 1.54178 Å) as the incident beam. A Gobel mirror was employed as a monochromator. The sample powder was loaded to a glass holder and leveled with a glass slide before mounting it on the sample chamber. The specimens were scanned between 4 and 40°. The scan step-width was set to 0.01° and the scan rate to 0.01°/s.

Sorption Measurements: A Cahn C-1000 microgravimetric balance was used to measure the change in mass of samples suspended within a glass enclosure under a chosen atmosphere. Sample MOF-508a of about 500 mg was cooled by a liquid nitrogen bath and the temperature was monitored using a thermocouple suspended in close proximity to the sample bucket. Activation of the porous materials was achieved by removing the labile guest molecules by heating at 120 °C for 24 hours under vacuum (< 10^{-3} Torr) in a microgravimetric sorption apparatus. Prior to admittance of the analyte gas, the entire chamber and manifold were evacuated overnight while the walls were heated several times using a heat gun. The system was purged at room temperature three times with the analyte gas (ultra high purity grade) before cooling to 77 K and gases were passed through a molecular sieve trap before being exposed to the sample. When hydrogen gas was used, the trap was additionally immersed in liquid nitrogen to remove any condensable impurities. Pressures were measured with two MKS Baratron transducers 622A with the range covering 0-10 and 0-1000 Torr (accuracy 0.25%). The adsorbate was added incrementally and data points were recorded when no further change in mass was observed (within 0.05 mg). An empirical buoyancy correction was applied to

all data points based on the change in mass of standard aluminum foil weights within the analyte gas at 77 K. CO_2 sorption measurements were carried out at 195 K by a acetone/dry ice slush.

Column Packing: MOF-508a were dried overnight in a vacuum oven at 120 °C to form MOF-508b particles. All particles were sieved to 50 to 100 μm before packing. A piece of 1/8 inch 304 stainless steel tubing was precut to 120cm. Both ends were polished with a fine dental file. The tube was positioned vertically against the floor. 2 cm from lower end of the tube was filled with glass wool that retains the MOF-508b particle during the column packing. The upper open end of the tube was connected to a glass funnel through a piece of 2cm-length rubber tubing. Aliquots of 100 mg of MOF-508b particles were slowly fed into the tubing through the funnel with gentle tapping along the tubing. At feeding intervals, the column was shaken for several times to ensure no void left in the tube. The column was filled with MOF-508b particles to 2 cm below the upper end of the tube. The upper 2 cm of the tubing was then filled with glass wool. A total amount of 3 grams of MOF-508b particles were packed into the column. 2 piece of 1/8' to 1/16' reduce union were fixed to the column ends. Afterwards, the column was bended into a 10cm diameter coil, which can fit into the GC column compartment. The column was connected to the GC system through 1/16' fittings.

Single-crystal X-ray Crystallography: Crystals of MOF-508a and MOF-508b were transferred from a crystallization vessel to a drop of polybutanes oil on a microscope slide. Using a nylon loop, a single crystal was than picked and mounted on a Bruker X8 APEX II diffractometer (Mo radiation) in a cold (-100 ºC) nitrogen stream. Data collection and reduction were done using Bruker Apex2 software package. For MOF-508a, overall 18551 reflections were collected, 5144 were unique (R_{int} = 0.0729); with 3426 'strong' reflections having Fo > 4σFo. The structure was solved by direct method and subsequent difference Fourier techniques (SHEXLTL). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added to a model in their geometrically ideal positions. C6 rings were statistically disordered into two positions each. Due to highly disordered solvent pockets, the data were corrected by PLATON Squeeze program. Final R_1 = 6.55% for 417 refined parameters. For MOF-508b, overall 13286 reflections were collected, 2507 were unique (R_{int} = 0.0301); with 2225 reflections having Fo > 4σFo. The structure was solved by direct method and subsequent difference Fourier techniques (SHEXLTL). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were either located from a difference electron density map or added to a model in their geometrically ideal positions. C6 rings were statistically disordered into two positions each. Final R_1 = 3.25% for 207 parameters. Residual electron densities were less than 1.02 e/ $Å^3$. The contents of the asymmetric units for MOF-508a and MOF-508b are shown in Fig. S3.

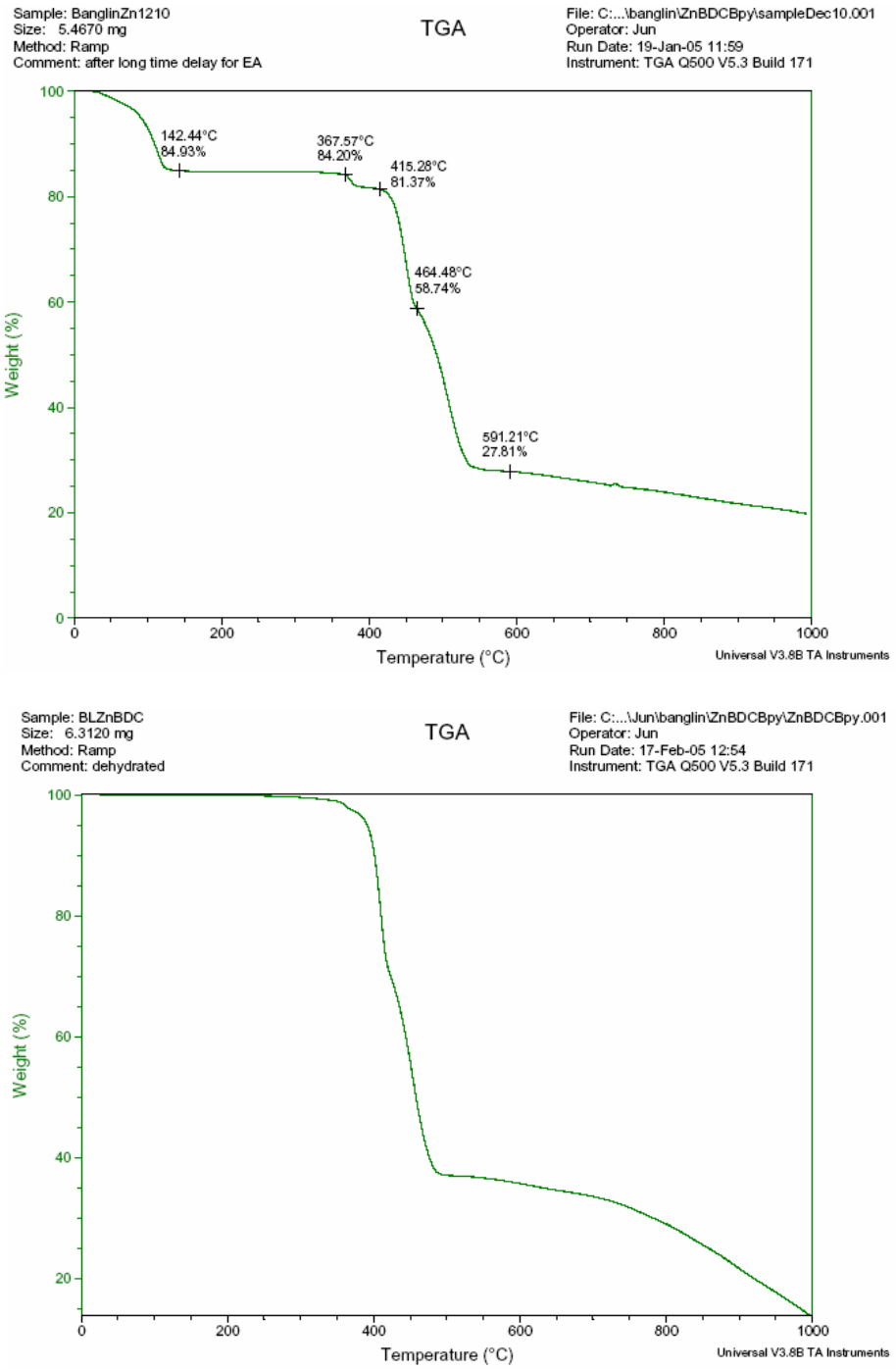

Figure S1. TGA plots of MOF-508a (top) and MOF-508b (bottom).

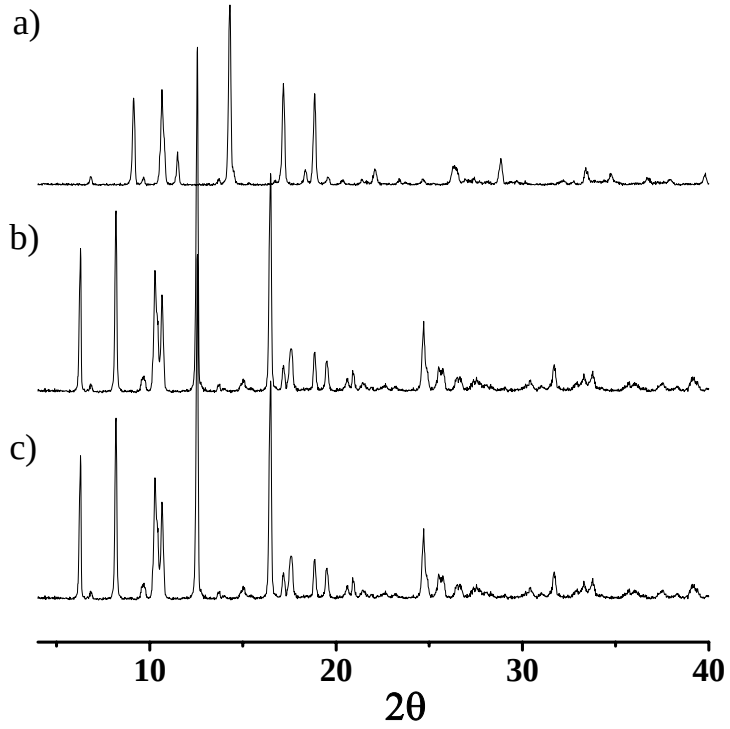

Figure S2. Powder X-ray diffraction (PXRD) patterns of (a) guest-free dense phase MOF-508b, (b) as-synthesized open phase MOF-508a and (c) regenerated open phase MOF-508a.

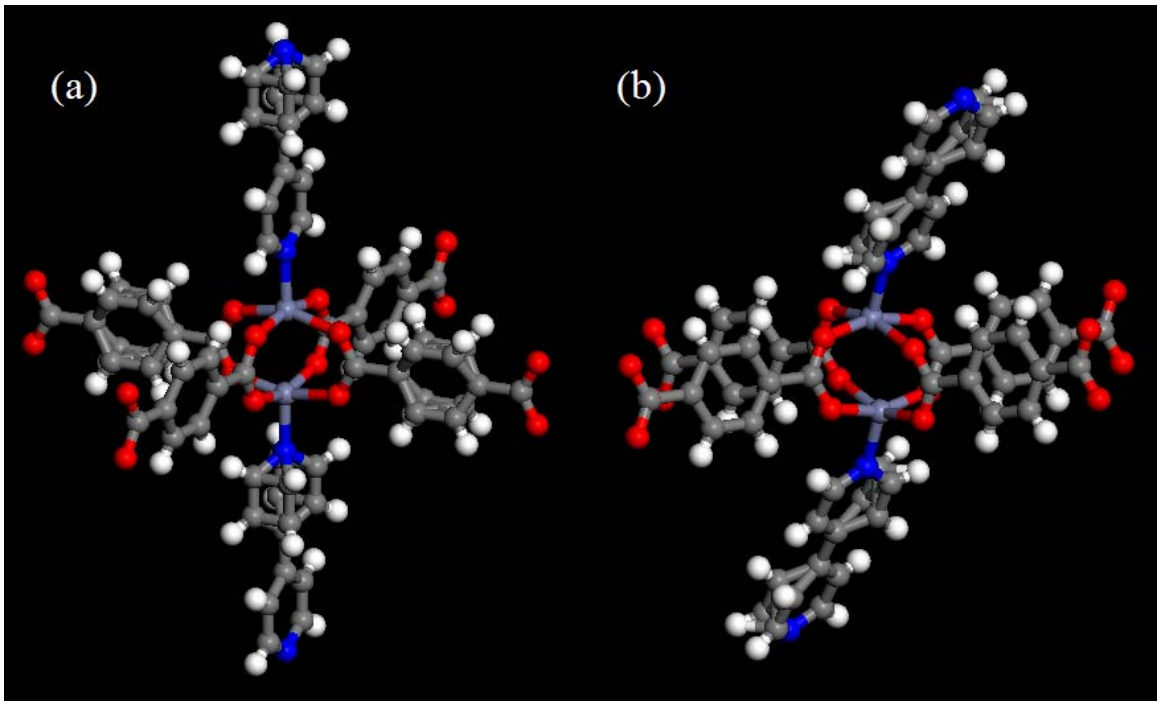

Figure S3. Asymmetrical paddle wheel $Zn_2(BDC)_2$(4,4'-Bipy) units and their coordination geometries in (a) MOF-508a and (b) MOF-508b. (Zn, medium purple; C, gray; O, red; N, blue; H, white)

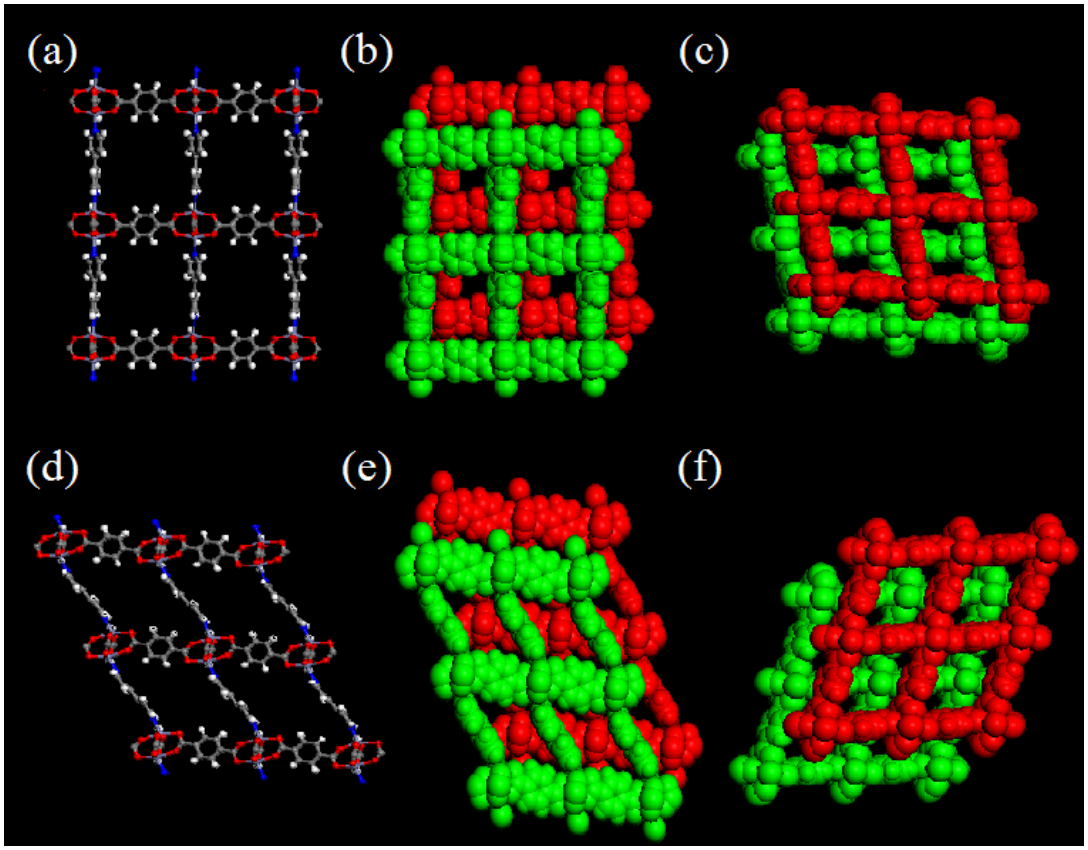

Figure S4. The single crystal x-ray structure of open phase Zn(BDC)(4,4'-Bipy)$_{0.5}$·(DMF)(H_2O)$_{0.5}$ (MOF-508a) showing (a) an elongated primitive cubic α-Po net viewed along *a* axis and its doubly interpenetrating 3D frameworks (red and green) with (b) channel of 2.3 x 3.4 Å along the *a* axis and (c) channel of 2.0 x 4.0 Å along the *c* axis; The single crystal x-ray structure of dense phase Zn(BDC)(4,4'-Bipy)$_{0.5}$ (MOF-508b) showing (d) an highly distorted α-Po net and its doubly interpenetrating 3D frameworks (red and green) with the condensed structure viewed along (e) the rectangular square and (f) the distorted square. (Zn, medium purple; C, gray; O, red; N, blue; H, white)

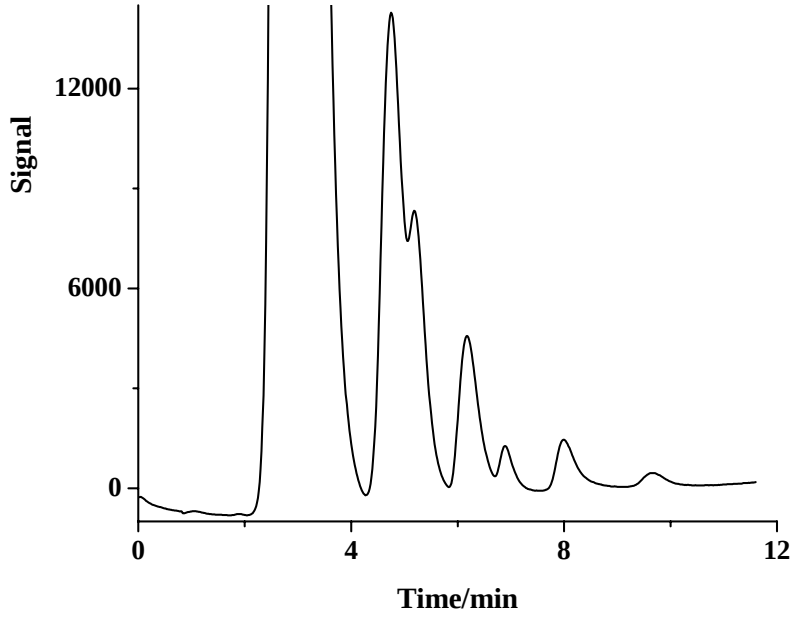

Figure S5. Chromatogram of natural gas mixtures obtained on MOF-508 column (Signal = TCD response).