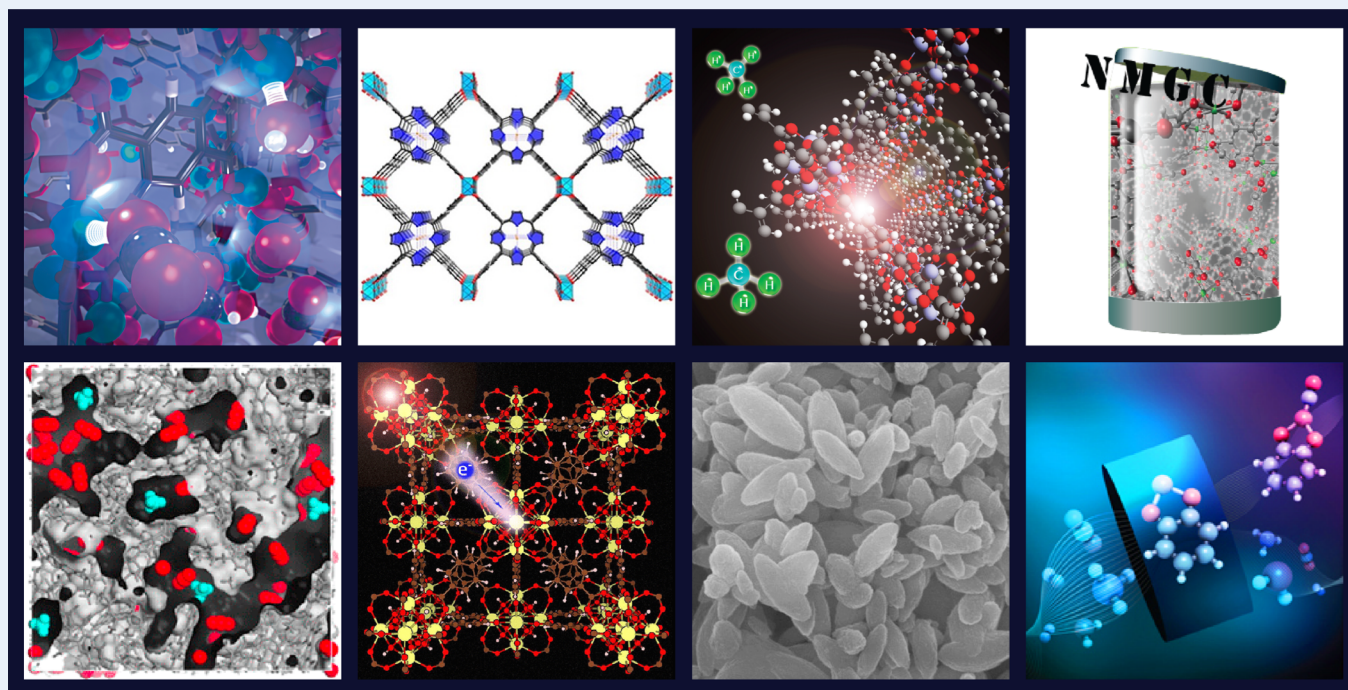


NANOPOROUS MATERIALS GENOME CENTER

2018 ALL-HANDS MEETING



SEPTEMBER 16 - 17, 2018

UNIVERSITY OF MINNESOTA

SEPTEMBER 16 - 17, 2018 | UNIVERSITY OF MINNESOTA

Sunday, September 16, 2018

Registration opens at 8 a.m. in The Commons

8:30 a.m. Continental breakfast buffet, The Commons

9:30 a.m. Meeting begins in the Thomas Swain Room

9:30 a.m. Welcome & update on the Center - Ilja Siepmann

9:40 a.m. Fast and Accurate Prediction of Hydrogen Adsorption in Nanoporous Materials Thrust A
Arun Gopalan, Benjamin Bucior, N. Scott Bobbitt, and Randall Q. Snurr

10:05 a.m. Deep neural network learning of binary sorption equilibria from molecular simulation data Thrust A
Andrew Yangzesheng Sun, Robert F. DeJaco, and J. Ilja Siepmann

10:30 a.m. Nuclear Quantum Effects in Molecular Adsorption and Diffusion Rates Through Zeolites Thrust B
Britta Johnson and Nandini Ananth

10:55 a.m. Coffee Break

11:15 a.m. Computational Screening of Metal-Catecholate Functionalized Metal-Organic Frameworks for Thrust B
O₂/N₂ Separation
Hakan Demir, WooSeok Jeong, Samuel J. Stoneburner, Debmalaya Ray, Christopher J. Cramer,
J. Ilja Siepmann, and Laura Gagliardi

11:40 a.m. Small Gas Molecule Adsorption in Metal Catecholate Incorporated UiO-66, -67, and -68 Structures Thrust B
Hakan Demir, Laura Gagliardi, Christopher J. Cramer, and J. Ilja Siepmann

Methane Recovery from Biogas and Sour Natural Gas Using CoRE MOFs Thrust B
Hakan Demir, Laura Gagliardi, Christopher J. Cramer, and J. Ilja Siepmann

12:15 p.m. Buffet lunch and discussion of collaborative research projects, The Commons (dining in the Thomas Swain Room)

12:15 p.m. PI Lunch, Gateway Room

1:45 p.m. Facilitating the design of mixed-matrices materials Thrust B
Ping Lin, Grit Kuppen, Alex Demidov, and Coray M. Colina

2:10 p.m. Exploiting pi – pi Interactions to Efficiently Extract Atrazine from Water Thrust B
Riki J. Drouot, Isil Akpınar, Satoshi Kato, Timur Islamoglu, and Omar K. Farha

2:35 p.m. Solution Phase Adsorption of Furan and Carboxylic Acid in Hierarchical Zeolites: Insights from Thrust B
Molecular Simulation
Tyler R. Josephson, Kristeen E. Joseph, Paul J. Dauenhauer, and J. Ilja Siepmann

3:00 p.m. Coffee Break

3:30 p.m. Investigation of the Hydrogen Evolving Activity of a Cobalt Dithiolene Metal-Organic Thrust C
Framework
Keying Chen, Courtney Downes, and Smaranda Marinescu

3:55 p.m. Post-Synthetic Modification of Electronic Structure in Metal-Organic Frameworks with Thrust C
Electrochemistry and Mechanical Pressure
Michael E. Ziebel, Lucy E. Darago, Carlo A. Gaggioli, Jingyun Ye, Laura Gagliardi, and Jeffrey R.
Long

4:20 p.m. Applications of Absolutely Localized Huzinaga Operator WF-in-DFT Embedding Thrust C
Daniel Graham, Dhabih Chulhai, and Jason Goodpaster

5:00 p.m. Reception, Heritage Gallery

6:00 p.m. Buffet dinner, Heritage Gallery

7:30 p.m. Poster session and dessert, The Commons

9:30 p.m. End of poster session

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Monday, September 17, 2018

Registration opens at 7:30 a.m. in the Commons Room

- 7:45 a.m. Continental breakfast buffet, The Commons (dining in the Thomas Swain Room)**
- 7:45 a.m. Scientific Advisory Committee and Executive Committee Breakfast, Gateway Room**
- 8:30 a.m. Meeting begins in the Thomas Swain Room**
- 8:30 a.m. Invited Speaker - Matthias Thommes
Institute for Separation Science & Technology, Department of Chemical and Biological Engineering (CBI), Friedrich-Alexander-University Erlangen-Nürnberg, Germany
Progress and Challenges in the Structural Characterization of Nanoporous Materials by Physical Adsorption
- 9:20 a.m. Electronic properties of the Cu[Ni(pdt)₂] conductive metal-organic framework: a periodic-DFT investigation Thrust D
Davide Presti, Michael L. Aubrey, Matthew T. Kapelewski, Jonathan F. Melville, Laura Gagliardi, and Jeffrey R. Long
- 9:45 a.m. Understanding the Electronic Structure and Conductivity in 2D Metal-Semiquinoid Frameworks of Fe, Ti, V and Cr Thrust D
Carlo Alberto Gaggioli and Laura Gagliardi
- 10:10 a.m. Coffee Break
- 10:40 a.m. Software Plan
- 12:00 p.m. Small Working Groups**
- 12:00 p.m. Box lunches served, The Commons**
- 2:00 p.m. Adjourn**

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Presenters of odd-numbered posters are kindly requested to stay near their posters during the first hour and presenters of even-numbered abstracts are kindly requested to stay near their posters during the second hour of the poster session.

1. Energy-Based Descriptors to Rapidly Predict Hydrogen Storage in MOFs
Benjamin Bucior, N. Scott Bobbitt, Timur Islamoglu, Subhadip Goswami, Arun Gopalan, Taner Yildirim, Omar Farha, Neda Bagheri, and Randall Snurr
2. Photocatalytic Newman-Kwart Rearrangement
Sina Chiniforush and Christopher J. Cramer
3. Machine Learning for Quantum Electron Correlation
Dhabih V. Chulhai, Elizabeth R. Smithwick, and Jason D. Goodpaster
4. Modeling Magnetic Metal Organic Frameworks using Density Functional Th
Brianna A. Collins and Jason D. Goodpaster
5. Separation of Butane Isomers on All-Silica Zeolites
Robert F. DeJaco, Andrew Yangzesheng Sun, and J. Ilja Siepmann
6. Small Gas Molecule Adsorption in Metal Catecholate Incorporated UiO-66, -67, and -68 Structures
Hakan Demir, Laura Gagliardi, Christopher J. Cramer, and J. Ilja Siepmann
7. A porous, electrically conductive hexa-zirconium(IV) metal-organic framework
Subhadip Goswami, Debmalya Ray, Ken-ichi Otake, Chung-Wei Kung, Sergio J. Garibay, Timur Islamoglu, Ahmet Atilgan, Yuexing Cui, Christopher J. Cramer, Omar K. Farha, and Joseph T. Hupp
8. Computational Screening of Metal-Catecholate Functionalized Metal-Organic Frameworks for O₂/N₂ Separation
Hakan Demir, WooSeok Jeong, Samuel J. Stoneburner, Debmalya Ray, Christopher J. Cramer, J. Ilja Siepmann, and Laura Gagliardi
9. Acid Modified Metal Organic Framework in Pd-Catalyzed Oxidative Heck Coupling Reaction
Mukunda Mandal, Jingyun Ye, Ken-ichi Otake, Omar K. Farha, Donald G. Truhlar and Christopher J. Cramer
10. Electrochemical CO₂ Reduction using Metal Organic Framework (MOF)
Saied Md Pratik, Mukunda Mandal, and Christopher J. Cramer

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11. Tuning the Electrical Conductivity of a Hexa-M(IV) Metal-Organic Frameworks, where M = Zr, Hf, Ce and Th
Debmalya Ray, Subhadip Goswami, Ravithree Senanayake, Omar K. Farha, Joseph T. Hupp, Christopher J. Cramer and Laura Gagliardi
12. Determination of hydrogen evolution mechanisms in cobalt dithiolene metal organic frameworks using Density Functional Theory
Eugene A. Schneider and Jason D. Goodpaster
13. Redox depressed O₂ adsorption in Co-based MOFs
Jenny G. Vitillo, Varinia Bernales, Julia Oktawiec, Jeffrey R. Long, and Laura Gagliardi
14. Cerium-Based Metal-Organic Frameworks for Photocatalysis
Xin-Ping Wu, Laura Gagliardi, and Donald G. Truhlar
15. Computational Study of Electrocatalytic Hydrogen Evolution from Water by a Mononuclear Molybdenum Sulfide-Functionalized Metal-Organic Framework
Jing Xie, Hyunho Noh, Omar K. Farha, Joseph T. Hupp, Christopher J. Cramer, Laura Gagliardi
16. Using cheminformatics to automate the design of nanoporous materials for clean energy applications
Zhenpeng Yao, N. Scott Bobbitt, Benjamin Bucior, Andrew Yangzesheng Sun, J Ilja Siepmann, Randall Q. Snurr, Alán Aspuru-Guzik
17. Post-Synthetic Modification of Electronic Structure in Metal–Organic Frameworks with Electrochemistry and Mechanical Pressure
Michael E. Ziebel, Lucy E. Darago, Carlo A. Gaggioli, Jingyun Ye, Laura Gagliardi, and Jeffrey R. Long

ABSTRACTS

LISTED IN ALPHABETICAL ORDER BY FIRST AUTHOR'S LAST NAME

Energy-Based Descriptors to Rapidly Predict Hydrogen Storage in MOFs

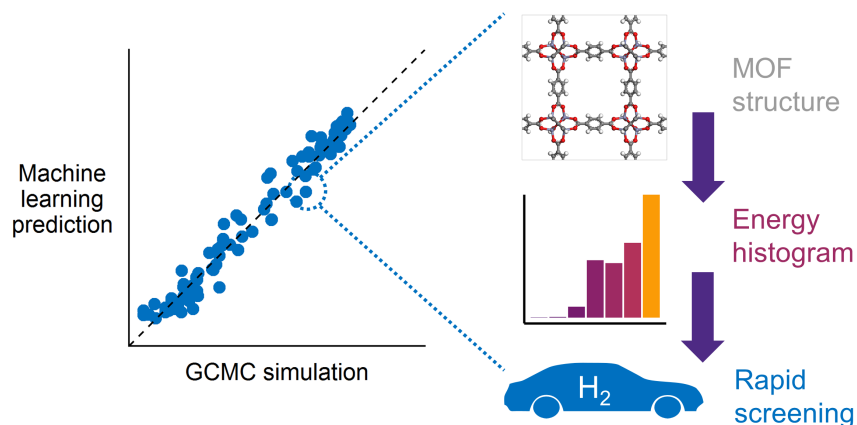
**Benjamin Bucior^a, N. Scott Bobbitt^a, Timur Islamoglu^b, Subhadip Goswami^b, Arun Gopalan^a,
Taner Yildirim^c, Omar Farha^{a,b}, Neda Bagheri^a, and Randall Snurr^a**

^a Department of Chemical & Biological Engineering, Northwestern University

^b Department of Chemistry, Northwestern University

^c NIST Center for Neutron Research, National Institute of Standards and Technology

High-throughput molecular simulations are a powerful tool for MOF design, particularly for adsorption applications like gas storage and separations. These methods can identify promising MOF candidates out of thousands of possibilities, and there are opportunities to better utilize the vast amounts of generated data. We applied machine learning methods to accelerate MOF screening and to develop better structure-property relationships. Our approach uses least absolute shrinkage and selection operator (LASSO) regression to extract insights from MOF energy landscapes, which are rapidly calculated using a probe molecule. The model is highly accurate, interpretable, robust, and three orders of magnitude faster than detailed molecular simulations. To demonstrate the usefulness of this model, we screened 55,000 MOFs and identified a candidate MOF with high hydrogen storage capacity, which we also confirmed experimentally. The approach can be easily applied to other classes of porous materials and adsorbate molecules such as methane.



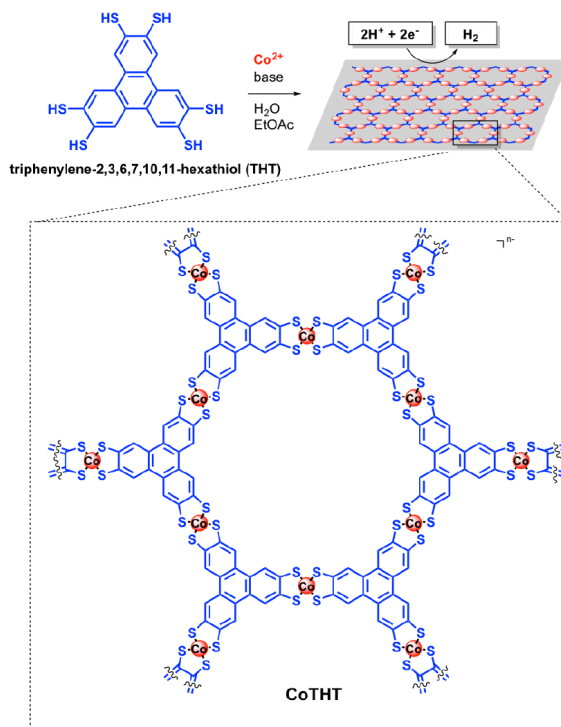
Investigation of the Hydrogen Evolving Activity of a Cobalt Dithiolene Metal-Organic Framework

Keying Chen, Courtney Downes, and Smaranda Marinescu*

Department of Chemistry, University of Southern California, Los Angeles, California, 90089

Metal-organic frameworks (MOFs) have recently emerged as a promising class of material for electrocatalysis, among which the 2-dimensional (2D) metal dithiolene MOFs are some of the earliest examples. Previous reports have shown the promising HER activities of metal dithiolene MOFs incorporating cobalt or nickel metal centers. However, no systematic electrochemical studies have been reported for these materials, largely due to the fact that the typical “top-down” deposition method of the catalyst cannot guarantee a good integration between the electrode and the catalyst. The deposited catalyst films invariably display significant cracking, rendering the assessment of the intrinsic catalytic activity of the material extremely difficult.

Herein, we modify the deposition method by fabricating an ink composite (**1**), comprised of cobalt 2,3,6,7,10,11-triphenylenehexathiolate framework (**CoTHT**), Nafion, and carbon black. **1** exhibited better adhesion to the electrode surface and was able to be electrochemically characterized in detail. Experimental results suggested the promising activity of **1** with an optimal overpotential of 143 mV to reach a current density of 10 mA/cm² and a Tafel slope of 70.6 mV/dec in pH 1.3 aqueous solution, which is by far one of the most active MOF-based catalysts for HER.

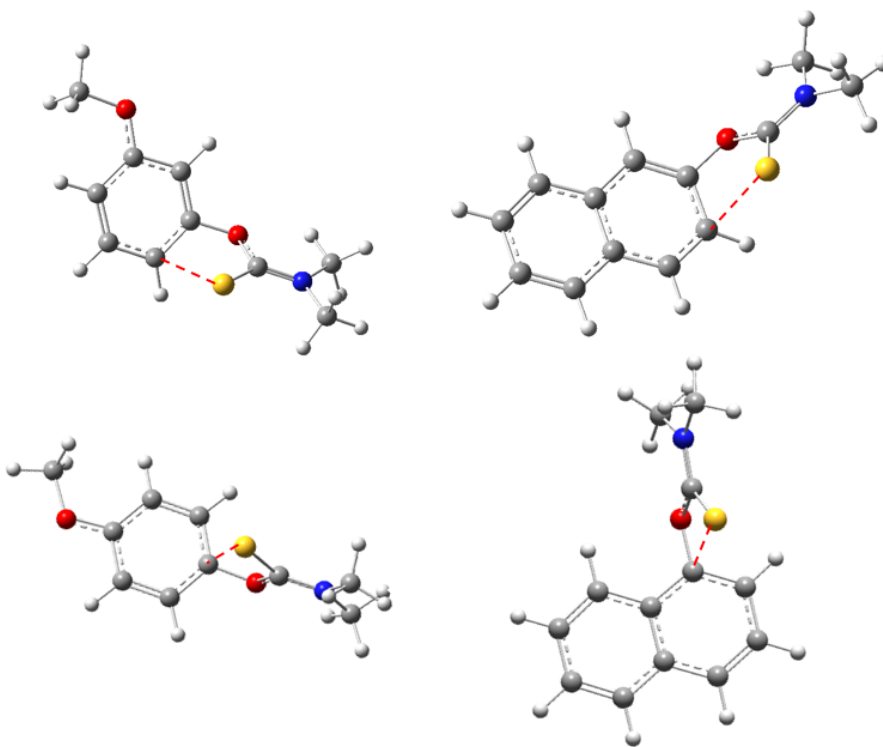


Photocatalytic Newman-Kwart Rearrangement

Sina Chiniforush and Christopher J. Cramer ^a

^aDepartment of Chemistry, University of Minnesota

Photo-redox catalysis is an important tool that allows access to regions of potential energy surface that typically inaccessible, which makes it useful in synthetic chemistry. Recently, photo-redox catalysis was utilized to achieve Newman-Kwart rearrangement in ambient temperature, which typically requires high temperatures. Interestingly, the selectivity of this reaction is different under photocatalytic conditions. To understand the mechanism of this reaction, density function theory calculations were utilized in this study. Potential modifications of the substrates are also introduced to improve the reactivity of the substrates.



Machine Learning for Quantum Electron Correlation

Dhabih V. Chulhai^a, Elizabeth R. Smithwick^b, and Jason D. Goodpaster^a

^a Department of Chemistry, University of Minnesota

^b Department of Chemistry, Duke University

We use machine learning to understand how electrons interact which allows us to solve the exact wave function for the many-electron Schrödinger equation within the full configuration interaction framework. The approach is further generalized to circumvent the construction of the wave function allowing for the direct calculation of properties of a molecule, such as the electronic energy and dipole moment. Our approach ‘learns’ how electrons correlate by solving the Schrödinger equation for subsets of the electrons in the molecule, which allows for the machine learning prediction of properties for the full molecule. The method is shown to be systematically improvable, essentially linear scaling, embarrassingly parallelizable, and highly accurate. This work has far reaching implications to a diverse set of many-body chemistry and physics problems.

Modeling Magnetic Metal Organic Frameworks using Density Functional Theory

Brianna A. Collins^a and Jason D. Goodpaster^b

^aChemistry Department, University of Minnesota – Twin Cities

^bChemistry Department, University of Minnesota – Twin Cities

We use spin-polarized Density Functional Theory (DFT) to study the magnetic properties of Metal Organic Frameworks (MOFs). Porous nanomaterials are able to perform separation of gas or liquid mixtures, typically by chemical adsorption of one of the components within the nanomaterial. Recently, an alternative approach has been suggested to leverage differences in molecular magnetization to perform the separation. Our aim is to be able to model and predict this phenomenon. In order to achieve this, we study MOFs, which are porous materials made of transition metals nodes bonded by organic linkers, using various computational methods. However, modeling magnetic properties in these systems faces extraordinary challenges and requires careful investigation. Spin-Polarized Density Functional Theory (DFT) is an attractive method to study magnetic moments because the spin density, that gives rise to the magnetic moments, is well defined in these calculations. Additionally, DFT is computationally efficient and can be applied to these large MOF systems. However, there are well-known obstacles with modeling magnetic moments in DFT, such as the lack of proper electron localization. Therefore, we perform various DFT, DFT+U, and exchange-correlated method calculations to build an appropriate protocol for the study of magnetic MOFs.

Separation of Butane Isomers on All-Silica Zeolites

Robert F. DeJaco^{ab}, Andrew Yangzesheng Sun^b, and J. Ilja Siepmann^{ab}

^a Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN, 55455-0132

^b Department of Chemistry and Chemical Theory Center, University of Minnesota, Minneapolis, MN, 55455-0431

Multi-component mixtures are commonly encountered in separation processes where nanoporous materials have the potential to be advantageous over conventional approaches. However, as the number of components in a mixture increases by one, so does the dimension of the phase equilibria necessary for evaluation of a separation process. As a result of the increased computational or experimental cost, many studies for mixture adsorption onto nanoporous materials only investigate a small slice of this phase equilibria hyper-surface—typically the equimolar slice—and a comprehensive study of mixture equilibria has not been reported. In this work, Mira, a large-scale supercomputer at Argonne National Lab, is used to obtain the entire p_{total}, y_i surface for adsorption of *n*-butane and 2-methylpropane mixtures onto 256 all-silica zeolites selected from the IZA database.¹ NpT Gibbs ensemble Monte Carlo simulations are performed at $T = 343$ K with a number of molecules higher than the saturation loading for each zeolite supercell. The total pressure and overall composition are varied as eight logarithmically-spaced points from 0.01% to 90% of the *n*-butane saturation pressure and by eight linearly-spaced points from 0 to 1 mole fraction *n*-butane, respectively. At each state point, eight independent simulations are carried out, and the ensemble of 131,072 simulations are bundled in one job submission on Mira. Subsets of the mixture adsorption isotherms are fit to Real Adsorbed Solution Theory using activity coefficient models based on the Wilson equation and using deep neural networks. The results for the entire phase envelope are discussed in light of conventional approaches to investigate mixture adsorption by the molecular simulation community.

References

[1] C. Baerlocher, and L. B. McCusker, “Database of zeolite structures,” <http://www.iza-structure.org/databases/> 2016.

Methane Recovery from Biogas and Sour Natural Gas Using CoRE MOFs

Hakan Demir^a, Laura Gagliardi^a, Christopher J. Cramer^a, and J. Ilja Siepmann^{a,b}

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^bDepartment of Chemical Engineering and Materials Science, University of Minnesota, 421 Washington Avenue SE, Minneapolis, MN 55455-0431, United States.

Over the last century, the high consumption level of fossil fuels has become concerning for the society and the environment due to the increasing pollution in nature. To mitigate the detrimental effects of fossil fuel usage, cleaner energy sources are being sought. Methane is deemed to be the fuel to be used during the transition period connecting the era of fossil fuels to that of the clean and efficient energy sources (i.e. hydrogen). Although its combustion generates greenhouse gases like fossil fuels do, owing to methane's high hydrogen/carbon ratio, less CO₂ is produced compared to conventional fuels such as oil and coal. Thus, the production and the usage of methane is crucial to slow down the growth of the environmental problems.

Metal-organic frameworks (MOFs) are promising candidates for many gas separation applications including methane purification since their tailorable structures can allow creating pores that can hold a specific gas while letting others pass through the material. The Computation-Ready Experimental (CoRE) MOF database is a collection of experimentally synthesized MOFs made ready for computational studies which has been the focus of materials for this talk.

In this talk, using CoRE MOFs, two possible methane recovery scenarios will be discussed: Methane recovery from five-component biogas mixture (CH₄, N₂, CO₂, H₂S, NH₃) and three-component sour natural gas (CO₂, H₂S, CH₄). These scenarios are less studied in the literature however more realistic than typical studies where binary mixtures of natural gas are assumed with the presence of equimolar methane and a contaminant gas. Through the use of Grand Canonical Monte Carlo (GCMC) simulations, MOFs that can have high working capacity, selectivity and regenerability are identified and the correlation between performance metrics and the structural properties of MOFs is discussed.

Small Gas Molecule Adsorption in Metal Catecholate Incorporated UiO-66, -67, and -68 Structures

Hakan Demir^a, Laura Gagliardi^a, Christopher J. Cramer^a, and J. Ilja Siepmann^{a,b}

^aDepartment of Chemistry, Minnesota Supercomputing Institute, and Chemical Theory Center, University of Minnesota, 207 Pleasant Street Southeast, Minneapolis, MN 55455-0431, United States.

^bDepartment of Chemical Engineering and Materials Science, University of Minnesota, 421 Washington Avenue SE, Minneapolis, MN 55455-0431, United States.

Metal-organic frameworks (MOFs) are nanocrystalline materials which feature properties such as high porosity, wide chemical diversity and ease of functionalization. Owing to these desirable properties, MOFs have been one of the main focii of the material research and they have shown considerable potential for a number of applications including principally gas adsorption/separation, catalysis, and sensing. More recently, the modification of MOF structures with metal catecholates have attracted interest since it creates open metal sites that can strongly bind a gas molecule over another which is crucial for effective gas separation. Despite the structural versatility of MOFs, they generally suffer from low structural stability in different mediums. However, a specific class of MOFs, Zr-based UiO-type MOFs, has exhibited superior thermal, chemical stability which render them stand out from most of the other MOFs.

In this work, Zr-based pristine UiO-66, -67, and -68 structures are computationally doped with metal catecholates (Co, Mg, Ni, Zn) to study the effect of the open metal sites in metal catecholates on selective gas sorption for various small gas molecules (CH₄, N₂, CO₂, NH₃, H₂S, SO₂, H₂O). Given the fact that four different metals are used in the metal-catecholates, our study makes it possible to show which metal types can bring performance improvements for today's gas storage/separation challenges. In our DFT analysis employing PBE-D3 (BJ) functional, the absolute and relative binding energies of sorbates are considered to identify potentially useful UiO-type structures for several gas mixtures. Furthermore, the sorbate binding energies in pristine UiO-type structures are contrasted with those in their counterparts with metal catecholates to discuss the advantages of creating strong adsorption sites in the pores of UiO-type MOFs.

Exploiting π – π Interactions to Efficiently Extract Atrazine from Water

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^c Department of Chemistry, Faculty of Science, King Abdulaziz University

The United States Environmental Protection Agency (EPA) recognizes atrazine as an endocrine disrupting compound. Excessive use of this fertilizer results in contamination of surface and ground water supplies via agricultural runoff. Efficient removal of atrazine from contaminated water supplies is paramount. Here, we evaluated the atrazine affinity of an assortment of water-stable Zr_6 -based metal–organic frameworks (MOFs) and investigated the mechanism governing atrazine adsorption. We found that the mesopores of NU-1000 facilitated rapid atrazine uptake saturating in < 5 min and that the pyrene-based linkers offered abundant sites for π - π interactions with atrazine as demonstrated by the near 100% uptake. Without the presence of a pyrene-based linker, NU-1008, a MOF similar to NU-1000 with respect to surface area and pore size, removed <20% of the exposed atrazine. These results further suggest that exceptional atrazine uptake capacity stems from the presence of a pyrene core as found in NU-1000, affirming that π - π stacking is responsible for the atrazine adsorption. Furthermore, NU-1000 displays an exceptional atrazine removal capacity through 4 cycles of adsorption-desorption. Powder X-ray diffraction (PXRD) and Brunauer–Emmett–Teller (BET) surface area analysis confirmed the retention of MOF crystallinity and porosity throughout the adsorption-desorption cycles.

Understanding the Electronic Structure and Conductivity in 2D Metal-Semiquinoid Frameworks of Fe, Ti, V and Cr

Carlo Alberto Gaggioli and Laura Gagliardi

Department of Chemistry, Chemical Theory Center and Supercomputing Institute, University of Minnesota–Twin Cities,
207 Pleasant Street SE, Minneapolis, Minnesota 55455, United States

In the past years, an increasing number of Metal–Organic Frameworks (MOF) has been shown to display electronic conductivity that can be exploited for several applications, such as battery electrodes, thermo-electrics, electrochemical sensors, electrocatalysts.^[1] There have been proposed several ways to achieve electronic conductivity in MOFs, such as using metal thiolate chains, infinite π – π stacking, donor–acceptor charge transfer chains, and π – d conjugated square planar metal sites. Another strategy that led to improved conductivities consists of using mixed-valence units that repeat in one, two, or three-dimensions. MOFs are particularly appealing cause it is possible to tune their surface chemistry and electronic structure via modification of metal, ligand, and network topology.

Recently, it has been shown that mixed valence 2D-Metal Semiquinoid Frameworks are an appealing class of materials for conductivity applications, and the Fe, Ti, V and Cr phases have been analyzed experimentally, revealing an exciting high tunability of the electronic structure and conductivity.[2] In this contribution, we employ computational methods to understand the electronic structure and the mechanism of conductivity in these materials. A systematic DFT study have been performed in order to find a reliable computational strategy that can reproduce experimental data, in order to be predictive for the analysis of new materials not yet synthesized.

References

[1] (a) Sun, L.; Campbell, M. G.; Dinca, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 3566. (b) D’Alessandro, D. M.; Kanga, J.; Caddy, J. S. *Aust. J. Chem.* **2013**, *64*, 718. (c) Morozan, A.; Jaouen, F. *Energy Environ.Sci.* **2012**, *5*, 9269. (d) Erickson, K. J.; Léonard, F.; Stavila, V.; Foster, M. E.; Spataru, C. D.; Jones, R. E.; Foley, B. M.; Hopkins, P. E.; Allendorf, M. D.; Talin, A. A. *Adv. Mater.* **2015**, *27*, 3453.

[2] Ziebel, M. E.; Darago, L. E.; Long, J. R. *J. Am. Chem. Soc.* **2018**, *140*, 3040-3051.

Fast and Accurate Prediction of Hydrogen Adsorption in Nanoporous Materials

Arun Gopalan^a, Benjamin Bucior^a, N. Scott Bobbitt^a, and Randall Q. Snurr^a

^aChemical and Biological Engineering, Northwestern University

We present a fast and accurate, semi-analytical method for predicting hydrogen adsorption in nanoporous materials. For any given set of conditions (T, P), the adsorption in a material is calculated as an integral average over all adsorption sites (guest-host interactions) plus the guest-guest contribution as a function of the adsorption pressure (P) and including the effects of confinement. The guest-host interaction energy is calculated using a classical force field¹, where the material is probed using a single-site hydrogen probe² to obtain the energy distribution of adsorption sites ($\rho(E)$). Local adsorption at each site is then modeled as a Langmuir isotherm, which when coupled with the density distribution of sites gives an accurate description of adsorption at low loading (Henry's constant). To capture the guest-guest interactions correctly, we consider each adsorbed molecule to have an average coordination number³, which is regressed using Gaussian Process Regression (GPR) as a function of the adsorption conditions (T, P) and the textural properties of the material. The coordination number multiplied by the well depth (ϵ) of the Lennard-Jones potential for hydrogen accounts for the guest-guest interactions in the local isotherm. The method is tested by predicting hydrogen adsorption on selected metal-organic frameworks (MOFs) from the Computation Ready MOF (CoRe-MOF) database⁴ at 77 K over the broad pressure range of 1 Pa to 100 bar, and the results are compared against predictions from GCMC simulations. Once fully tested, the method can be used to screen large numbers of materials and identify top candidates and design strategies for hydrogen storage and other applications.

References

- [1] A.K. Rappé, C.J. Casewit, K.S. Colwell, W.A. Goddard III, W.M. Skiff. UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations. *Journal of the American Chemical Society*. 1992 Dec;114(25):10024-35.
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A porous, electrically conductive hexa-zirconium(IV) metal–organic framework¹

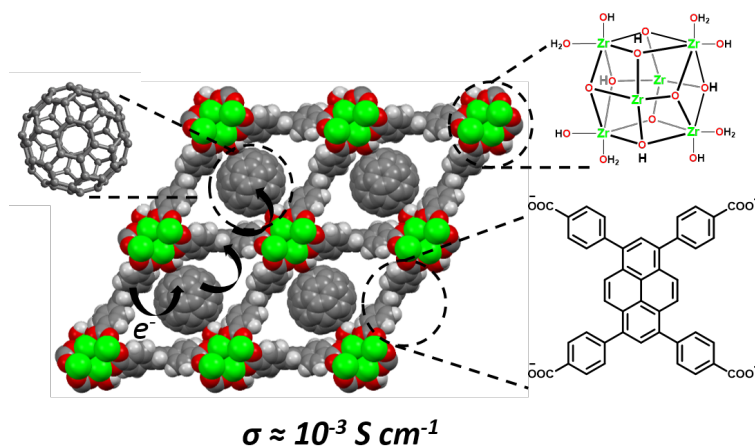
Subhadip Goswami,^a Debmalya Ray,^b Ken-ichi Otake,^a Chung-Wei Kung,^a Sergio J. Garibay,^a Timur Islamoglu,^a Ahmet Atilgan,^a Yuexing Cui,^a Christopher J. Cramer,^b Omar K. Farha^{a,c} and Joseph T. Hupp^{*a}

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^b Department of Chemistry, Chemical Theory Center, Minnesota Supercomputing Institute, University of Minnesota, 207 Pleasant Street SE, Minneapolis, USA

^c Department of Chemistry, King Abdulaziz University, Jeddah 21589, Saudi Arabia

Engendering electrical conductivity in high-porosity metal–organic frameworks (MOFs) promises to unlock the full potential of MOFs for electrical energy storage, electrocatalysis, or integration of MOFs with conventional electronic materials. Here we report that a porous zirconium-node-containing MOF, NU-901, can be rendered electronically conductive by physically encapsulating C60, an excellent electron acceptor, within a fraction (ca. 60%) of the diamond-shaped cavities of the MOF. The cavities are defined by node-connected tetra-phenyl-carboxylated pyrene linkers, i.e. species that are excellent electron donors. The bulk electrical conductivity of the MOF is shown to increase from immeasurably low to $10^{-3} \text{ S cm}^{-1}$, following fullerene incorporation. The observed conductivity originates from electron donor–acceptor interactions, i.e. charge-transfer interactions – a conclusion that is supported by density functional theory calculations and by the observation of a charge-transfer-derived band in the electronic absorption spectrum of the hybrid material. Notably, the conductive version of the MOF retains substantial nanoscale porosity and continues to display a sizable internal surface area, suggesting potential future applications that capitalize on the ability of the material to sorb molecular species.



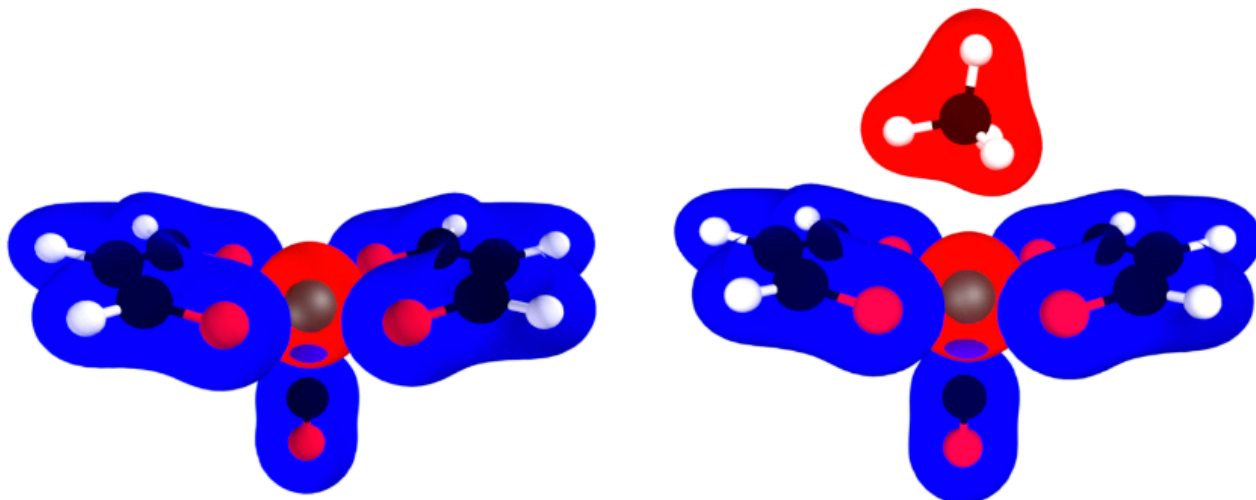
¹ Goswami et. al, *Chem. Sci.*, 2018, **9**, 4477-4482.

Applications of Absolutely Localized Huzinaga Operator WF-in-DFT Embedding

Daniel Graham^a, Dhabih Chulhai^a, and Jason Goodpaster^a

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Quantum embedding methods provide a strategy for performing localized highly accurate calculations on chemical systems while not incurring high cost computational scaling for the full system. The Huzinaga projection operator based absolute localization wavefunction embedded in density functional theory (WF-in-DFT) embedding methods match full system WF energy differences across a diverse test set. This test set includes systems with bond formation and dissociation, embedding within a conjugated system, and multi-reference WF calculations embedded in DFT. In all test cases, the embedding method demonstrates high accuracy for a relatively small WF region and systematic improvement with increasing size of the WF region. Additionally, the method is being applied to gas adsorption on large metal organic framework (MOF) cluster models, specifically cluster models of MOF-74 (see figure) and MOF-5. Preliminary results for these cluster models are promising, however some require special treatment to calculate accurate energies. The absolute localization WF-in-DFT method can be applied to systems at the DFT size limit, as long as the size of the WF region is small compared to the system at large.



Computational Screening of Metal-Catecholate Functionalized Metal-Organic Frameworks for O₂/N₂ Separation

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Metal-catecholate functionalized metal-organic frameworks (MOFs) can be employed in gas separations, gas storage, and catalysis. For O₂/N₂ separation, it was shown that metal-catecholate systems with a first-row transition metal show a stronger O₂ binding energy than that of N₂ by performing density functional theory (DFT) and multireference wave function calculations [1]. However, the above calculations were based on metal-catecholate cluster models. The next step is to test whether MOFs with a metal-catecholate moiety show preferential binding to O₂ over N₂. In this work, pristine MOF structures that are appropriate platforms to insert a metal-catecholate moiety were identified through screening for subsequent DFT calculations. Among 5109 CoRE MOF structures [2], 201 structures were selected by considering the pore size, the presence of 6-membered rings for potential metalation sites, the O₂/N₂ uptake selectivity obtained from Grand Canonical Monte Carlo (GCMC) simulations, and the unit cell size for the feasibility of high-level calculations. Since multiple metalation sites can exist in one MOF structure, there are in total 4783 metalated MOF structures that can be created from the prescreened 201 pristine MOF structures when only one metal-catecholate complex is added to each metalation site. To narrow down the number of potential candidates for DFT calculations, we developed a code that identifies unique metalation sites and excludes structures with unphysical metalation sites due to the closeness to framework atoms. Duplicate metalation sites are excluded. Through the screening four MOFs that have only one unique metalation site are chosen which are then modified with the addition of Co, Mg, Ni, and Zn-catecholates. O₂ and N₂ binding energies in these four MOFs are studied with DFT using periodic models. Considering the DFT binding energies of O₂ and N₂, the potential of identified CoRE MOFs for several applications including O₂/N₂ separation is discussed.

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Nuclear Quantum Effects in Molecular Adsorption and Diffusion Rates Through Zeolites

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Nanoporous materials (NPMs) like zeolites and metal organic frameworks (MOFs) have been extensively studied for their gas capture and separation abilities. In order to develop accurate simulations to explain these properties, we need to understand both the adsorption between the gas adsorbates and the complex frameworks as well as the molecular diffusivities through the pores. Previous studies have indicated the need for the inclusion of additional interactions in order to explain more complex behaviors. One such example is the importance of nuclear quantum effects when calculating rates through NPMs with small diameter nanopores. In general, systems in which the pore size and molecular diameter are similar experience significant nuclear zero-point effects. Because of the large system size of NPMs and the time scales necessary to capture relevant processes, calculating quantum effects using traditional methods is infeasible.

We use path integral and ring polymer molecular dynamics (PIMD/RPMD) methods to calculate the quantum effects in various molecule-NPM systems. RPMD methods are attractive because they scale classically with system size but are able to capture quantum effects like zero-point energy and tunneling. By employing a combination of simple models and PIMD, we evaluate the role of nuclear quantum effects in the static properties of a series of molecule-zeolite systems. In particular, we compare the classical and quantum insertion barrier for H₂/D₂ into different zeolite pores. We leverage these results to move towards obtaining RPMD simulations and rates for H₂/D₂ diffusion through the relevant zeolite structures. Our target is to use RPMD to model the diffusion of ethane and ethylene through a series of zeolites with narrow pores to determine the role nuclear quantum effects play in ethane/ethylene separation. We will also discuss our strategies in implementing mixed quantum-classical PIMD/RPMD into CP2K.

Solution Phase Adsorption of Furan and Carboxylic Acid in Hierarchical Zeolites: Insights from Molecular Simulation

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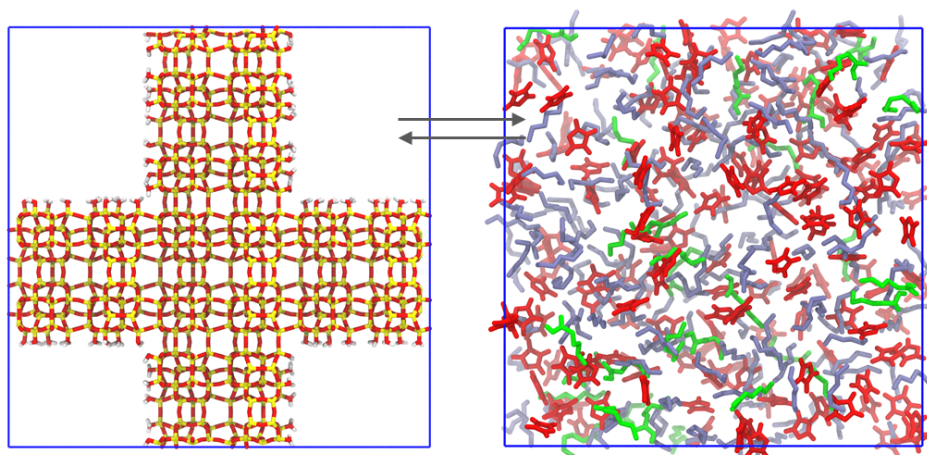
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Oleo-furans¹ are a novel class of bio-renewable surfactants with superior hard-water stability compared to petroleum-derived surfactants. During their synthesis, sugar-derived furans react with triglyceride-derived fatty acids via acid-catalyzed acylation. Their synthesis is promoted by hierarchical zeolites, such as self-pillared pentasil (SPP) zeolites², which combine microporous and mesoporous functionalities to perform selective catalysis and accommodate diffusion of large molecules.

To improve fundamental understanding and enable improvements in catalyst and process design, the co-adsorption of furan, hexanoic acid, and various solvents from solution into SPP was investigated using Monte Carlo simulations in the Gibbs Ensemble. Solution composition and reaction conditions significantly affect adsorption selectivity, as well as the distribution of species in the meso- and micropores of SPP. Silanols on the surface of SPP strongly hydrogen bond with hexanoic acid, promoting selective adsorption of acid from the solution phase onto the mesopore walls, while furan and hexane solvent are more evenly distributed throughout the mesopore and micropore volumes. The influence of several process variables on the adsorption selectivity and spatial distribution in the zeolite was also investigated, including solution composition, the chain length and degree of branching of the solvent, and adsorption in both subcritical and supercritical regimes.

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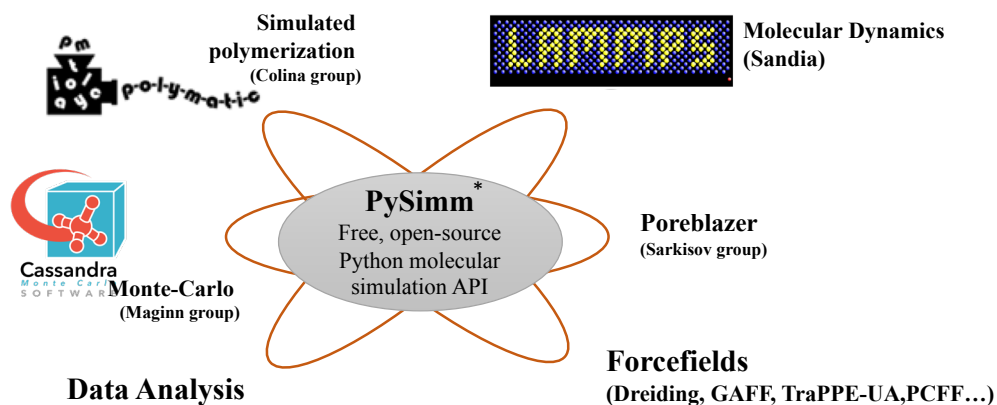
Facilitating the design of mixed-matrices materials

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There is a great need for new easy-to-use tools to perform computational studies of mixed-matrices materials, that include amorphous polymers and ordered structures. Several approaches have been attempted to generate these network structures such as assuming ordered structures or combining smaller network fragments which are not ideal for many scenarios such as highly crosslinked amorphous systems. Moreover, most studies to date consider the systems as static, which might be an unrealistic assumption especially at high pressures. In particular, phenomena such as swelling, plasticization, and aging are known to affect the properties of polymers in general. In this talk, we will discuss the capabilities of a simulation tool, *pysimm*, designed to facilitate the structure generation, simulation and characterization of complex molecular systems. In general, the properties of polymeric materials depend greatly on the specifics of each polymeric sample such as the monomeric composition, tacticity, molecular weight distribution, degree of branching and network structure. Examples showing the use of the tool for different systems (Organic Molecules and Polymers of Intrinsic Microporosity, zeolites, MOFs) will be provided, including the development of a new computational polymer growth algorithm using *pysimm* to control molecular weight and build copolymers. The *pysimm* (<http://pysimm.org>), short for python simulation interface for molecular modeling, is a python package that provides a collection of different simulation tools while offering smooth integration with highly optimized third party software for specialized tasks. The modular tools in the *pysimm* package provide a toolbox for researchers to build applications with complex workflows through easy to use functions and fully object oriented representations of molecular systems. Pysimm interfaces with existing software, such as the LAMMPS, Poreblazer and Cassandra.



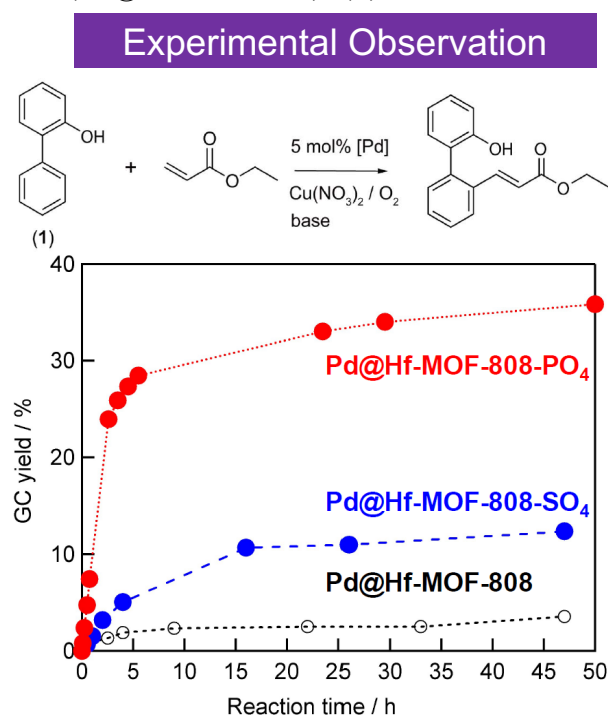
Acid Modified Metal Organic Framework in Pd-Catalyzed Oxidative Heck Coupling Reaction

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Palladium catalyzed Heck coupling reaction is one of the most powerful methods for C-H bond functionalization.¹ In contrast to traditional Heck reaction, where electrophiles act as self-oxidant for generating Pd(II) from Pd(0), oxidative Heck coupling generally uses an external oxidant.² In this work, we have used the oxidative Heck coupling scheme for selective alkenylation of C-H bond at the 2'-position of 2-hydroxybiphenyl. For catalysis, three variants of palladium source have been used: Pd-deposited on (i) hafnium substituted MOF-808 (Pd@Hf-MOF-808), (ii) H₂SO₄ treated Hf-MOF-808 (Pd@Hf-MOF-808-SO₄), and (iii) H₃PO₄ treated Hf-



MOF-808 (Pd@Hf-MOF-808-PO₄). Experimentally, both acid modified MOFs showed higher reactivity than the bare MOF, with the phosphate modified variant showing maximum reactivity. Unfortunately, solely based on the crystal structure data, the geometry of neither the acidified MOFs, nor their Pd-deposited analogs could be recognized with certainty. To better understand the structural features and the origin of differential reactivity, density functional modeling of various species was performed. Various conformers with different binding modes (with SO₄/PO₄) and different proton topology were explored. Presumably, the phosphate modified MOF is able to stabilize the Pd(II) species—the active species responsible for the oxidative Heck coupling reaction; thus eliminating catalyst deactivation pathway leading to the formation of Pd-nano particles. We believe, these detailed understanding could be efficiently used for future material design efforts.

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Electrochemical CO₂ Reduction using Metal Organic Framework (MOF)

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Increasing concentrations of atmospheric CO₂ are a consequence of rising fossil fuel combustion, a situation that confronts human civilization with unprecedented challenges like global warming and restrictions on energy consumption. As such, the development of economically feasible and environmentally benign technologies to generate electrical energy and chemical fuels is essential for a sustainable future. Among various strategies, electrochemical CO₂ reduction is one promising approach to produce hydrocarbons, alcohols, and other organic products from CO₂.¹ The major challenges that must be addressed to improve the efficiency of current electrochemical CO₂ reductions are high overpotentials, poor faradaic efficiencies, and poor product selectivities. High overpotentials and poor product selectivities derive from poorly tuned adsorption energies of critical intermediates in the reaction cycle(s), while low faradaic efficiencies are typically attributable to competitive hydrogen evolution occurring in the same range of potentials as CO₂ reduction. Improved catalysts should address these various issues. Among known homogeneous and heterogeneous electrocatalysts, metallic copper is unique for its wide range of product distribution. Unfortunately, the Cu catalyzed CO₂ reduction reaction also requires a high overpotential. However, bimetallic Cu-containing electrocatalysts, including Cu-Ni, Cu-Sn, Cu-Au, Cu-Pt, and Cu-In, have been developed for CO₂ reduction and show improved selectivity compared to pristine Cu.

Metal-organic frameworks (MOFs) comprise a class of porous, crystalline materials. MOFs show promise for a wide range of application due to their unique electronic, optical, and catalytic properties.² Recently, our experimental collaborators at Northwestern University synthesized novel heterostructures where metallic copper nanoparticles are deposited in the thin film of a water-stable MOF (NU-1000). They used solvothermal deposition in MOFs (SIM) followed by electrochemical reduction of Cu(II) to generate metallic Cu and studied electrochemical CO₂ reduction in its presence. This copper nanoparticle deposited NU-1000 was found to exhibit a promising catalytic efficiency towards electrochemical reduction of CO₂ in an aqueous electrolyte.³ Interestingly, our collaborators have also found that copper-indium nanoparticles deposited in NU-1000 exhibit better product selectivity in aqueous electrolyte compared to pure Cu or In. More specifically, methanol is obtained as a major product at an applied potential of -0.82 V with respect to the reversible hydrogen electrode.

Our goal is to use theory to elucidate the mechanistic details of electrochemical CO₂ reduction taking place on Cu and Cu-In nanoparticles embedded in NU-1000. Cluster and periodic calculations should shed light on key atomistic details, electronic factors, steric, and strain energies that dictate overall thermochemistry, kinetics, and finally product selectivity. Insights won from fundamental studies should help both experimentalists and theorists to design improved MOF-based electrocatalysts for efficient electrochemical CO₂ reduction.

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Electronic properties of the Cu[Ni(pdt)₂] conductive metal-organic framework: a periodic-DFT investigation

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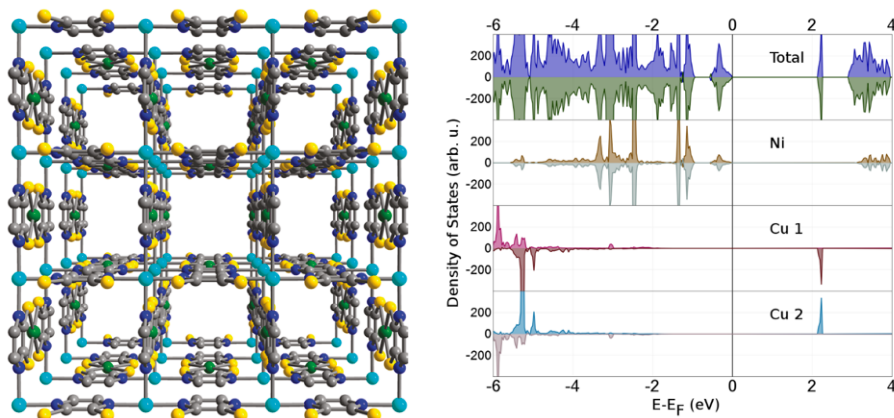
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Conductive and chemiresistive metal-organic frameworks (MOFs) are an emerging class of materials that can be employed as chemical sensors.^{1,2} Moreover, because of their porosity and crystallinity they show remarkable gas-adsorption properties. A wise combination of such features can lead to a smart design of conductive materials that operate at near-ambient conditions.

The electronic nature of Cu[Ni(pdt)₂] (pdt²⁻ = 2,3-pyrazinedithiolate) MOF is investigated by means of density functional theory (DFT) calculations, and related to the experimental characterization of its conductivity, which in the pristine material is 200-fold greater than in the solvated material.

Possible reasons and mechanisms for conductivity of the pristine MOF are explored, through the study of band structure, density of states and polaron formation.

Further computational investigations will be focused on the understanding of the experimentally observed chemiresistivity, which, rather than being correlated to the binding strength of the adsorbate, is proportional to the quantity of adsorbed species.



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Tuning the Electrical Conductivity of a Hexa-M(IV) Metal-Organic Frameworks,
where M = Zr, Hf, Ce and Th

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Engineering electrical conductivity into high-porosity metal-organic frameworks (MOFs) promises to unlock the full potential of MOFs for electrical energy storage, electrocatalysis, and integration with more conventional electronic materials. In recent work¹ we showed that the electrical conductivity of a porous zirconium-node-containing MOF, NU-901, can be tuned by physically incorporating into its pores fullerene (C₆₀) molecules, which can in principle act as electron acceptors interdigitated between the electron-rich 1,3,6,8-tetrakis(*p*-benzoate)pyrene linkers of the MOF. The bulk electrical conductivity of NU-901 increases by 11 orders of magnitude upon incorporation of the C₆₀ molecule into it.

As part of our study, we used density functional theory to examine variations in the electrical conductivity of doped MOFs like NU-901 as a function of several different variations in composition. In particular, we considered:

- 1) Introduction of C₆₀ into the triangular pore of NU-1000.
- 2) Replacement of Zr(IV) with Hf(IV), Ce(IV), and Th(IV).
- 3) Incorporation of 1,4-fullerene derivatives in place of C₆₀.

¹ Goswami et. al, *Chem. Sci.*, 2018, **9**, 4477-4482

Determination of hydrogen evolution mechanisms in cobalt dithiolene metal organic frameworks using Density Functional Theory

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Cobalt dithiolene metal organic frameworks (MOFs) were examined using plane wave density functional theory (DFT) in order to understand the mechanism of the hydrogen evolution reaction (HER) in these MOFs. The design of effective hydrogen evolving catalysts from earth abundant materials is an important factor for developing alternative energy sources. Cobalt dithiolene complexes have been shown to mediate hydrogen evolution under electrocatalytic conditions, and are among the most efficient molecular catalysts for HER. These complexes have high charge carrier mobility and high surface-to-volume ratio, making them attractive choices for HER. These systems are of interest due to their potential for developing integrated photoanode and photocathode material for a solar fuel cell.

Results show that the position of hydrogen atoms in a system when two or more are present on sulfur atoms does not have a large effect on the free energy of the system. When one hydrogen atom is present in the system, the lowest energy position is on a cobalt atom for both systems of interest. When two hydrogen atoms are present the lowest energy position is two H atoms coordinated in between two cobalt atoms. Slightly higher in energy than that is a system with one hydrogen on both a cobalt atom and a sulfur atom. This suggests that the mechanism proceeds by first a hydrogen coordination to a cobalt, and a second hydrogen then coordinating to a sulfur. This is followed by the movement of a hydrogen atom to the center cobalt so that both hydrogen atoms are coordinated in between cobalt centers. The H₂ molecule is then released and the process repeats.

Deep neural network learning of binary sorption equilibria from molecular simulation data

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We employed deep neural networks as an efficient and intelligent surrogate of molecular simulations for complex sorption processes on a probabilistic foundation loosely based on variational inference. Gibbs ensemble Monte Carlo simulations in the canonical (NVT) ensemble were performed to model a desorption process for alkanediol-solvent binary mixtures from all-silica zeolites, and a multi-task deep neural network was trained on the simulation data to predict desorption loading from simulation parameters. We demonstrate that the deep neural network accurately reproduces simulation results and is able to obtain a continuous isotherm function. The neural network prediction can be therefore utilized to greatly accelerate optimization of desorption conditions, which requires laborious parameter search if accomplished by simulation. Furthermore, a deep neural network learns information about the binary sorption equilibria as hidden layer representations. This allows for application of transfer learning by fine-tuning a pretrained neural network to achieve better generalization performance for a new system with less available data.

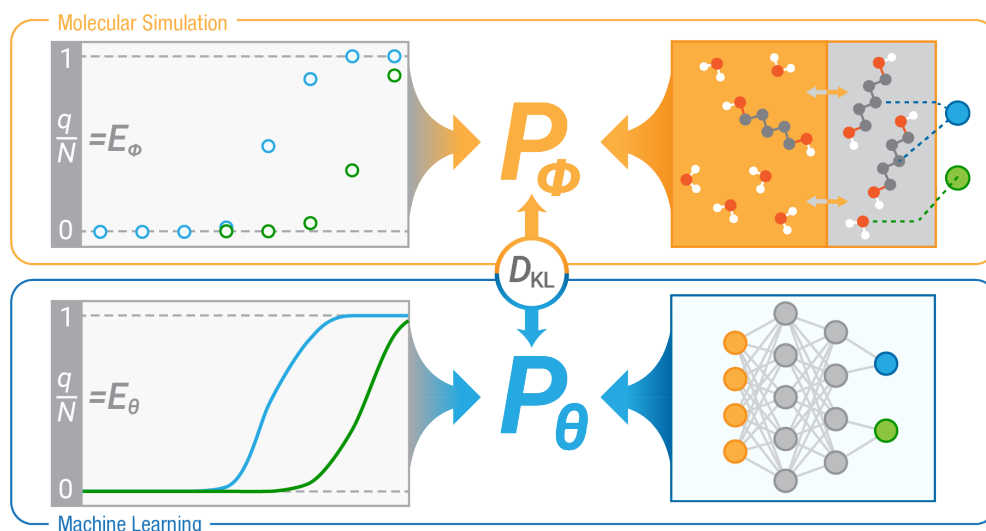


Figure: A machine learning model is trained on simulation data to approximate the underlying probability distribution for the simulation system and thus reproduces and interpolates simulation results.

Progress and Challenges in the Structural Characterization of Nanoporous Materials by Physical Adsorption

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Assessing adsorption properties of nanoporous materials and their structural characterization is crucial for advancing their application in catalysis, separations, and other industrial processes. In this lecture we will review the major progress made within the last two decades in the area of physical adsorption characterization [1], but will also discuss the existing challenges in the characterization of advanced porous materials exhibiting hierarchical pore-network structures [2].

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Redox depressed O₂ adsorption in Co-based MOFs

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Separation of O₂ from air is a key large-scale industrial process that is still carried out via cryogenic distillation.¹ Cobalt-based MOFs constitute promising materials for this purpose, as some are able to adsorb selectively O₂ over N₂ with high stability. In this computational work, the air-stable MOFs Co₂Cl₂(bbta) and Co₂(OH)₂(bbta) (H₂bbta = 1*H*,5*H*-benzo(1,2-*d*:4,5-*d'*)bistriazole)² have been investigated by a two-fold protocol combining Kohn-Sham density functional calculations on periodic and cluster models with calculations based on multireference wave function based methods. Both levels of theory revealed a high-spin configuration Co-centers, despite the strong coordination environment provided by the triazolate ligands and suggested an antiferromagnetic coupling among the Co-centers, in agreement with experimental magnetic measurements.

Our results show a lower affinity of O₂ towards Co₂Cl₂(bbta) than towards the Co₂(OH)₂(bbta) variant, in agreement with experiment, unravelling a complex mechanism of adsorption of O₂ by these MOFs.

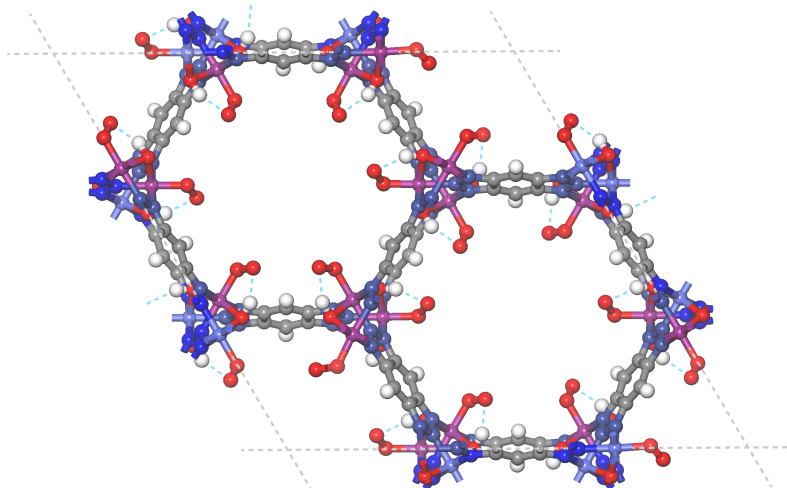


Figure: 1:1 coverage of O₂: Co in Co₂(OH)₂(bbta). Color code: Co (purple), C (grey), N (blue), O (red), H (white).

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Cerium-Based Metal-Organic Frameworks for Photocatalysis

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Separation of photo-excited charges (electrons and holes) can exert important control over the lifetimes of photoexcited states. We address this issue in metal-organic frameworks (MOFs), which are potential photocatalysts due to their tunability that provides greater photoredox possibilities and their porosity that facilitates the diffusion of reactants, with the potential to overcome the low charge mobility of many nonporous semiconductors. We studied UiO-66, which is built from $Zr_6O_4(OH)_4$ nodes and 1,4-benzene-dicarboxylate linkers, because it has superior tunability, such as complete or partial metal (Hf, Th, Ti, U, Ce) substitutions in the nodes and a variety of possible linker functionalizations. We found that ligand-to-metal charge transfer (LMCT) can lead to separation of photo-excited charges in the MOF, and that – with pure metals (Zr, Hf, Th, Ti, U, or Ce) in the nodes – LMCT is favorable only for Ce, where it is promoted by the low-lying empty $4f$ states of Ce^{4+} . We propose that incorporating Ce^{4+} into the nodes is an effective way to facilitate LMCT in a MOF. We also found that linker functionalization is possible to engineer the electronic structure of the Ce-MOF for a desired reaction (e.g., water splitting) while preserving favorable LMCT. We also considered partial metal (Zr and Ti) substitution in the Ce-MOF and found that it can promote the photocatalytic catalytic performance of the Ce-MOF. In the final analysis we propose four combinations of node constitutions (with mixed Ce-Zr or mixed Ti-Zr nodes) and linker substitutions (by I, OH, or Br) that are recommended for experimental consideration because our density functional calculations satisfy all of the following criteria: synthetically feasible, light absorption by the linker in the visible, HOCO–LUCO gap greater than 1.48 eV (1.23 eV required for water splitting plus 0.25 eV allowed for overpotential), valence band maximum below the absolute potential for the reduction step in water splitting, and conduction band minimum above the absolute potential for the oxidation step in water splitting. Some materials may also be candidates for the reduction of CO_2 .

Computational Study of Electrocatalytic Hydrogen Evolution from Water by a Mononuclear Molybdenum Sulfide-Functionalized Metal-Organic Framework

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A molybdenum sulfide functionalized NU-1000, the latter a Zr₆-based metal-organic framework, was synthesized via SIM (solvothermal deposition in MOFs) of molybdenum(VI) and subsequent exposure to H₂S. The catalyst, named **MoS_x-SIM**, is established to be mononuclear via single crystal X-ray diffraction measurement and exhibits low electrocatalytic behavior for evolution of molecular hydrogen from aqueous acid. Meanwhile, introduction of a redox mediator (RM), methyl viologen (MV²⁺), enhances the catalytic performance, presumably through facilitation of electron transfer from the reduced RM. Kinetic study reveals an unexpected square-root dependence of the overall reaction rate on the mediator concentration and a potential-dependent pH-effect.

To gain a microscopic understanding of the mechanism of hydrogen evolution from aqueous acid by this MOF-affixed mononuclear **MoS_x-SIM** catalyst, we performed density functional theory calculations on a cluster model (Figure 1). We substituted the linkers with formate and used the M06-L/6-31G(d)&SDD method in the Gaussian 09 software package. An electrocatalytic cycle of hydrogen evolution requires the addition of two protons, two electrons, and the release of H₂, with the proton and electron transfer steps potentially proceeding in any order. A metal-hydride intermediate is formed, followed by reacting with a proton from the system to form H₂. Considering multiple possible protonation sites, -Mo, -O, -OH, and -HS, several mechanisms were explored. Preliminary results suggest the favored pathway is protonation → reduction → protonation → reduction → H₂ release, and that the formation of H₂ on the metal is the rate limiting step. Our current model suggests that using MV²⁺ as the redox mediator, proton transfers and electron transfers are highly feasible. Investigations on the effect of linker, formate vs. benzoate, and functional are undergoing.

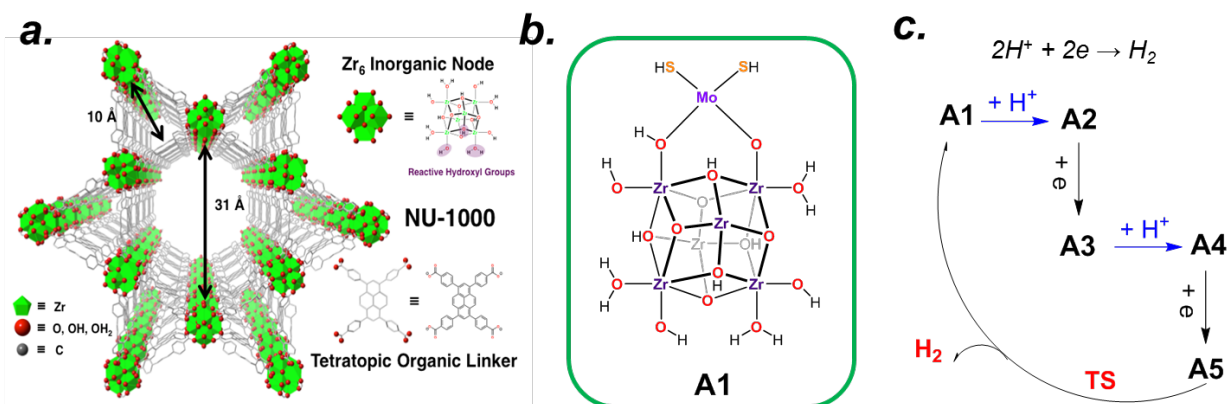


Figure 1. **a.** Non-functionalized metal-organic framework, NU-1000. **b.** Cluster model of MoS_x-SIM. **c.** Catalytic hydrogen evolution reaction scheme.

Using cheminformatics to automate the design of nanoporous materials for clean energy applications

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Nanoporous materials, including metal-organic frameworks (MOFs) and zeolites, are a class of crystalline materials with ultrahigh porosity and high internal surface areas which make them of great interest for clean energy applications, such as gas separations and gas storage. MOFs are nanoporous materials made of inorganic nodes connected by organic linkers. There are many different nodes, linkers, and functional groups which can be combined into a huge number of plausible MOF structures. The chemical space of all possible MOFs is far too large to thoroughly sample using brute force; therefore, we must turn to automated search methods to identify promising candidates tailored for a specific application. In this work, we trained a deep neural network on thousands of SMILES codes derived from unique MOFs, which are encoded into a continuous vector representation. The continuous vector allows us to generate new materials *via* perturbations to the vector, which can then be decoded back into a SMILES code that corresponds to a 3D MOF. We estimate the chemical properties of the MOF from the latent continuous vector representation of the codes and therefore guide the search for optimized MOFs. For this work, we have chosen CO₂ separation from CO₂/N₂ and CO₂/CH₄ mixtures as an example application for this design algorithm. Also, we have trained a Gaussian process model with the ethane/ethylene separation properties of tabulated 3D potential grids for known zeolites from the IZA database. The potential grid stores the interaction of the rigid framework with guest molecules in separate energy terms (repulsive and attractive Lennard-Jones and Coulomb) as data channels and contains information directly related to adsorption thermodynamics. We used the Gaussian process model to extract the information from these potential grids and to predict the ethane/ethylene separation performances for zeolites.

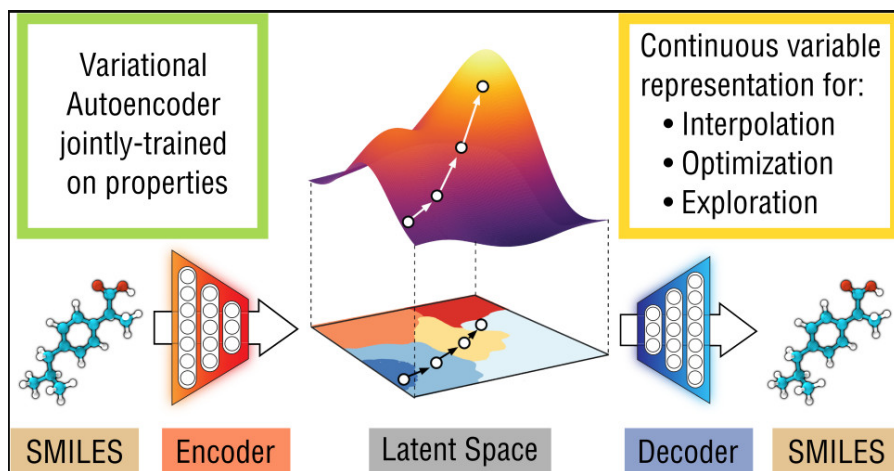


Figure: Diagram of workflow for design of MOFs using a variational autoencoder.
Image from Gómez-Bombarelli et al. ACS Cent. Sci. 2018, 4, 268-276

Post-Synthetic Modification of Electronic Structure in Metal–Organic Frameworks with Electrochemistry and Mechanical Pressure

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The electronic structure of metal–organic materials can be readily tuned through precise control of metal, ligand, and topology to access novel electronic and magnetic properties. However, many frameworks are limited to short-range electron communication due to a lack of charge carriers and the absence of strong orbital interactions. Several strategies have emerged for accessing more delocalized electronic structures in these materials, including metal mixed-valence, π - π stacking, and π - d conjugation with redox-active ligands. While chemical reduction and oxidation have been used to post-synthetically alter the electronic properties of these materials, comparatively few studies have investigated the possibility of electrochemistry or high pressure to access electronic structures challenging to achieve through chemical routes. Electrochemical reduction of an iron–semiquinoid framework has been used to access simultaneous metal- and ligand-redox chemistry not observed in a similar chromium phase. The experimental characterization of this reduced phase will be discussed, in addition to the potential of this system as a high capacity cathode material. Additionally, high pressure studies of a cobalt-semiquinoid framework revealed a valence-tautomeric transition above 10 GPa. Spectroscopic evidence for this transition will be discussed, as well as the effects of this electronic phase transition of conductivity.

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* Thrust A: Development of Methods to Accelerate Discovery of Functional Porous Materials

Thrust B: Discovery of Porous Materials for Challenging Chemical Separations

Thrust C: Discovery of Porous Materials for Challenging Chemical Transformations

Thrust D: Engineering of Nanoporous Materials with Tailored Electronic Structures

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