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14. ABSTRACT
The objective of this research was to identify new sorbents for removal of toxic compounds including ammonia, phosphine, arsine, and methyl bromide from air, particularly in the presence of humidity. Included in this goal was the systematic computational study of strong chemisorption of target molecules and functionalized surfaces, including nanoporous metal-organic framework (MOF) materials, as well as functional groups and metal catecholates that could be incorporated into MOFs to improve adsorption of the target molecules. Cu-MOF-74 (Cu-CPO-27) and ZIF-78 are predicted to be good sorbents for ammonia in the presence of humidity. We devised

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19a. NAME OF RESPONSIBLE PERSON
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Report Title

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ABSTRACT

The objective of this research was to identify new sorbents for removal of toxic compounds including ammonia, phosphine, arsine, and methyl bromide from air, particularly in the presence of humidity. Included in this goal was the systematic computational study of strong chemisorption of target molecules and functionalized surfaces, including nanoporous metal-organic framework (MOF) materials, as well as functional groups and metal catecholates that could be incorporated into MOFs to improve adsorption of the target molecules. Cu-MOF-74 (Cu-CPO-27) and ZIF-78 are predicted to be good sorbents for ammonia in the presence of humidity. We devised an efficient way to identify hydrophobic MOFs using Henry's constants and screened 137,953 hypothetical MOFs, finding 2777 hydrophobic structures which are selective for ammonia instead of water. Aromatic rings modified with a variety of functional groups were screened for interactions with ammonia, phosphine, and water. We predict that groups containing transition metals like copper and silver provide the strongest binding and best selectivity over water. A number of metal catecholates were tested for binding strength with ammonia, phosphine, arsine, and methyl bromide, and promising targets were identified.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
01/31/2017	8	Michael J. Katz, Ashlee J. Howarth, Peyman Z. Moghadam, Jared B. DeCoste, Randall Q. Snurr, Joseph T. Hupp, Omar K. Farha. High volumetric uptake of ammonia using Cu-MOF-74/Cu-CPO-27, Dalton Trans., ( ): 4150. doi:
01/31/2017	9	Peyman Z. Moghadam, David Fairen-Jimenez, Randall Q. Snurr. Efficient identification of hydrophobic MOFs: application in the capture of toxic industrial chemicals, J. Mater. Chem. A, ( ): 529. doi:
TOTAL:		2

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper
TOTAL:	

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper

TOTAL:

Number of Manuscripts:

Books

Received	Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Randall Q. Snurr: Ernest W. Thiele Award from the Chicago Local Section of AIChE, 2015
Randall Q. Snurr: Highly Cited Researcher, Thomson Reuters, 2016

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Peyman Moghadam	0.50
N. Scott Bobbitt	0.50
FTE Equivalent:	**1.00**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Randall Q. Snurr	0.01	
FTE Equivalent:	**0.01**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Paul McCullough	0.00	Chemical Engineering
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):......	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:......	0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment.

Technology Transfer

Joint publication with Jared B. DeCoste at Edgewood Chemical Biological Center.

Interactions with Gregory Peterson at Edgewood Chemical Biological Center.

Computational Analysis and Screening of Materials for Capture of Toxic Compounds (Topic 8.5)

W911NF1210130

Randall Snurr, Northwestern University

FINAL REPORT

Apr 1, 2012 to Sep 30, 2016

Abstract

The objective of this research was to identify new sorbents for removal of toxic compounds including ammonia, phosphine, arsine, and methyl bromide from air, particularly in the presence of humidity. Included in this goal was the systematic computational study of strong chemisorption of target molecules and functionalized surfaces, including nanoporous metal-organic framework (MOF) materials, as well as functional groups and metal catecholates that could be incorporated into MOFs to improve adsorption of the target molecules. Cu-MOF-74 (Cu-CPO-27) and ZIF-78 are predicted to be good sorbents for ammonia in the presence of humidity. We devised an efficient way to identify hydrophobic MOFs using Henry's constants and screened 137,953 hypothetical MOFs, finding 2777 hydrophobic structures which are selective for ammonia instead of water. Aromatic rings modified with a variety of functional groups were screened for interactions with ammonia, phosphine, and water. We predict that groups containing transition metals like copper and silver provide the strongest binding and best selectivity over water. A number of metal catecholates were tested for binding strength with ammonia, phosphine, arsine, and methyl bromide, and promising targets were identified.

Scientific Progress and Accomplishments

1. NH_3 adsorption in CPO-27(M)

M.J. Katz, A.J. Howarth, P.Z. Moghadam, J.B. DeCoste, R.Q. Snurr, J.T. Hupp, O.K. Farha, "High volumetric uptake of ammonia using Cu-MOF-74/Cu-CPO-27," *Dalton Trans.* **45**, 4150-4153 (2016).

In this part of the project, we calculated the binding energies of ammonia and water with CPO-27(M) analogues containing different metals; M= Cu, Ni, Mg, Zn, and Co. This MOF is also known as MOF-74 or M-DOBDC. The geometry optimizations and energy calculations were performed using density functional theory (DFT). Figure 1 compares the ammonia binding energies for different metals in CPO-27. It can be seen that ammonia interacts with CPO-27(Cu) with a binding energy of -76 kJ/mol, which is lower in magnitude than the binding energies calculated for the other metals. Interestingly, in our previous quantum mechanical study on CO_2 adsorption [2], it was also found that CPO-27(Cu) binds with CO_2 weakly compared to the other metals studied in either periodic or cluster models.

The low ammonia binding with CPO-27(Cu) is in agreement with breakthrough experiments where CPO-27(Cu) adsorbs ammonia poorly in dry conditions. The breakthrough measurements were performed by Jared DeCoste at Edgewood Chemical Biological Center (ECBC) on materials synthesized by the group of Joseph Hupp and Omar Farha at Northwestern University. The breakthrough experiments also show that CPO-27(Cu) outperforms other CPO-27 structures in humid conditions, with ammonia uptake of 7.6 mmol/g. Under dry conditions CPO-27(Cu) exhibited a respectable performance (2.6 *vs.* 2.9 NH_3 per nm^3 for the previous record holder HKUST-1), and under 80% relative humidity, the MOF outperformed HKUST-1 (5.9 *vs.* 3.9 NH_3 per nm^3, respectively).

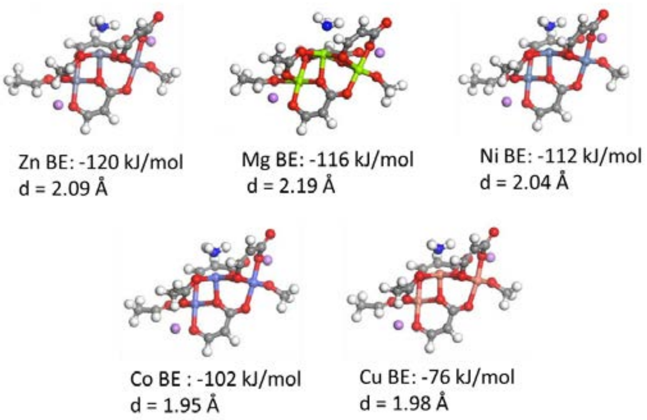


Figure 1: The most stable position of an ammonia molecule binding with different metals in CPO-27. The numbers below each configuration represent the ammonia binding energy (BE) and the center-to-center distance between ammonia nitrogen and the metal.

In an attempt to calculate the binding affinity of ammonia in the presence of water, we initially pre-adsorbed a single water molecule with CPO-27(Cu) and CPO-27(Zn). Water binds with CPO-27(Zn) (BE = −91 kJ/mol) stronger than CPO-27(Cu) (BE = −48 kJ/mol), and the water oxygen-metal distance is shorter for CPO-27(Zn) by ~0.2 Å.

We then used the optimized structures and calculated the ammonia binding energy in the presence of water (Figure 2). It can be seen that the largest decrease in ammonia binding energy occurs in CPO-27(Zn), where the binding energy decreases from −120 kJ/mol in dry conditions to −45 kJ/mol in the presence of water. Interestingly, in the presence of water, the ammonia binding energy in CPO-27(Cu) (−64 kJ/mol) is stronger than CPO-27(Zn). As illustrated in the final configurations, this is because with Cu, the ammonia is energetically favored and replaces water to interact directly with the metal. In the case of Zn, ammonia only hydrogen bonds with the pre-adsorbed water and does not interact with the metal. These results support the experimental observation that in humid conditions Cu has the highest ammonia uptake while all other CPO-27 analogues show lower ammonia adsorption compared to dry conditions. It should be noted, however, that FTIR and XRD experiments indicate degradation of CPO-27(Cu) especially in humid conditions.

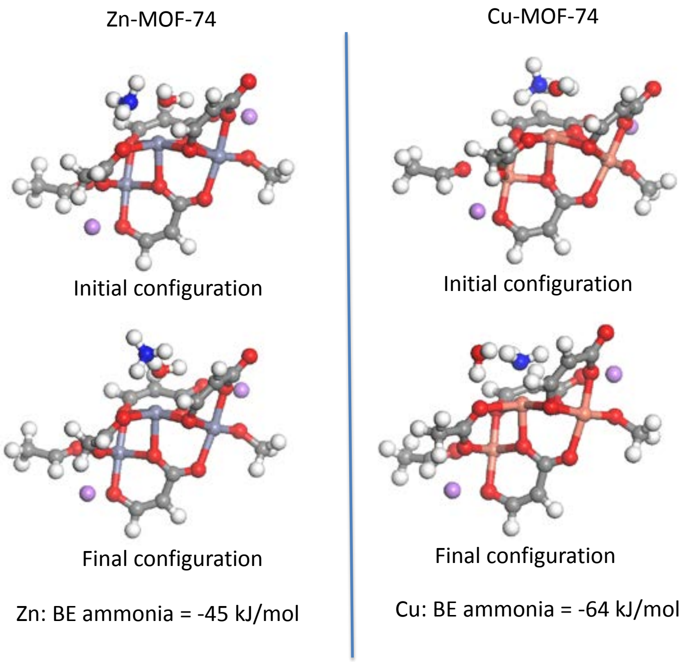


Figure 2: The initial and the final most stable position of an ammonia molecule binding with CPO-27-Zn (left) and CPO-27-Cu (right) in the presence of a single water molecule. The numbers below each configuration represent the ammonia binding energy with the corresponding cluster.

2. Ammonia adsorption in ZIFs with GME topology

We examined a number of water-stable ZIFs with the GME topology and a wide range of functionalities for ammonia capture. The structure of the ZIFs considered in this work consists of tetrahedrally coordinated Zn atoms connected to imidazolate or functionalized imidazolate linkers (ZnN_4). There are two types of interconnected 1-D channels in GME ZIFs. The large channels contain so-called KNO cages and the small channels consist of so-called GME cages.

To investigate how the studied ZIFs perform for ammonia adsorption, we carried out grand canonical Monte Carlo (GCMC) simulations of adsorption for ammonia at 298 K. In Figure 3, we show the amount of ammonia adsorbed for the low pressure range up to 1 bar and high pressures up to 8 bar. For pressures up to 0.1 bar, ZIF-78 exhibits the highest uptake (~ 5 mol/kg) due to the presence of polar $–NO_2$ groups that interact strongly with ammonia. This means that functionalizing the linkers in GME ZIFs can greatly enhance ammonia-framework interaction strength especially in the low pressure regime as shown for ZIF-78. The calculated capacity of ZIF-78 is near the target value of 6 mol/kg for ammonia uptake. Our results show that at 1 bar, ammonia is preferentially adsorbed in a mixture simulation with water even at 80% RH. Even when mixture simulations were repeated with pre-adsorbed amounts of water in the pores, ammonia is predicted to quickly replace water molecules.

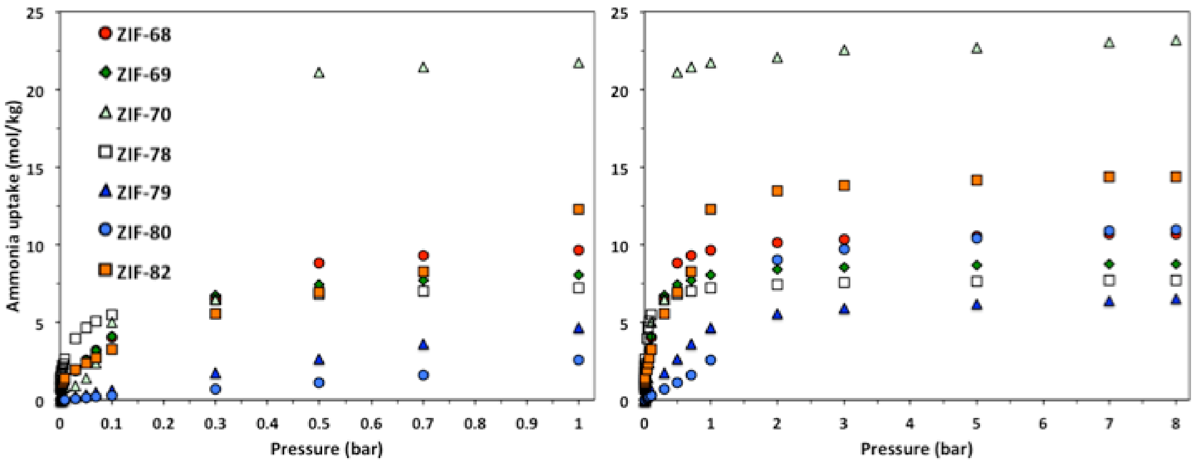


Figure 3: Simulated ammonia adsorption isotherms in ZIFs with GME topology at 300 K for low pressure (left) and high pressure (right).

3. Identification of hydrophobic MOFs for capture of toxic industrial chemicals

P. Z. Moghadam, D. J. Fairen-Jimenez, R. Q. Snurr, "Efficient Identification of Hydrophobic MOFs: Application in the Capture of Toxic Industrial Chemicals," *J. Mater. Chem. A* 4, 529-536 (2016).

Water is an ever-present component in the air, and competitive adsorption of water is a major challenge in many applications of adsorbents, including capture of toxic industrial chemicals (TICs) from the atmosphere. For metal–organic framework (MOF) adsorbents, the presence of water often leads to major material instabilities that could limit their practical performance. MOFs displaying hydrophobic behavior might be useful in overcoming these problems. In this work, we devised a new computational strategy to quickly identify hydrophobic MOFs based on their water Henry's constants. Starting with a database of 137 953 hypothetical MOFs, we identified 45 975 structures as hydrophobic based on their simulated water Henry's constants. Henry's constants were calculated using the Widom insertion method, which is orders of magnitude faster than deriving them from an adsorption isotherm using GCMC calculations.

Using GCMC simulations, we further analyzed 2777 of these hydrophobic materials whose linkers did not contain chemical functionalization. The results show insignificant water uptake in the identified MOFs, confirming their hydrophobic nature. The capability of the hydrophobic MOFs was assessed for ammonia capture under humid conditions, and analysis of the data generated from this high-throughput computational screening revealed the role of the textural properties and surface chemistry on the removal of toxic compounds. Figure 4 shows the selectivity for ammonia over water as a function of pore diameter and pore volume. MOFs with pore sizes near the kinetic diameter of ammonia (3.6 Å) show the greatest selectivity, although MOFs with pore diameters up to around 8 Å and 1.0 cm^3/g pore volume are capable of attaining a selectivity of about 10.

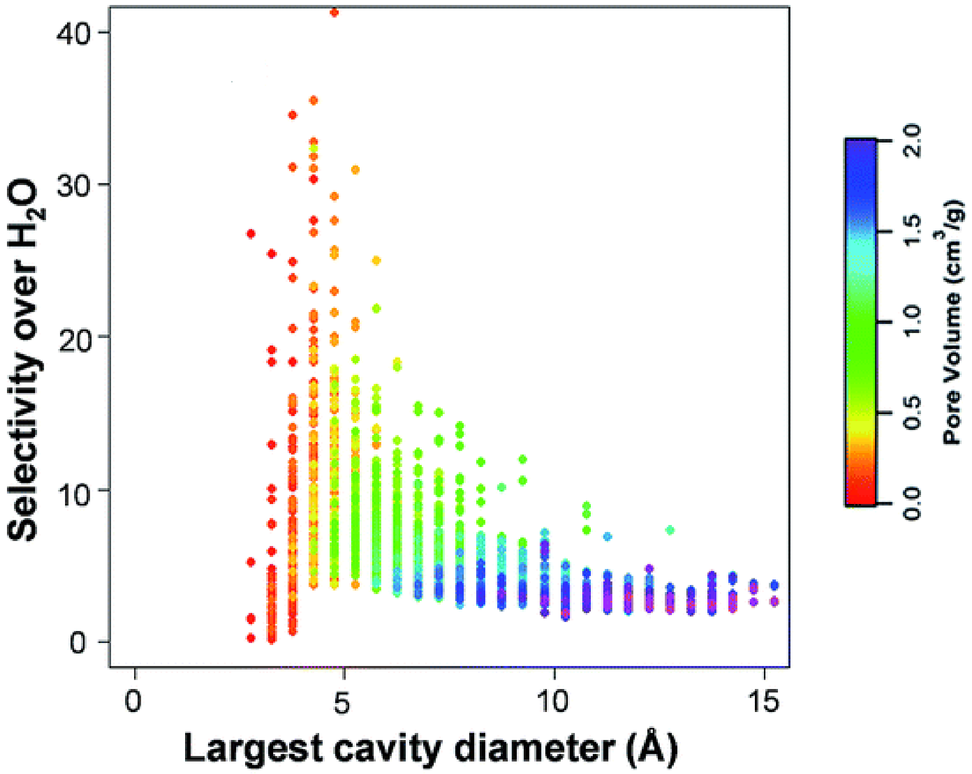


Figure 4 - Calculated ammonia selectivity over water as a function of largest cavity diameter for non-functionalized hydrophobic MOFs at 298 K. The color indicates the specific pore volume.

4. Effects of pre-adsorbed perfluoroalkanes on ammonia and water adsorption in MOFs

P. Z. Moghadam, P. Ghosh, R. Q. Snurr, "Understanding the effects of pre-adsorbed perfluoroalkanes on the adsorption of water and ammonia in MOFs," *J. Phys. Chem. C, 119*, 3163–3170 (2015).

Since hydrophobicity has been shown to improve the selectivity for ammonia over water, we considered modifying MOFs to increase their hydrophobic nature. Building on published work of Jared DeCoste and Greg Peterson at ECBC, we performed GCMC simulations to determine if preadsorbed perfluoroalkanes enhance ammonia adsorption, suppress water uptake, and reduce clustering of water molecules. Ammonia adsorption results under dry and humid conditions were compared with experiments where available. To assess the generality of the results, the Henry's constants of ammonia and water were calculated in 50 hypothetical MOFs with different loadings of preadsorbed perfluorohexane (PFH).

Molecular simulations indicate that the presence of preadsorbed perfluoroalkanes has little effect on ammonia and water uptake in the MOF Cu−BTC in the Henry's region. However, due to the bulky nature of perfluoroalkanes, they reduce the accessible pore volume leading to lower saturation capacity for both compounds, as shown in Figure 5. The distribution of hydrogen bonds revealed less water clustering when perfluoroalkanes were present in the pores. However, no significant shift in the water condensation step, and hence no enhanced hydrophobicity within the Cu−BTC cavities, was observed. Furthermore, the potential energy calculations showed that water and ammonia molecules interact more strongly with the hydrated copper sites and with each other than with PFH molecules.

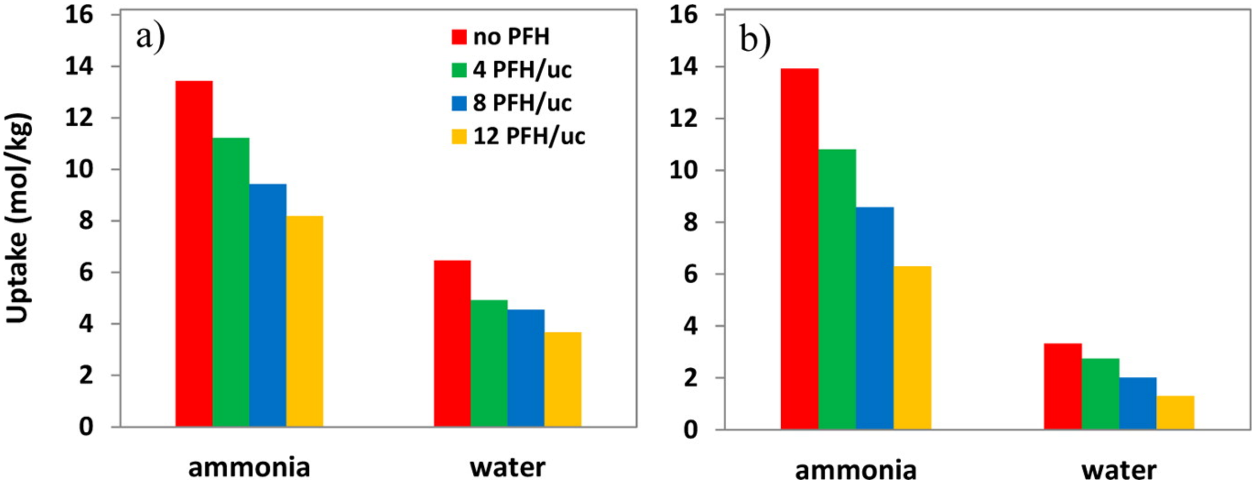


Figure 5 - Mixture simulations of ammonia and water in Cu-BTC (HKUST-1) at 1 bar of ammonia pressure and 298 K with and without preadsorbed PFH at (a) 80% RH and (b) 40% RH.

5. Screening of functional groups for ammonia capture in MOFs

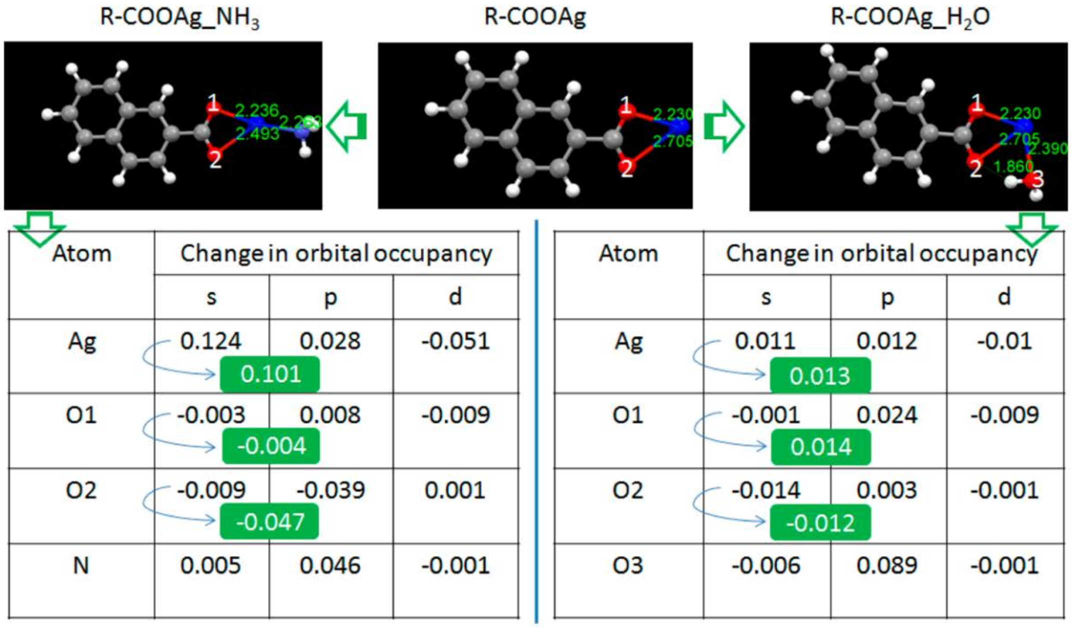
K.C. Kim, D. Yu, R.Q. Snurr, "Computational screening of functional groups for ammonia capture in metal-organic frameworks," *Langmuir* 29, 1446-1456 (2013).

Metal−organic frameworks (MOFs) containing functional groups that strongly bind ammonia could be promising candidates for ammonia capture from air. To identify functional groups that preferentially bind ammonia versus water, we used quantum chemical methods to calculate the binding energies of ammonia and water with 21 different functional groups attached to aromatic rings, such as are common in MOF linkers. Functionalized naphthalene was used as a surrogate for the MOF linkers, and the binding energies were calculated by optimizing an ammonia molecule interacting with the functional group from several different initial positions and taking the lowest energy configuration. Binding energies for water were also calculated for comparison.

Our examination reveals that 10 functional groups have stronger binding with ammonia than water. Among them, R−COOCu and R− COOAg are the top two promising candidates for ammonia capture under humid conditions. Under dry conditions, R− COOCu binds ammonia most strongly among the 21 functional groups examined.

The adsorption of ammonia or water on R−COOCu and R−COOAg gives rise to an asymmetric positioning of the copper and silver atoms. NBO and charge analyses reveal that the orbitals and charge distributions between two oxygen atoms of the R−COOCu and R−COOAg are asymmetrically changed after the adsorption of ammonia or water, with the electron-deficient copper and silver atoms moving toward the electron-rich oxygen atom, as shown in Figure 6.

We also examined the effects of solvents with a wide range of dielectric constants on ammonia protonation while interacting with the Bronsted acid functional groups. We found that increasing acidity and dielectric constant promote protonation of ammonia.



Atom	Change in orbital occupancy		
	s	p	d
Ag	0.124 0.101	0.028	-0.051
O1	-0.003 -0.004	0.008	-0.009
O2	-0.009 -0.047	-0.039	0.001
N	0.005	0.046	-0.001

Atom	Change in orbital occupancy		
	s	p	d
Ag	0.011 0.013	0.012	-0.01
O1	-0.001 0.014	0.024	-0.009
O2	-0.014 -0.012	0.003	-0.001
O3	-0.006	0.089	-0.001

Figure 6 - Change in orbital occupancy for R-COOAg when ammonia and water bind. Values in white represent the change in the s, p, and d orbitals and the values in green are the total change. Note the asymmetric change in the oxygen orbitals.

6. Phosphine adsorption on functional groups

N. S. Bobbitt, R.Q. Snurr, "*Ab initio* screening of metal catecholates for adsorption of toxic pnictogen hydride gases," *in preparation.*

We have calculated binding energies for phosphine with several common functional groups that might be incorporated into a MOF, including R-F, R-OH, and R-COOH. The functional groups were represented as a functionalized benzene ring, and binding energies were calculated with DFT by optimizing the geometry for a phosphine molecule interacting with the functionalized ring, using several start positions and taking the minimum. We find that phosphine does not bind strongly to groups that do not contain transition metals. R-COOAu, R-COOAg, and R-COOCu all exhibit strong binding energies of -192, -145, and -106 kJ/mol, while the next closest is R-COOLi at -37 kJ/mol. The binding energy results for this screening are summarized in Table 1.

Functional Group	BE (kJ/mol)
R-COOAu	-192
R-COOCu	-145
R-COOAg	-106
R-COOLi	-37
R-COOTl	-33
R-OH	-33
R-COONa	-31
R-COORb	-29
R-SO3H	-25
R-OOH	-24
R-COOH	-21
R-SO2H	-19
R-CONH2	-19
R-OPH2	-17
R-NH2	-16
R-Cl	-14
R-F	-11
R	-10

Table 1. Binding energy for phosphine and various groups functionalized on benzene.

7. Screening of metal catecholates for ammonia capture in MOFs

K.C. Kim, P.Z. Moghadam, D. Fairen-Jimenez, R.Q. Snurr, "Computational screening of metal catecholates for ammonia capture in metal-organic frameworks," *Ind. Eng. Chem. Res.* 54, 3257-3267 (2015).

Catecholates are an interesting choice of functional group because they contain highly exposed metal atoms that can readily bind target molecules. Also, the most promising catecholates could potentially be incorporated into MOF linkers or attached to MOF nodes via solvent-assisted ligand incorporation (SALI). We screened a series of metal catecholate candidates using quantum chemical methods to identify the most promising metals for ammonia capture in the presence of water. Binding energies and free energies of binding were calculated first for ammonia and water separately with a series of metal catecholates.

Although selectively capturing ammonia is challenging due to competitive binding of ammonia and water, this thermodynamic study shows that 16 of the 18 proposed metals have a preferential binding toward ammonia vs water. In particular, Pt-, Cu-, and Be-catecholates are promising candidates to capture ammonia in humid conditions (although Be may not be practical). Our study also revealed that there is no reaction between ammonia and water when coadsorbed on the metal catecholates under a wide range of dielectric constants and thus the ionic complex, NH4 + OH−, is not formed.

We also performed an analysis of simultaneous binding of ammonia and water for Cu- and Zn-catecholates. The optimized geometries for co-adsorption are shown in Figure 7. In both cases, the competitive adsorption with water significantly weakens the ammonia-metal binding.

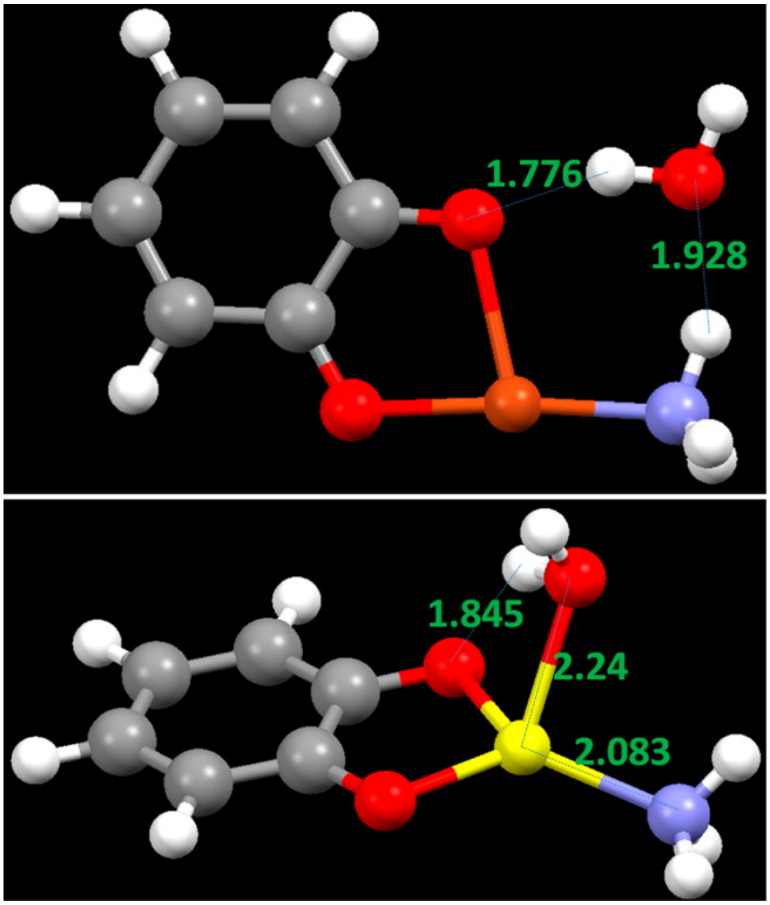


Figure 7- Most stable positions of ammonia binding to (top) Cu- and (bottom) Zn-catecholates in the presence of a water molecule. Gray, white, red, blue, brown, and yellow atoms are C, H, O, N, Cu, and Zn, respectively. Values in dark green represent the binding distances in Å.

8. Toxic hydride gas adsorption on metal catecholates

N. S. Bobbitt, R.Q. Snurr, "*Ab initio* screening of metal catecholates for adsorption of toxic pnictogen hydride gases," *in preparation.*

Inspired by results from the previous study of ammonia on metal catecholates, we expanded on that work and studied the adsorption of the related molecules ammonia, phosphine, and arsine on a larger number of metal catecholates, including the alkaline earth metals and almost all transition metals. This large-scale screening has allowed us to uncover some interesting periodic trends in the binding behavior of the metals.

To evaluate the various catecholates for toxic gas adsorption, we performed DFT calculations to find binding energies of phosphine interacting with the catecholate. In order to account for all possible adsorption sites, we performed optimizations using five different initial configurations of the adsorbate molecule and catecholate. In many cases, different initial positions still resulted in the same final optimized position. The lowest energy position was then used for the binding energy calculation, along with the energy of isolated target molecule and catecholate. Figure 8 shows the binding energies for ammonia, phosphine, and arsine on metal catecholates. Os, Ir, Pt, Mg, and Be exhibit particularly strong binding for ammonia, while Os, Ir, Pt, and Au have the strongest interactions with phosphine and arsine.

We find that phosphine and arsine have very similar behavior, which is markedly different from ammonia. Figure 9 plots the binding energy of all three gases against the binding energies for phosphine. Clearly, there is a strong correlation between the arsine and phosphine binding energy, while the ammonia data is more scattered. Phosphine and arsine binding is primarily driven by electron donation to the metal, forming a partial covalent bond between the metal and P or As atoms. Ammonia also donates some electron density; however, it is less than phosphine, and the ammonia binding process contains a substantial electrostatic component due to the large negative charge residing on the highly electronegative N atom. P and As are close to neutral and do not have this Coulomb contribution to binding. Therefore, alkaline earth metals and metals on the left side of the periodic table, which have high positive partial charges in the catecholate, exhibit strong Coulomb attraction with ammonia and not phosphine or arsine.

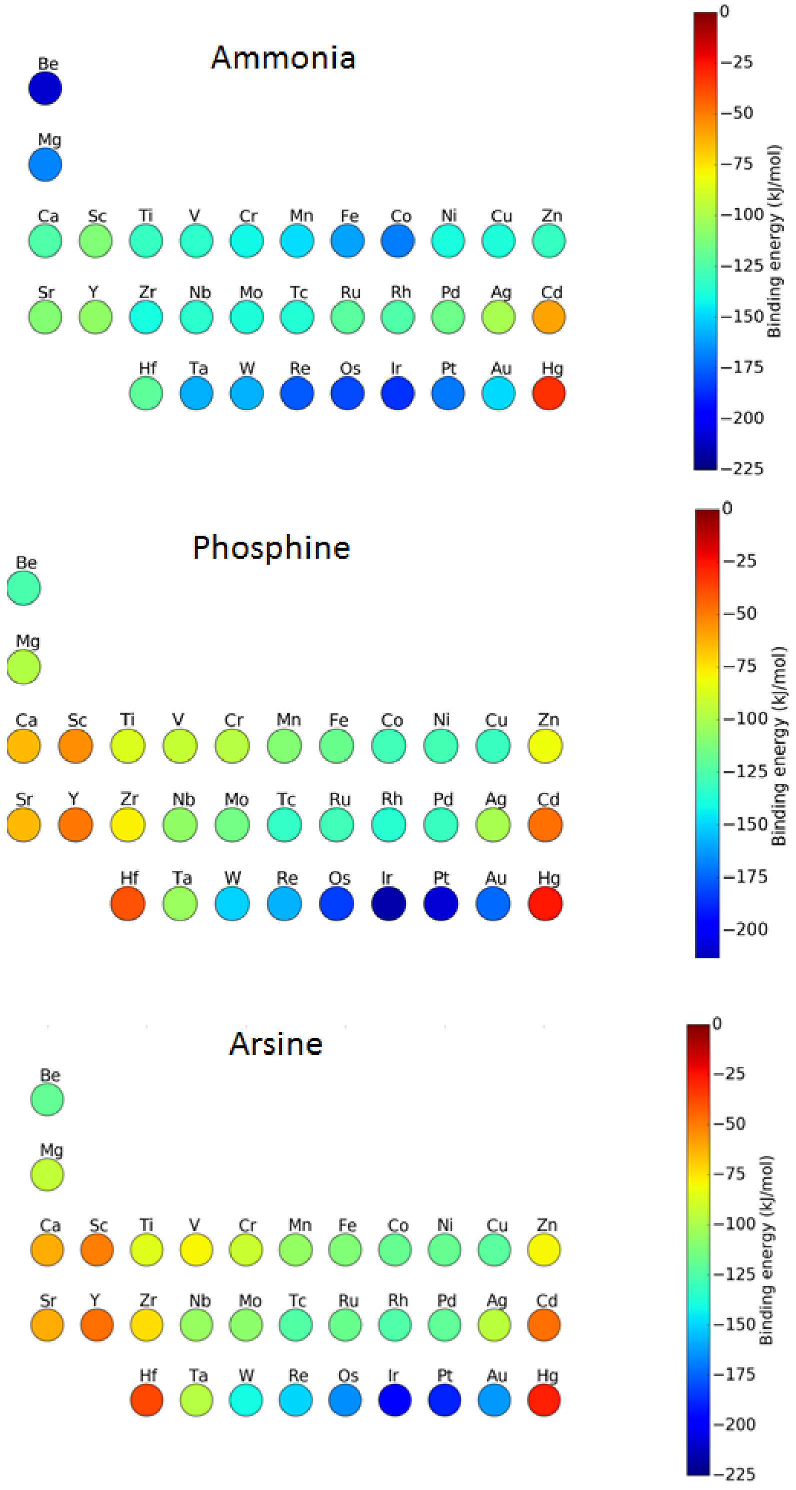


Figure 8: Binding energies for ammonia, phosphine, and arsine on metal catecholates.

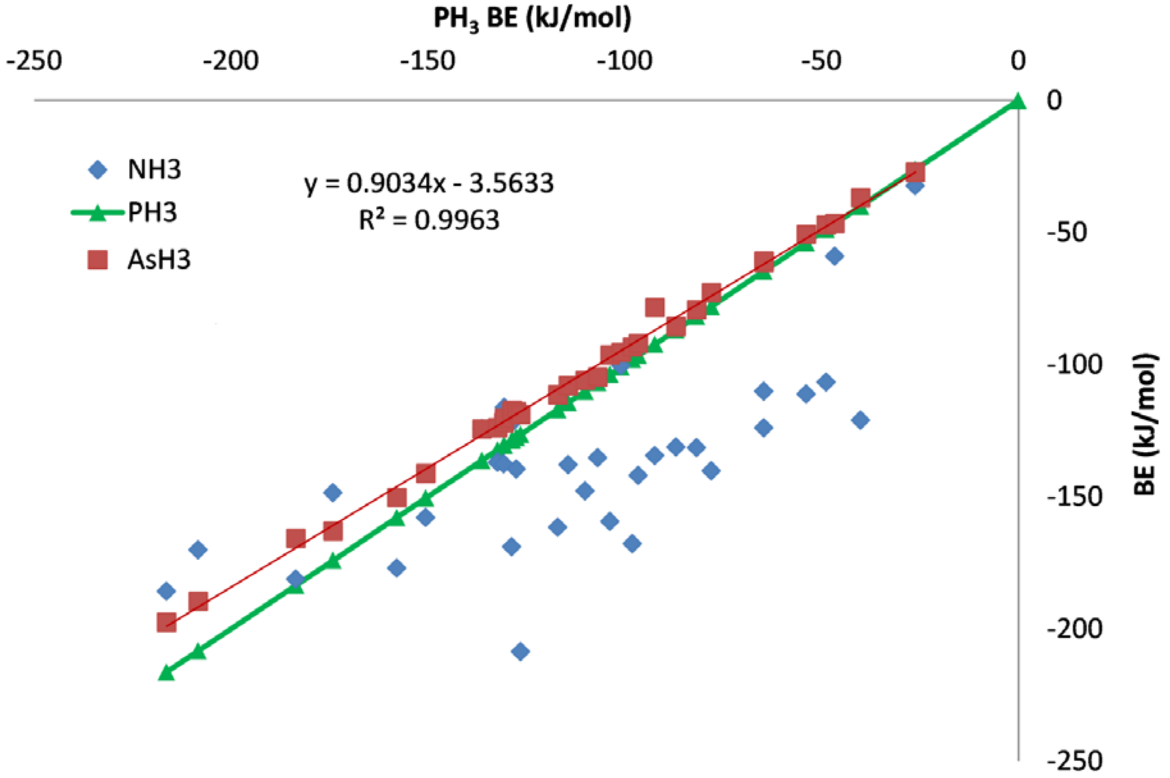


Figure 9 - Parity plot of binding energies for ammonia and arsine vs binding energy of phosphine on metal catecholates. The green line is phosphine vs phosphine, i.e., a slope of unity.

9. Methyl bromide adsorption on metal catecholates

N. S. Bobbitt, R. Q. Snurr, “Methyl bromide binding on metal catecholates,” *in preparation.*

We also calculated binding energies for methyl bromide (MeBr) on metal catecholates using a similar process as previously described for ammonia. We found that the row 6 metals Os, Ir, Pt, and Au exhibit very strong binding for MeBr. In order to assess the selectivity of the metals for our target MeBr over water, we also calculated binding energies for water. Figure 10 shows the differences in these binding energies, with lower values (blue) indicating that the metal is more selective for MeBr. Ir, Pt, and Au are the most selective for MeBr and are the most promising candidates for MeBr adsorption under humidity.

We also observed an interesting phenomenon for MeBr binding to Y, Sc, and Ta catecholates, in which the methyl group and Br atom dissociate and bind separately to the metal, as shown in Figure 11. This results in a very large stabilization of about 280 kJ/mol for Y and Sc and 140 kJ/mol for Ta. This unexpected reactivity could potentially be exploited for irreversible capture of methyl bromide.

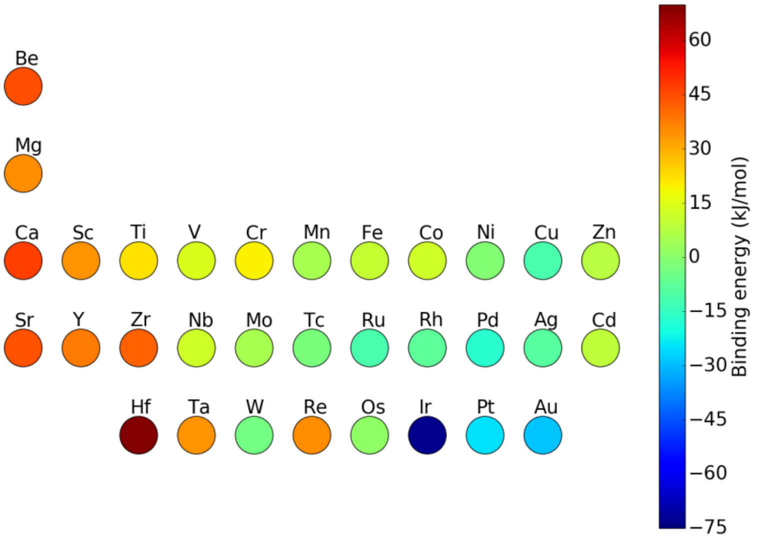


Figure 10 - Difference between binding energies of MeBr and water on metal catecholates. A more negative (blue) value in this figure indicates selectivity for MeBr over water, while red indicates the metal is selective for water.

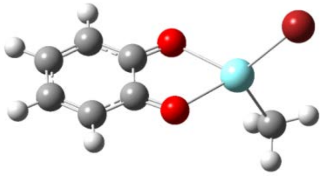


Figure 11 – Predicted MeBr binding to Y catecholate. The Me group and Br atom dissociate and bind separately to the Y atom. The grey atoms are C, the light blue is Y, the bright red are O, and the darker red is Br.

Final Conclusions

Among MOFs, Cu-MOF-74/Cu-CPO-27 has one of the highest densities of Cu(II) sites per unit volume. Under humid conditions, Cu-MOF-74/Cu-CPO-27 demonstrates the highest volumetric ammonia uptake of any MOF reported to date.

ZIF-78 is predicted to show high ammonia uptake capacity and selective adsorption of ammonia under humid conditions.

We developed a new computational strategy based on Henry's constants to quickly identify hydrophobic MOFs and applied it to identify 45 975 hydrophobic materials from a pool of 137 953 hypothetical MOFs. The simulations results show that, on the one hand, strongly hydrophilic MOFs present high competitive water adsorption and therefore exhibit poor selectivity towards TICs. On the other hand, MOFs that are too hydrophobic present low affinity for the TICs and therefore exhibit low selectivity as well. However, MOFs with moderate hydrophobicity and pore sizes comparable to the TIC’s kinetic diameter deliver the highest selectivities over water.

We analyzed the effects of preadsorbed perfluoroalkanes on the hydrophobic nature and ammonia uptake of MOFs. However, despite the expected hydrophobicity of perfluoroalkanes, their presence was not found to induce a more hydrophobic behavior in Cu−BTC, and the water condensation step was not significantly shifted. Ammonia uptake in Cu−BTC was not enhanced by perfluoroalkanes under dry or humid conditions.

DFT calculations indicate that ammonia and phosphine interact strongly with functional groups that contain transition metals, notably Ag and Cu. Interactions with functional groups that do not contain metal are fairly weak. Also, for Bronsted acid functional groups, increasing acidity and dielectric constant can promote protonation of ammonia.

We examined periodic trends in ammonia, phosphine, and arsine adsorption, as well as differences in the behaviors of these three gases. Ammonia exhibits notably different behavior from phosphine and arsine due to a strong Coulomb interaction between the charged N atom and the metal, while phosphine and arsine binding is primarily driven by electron donation. Therefore metals with higher electronegativity tend to bind phosphine and arsine stronger, while metals toward the left side of the periodic table bind ammonia stronger than phosphine and arsine. The Row 6 metals Ir, Pt, and Au show strong binding for all three gases.

We also calculated binding energies for methyl bromide with metal catecholates and found that Ir, Pt, and Au offer the best selectivity over water, while the alkaline earth metals actually select for water over methyl bromide. An intriguing dissociative adsorption is also predicted in a few cases.

Published papers

1. K.C. Kim, D. Yu, R.Q. Snurr, "Computational screening of functional groups for ammonia capture in metal-organic frameworks," *Langmuir* 29, 1446-1456 (2013). (**DOI:** 10.1021/la3045237)
2. D. Yu, A.O. Yazaydin, J.R. Lane, P.D.C. Dietzel, R.Q. Snurr, "A combined experimental and quantum chemical study of CO_2 adsorption in the metal-organic framework CPO-27 with different metals," *Chem. Sci.* 4, 3544-3556 (2013). (**DOI**: 10.1039/C3SC51319J)
3. P. Z. Moghadam, P. Ghosh, R. Q. Snurr, "Understanding the effects of pre-adsorbed perfluoroalkanes on the adsorption of water and ammonia in MOFs," *J. Phys. Chem. C*, *119*, 3163–3170 (2015). (**DOI:** 10.1021/jp511835d)
4. K.C. Kim, P.Z. Moghadam, D. Fairen-Jimenez, R.Q. Snurr, "Computational screening of metal catecholates for ammonia capture in metal-organic frameworks," *Ind. Eng. Chem. Res.* 54, 3257-3267 (2015). (**DOI:** 10.1021/ie504945w)
5. J.M. Holcroft, K.J. Hartlieb, P.Z. Moghadam, J.G. Bell, G. Barin, D.P. Ferris, E.D. Bloch, M.M. Algaradah, M.S. Nassar, Y.Y. Botros, K.M. Thomas, J.R. Long, R.Q. Snurr, J.F. Stoddart, "Carbohydrate-mediated purification of petrochemicals," *J. Am. Chem. Soc.* 137, 5706-5719 (2015). (**DOI:** 10.1021/ja511878b)
6. Y.P. Zeng, P.Z. Moghadam, R.Q. Snurr, "Pore size dependence of adsorption and separation of thiophene/benzene mixtures in zeolites," *J. Phys. Chem. C*, 119, 15263-15273 (2015). (**DOI:** 10.1021/acs.jpcc.5b03156)
7. P. R. McGonigal, P. Deria, I. Hod, P. Z. Moghadam, A. Avestro, N. E. Horwitz, I. C. Gibbs-Hall, A. K. Blackburn, D. Chen, Y. Y. Botros, M. R. Wasielewski, R. Q. Snurr, J. T. Hupp,

O. K. Farha, and J. F. Stoddart, “Electrochemically addressable trisradical rotaxanes organized within a metal–organic framework”, *Proc. Natl. Acad. Sci.*, 112, 11161-11168 (2015). (**DOI**: 10.1073/pnas.1514485112)

8. M.J. Katz, A.J. Howarth, P.Z. Moghadam, J.B. DeCoste, R.Q. Snurr, J.T. Hupp, O.K. Farha, “High volumetric uptake of ammonia using Cu-MOF-74/Cu-CPO-27,” *Dalton Trans.* **45**, 4150-4153 (2016). (**DOI**: 10.1039/C5DT03436A)
9. P. Z. Moghadam, D. J. Fairen-Jimenez, R. Q. Snurr, “Efficient Identification of Hydrophobic MOFs: Application in the Capture of Toxic Industrial Chemicals,” *J. Mater. Chem. A* 4, 529-536 (2016). (**DOI**: 10.1039/C5TA06472D)

Papers in preparation

1. N. S. Bobbitt, R.Q. Snurr, “*Ab initio* screening of metal catecholates for adsorption of toxic pnictogen hydride gases,” *in preparation.*
2. N. S. Bobbitt, R. Q. Snurr, “Methyl bromide binding on metal catecholates,” *in preparation.*

Recent Presentations

- **Pacifichem Conference, Honolulu, HI, USA** December 2015. Oral presentation, “Screening of functionalized or hydrophobic MOFs for capture of ammonia and other toxic compounds,” P. Z. Moghadam, K. C. Kim, Y. Zeng, P. Ghosh, D. Fairen-Jimenez, R. Q. Snurr.
- **Catalysis Club of Chicago Spring Symposium, Naperville, IL, USA** May 14, 2015. Poster presentation, “Efficient Identification of Hydrophobic MOFs,” P.Z. Moghadam, D. Fairen-Jimenez and R. Q. Snurr.
- **American Chemical Society Spring Meeting, Denver, CO, USA** March 2015. Oral presentation, “Screening of Functionalized or Hydrophobic MOFs for Capture of Ammonia and Other Toxic Compounds,” P.Z. Moghadam, K.C. Kim, D. Fairen-Jimenez, R.Q. Snurr
- **AIChE Annual Conference, Atlanta, GA, USA** November 16-21, 2014. Oral presentation, “Computational Screening of MOFs for the Separation of Toxic Chemicals,” P.Z. Moghadam and R. Q. Snurr.
- **Chem/Bio Filtration Strategies and Multifunctional Materials Conference, Arlington, VA, USA** October 22-24, 2014. Oral presentation, “Screening of metal-organic frameworks for Capture of Toxic Compounds,” P. Z. Moghadam and R. Q. Snurr