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14. ABSTRACT

Metal-organic frameworks (MOFs) with rigid, permanently porous structures have been shown to adsorb a variety of guests, including known carcinogens; however, little is known about the capacity of MOFs for dynamic gas adsorption properties. Therefore, dynamic adsorption experiments with various gases and CWA/simulants were performed. We first prepared M-MOF-74 (M = Zn, Mg, Co, Ni) series and tested their ability to separate ammonia from both dry and wet air. In dry conditions, all of the MOFs have excellent separation capacity (> 1 mol/kg). In

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Molecular nanoparks for CWAs, TICs, and TIMs

ABSTRACT

Metal-organic frameworks (MOFs) with rigid, permanently porous structures have been shown to adsorb a variety of guests, including known carcinogens; however, little is known about the capacity of MOFs for dynamic gas adsorption properties. Therefore, dynamic adsorption experiments with various gases and CWA/simulants were performed. We first prepared M-MOF-74 (M = Zn, Mg, Co, Ni) series and tested their ability to separate ammonia from both dry and wet air. In dry conditions, all of the MOFs have excellent separation capacity (> 1 mol/kg). In humid conditions, the uptake drops in every case, but ammonia uptake remains high. After the clear demonstration of metal effects on gas selectivity, we extended our strategy to create metalated nanoparks; we synthesized MOF-253 for successive metalation reactions. We tested the ammonia separation capacity for Cu, Zn, and Fe impregnated MOF-253 materials. Based on the dynamic loading melataed MOF-253 samples clearly outperform the pristine MOF-253, and ammonia loading values are comparable to those for M-MOF-74 series. More importantly, the metalated MOF-253 series showed significant saturation loading capacity for ammonia in a humid environment.

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
10/07/2011	1.00	David Britt, Chain Lee, Fernando J. Uribe-Romo, Hiroyasu Furukawa, Omar M. Yaghi. Ring-Opening Reactions within Porous Meta-Organic Frameworks, Inorganic Chemistry, (07 2010): 6387. doi: 10.1021/ic100652x
10/07/2011	2.00	T. Grant Glover, Gregory W. Peterson, Bryan J. Schindler, David Britt, Omar Yaghi. MOF-74 building unit has a direct impact on toxic gas adsorption, Chemical Engineering Science, (01 2011): 163. doi: 10.1016/j.ces.2010.10.002
12/04/2012	6.00	Joseph R. Hunt, Christian J. Doonan, James D. LeVangie, Adrien P. Co?te?, Omar M. Yaghi. Reticular Synthesis of Covalent Organic Borosilicate Frameworks, Journal of the American Chemical Society, (09 2008): 0. doi: 10.1021/ja805064f
12/04/2012	3.00	Qiaowei Li, Hiroyasu Furukawa, Alexander U. Czaja, Omar M. Yaghi, Kounosuke Oisaki. A Metal-Organic Framework with Covalently Bound Organometallic Complexes, Journal of the American Chemical Society, (07 2010): 0. doi: 10.1021/ja103016y
12/04/2012	4.00	Christian J. Doonan, David J. Tranchemontagne, T. Grant Glover, Joseph R. Hunt, Omar M. Yaghi. Exceptional ammonia uptake by a covalent organic framework, Nature Chemistry, (02 2010): 0. doi: 10.1038/nchem.548
12/04/2012	5.00	Omar M. Yaghi, Qiaowei Li. Reticular Chemistry and Metal-Organic Frameworks for Clean Energy, MRS Bulletin, (01 2011): 0. doi: 10.1557/mrs2009.180
12/04/2012	7.00	David Britt, David Tranchemontagne, Omar Yaghi. Metal-organic frameworks with high capacity and selectivity for harmful gases, Proc National Academy of Sciences, (08 2008): 11623. doi:

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Number of Papers published in peer-reviewed journals:

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Received   Paper

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Number of Papers published in non peer-reviewed journals:

(c) Presentations

D. Britt, D. Tranchemontagne, O. M. Yaghi, Metal-organic frameworks for air purification. IPE 2007, October 2007, Melbourne, Australia.

D. Britt, Challenges in the application of metal-organic frameworks to air purification, the Advanced Filtration Workshop, September 2009, Arlington, VA.

O. M. Yaghi, Chemistry and porosity of metal-organic frameworks, Seminar in the Dept. of Chemistry, UC Berkeley, October 2009, Berkeley, CA.

O. M. Yaghi, Reticular chemistry where geometry becomes beautifully real and useful, ACS Southern Regional Meeting, October 2009, San Juan, Puerto Rico.

O. M. Yaghi, Porous crystals as molecules, Eleventh International Conference on Organic Chem., November 2009, Kyoto, Japan (Plenary talk).

D. Britt, Controlled post-synthesis incorporation of accessible metal sites in a metal-organic framework, the 2009 Chemical and Biological Defense Science and Technology (CBD S&T) Conference, November 2009, Dallas, TX.

O. M. Yaghi, Metal-organic frameworks and their applications to clean energy, 5th Intl. Symposium on Macrocyclic and Supramolecular Chemistry, June 2010, Nara, Japan (Plenary talk).

O. M. Yaghi, Zeolitic imidazolate frameworks, 5th International Zeolite Membrane Meeting, May 2010, Loutraki, Greece (Plenary talk).

O. M. Yaghi, Reticular chemistry and its applications to clean energy, Seminar in University of Milan, May 2010, Italy.

O. M. Yaghi, Frontiers in materials chemistry, 239th ACS National Meeting & Exposition, March 2010, San Francisco, CA (Plenary talk).

H. Furukawa, Inclusion of reactive sites within metal-organic frameworks: synthesis and characterization, the Advanced Filtration Workshop, September 2010, Arlington, VA.

O. M. Yaghi, Metal-organic frameworks and their applications to clean energy, Welch Conference on Green Chemistry and Sustainable Energy, October 2010, Houston, TX.

O. M. Yaghi, Metal-organic frameworks and their applications to clean energy, 1st United Arab Emirates Conference on Pure and Applied Chemistry (ECPAC11), March 2011, Sharjah, UAE.

O. M. Yaghi, Perspectives on MOF research and the UCLA center for global mentoring, VNUHCM-UCLA Symposium: Chemistry of MOFs and Related Materials, March 2011, Ho Chi Minh City, Vietnam.

O. M. Yaghi, Metal-organic frameworks and their applications to carbon capture, 8th U.S.-Korea Forum on Nanotechnology, April 2011, Pasadena, CA.

O. M. Yaghi, The 'Gene' Within Metal-Organic Frameworks, Eyring Lectures in Chemistry & Biochemistry, April 2011, Arizona State University, Tempe, AZ.

O. M. Yaghi, Metal-organic frameworks and their applications to clean energy, Saudi International Petrochemicals Technologies Conference 2011, June 2011, KACST, Saudi Arabia.

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Received   Paper

  TOTAL:

Number of Manuscripts:

Books

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  TOTAL:

Patents Submitted

20120259135, O. M. Yaghi, C. J. Doonan, H. Deng, Complex mixed ligand open framework materials

20120186449, O. M. Yaghi, F. J. Uribe-Romo, F. Gandara-Barragan, D. K. Britt, Preparation of metal-triazolate frameworks

20120031268, O. M. Yaghi, D. K. Britt, A. U. Czaja, Reversible ethylene oxide capture in porous frameworks

20110319630, O. M. Yaghi, A. U. Czaja, W. Morris, J. R. Hunt, D. K. Britt, C. Lee, Porous reactive framework

20110277767, O. M. Yaghi, D. K. Britt, D. J. Tranchemontagne, Metal organic frameworks (MOFs) for air purification

20110137025, O. M. Yaghi, Q. Li, O. S. Miljanic, W. Zhang, J. F. Stoddart, Chemical framework compositions and methods of use

Patents Awarded

Awards

2011	TOP 2 most cited chemist worldwide (ISI Thomson)
2011	Distinguished Professor, Vietnam National University, Vietnam
2011	Icon Professor, University of Malaya, Malaysia
2010	Royal Society of Chemistry Centenary Prize
2009	World Class Professor, KAIST, Korea
2009	Izatt-Christensen International Award in Macrocyclic Chemistry
2009	American Chemical Society, ACS Award in the Chemistry of Materials
2009	Musher Lectureship, Hebrew University, Israel
2009	The Gooch-Stephens Lectures, Baylor University
2009	Miller Visiting Professorship at University of California-Berkeley
2008	AAAS Newcomb Cleveland Prize for the most outstanding paper in Science
2008	US National Science Foundation Distinguished Lecturer
2008	Guggenheim Lectureship, Reading University, UK
2008	G. Schmidt Lectureship, Weizmann Institute, Israel
2007	Materials Research Society, MRS Medal Sole Recipient
2007	Deans Recognition Award, UCLA

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
David Britt	0.21	
Eunwoo Choi	0.07	
Hexiang Deng	0.04	
Qiaowei Li	0.02	
Anh Thi Phuong Phan	0.05	
David Tranchemontagne	0.09	
Chi-Hau Sue	0.02	
Kyle Cordova	0.05	
Kyle Davia	0.01	
Iris Rauda	0.02	
Lisa Wang	0.05	
FTE Equivalent:	**0.63**	
Total Number:	**11**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Rahul Banerjee	0.03
Hiroyasu Furukawa	0.03
Yongbok Go	0.02
Sungjun Hong	0.19
Joseph Hunt	0.03
Jeremy Klosterman	0.07
Dani Peri	0.03
Bhaskar Ramachandran	0.11
Qiang Wei	0.10
FTE Equivalent:	**0.61**
Total Number:	**9**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Omar Yaghi	0.07	
FTE Equivalent:	**0.07**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

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
Kyle Davia
Total Number: **1**

Names of personnel receiving PHDs

NAME	
David Britt	
Eunwoo Choi	
Hexiang Deng	
Qiaowei Li	
Anh Thi Phuong Phan	
David Tranchemontagne	
Total Number:	**6**

Names of other research staff

NAME	PERCENT_SUPPORTED
Cornelius Klock	0.03
Chain Lee	0.12
Jose Mendoza-Cortes	0.10
FTE Equivalent:	**0.25**
Total Number:	**3**

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

FINAL REPORT

Dates covered: Aug 20, 2006 to Aug 19, 2012

Molecular nanoparks for CWAs, TICs, and TIMs

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1. PROJECT AND REPORT OVERVIEW

a. The objective of this project is to incorporate MOFs and COFs in personal protection technologies for protection against CWA and other TIC/TIM.

MOFs with rigid, permanently porous structures have been shown to adsorb a variety of guests, including known carcinogens (e.g. CCl_4). These materials have high surface area and free volume, as well as controllable functionality and metrics; however, little is known about the capacity of MOFs for dynamic gas adsorption properties. Therefore, dynamic adsorption experiments with various gases and CWA/simulants were performed to glean some insight into the adsorption mechanism. The primary conclusion is that reactive functionality is necessary for high capacity. In particular, we see success in MOFs containing coordinatively unsaturated metal sites and amino groups. This leads us to develop our idea; precisely controlling dispersability of reactive and/or strong binding sites in the crystalline porous solids would be important to achieve desired function and requires development.

We first prepared M-MOF-74 (M = Zn, Mg, Co, Ni) series and tested their ability to separate ammonia from both dry and wet air. In dry conditions, all of the MOFs have excellent separation capacity (> 1 mol/kg). In humid conditions, the uptake drops in every case, but ammonia uptake remains high. It should be noted that the post-desorption loading of Ni-MOF-74 is almost unchanged upon introduction of humidity. This is the first example of a MOF that does not show any reduction in chemisorption of a gas in the presence of water.

After the clear demonstration of metal effects on gas selectivity, we are extending our strategy to create metalated nanoparks; MOF with (i) covalently bound organometallic complexes and (ii) 2,2′-bipyridine link. In the former case, we prepared a metalated link containing an N-heterocyclic carbene (Pd(II)-NHC) and then assembled it into a MOF-5 type structure (IRMOF-77). We showed the permanent porosity of IRMOF-77 and the successful substitution of the pyridine coligand in IRMOF-77 without affecting the integrity of the MOF.

In the latter case, we synthesized MOF-253 for successive metalation reactions. We tested the ammonia separation capacity for Cu, Zn, and Fe impregnated MOF-253 materials. Based on the dynamic loading melataed MOF-253 samples clearly outperform the pristine MOF-253, and ammonia loading values are comparable to those for M-MOF-74 series. More importantly, the metalated MOF-253 series showed significant saturation loading capacity for ammonia in a humid environment.

We also studied ammonia storage capacity using another class of crystalline porous solid (covalent organic frameworks (COFs)). We tested COFs which contain a high density of Lewis acid boron sites that can strongly interact with Lewis basic guests. COF-10 shows the highest uptake capacity (15 mol/kg, 298 K, 1 bar) of any porous material. Ammonia can be removed from the pores of COF-10 by heating samples under vacuum, and the total uptake capacity of ammonia were maintained after several cycles of adsorption/desorption.

b. Key achievements

1. A benchmark for the dynamic capacity of MOFs for harmful gases of many types was established. The primary conclusion is that reactive functionality is necessary for high capacity. In particular, we see success in MOFs containing coordinatively unsaturated metal sites and amino groups. In fact, based on capacity alone, these MOFs are superior to activated carbon adsorbents.

2. Alkylsulfonate and primary amine groups were introduced in MOF structures by ring-opening reaction of 1,3-propanesultone and 2-methylaziridine.

3. COF-10 shows the highest uptake capacity (15 mol/kg, 298 K, 1 bar) of any porous material, including zeolite, cation exchange resin, and mesoporous silica.

4. The gas separation properties of the Zn, Co, Ni, and Mg versions of MOF-74 on both dry and wet mixtures of ammonia were studied in fixed-bed breakthrough experiments. We found the separation properties of MOF-74 depend heavily on the identity of the metal ion.

5. The successful preparation of highly porous MOF (IRMOF-77) with Pd(II)- N-heterocyclic carbene organometallic complexes.

6. First MOF featuring open 2,2′-bipyridine ligand sites was prepared, and subsequent complexation of Cu^{2+}, Zn^{2+}, and Fe^{2+} was also performed. Ammonia breakthrough experiments indicate the usefulness of metalation in dried and humid conditions.


2. TECHNICAL PROGRESS DURING THE REPORTING PERIOD

a. Tasks 1-6: MOFs with high capacity and selectivity for harmful gases

Effective capture of harmful chemicals is of great importance to those who are at risk for being exposed to such materials. General purpose filters are often comprised of activated carbon impregnated with copper, silver, zinc, and molybdenum salts; however, they are not adequately effective against all potential threats [1,2]. MOFs whose pore metrics and functionality can be designed have exceptional surface area so that it is likely that MOFs provides limitless potential for the application to gas filtration.

The eight "challenge" gases were selected to include several for which activated carbons have poor uptake, such as ammonia and ethylene oxide (EtO), as well as several for which they have good uptake, such as chlorine and benzene. Also chosen were carbon monoxide, sulfur dioxide, dichloromethane, and tetrahydrothiophene (THT). We sample a wide range of size, acidity, vapor pressure, and other variables to span the entire breadth of potential hazards. In a similar manner, six "benchmark" MOFs (Figure 1) were chosen to explore a range of surface area, functionality, and pore dimensions [3-7]. The separation capacities of the MOFs have been compared in each case to a sample of BPL-carbon.

Breakthrough curves for SO_2, NH_3, and Cl_2 adsorption in MOF-5, IRMOF-3, IRMOF-62, MOF-74, MOF-177, MOF-199 (the benchmark MOFs), and BPL-carbon were recorded. Plots of breakthrough curves and estimated separation capacities for gaseous contaminants are presented in Figure 2(A-C). We find retention of ammonia in all the benchmark MOFs to be a vast improvement relative to BPL-carbon, three of the MOFs (IRMOF-3, MOF-74, MOF-199) attaining at least 59-fold improvement in separation capacity. From this, it is presumed that MOFs lacking reactive adsorption sites are ineffective in kinetic gas adsorption.

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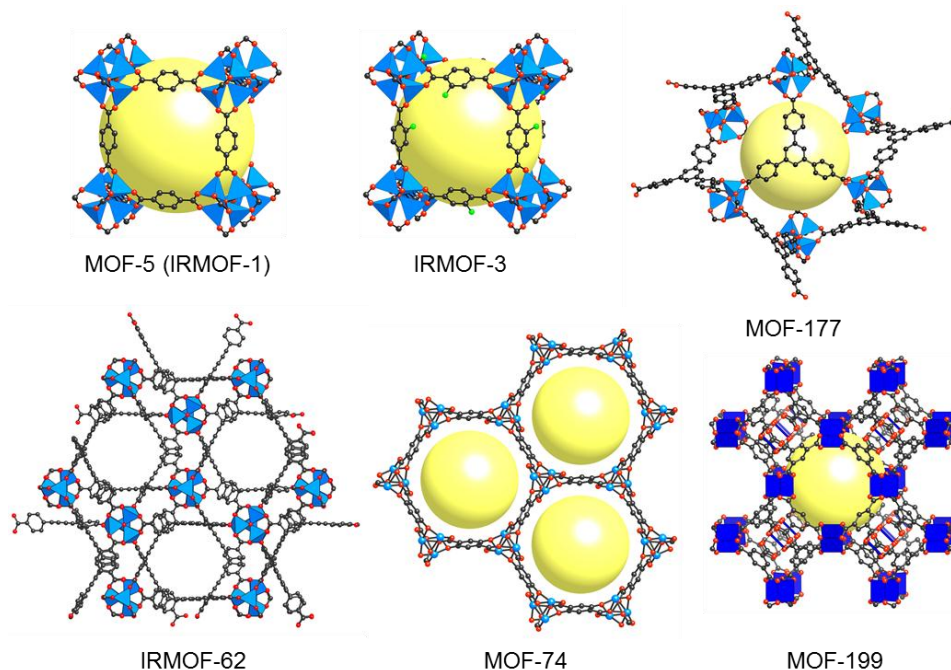
Figure 1. The single-crystal x-ray structures of the benchmark MOFs: the $Zn_4O(CO_2)_6$ cluster linked by terephthalate (MOF-5), 2-aminoterephthalate (IRMOF-3), benzene-1,3,5-tris(4-benzoate) (MOF-177), and diacetylene-1,4-bis(4-benzoic acid) (IRMOF-62); 1D $Zn_2O_2(CO_2)_2$ chains linked by 2,5-dihydroxyterephthalate (MOF-74) and the $Cu_2(CO_2)_4$ cluster linked by trimesate (MOF-199). Atom colors: C, black; O, red; N, green; Zn, light blue tetrahedral or light blue sphere; Cu, dark blue squares.

Coordinatively unsaturated metal sites are known to be reactive as Lewis acids. They demonstrate efficacy as adsorption sites in testing of MOF-199 and MOF-74. MOF-199 outperforms BPL-carbon by a factor of 59 in NH_3 adsorption and performs equally well in adsorbing SO_2. MOF-74 is even more effective, adsorbing more than 62 times the amount of NH_3 and nearly 6 times the amount of SO_2 as the activated carbon sample. In both cases, the highly reactive 5-coordinate zinc species in MOF-74 may contribute to the highly successful kinetic adsorption. MOF-199 is less successful when challenged with Cl_2 due to the fact that Cl_2 does not typically act as a ligand. However, it is clear that MOFs with open metal sites tend to be Lewis acidic; therefore, highly effective as adsorption media for gases that can act as Lewis bases, which is a weakness in activated carbons [8,9].

While open metal sites are reactive electron deficient groups, amines constitute a common reactive electron rich group that is available for hydrogen bonding as well. As noted above, the presence of the amine in IRMOF-3 affords a vast improvement relative to MOF-5 in adsorption of NH_3, a molecule that readily forms hydrogen bonds. Relative to BPL-carbon, IRMOF-3 adsorbs almost 71 times as much NH_3 before breakthrough. Furthermore, IRMOF-3 is observed to outperform BPL-carbon by a factor of 1.76 in adsorption of Cl_2, against which the open metal site MOFs were ineffective. Clearly it is possible to adsorb a range of contaminants that will react either as Lewis acids or Lewis

bases simply by including a reactive functionality of the opposite nature in a MOF structure.
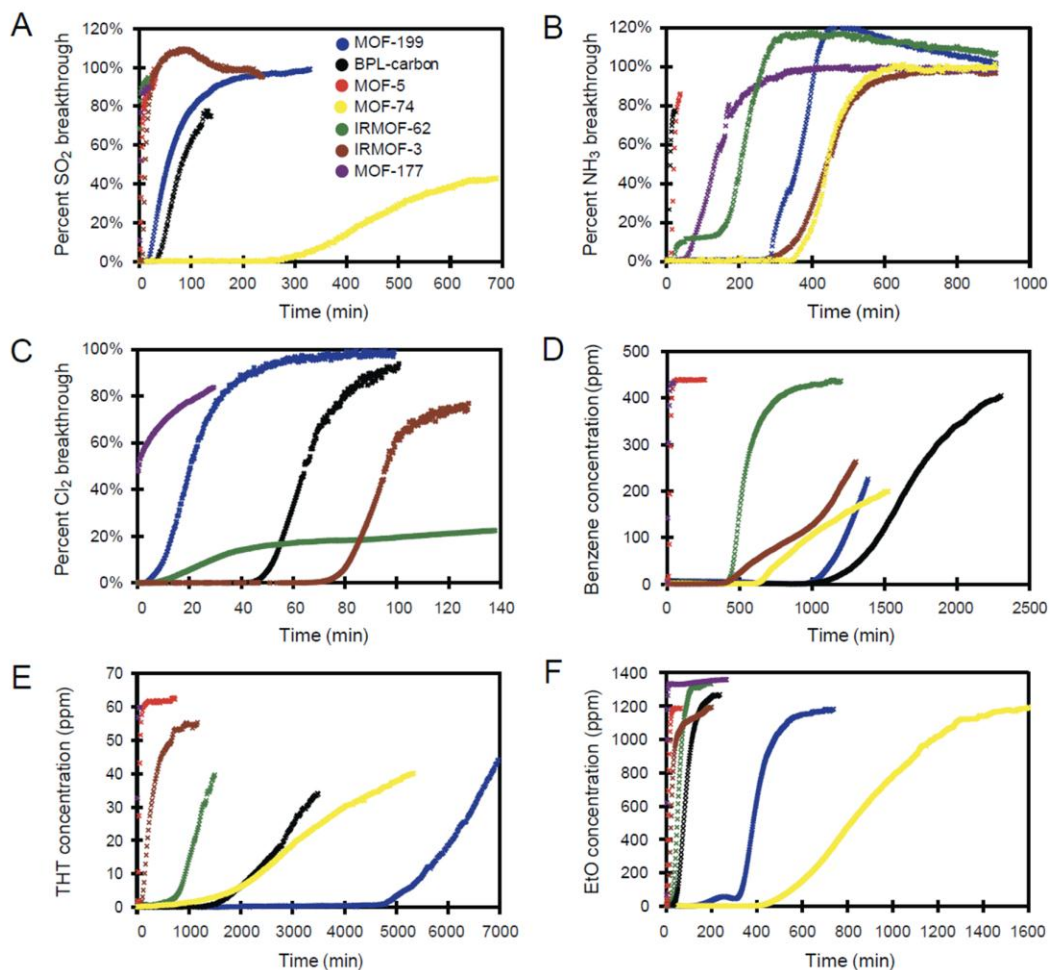
Figure 2. Kinetic breakthrough curves of SO_2 (A), NH_3 (B), Cl_2 (C), benzene (D), tetrahydro-thiophene (THT) (E), and ethylene oxide (EtO) (F) in the benchmark MOFs.

Breakthrough curves for tetrahydrothiophene (THT), benzene, and ethylene oxide (EtO) were recorded using the benchmark MOFs and BPL-carbon. Plots of the breakthrough curves and estimated separation capacity for vaporous contaminants are presented in Figure 2(D-F).

In following with the results of breakthrough experiments on gaseous contaminants, MOF-5 and MOF-177 do not perform well as kinetic adsorption media. IRMOF-62 also has low separation capacity values in comparison to BPL-carbon except in the case of EtO adsorption, where IRMOF-62 and BPL-carbon are equally ineffective. We also observe that IRMOF-3 is a poor adsorbent for the vapors chosen, as none behave as good Lewis acids. Open metal sites, particularly the copper sites found in MOF-199, prove to be the most effective in removing vapors from the gas stream. Both MOF-74 and MOF-199 outperform BPL-carbon by an order of magnitude. However, MOF-74 is not effective against the entire range of vapors, while MOF-199 is. There is some

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improvement over BPL-carbon in benzene adsorption and improvement by nearly a factor of 3 in adsorption of THT. In each case MOF-199 exhibits a color change identical to that observed upon exposure to water or NH_3, indicating a strong interaction with the open copper site.

Coordinatively unsaturated metal sites (MOF-74 and MOF-199) and amino functionality (IRMOF-3) prove effective in adsorbing contaminants that interact strongly with those groups. In particular, MOF-199 demonstrates efficacy equal to or greater than BPL-carbon against all gases and vapors tested except chlorine. It is clear that a successful dynamic adsorption medium will contain some reactive functionality, often in the form of a coordinatively unsaturated metal site. Our results open up an area of inquiry in the field of MOFs and indicate their great potential to supplement and eventually replace activated carbons as dynamic adsorption media.

b. Task10:

We have developed the isoreticular chemistry how to design high surface area MOFs such as MOF-177 [4]; however, in many cases these materials do not show exceptional gas selectivity, which is indicative of the relatively weak interaction with guests, as shown in previous section. In other words, greater interaction with guests must be the key issue for the air purification. We believe that MOFs with accessible reactive metal sites are one of the best candidates to capture CWAs, TICs, and TIMs. To that end, we started the isoreticular modification of MOFs followed by the isoreticular metalation.
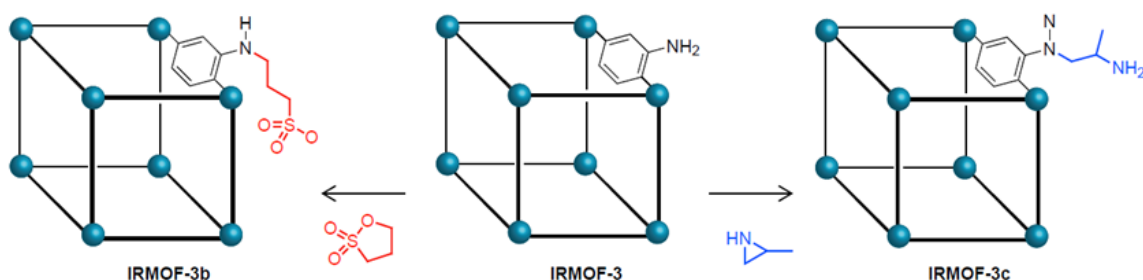
Figure 3. Ring-opening reactions performed on IRMOF-3 leading to covalently functionalized products IRMOF-3b and 3c. The cage of the MOF is represented as a cube where blue balls replace Zn_4O units and edges replace the organic linkers.

For the ring-opening reactions, IRMOF-3 was immersed in 1,3-propanesultone or 2-methylaziridne containing chloroform (Figure 3). The reaction products, here termed IRMOF-3b and IRMOF-3c respectively, maintained their structural topology throughout the reaction as evidenced by powder X-ray diffraction (PXRD) experiments. From elemental analysis, the approximate reaction yield per organic linker of IRMOF-3b and IRMOF-3c was estimated to be 57% and 108%, respectively.

The high porosity of the parent IRMOF-3 structure is retained after reaction, as evidenced by N_2 adsorption isotherms collected for the reaction products. IRMOF-3b has the BET surface area of 1380 m^2/g, which is 67% of IRMOF-3. This reduction in surface area is expected with the added mass of the alkylsulfonate groups. IRMOF-3c has the BET surface area of 530 m^2/g, 26% of IRMOF-3. This reduction is more than what is

expected for the added mass of alkylamine groups, though the material is still highly porous.
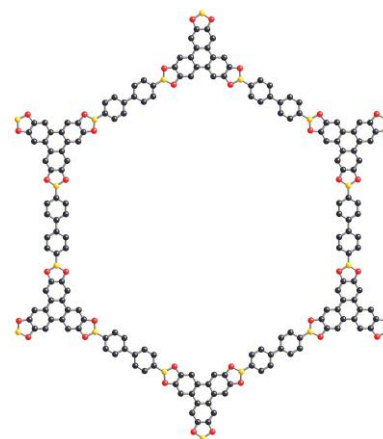
Originally IRMOF-3c was immersed in the solution containing Fe(II) ions for the metalation reaction. However, the metal composition of the IRMOF-3 derivative implies that zinc ions leached out from the IRMOF and were coordinated to alkylamine groups. Therefore, we prepared a new amino-functionalized MOF with a larger cavity (termed MOF-202). The topology of MOF-202 is the same as MIL-101 [11]. Since MOF-202 has large pore openings (> 10 Å) and two types of large cages (25 – 30 Å), we expected that the pore aperture/diameter of MOF-202 after the reaction with aziridine would remain large enough for gas diffusion. However, the BET surface area of MOF-202n (modified material) was much smaller than that of the pristine material (2000 and 525 m^2/g for MOF-202 and MOF-202n, respectively). The reason for the surface area decrease is not clear, but pore openings of MOF-202n could be partly blocked by the post-modification process.

After modification, MOF-202n was immersed in a solution containing Cr(III) ions (terms MOF-202n-Cr). The BET surface area of MOF-202n-Cr was estimated to be 200 m^2/g, which is smaller than MOF-202n probably due to the mass added as a result of metal impregnation. The successful isoreticular covalent transformation followed by metalation opens a route for incorporating metal ions into a wide range of frameworks. This is an important first step toward exploiting such metallated frameworks in gas and vapor capture.

c. Task 12: Prepare COFs to investigate their ammonia uptake behaviors

Covalent organic frameworks (COFs) are porous crystalline materials constructed by linking light elements such as carbon, boron, oxygen and silicon through strong covalent bonds. An attractive feature of some COFs is the high density of Lewis acidic boron atoms, present in boroxine (B_3O_3) or boronate ester (C_2O_2B) rings, which are an integral component of their frameworks. These boron sites present a unique adsorbent surface ready for interaction with Lewis basic gases such as ammonia, in a manner similar to the classical ammonia-borane coordinative bond. Therefore we sought to examine the ability of COF materials for ammonia capture.

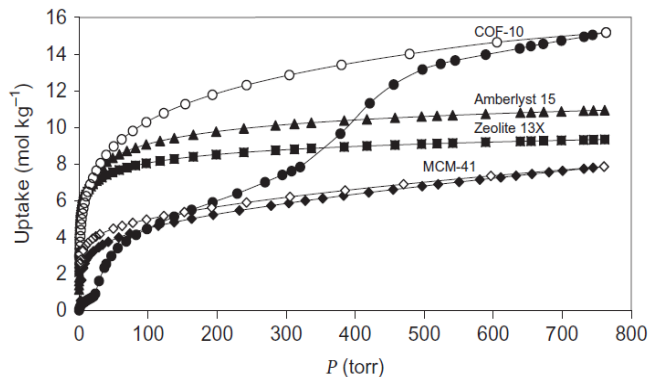**Figure 4.** Atomic connectivity and structure of crystalline COF-10. B, orange; O, red; C, black.

COF-10 was prepared according to previously published procedures (Figure 4) [11]. Its structure comprises hexahydroxytriphenylene (HHTP) and biphenyldiboronic acid (BPDA) building units linked into porous hexagonal layers. These layers are stacked in an approximately eclipsed pattern to give a **bnn** type structure with one-dimensional pores with diameters of 34 Å. Each hexagonal ring contains 12 boron atoms as part of the five-membered boronate ester rings (C_2O_2B).
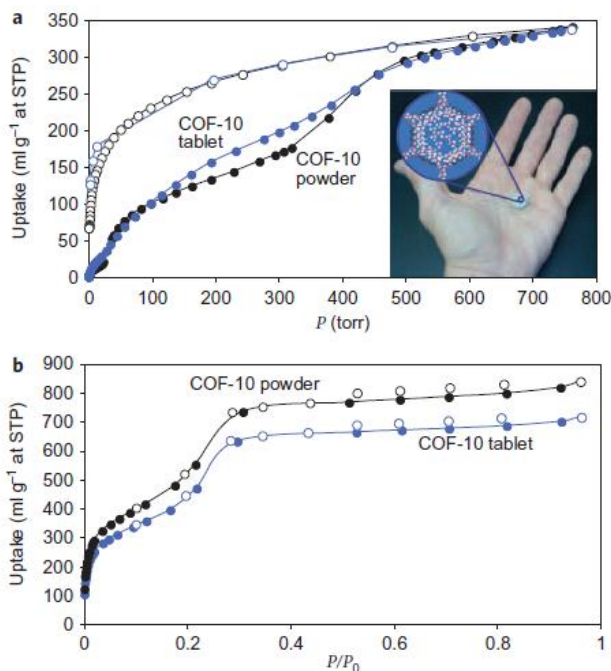
An ammonia adsorption isotherm was measured on COF-10 at 25 °C (Figure 5). The isotherm profile is best described as Type IV, which is indicative of a mesoporous material. Further evidence for this is provided by the low uptake at pressures below 150 Torr, beyond which COF-10 shows exceptional uptake (15 mol/kg), significantly outperforming the state-of-the-art materials Zeolite 13X (9 mol/kg) and Amberlyst 15 (11 mol/kg) [12]. The hysteresis observed for COF-10 is attributed to the

Figure 5. Ammonia isotherm for COF-10 at 298 K. Isotherms for Amberlyst 15, Zeolite 13X and MCM-41 were overlaid for comparison.

strong adsorption behavior of ammonia. However, 80% of the adsorbed ammonia can be removed by applying vacuum, and the remaining ammonia can be completely removed by heating to 200 °C under vacuum. The ammonia isotherm of MCM-41 at 298 K was collected for comparison because of its similar pore dimensions to COF-10 (Figure 5). In this pressure region, the MCM-41 ammonia isotherm most resembles a Type I profile, with a total ammonia uptake capacity of 7.9 mol/kg at 760 Torr, approximately half that of COF-10.

To investigate the potential for such applications, a binder-free tablet of pure COF-10 crystals was made using a conventional press at 2,000 psi. The nitrogen and ammonia adsorption capacity of the tablet was only slightly less than that of the pure COF-10 crystalline powder (Figure 6). The loss of the mesoporous step at 300 Torr results from the mechanical disruption of the walls of the framework, leading to the material no longer providing the appropriate adsorbate-adsorbent wall interactions that produce rapid pore filling en route to condensation. Such behavior is consistent with that observed for compressed samples of MCM-41. These results illustrate that COF materials not only have an exceptionally high capacity for ammonia, but also are sufficiently structurally robust to be

Figure 6. Ammonia (**a**) and nitrogen (**b**) isotherms for COF-10 powder (black) and COF-10 tablet (blue). Inset, pressed tablet of COF-10 loaded with ammonia.

compressed into tablets and pellets, which are the typical forms applied in industry when using adsorbent materials. Furthermore, the structural stability of COF tablets provides a
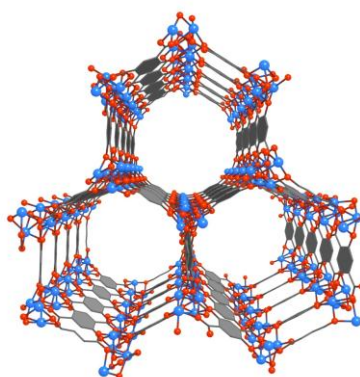
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means of taking advantage of this class of ultralow-density crystals in a more compact volume.

This work presents the exceptionally high uptake of ammonia by COF-10 compared with state-of-the-art materials. The layered morphology of COF-10 seems to be disrupted during the adsorption cycles of ammonia, but atom connectivity and periodicity are maintained. We also show the full adsorption isotherms subsequent to the second and third cycles of ammonia and the remarkable result that, given that the handling and regeneration conditions are not optimized, only 4.5% of total uptake capacity is lost. It is noteworthy that the slight reduction in total uptake capacity is accompanied by a larger uptake at low pressure. The rich adsorption chemistry revealed in this work suggests that COF-10 may be a potentially viable material for the uptake and release of ammonia. Furthermore, we anticipate that analogous COF materials may be optimized for the capture and storage of other Lewis bases by taking advantage of the interlayer adsorption interactions induced by their Lewis acidic surfaces.

d.   Tasks 14, 18: Synthesize M-MOF-74 series for gas separation

Effective gas separation in a porous framework material relies on the presence of some reactive center that interacts sufficiently strongly with guests within the framework. MOF-74 is a framework based on Zn(II) ions and 2,5-dioxidoterephthalate that features linear hexagonal channels decorated densely with 5-coordinated Zn sites (Figure 7).[13] Since its report, analogous materials have been synthesized using Co(II), Ni(II), Mg(II), and Mn(II).[14-16] Each material in the series is highly porous and features the 5-coordinate metal with an accessible sixth coordination site. The MOF-74 series presents an excellent opportunity for study of open metal site-based separation as it depends on the identity of the metal. Here we studied the gas separation properties of the Zn, Co, Ni, and Mg versions of MOF-74 on both dry (0% relative humidity, RH) and wet (80% RH) mixtures of

Figure 7. MOF-74 single crystal X-ray structure. Zn atoms are represented in blue, O atoms in red, and C atoms in grey. H atoms are omitted for clarity.

ammonia in fixed-bed breakthrough experiments. We found that the separation properties of MOF-74 depend heavily on the identity of the metal ion.

The breakthrough data for the separation of dry ammonia on the MOF-74 series (Figure 8(left)) provide an illustration of the impact that the metal site has on separation capacity. Based on the dynamic loading calculated from these data, the Mg and Co materials, with capacity of 13.0 and 11.2 wt%, respectively, clearly outperform the Ni and Zn materials (Table 1). Furthermore, when ammonia is loaded on these materials in dry conditions a significant portion of the adsorbed ammonia is retained when the materials are exposed to dry air during a desorption experiment (70% and 83% retention by the Co and Mg analogs, respectively). This result is noteworthy because NaX zeolite, one of the most widely used porous adsorbents, does not retain any of the adsorbed ammonia in dry conditions after desorption under the same breakthrough conditions. The loading of

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ammonia at breakthrough on all the MOF-74 analogs is generally near to or exceeds the maximum loading of traditional materials, such as NaX zeolite, which has a separation capacity of 4.9 wt% when tested under the same conditions, and BPL activated carbon, which has effectively no capacity for dry ammonia. In dry conditions Mg-MOF-74 has nearly 3 times the separation capacity of NaX zeolite while Ni-MOF-74, the analog with lowest separation capacity, has 80% the capacity of NaX.
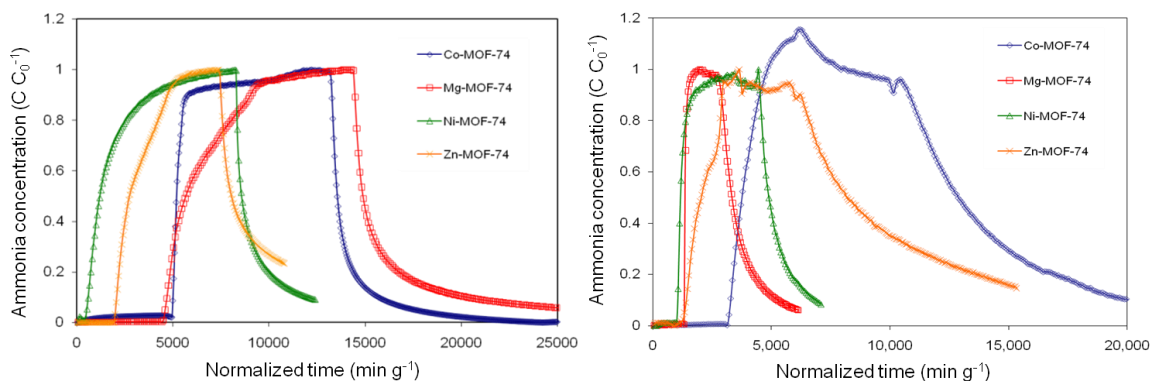
Figure 8. Breakthrough curves for ammonia at 0% RH (left) and 80% RH (right) in the MOF-74 series. Data courtesy of Greg Peterson (Edgewood Chemical and Biological Center (ECBC)).

Although the capacity of the MOF-74 analogs is reduced in a humid gas stream (Figure 8(right)), they maintain significant capacity for ammonia in a humid environment prior to desorption. For example, Mg-MOF-74, the worst performing MOF-74 analog for wet ammonia, has 6 times the capacity of BPL activated carbon, while the best analog, Co-MOF-74, has over 15 times the capacity of BPL and 7 times the capacity of NaX zeolite in humid experiments. However, the capacity of the Co, Mg, and Zn analogs drops considerably upon desorption. Indeed, the Co and Zn materials retain no ammonia after desorption under humid conditions. This result indicates that water is tightly bound to the framework, while ammonia is solvated rather than adsorbed. Notably, the post-desorption loading of Ni-MOF-74 is almost unchanged upon introduction of humidity. While the loading is not exceptionally high, this feature of selectivity over water is an important observation.

Table 1. Separation capacity of the MOF-74 series for ammonia measured as weight percent of adsorbed gas.

	Relative humidity /%	Capacity before desorption / wt%	Capacity after desorption / wt%
Co-MOF-74	0	11.2	9.4
	80	7.3	< 0.1
Mg-MOF-74	0	13.0	9.1
	80	2.8	0.9
Ni-MOF-74	0	3.9	2
	80	3.3	1.9
Zn-MOF-74	0	6.3	3.7
	80	4.8	< 0.1

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e. Task 15: MOF with covalently bound organometallic complexes

MOFs are ordered porous solids in which inorganic building units are joined by organic links. An important aspect of their chemistry is the ability to build structures with functionalized pores. This is achieved either by (1) employing an appropriately functionalized link in the assembly of the structure or (2) functionalizing the links after the structure has formed. Although these approaches have been employed to yield MOFs with pores that are functionalized by organic units and noncovalently or covalently bound coordination complexes, strategies for introducing covalently bound organometallic complexes in which metal ions are directly bound to carbon atoms remain largely undeveloped. The first approach works only in cases where the functional unit does not interfere with the assembly of a given structure, and the second one is limited by the overall stability of the framework under the reaction conditions necessary for postsynthetic functionalization.

Here we show how to make covalently linked organometallic complexes within the pores of MOFs. We initially prepared a link containing an *N*-heterocyclic carbene (NHC) precursor (**L0**, Figure 9a) and then assembled it into a MOF-5 type structure (IRMOF-76). After unsuccessful attempts at producing a covalently bound organometallic complex in the MOF, we metalated the link first (**L1**, Figure 9b) and then assembled it into the desired metalated MOF structure (IRMOF-77).
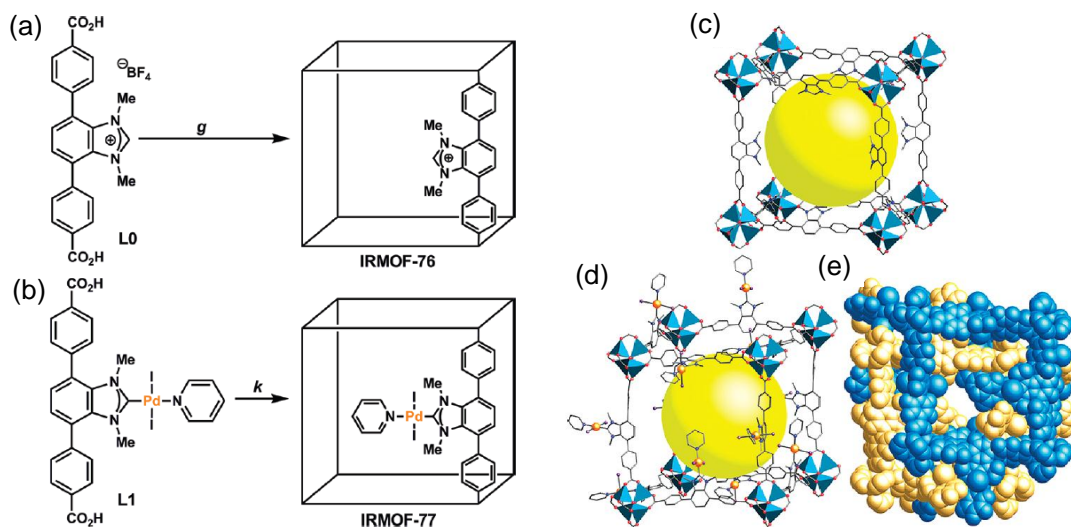
Figure 9. Reaction scheme for IRMOF-76 (a) and -77 (b). Single-crystal structure of IRMOF-76 (c) and -77 (d, shown with only one **pcu** net). Atom colors: blue tetrahedron, Zn; purple, I; orange, Pd; red, O; blue sphere, N. (e) Space-filling illustration of IRMOF-77. Two interwoven **pcu** nets are shown with blue and gold colors, respectively.
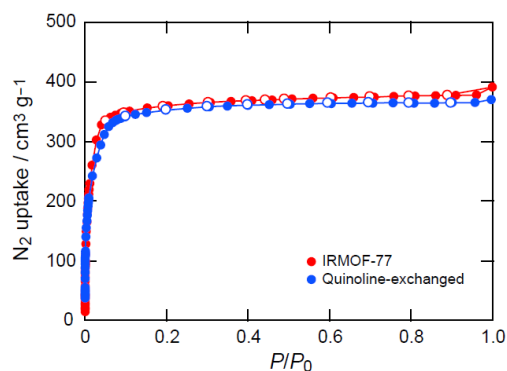
The synthesis of IRMOF-76 was carried out using a mixture of $Zn(BF_4)_2$, KPF_6, and **L0** in *N,N*-dimethylformamide (DMF). The mixture was heated at 100 °C for 36 h, whereupon colorless crystals of IRMOF-76 [$Zn_4O(C_{23}H_{15}N_2O_4)_3(X)_3$, X = BF_4, PF_6, OH] were obtained. Single-crystal X-ray diffraction analysis revealed that IRMOF-76 is isoreticular

with MOF-5. Here, Zn_4O units are connected to six **L0** links to form a cubic framework of **pcu** topology (Figure 9c). IRMOF-76 is a non-interpenetrated cationic MOF possessing imidazolium moieties (NHC precursors) on each link. We then aimed to produce an NHC or its metal complex in IRMOF-76 by a postsynthetic approach. However, none of the conditions examined were successful for this system. These results led us to seek an alternative strategy using a link possessing a metal-NHC complex (**L1**).
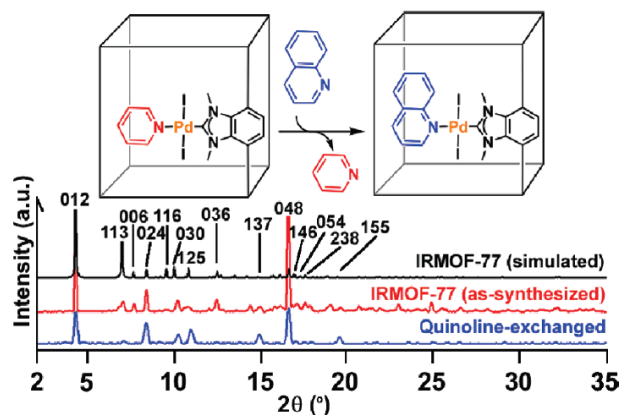
The synthesis of IRMOF-77 was conducted using $Zn(NO_3)_2$ and **L1** in a solvent mixture of *N,N*-diethylformamide (DEF) and pyridine (75:1). The mixture was heated at 100 °C for 30 h, whereupon orange crystals of IRMOF-77 [$Zn_4O(C_{28}H_{21}I_2N_3O_4Pd)_3$] were obtained. X-ray single-crystal structure analysis reveals that IRMOF-77 is also isoreticular with MOF-5. The X-ray crystal structure verifies the presence of the $NHC\text{-}PdI_2$(pyridine) moiety (Figure 9d). The Zn ions used for the construction of the framework are not involved in binding with the metal-NHC moiety. Two interwoven frameworks were formed with ca. 7 Å offset distance

Figure 10. N_2 isotherms for IRMOF-77 and quinoline-exchanged IRMOF-77 measured at 77 K.

(Figure 9e), presumably to mitigate the interference of the metal-NHC moieties with each other, with 4.06 Å shortest distances between two methyl carbons from two frameworks. Due to the interwoven nature of the structure, the pore aperture is ca. 5 Å × 10 Å. All immobilized Pd(II) centers protrude into the pores without blocking each other.

To confirm the presence of void space and the architectural stability of IRMOF-77, the permanent porosity was demonstrated by the N_2 adsorption isotherm of the guest-free samples. The isotherm shows steep N_2 uptake in the low-pressure region, which indicates that the material is microporous (Figure 10). The Langmuir and BET surface areas of activated IRMOF-77 are calculated to be 1610 and 1590 m^2 g^{-1}, respectively.

To examine the reactivity of the immobilized Pd(II) centers of IRMOF-77, ligand exchange experiments were carried out by immersing as-synthesized crystals of IRMOF-77 in 4% v/v quinoline/DMF solution for 1 day at room temperature. A comparison between the powder X-ray diffraction (PXRD) patterns before and after exchange reveals that the framework remains intact during the exchange process (Figure 11), which is also


Figure 11. PXRD patterns of as-synthesized IRMOF-77 (red) and quinoline exchanged IRMOF-77 (blue) and simulated PXRD pattern from single crystal X-ray structure (black).

supported by porosity measurements. No signal from the pyridine protons is observed in the ^{1}H NMR spectrum of the digested MOF after ligand exchange. Only the signals from quinoline are observed, with the expected molar stoichiometry (carboxylate link:quinoline = 1:1). Retention of the NHC-Pd bond is confirmed by the ^{13}C CP/MAS solid-state NMR spectrum (before, 154.1 ppm; after, 152.9 ppm). These results indicate the presence of an NHC-PdI$_2$(quinoline) complex after ligand exchange.

In conclusion, the structures of IRMOF-76 and -77 demonstrate the successful application of our strategy to immobilize Pd(II)-NHC organometallic complexes in MOFs without losing the MOF's porosity and its structural order.

f. Task 16: Scale-up MOF-253, and successive metalation reaction and characterization
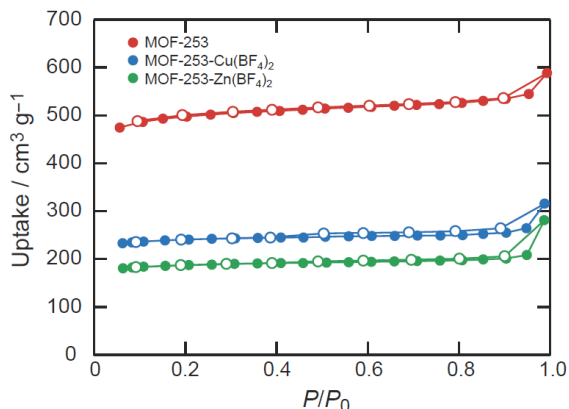
High surface area MOFs (such as MOF-5 and -177 [3,4]) show excellent gas storage capacity in high-pressure region, but their gas uptake capacity below ambient pressure is generally poor. As demonstrated above [17], we found that pore functionality, especially coordinatively unsaturated metal site, plays a dominant role in determining the dynamic adsorption performance of MOFs, since exposed metal centers can dramatically enhance (selective) gas uptake or serve as a source of catalytic activity. Since the first report of successful postsynthetic modification of MOFs, we and others have developed metalation protocols which would be applicable to the selective gas uptake and catalysis [18,19]. More importantly, our preliminary results show that metalated MOFs hold 5-10 mol/kg of ammonia even under humid conditions. Therefore, we considered the possibility that a hard oxophilic metal cation might preferentially coordinate the carboxylate groups of a mixed donor ligand such as 2,2′-bipyridine-5,5′-dicarboxylate (BPyDC^{2-}), leading to a framework with the softer donor groups available to bind metals.
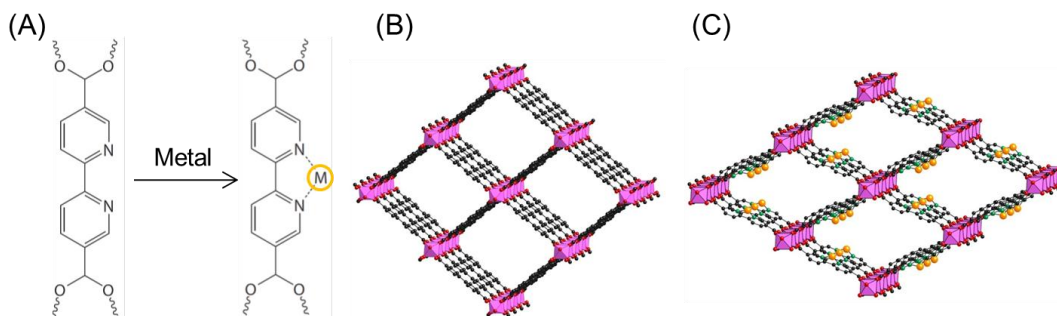
Figure 12. (A) General schematic representation of the metalation. Modeled crystal structure of MOF-253 before (B) and after the metalation (C). Atom colors: C black, O red, N green, Al pink polyhedra, Zn orange. All hydrogen atoms and leaving groups are omitted.

The synthesis of Al(OH)(BPyDC) (MOF-253) was accomplished in direct analogy with the recently reported framework Al(OH)(BPDC) (BPCD^{2-} = 4,4′-biphenyldicarboxylate). Reaction of H$_2$BPyDC with AlCl$_3$·6H$_2$O in DMF at 120 °C for 24 h afforded Al(OH)(BPyDC) as a white microcrystalline solid. The solid was soaked in methanol and then heated at 250 °C under dynamic vacuum for 24 h to yield the activated MOF-253. X-ray powder diffraction data show MOF-253 to be isostructural with Al(OH)(BPDC) [20].

The accessibility of the chelating BPy units within the framework of MOF-253 was confirmed by soaking the solid in methanol solutions of $Zn(BF_4)_2$ and $Cu(BF_4)_2$ to afford MOF-253-Zn and MOF-253-Cu. However while characterizing our samples, we noticed the peak positions in the PXRD pattern are vastly different from the original MOF-253 and reported results. To determine the atomistic connectivity, we analyzed the PXRD pattern of 100% loading sample (MOF-253-Zn(BF$_4$)$_2$). The PXRD pattern was indexed on a monoclinic unit cell (*Cc*) and refined on *Materials Studio* yielding cell parameters *a* =

Figure 13. N$_2$ isotherms for MOF-253 (red), MOF-253-Zn (green), and MOF-253-Cu (blue).

26.060 Å, *b* = 14.915 Å, *c* = 6.3421 Å, β = 109.14°. Surprisingly, the unit cell volume decreased from 2885.28 Å^3 to 2328.81 Å^3 or 20% cell volume variation after the metalation. Figure 12 shows the proposed structure of MOF-253 before and after the metalation. In the metalated MOF structure, the bipyridine linkers are rotated to accommodate metal ions and their corresponding counter anions.

Low-pressure N$_2$ adsorption measurements performed on MOF-253 and metaleted materials at 77 K. These revealed type I adsorption isotherms characteristic of a microporous solid (Figure 13). The BET surface area of pristine, Cu, and Zn impregnated MOF-253 are estimated to be 1840, 900, and 700 m^2/g, respectively.

Breakthrough experiments using toxic compounds were performed at ECBC. The breakthrough data for the separation of dry ammonia on the metalated MOF-253 series (Figure 14(left)) provide an illustration of the impact that the metal site has on separation capacity. Based on the dynamic loading calculated from these data, the Cu, Zn, and Fe materials, with capacity of 3.4 and 3.2 and 8 mol/kg, respectively, clearly outperform the pristine MOF-253 (0.7 mol/kg). These values are comparable to those for M-MOF-74 series (2.3-6.6 mol/kg). More importantly, the metalated MOF-253 series showed significant saturation loading capacity for ammonia in a humid environment (Figure 14(right)). For example, MOF-253-Cu in humid condition has 3 times greater capacity (11.0 mol/kg) than that in dried condition. The capacity of the Zn and Fe metalated materials also maintained considerable capacity (7.3 and 6.0 mol/kg), and again these values are greater than MOF-253 (2.3 mol/kg).

Since metalated materials show better ammonia breakthgouh performance under both dry and humid conditions, we tested the water isotherms of Cu and Zn impregnated MOF-253 as well as pristine MOF-253. Figure 15 demonstrates the water isotherms of these MOF samples. The uptake for MOF-253 in the low pressure region is low. This implies that the micropore environment is hydrophobic despite the presence of the OH moiety of the 1D rod inorganic SBU. Around P/P_0 = 0.5, the isotherm showed steep rise and finally the uptake reached 500 cm^3/g. The profile of the isotherm is reminiscent of DUT-4 [21]; therefore, it is likely that the nitrogen atom of the bipyridine linker may not show strong interaction with water. However, it is not clear the reason why significant hysteresis was observed.
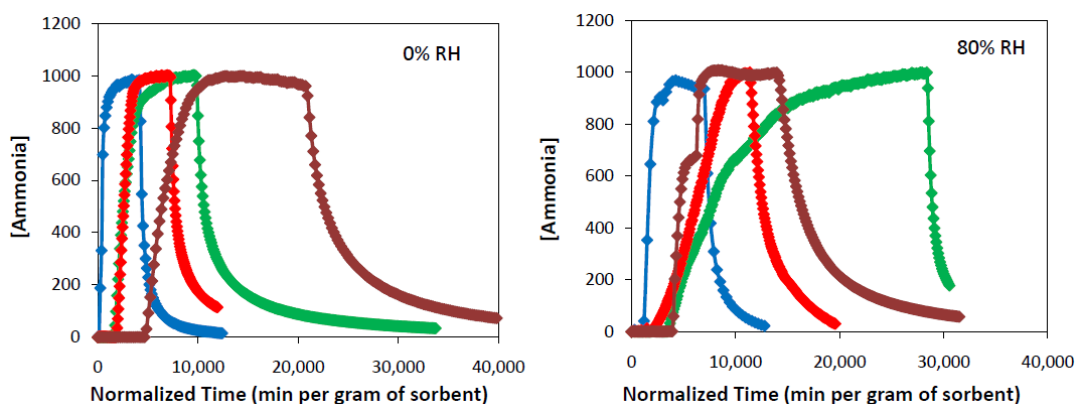
Figure 14. Selected kinetic breakthrough curves of gaseous ammonia in the metalated MOF-253 under dried (left) and humid conditions (right). MOF-253, blue; MOF-253-Zn(BF$_4$)$_2$, red; MOF-253-Cu(BF$_4$)$_2$, green; MOF-253-FeCl$_2$, brown. Data courtesy of Greg Peterson (ECBC).

When MOF-253 was impregnated, the profile of the water isotherm changed drastically. The water uptake in the low-pressure region was much higher than that of the pristine sample, and almost saturated at P/P_0 = 0.15. This hydrophilic nature (or polarized environment in the micoropore) could be one of the reasons why ammonia uptake was higher for the metal impregnated MOFs than for the original MOF-253. The total water uptake for MOF-253 was less perhaps because of the smaller BET surface area. Interestingly, the profile of the Cu metalated sample was similar to that of the Zn metalated MOF-253, indicating that the water sensitivity of these metals is nearly the same.

It is important to assess whether these metalated samples are stable under humid conditions. After the water vapor exposure, the profile of the PXRD pattern and its intensity did not show significant changes, indicating that the crystallinity retained. However, unexpectedly, the BET surface area of these materials is roughly half the value of the sample without water exposure. Therefore, we also measured an N$_2$ isotherm of MOF-253 after the water adsorption measurement. The sample showed much lower BET surface area (70 m^2/g), and the intensity of the PXRD pattern decreased. This implies that part of the structure was damaged, but we do not know how the MOF structure was influenced by water.

In summary, we demonstrated the synthesis of MOFs containing a free coordinating organic group within the pore. This BPy group affords the ability to include metal ions (e.g. Cu, Zn) within the pore of the MOF in many coordination environments. Preliminary ammonia breakthrough experiments
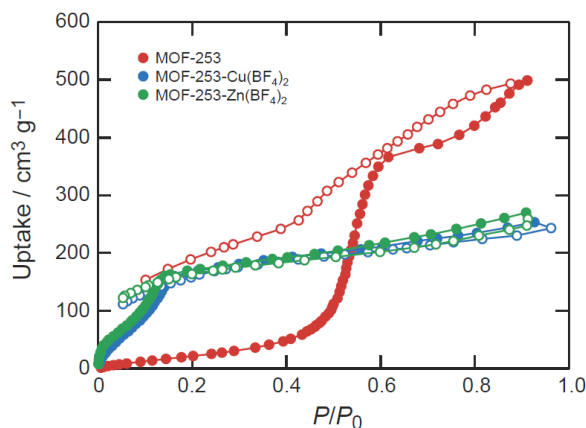
Figure 15. Water isotherms of fresh MOF-253 (red), and Cu(BF$_4$)$_2$ and Zn(BF$_4$)$_2$ loaded MOF-253 (blue and green).

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indicate the usefulness of metalation in dried and humid conditions. This clearly proves the effectiveness of metalation, and further development will be expected by additional strategies and materials.

g. Concluding remarks

We aimed to incorporate MOFs in personal protection technologies for protection against CWA and other TIC/TIM. During the project period, we endeavored to understand the fundamentals of gas separation in MOFs in addition to the equilibrium gas uptake, because much less was known about the interaction between MOFs and gases under kinetic conditions. Important conclusion in this project is that the presence of reactive sites in the pore that interact strongly with guest molecules is absolutely necessary for almost all relevant separations.

In this study, we showed that MOFs can have excellent separation capacity for ammonia and ethylene oxide, two common representative Lewis basic gases, which have been problematic for traditional porous materials for some time. The success of the MOF-74 series in separations including ammonia and sulfur dioxide should encourage further study in the field of MOFs, because the identity of the metal can be altered, which is in sharp contrast to zeolites.

The derivatives of IRMOF-3 and particularly MOF-253 should demonstrate such nature when they are metalated. Indeed, MOF-253 represents a rich possibility regarding the application of gas separation. Therefore, we believe that further exploration of the space of metalated MOF-253 compounds leads to materials with excellent separation capacity for harmful gases even in high humidity.

Our understanding of the synthesis of MOFs is still in its early stages; however, it is clear that the metalated MOFs are fertile ground for exploration. More importantly, the presented strategy should be applicable to other classes of porous solids, such as covalent organic and zeolitic imidazolate frameworks (COFs and ZIFs). In the continuous project under the DTRA support (Metalated Nanoparks for CWAs, TICs and TIMs), we plan to develop the synthesis and characterization of metalated MOFs, COFs, and ZIFs as well as mixed metal MOFs and ZIFs synthesis to improve adsorption capacity of various gases and CWA/simulants.

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