

PSTC 2016 Publications – Jeff Long

1. “Enhanced Ethylene Separation and Plasticization Resistance in Polymer Membranes Incorporating Metal-Organic Framework Nanocrystals” Bachman, J. E.; Smith, Z. P.; Li, T.; Xu, T.; Long, J. R. *Nature Mater.* **2016**, *15*, 845-849.

The implementation of membrane-based separations in the petrochemical industry has the potential to reduce energy consumption significantly relative to conventional separation processes. Achieving this goal, however, requires the development of new membrane materials with greater selectivity, permeability and stability than available at present. Here, we report composite materials consisting of nanocrystals of metal–organic frameworks dispersed within a highperformance polyimide, which can exhibit enhanced selectivity for ethylene over ethane, greater ethylene permeability and improved membrane stability. Our results suggest that framework–polymer interactions reduce chain mobility of the polymer while simultaneously boosting membrane separation performance. The increased stability, or plasticization resistance, is expected to improve membrane utility under real process conditions for petrochemical separations and natural gas purification. Furthermore, this approach can be broadly applied to numerous polymers that encounter aggressive environments, potentially making gas separations possible that were previously inaccessible to membranes.

2. “Plasticization-Resistant Ni₂(dobdc)/Polyimide Composite Membranes for the Removal of CO₂ from Natural Gas” Bachman, J. E.; Long, J. R. *Energy Env. Sci.* **2016**, *9*, 2031-2036.

We demonstrate that the incorporation of Ni₂(dobdc) metal–organic framework nanocrystals into various polyimides can improve the performance of membranes for separating CO₂ from CH₄ under mixed-gas conditions. Four upper-bound 6FDA-based polyimides, as well as the commercial polymer Matrimids, show improved selectivity under mixed-gas feeds when loaded with 15–25 wt% Ni₂(dobdc), while the neat polyimides show diminishing selectivity upon increasing feed pressure. This approach presents an alternative to chemical crosslinking for achieving plasticization resistance, with the added benefit of retaining or increasing permeability while simultaneously reducing chain mobility.

3. “Reversible CO Scavenging via Adsorbate-Dependent Spin State Transitions in an Iron(II)-Triazolate Metal-Organic Framework” Reed, D. A.; Xiao, D. J.; Gonzalez, M. I.; Darago, L. E.; Herm, Z. R.; Grandjean, F.; Long, J. R. *J. Am. Chem. Soc.* **2016**, *138*, 5594-5602.

A new metal–organic framework, Fe-BTTri (Fe₃[(Fe₄Cl)₃(BTTri)₈]₂·18CH₃OH, H₃BTTri =1,3,5-tris(1*H*-1,2,3-triazol-5-yl)benzene)), is found to be highly selective in the adsorption of CO over a variety of other gas molecules, making it extremely effective, for example, in the removal of trace CO from mixtures with H₂, N₂, and CH₄. This framework not only displays significant CO adsorption capacity at very low pressures (1.45 mmol/g at just 100 μbar), but, importantly, also exhibits readily reversible CO binding. Fe-BTTri utilizes a unique spin state change mechanism to bind CO in which

the coordinatively unsaturated, high-spin Fe^{II} centers of the framework convert to octahedral, low-spin Fe^{II} centers upon CO coordination. Desorption of CO converts the Fe^{II} sites back to a high-spin ground state, enabling the facile regeneration and recyclability of the material. This spin state change is supported by characterization via infrared spectroscopy, single crystal X-ray analysis, Mössbauer spectroscopy, and magnetic susceptibility measurements. Importantly, the spin state change is selective for CO and is not observed in the presence of other gases, such as H₂, N₂, CO₂, CH₄, or other hydrocarbons, resulting in unprecedentedly high selectivities for CO adsorption for use in CO/H₂, CO/N₂, and CO/CH₄ separations and in preferential CO adsorption over typical strongly adsorbing gases like CO₂ and ethylene. While adsorbate-induced spin state transitions are well-known in molecular chemistry, particularly for CO, to our knowledge this is the first time such behavior has been observed in a porous material suitable for use in a gas separation process. Potentially, this effect can be extended to selective separations involving other π -acids.

4. “Selective, Tunable O₂ Binding in Cobalt(II)-Triazolate/Pyrazolate Metal-Organic Frameworks” Xiao, D. J.; Gonzalez, M. I.; Darago, L. E.; Vogiatzis, K. D.; Haldoupis, E.; Gagliardi, L.; Long, J. R. *J. Am. Chem. Soc.* **2016**, *138*, 7161-7170.

The air-free reaction of CoCl₂ with 1,3,5-tri(1*H*-1,2,3-triazol-5-yl)benzene (H₃BTTri) in *N,N*-dimethylformamide (DMF) and methanol leads to the formation of CoBTTri (Co₃[(Co₄Cl)₃(BTTri)₈]₂·DMF), a sodalite-type metal-organic framework. Desolvation of this material generates coordinatively unsaturated low-spin cobalt(II) centers that exhibit a strong preference for binding O₂ over N₂, with isosteric heats of adsorption (Q_{st}) of -34(1) and -12(1) kJ/mol, respectively. The low-spin ($S = 1/2$) electronic configuration of the metal centers in the desolvated framework is supported by structural, magnetic susceptibility, and computational studies. A single-crystal X-ray structure determination reveals that O₂ binds end-on to each framework cobalt center in a 1:1 ratio with a Co-O₂ bond distance of 1.973(6) Å. Replacement of one of the triazolate linkers with a more electron-donating pyrazolate group leads to the isostructural framework Co-BDTriP (Co₃[(Co₄Cl)₃(BDTriP)₈]₂·DMF; H₃BDTriP = 5,5'-(5-(1*H*-pyrazol-4-yl)-1,3-phenylene)bis(1*H*-1,2,3-triazole)), which demonstrates markedly higher yet still fully reversible O₂ affinities ($Q_{st} = -47(1)$ kJ/mol at low loadings). Electronic structure calculations suggest that the O₂ adducts in Co-BTTri are best described as cobalt(II)-dioxygen species with partial electron transfer, while the stronger binding sites in Co-BDTriP form cobalt(III)-superoxo moieties. The stability, selectivity, and high O₂ adsorption capacity of these materials render them promising new adsorbents for air separation processes.

5. “Olsalazine-Based Metal-Organic Frameworks as Biocompatible Platforms for H₂ Adsorption and Drug Delivery” Levine, D. J.; Runčevski, T.; Kapelewski, M. T.; Keitz, B. K.; Oktawiec, J.; Reed, D. A.; Mason, J. A.; Jiang, H. Z. H.; Colwell, K. A.; Legendre, C.; FitzGerald, S. A.; Long, J. R. *J. Am. Chem. Soc.* **2016**, *138*, 10143-10150.

The drug olsalazine (H₄olz) was employed as a ligand to synthesize a new series of mesoporous metal-organic frameworks that are expanded analogues of the well-known M₂(dobdc) materials

(dobdc⁴⁻ = 2,5-dioxido-1,4-benzenedicarboxylate; M-MOF-74). The M₂(olz) frameworks (M = Mg, Fe, Co, Ni, and Zn) exhibit high surface areas with large hexagonal pore apertures that are approximately 27 Å in diameter. Variable temperature H₂ adsorption isotherms revealed strong adsorption at the open metal sites, and in situ infrared spectroscopy experiments on Mg₂(olz) and Ni₂(olz) were used to determine site-specific H₂ binding enthalpies. In addition to its capabilities for gas sorption, the highly biocompatible Mg₂(olz) framework was also evaluated as a platform for the delivery of olsalazine and other encapsulated therapeutics. The Mg₂(olz) material (86 wt % olsalazine) was shown to release the therapeutic linker through dissolution of the framework under simulated physiological conditions. Furthermore, Mg₂(olz) was used to encapsulate phenethylamine (PEA), a model drug for a broad class of bioactive compounds. Under simulated physiological conditions, Mg₂(olz)(PEA)₂ disassembled to release PEA from the pores and olsalazine from the framework itself, demonstrating that multiple therapeutic components can be delivered together at different rates. The low toxicity, high surface areas, and coordinatively unsaturated metal sites make these M₂(olz) materials promising for a range of potential applications, including drug delivery in the treatment of gastrointestinal diseases.

6. “Pore Environment Effects on Catalytic Cyclohexane Oxidation in Expanded Fe₂(dobdc) Analogues” Xiao, D. J.; Oktawiec, J.; Milner, P. J.; Long, J. R. *J. Am. Chem. Soc.* **2016**, *138*, 14371-14379.

Metal–organic frameworks are a new class of heterogeneous catalysts in which molecular-level control over both the immediate and long-range chemical environment surrounding a catalytic center can be readily achieved. Here, the oxidation of cyclohexane to cyclohexanol and cyclohexanone is used as a model reaction to investigate the effect of a hydrophobic pore environment on product selectivity and catalyst stability in a series of iron-based frameworks. Specifically, expanded analogues of Fe₂(dobdc) (dobdc⁴⁻ = 2,5-dioxido-1,4-benzenedicarboxylate) were synthesized and evaluated, including the biphenyl derivative Fe₂(dobpdc) (H₄dobpdc = 4,4'-dihydroxy-[1,1'-biphenyl]-3,3'-dicarboxylic acid), the terphenyl derivative Fe₂(dotpdc) (H₄dotpdc = 4,4''-dihydroxy-[1,1':4',1''-terphenyl]-3,3''-dicarboxylic acid), and three modified terphenyl derivatives in which the central ring is replaced with tetrafluoro-, tetramethyl-, or di-tert-butylaryl groups. Within these five materials, a remarkable 3-fold enhancement of the alcohol:ketone (A:K) ratio and an order of magnitude increase in turnover number are achieved by simply altering the framework pore diameter and installing nonpolar functional groups near the iron site. Mössbauer spectroscopy, kinetic isotope effect, and gas adsorption measurements reveal that variations in the A:K selectivities arise from differences in the cyclohexane adsorption enthalpies of these frameworks, which become more favorable as the number of hydrophobic residues and thus van der Waals interactions increase.

7. “Tuning the Methane Adsorption-Induced Phase Change in the Flexible Metal–Organic Framework Co(bdp)” Taylor, M. K.; Runčevski, T.; Oktawiec, J.; Gonzalez, M. I.; Siegelman, R. L.; Mason, J. A.; Ye, X.; Brown, C. M.; Long, J. R. *J. Am. Chem. Soc.* **2016**, *138*, 15019-15026.

Metal–organic frameworks that flex to undergo structural phase changes upon gas adsorption are promising materials for gas storage and separations, and achieving synthetic control over the pressure

at which these changes occur is crucial to the design of such materials for specific applications. To this end, a new family of materials based on the flexible metal–organic framework Co(bdp) (bdp²⁻ = 1,4- benzenedipyrazolate) has been prepared via the introduction of fluorine, deuterium, and methyl functional groups on the bdp²⁻ ligand. These frameworks are isorecticular to the parent framework and exhibit similar structural flexibility, transitioning from a low-porosity, collapsed phase to high-porosity, expanded phases with increasing gas pressure. Powder X-ray diffraction studies reveal that fluorination of the aryl ring disrupts edge-to-face π – π interactions, which work to stabilize the collapsed phase at low gas pressures, while deuteration preserves these interactions and methylation strengthens them. In agreement with these observations, high-pressure CH₄ adsorption isotherms show that the pressure of the CH₄-induced framework expansion can be systematically controlled by ligand functionalization, as materials without edge-to-face interactions in the collapsed phase expand at lower CH₄ pressures, while frameworks with strengthened edge-to-face interactions expand at higher pressures. Importantly, this work puts forth a general design strategy relevant to many other families of flexible metal–organic frameworks, which will be a powerful tool in optimizing these phase-change materials for industrial applications.

8. “Hydrogen Storage and Selective, Reversible O₂ Adsorption in a Metal-Organic Framework with Open Chromium(II) Sites” Bloch, E. D.; Queen, W. L.; Hudson, M. R.; Mason, J. A.; Xiao, D. J.; Murray, L. J.; Flacau, R.; Brown, C. M.; Long, J. R. *Angew. Chem., Int. Ed.* **2016**, *55*, 8605-8609.

A chromium(II)-based metal–organic framework Cr₃[(Cr₄Cl)₃(BTT)₈]₂ (Cr-BTT; BTT³⁻ = 1,3,5-benzenetristetrazolate), featuring coordinatively unsaturated, redox-active Cr²⁺ cation sites, was synthesized and investigated for potential applications in H₂ storage and O₂ production. Low-pressure H₂ adsorption and neutron powder diffraction experiments reveal moderately strong Cr–H₂ interactions, in line with results from previously reported M-BTT frameworks. Notably, gas adsorption measurements also reveal excellent O₂/N₂ selectivity with substantial O₂ reversibility at room temperature, based on selective electron transfer to form Cr^{III} superoxide moieties. Infrared spectroscopy and powder neutron diffraction experiments were used to confirm this mechanism of selective O₂ binding.

9. “Hydrogen Storage in the Expanded Pore Metal-Organic Frameworks M₂(dobpdc) (M = Mg, Mn, Fe, Co, Ni, Zn)” Gygi, D.; Bloch, E. D.; Mason, J. A.; Hudson, M. R.; Gonzalez, M. I.; Siegelman, R. L.; Darwish, T. A.; Queen, W. L.; Brown, C. M.; Long, J. R. *Chem. Mater.* **2016**, *28*, 1128-1138.

The hydrogen storage properties of a new family of isostructural metal–organic frameworks are reported. The frameworks M₂(dobpdc) (M = Mg, Mn, Fe, Co, Ni, Zn; dobpdc⁴⁻ = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate) are analogous to the widely studied M₂(dobdc) (M = Mg, Mn, Fe, Co, Ni, Cu, Zn; dobdc⁴⁻ = 2,5-dioxido-1,4-benzenedicarboxylate) family of materials, featuring the same weak-field oxo-based ligand environment for the M²⁺ metal centers, but with a larger pore volume resulting from the extended length of the dobpdc⁴⁻ linker. Hydrogen gas adsorption isotherms measured at 77 and 87 K indicate strong H₂ binding at low pressures, corresponding to the adsorption of one molecule per M²⁺ site. Isosteric heats of adsorption indicate adsorption enthalpies ranging from

−8.8 to −12.0 kJ/mol, with the trend Zn < Mn < Fe < Mg < Co < Ni. Room-temperature high-pressure adsorption isotherms indicate enhanced gravimetric uptakes compared to the M₂(dobdc) analogues, a result of the higher surface areas and pore volumes of the expanded frameworks. Indeed, powder neutron diffraction experiments performed on Fe₂(dobpdc) reveal two additional secondary H₂ adsorption sites not observed for the nonexpanded framework. While displaying higher gravimetric capacities than their nonexpanded counterparts, the larger pore volumes result in lower volumetric capacities. Upon comparison with other promising frameworks for hydrogen storage, it becomes evident that in order to design future materials for on-board hydrogen storage, care must be placed in achieving both a high surface area and a high volumetric density of exposed metal cation sites in order to maximize gravimetric and volumetric capacities simultaneously.

10. “Adsorption of Two Gas Molecules at a Single Metal Site in a Metal-Organic Framework” Runčevski, T.; Kapelewski, M. T.; Torres-Gavosto, R. M.; Tarver, J. D.; Brown, C. M.; Long, J. R. *Chem. Commun.* **2016**, 52, 8251-8254.

One strategy to markedly increase the gas storage capacity of metal–organic frameworks is to introduce coordinatively-unsaturated metal centers capable of binding multiple gas molecules. Herein, we provide an initial demonstration that a single metal site within a framework can support the terminal coordination of two gas molecules—specifically hydrogen, methane, or carbon dioxide.