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Elisha North
Taylor University

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Introduction

Metal-organic frameworks (MOFs) are a class of highly porous materials that have a wide range of possible uses. These frameworks include a transition metal linked with organic compounds (linking molecules) to result in a large, repeating crystalline structure with high porosity. This high porosity combined with the unique chemical makeup has attracted much attention from chemists over the years because of the predicted plethora of chemical and physical attributes unique to MOFs.[1]

A notable instance of such a metal-organic framework was published in *Nature Magazine* by Li, et al. in 1999.[1] Prior to the then-novel synthesis of the particular MOF reported in this article, no stable MOF had been reported because the first attempted MOF structures would collapse if they had no guest molecules in the pores, effectively rendering them useless. The possibility of a stable MOF had effectively been realized according to this article, and many of the imagined possible uses of these types of frameworks now seemed more feasible to achieve. The findings in this article seemed to inspire many more attempts to synthesize stable MOFs because of the new-found viability of MOFs as useful compounds for gas storage due to the stable, porous structure, as well as the plausibility of implementing these compounds as chemical sensors.[1–19]

The most well-known trait of MOFs is the high porosity they exhibit. This porosity mostly comes from the crystalline, repeating structure of organic compounds with cyclic, and often aromatic, substructures. A wide range of these MOFs is possible because of the many possible combinations of transition metals and organic linking molecules within these frameworks. The porosity exhibited by the framework is largely dependent upon the chosen linking molecule, so a careful selection of organic linking molecules used in the frameworks

could possibly result in a usefully large span of pore sizes. Inside the very small pores within these MOFs, it is possible to store various gas molecules, to allow for quantifiable, light-emitting or light-quenching electron interactions between the guest and the framework, as well as to adsorb medicine for controlled delivery within the body.[20] The ability to employ MOFs with all of these uses is known as "tunability" which is a key attribute to be explained in greater detail later. Useful real-world applications of these compounds as well as some limitations thereof will be discussed in the last two sections of this paper. Remarkably, all three of the listed uses of these porous MOFs have been reported in the literature and will be explored further over the course of this paper, but before further examination of these uses takes place, the synthesis of these compounds must be explained.

Synthesis

Methods of synthesis of these metal-organic frameworks are fairly straightforward at present, even though historically we have seen slow reactions with poor yields.[13] Synthesis in the past typically involved a slow, deliberate diffusion of an organic base into a solution of an inorganic salt in dimethylformamide (DMF).[1] This synthesis was, however, not too far from syntheses carried out at present. Currently, it is more common simply to mix together the linking molecules and an inorganic salt in an organic solvent, usually DMF. Sometimes this process can take several days, but other times it can take only several hours; however, the yields are overall consistently better than those reported using the diffusion method.[13] A helpful part of the synthesis is that it can be carried out at reasonable conditions, approximately 100° C and 1 atmosphere. No purging of glassware is necessary, either, and in many cases, the reaction carries with no side reactions occurring simultaneously. The reactions do not even need to be stirred or watched closely—only monitored periodically to check for products—so this is a particularly

easy method of synthesis. This ease of synthesis of these compounds has resulted in a large and quickly-growing number of reported novel MOFs. By the end of the simple reaction, crystalline product is typically visible in the solvent.

What physically happens during the course of the crystallization is the coming together of what are called secondary building units (SBUs). The acronym SBU refers to the observed structures at the vertices of each framework. These SBUs are observed and discussed in numerous papers on the subject of MOFs.[1–4,7,8,10,12,13] Essentially, they work as the building blocks of the crystal structure, hence the name "building unit." It becomes apparent upon viewing the models that each MOF holds a metal-containing SBU at each vertex of a unit cell. These SBUs link together by way of the organic linking molecules which build the framework. One particularly helpful SBU is the "paddle-wheel" SBU formed by back-to-back metal-dicarboxylate groups. In these paddle-wheels, we see that the metal is tetrahedrally bonded to four oxygen atoms, each oxygen provided from an adjacent carboxylate group, providing the ubiquitous metal-oxygen-carbon motif among MOFs. Furthermore, the metal-carboxylate tetrahedra are back-to-back, creating a particularly strong structure.[1,2,4,8,10] This square SBU helps with the tessellation of the crystal material because it is the junction between the organic linking molecules and the metal ions. The metal-containing SBUs are what provide both the rigidity necessary to uphold successive tessellations and the necessary angles to create the desired structure.[3] The observed structures in these MOFs are incredibly porous due to the distance between the metal SBUs at the vertices of the formula unit. Since the distance between the vertices is basically the length of the linking molecule, it is clear to see that the pore size within these frameworks is determined almost entirely by the length of the linking molecules therein. Therefore, it is possible to create a large variety of pore sizes in these frameworks

because there is a large number of possible linking molecules from which to choose. This variability of structure size and composition of MOFs makes up just one of the many nuances of tunability.

Tunability

Undoubtedly since the first synthesis of a legitimate metal-organic framework, there has been a seeming explosion of new MOFs. The key structural motif of the metallic secondary building units at the vertices of the frameworks has been markedly influential in the production of these new compounds. As mentioned above, the paddle-wheel SBU in particular has shown up quite frequently, both with copper, $Cu_2(CO_2)_4$, and with zinc, $Zn_2(CO_2)_4$.[1,3,8,10] This kind of SBU arises only because another common part of these frameworks is a carboxylate structure supplied by the linking molecules. It is fairly common to see some form of a benzene carboxylate derivative between the vertices of these frameworks.[1–4,7,8,10,13] The terminal carboxylic acid in the chosen linking molecules supplies the oxygen atoms necessary to provide the metal-oxygen-carbon motif observed at most vertices in these frameworks. The best example of this process is observed in the structure of the first viable MOF reported, initially called MOF-5, now re-named MOF-1.[1,13] This MOF has a very simple linking molecule: benzene-1,4-dicarboxylic acid, or *p*-benzenedicarboxylic acid. Each carboxylic acid at the ends of this molecule is deprotonated during the synthetic steps to form two free carboxylates. It is these free carboxylates that provide the necessary oxygens to form the paddle-wheel SBUs.[1] Once the SBUs and the linking molecules have tessellated into crystals, the next step is to run an x-ray diffraction, either powder or single-crystal, depending on the apparent size of the crystals, and then to remove the stored solvent from the synthesized framework by heating the material. The final step is to run a second x-ray diffraction on the material to determine whether or not the

crystal structure was maintained during the desolvation process. Unfortunately, the heating step was where most previously-synthesized MOFs failed to retain their structure; upon viewing the x-ray diffraction data, it would be apparent that the structure was no longer retained after the guest solvent was removed, rendering them useless as standalone MOFs.[1] Fortunately, the discovery of the necessary structural metal-oxygen-carbon motif to prevail against this effect paved the way for other structures with different pore sizes to be explored. The best way to do this was to synthesize new MOFs in a similar manner, but by using different linking molecules.

Eddaoudi, et al. in 2000, reported four distinct MOFs each possessing a benzene-carboxylate-derived linking molecule as well as zinc-based SBUs in the observed unit cells.[2] This research group was the first to synthesize a variety of MOFs and observe just a few of the many possible crystal structures. To determine the actual achieved structure, the group used both single-crystal x-ray diffraction and powder x-ray diffraction. The results told them that the structure before the removal of the solvent was the same or very similar as after the removal of the solvent, proving that the framework was stable and legitimate as a standalone MOF. Interestingly, though, the pore sizes of the unit cells were quite different: the smallest reported pore cross-section was 7 Å for MOF-2 and the largest reported pore cross-section was 14 Å for MOF-4. Additionally, the calculated apparent surface area of the reported MOFs ranged from 140 m^2/g for MOF-3 to 2900 m^2/g for MOF-5. Note that the MOF with highest cross-sectional length did not also possess the highest surface area, nor did it posses the highest free volume (free volume being the amount of space a given molecule may wander in a fixed lattice structure per unit mass of the lattice material reported in cm^3/g). One thing to note about this is that when calculating the free volume of the pore, van der Waals radii of the involved atoms in the framework must be considered because van der Waals force will affect the available free space.[2]

This free volume and surface area variability give MOFs some attributes that make them particularly useful. One such attribute is that of gas storage capabilities.[14]

Gas Storage

Gas storage is a prime area of interest in the realm of finely porous materials, and especially is of interest in the realm of metal-organic frameworks. Important determining factors of gas storage capabilities are the pore size of the MOF and the apparent surface area, as shown by Frost, et al. in his paper on this subject.[6] Frost's research group examined the effects of the porosity on the uptake of H_2 by several isoreticular metal-organic frameworks (IRMOFs). Isoreticular simply means that the network observed in the selected MOFs is the same. The group found that free volume and surface area greatly affected the ability for certain IRMOFs to adsorb H_2. The cause of the difference in the IRMOF's ability to adsorb H_2, therefore, was the difference in the pore size of the IRMOFs involved, since pore size directly affects both free volume and surface area. Since most research groups use some sort of x-ray diffraction measurement system to derive molecular structures and calculate the pore sizes of the MOFs they create, Frost's group simply used reported powder x-ray diffraction data and single crystal x-ray diffraction data from the literature available at that time in order to input the correct information into the computer systems to generate models of the selected IRMOFs. Using these models, they ran Grand Canonical Monte Carlo (GCMC) calculations to determine the filling patterns of H_2 molecules within a MOF. This method of calculation is a way of finding the way a given molecule will fill an area of fixed volume—precisely the environment that a crystalline MOF provides. Unfortunately, a problem with GCMC is that it is only a calculation and can yield inaccurate results due to a high number of approximations.[10] To determine whether or not the calculations were accurate, Frost's group did compare their computational results with

experimental results of the corresponding MOFs retrieved from other publications and found that their calculations were within reasonable range of the literature values reported.[6] They also found an interesting correlation regarding the sorption capabilities and the physical properties of the MOFs: at low pressures, the amount of H_2 adsorbed correlates well with the heat of adsorption; at intermediate pressures, the amount of H_2 adsorbed strongly correlates with the surface area of the MOF; and finally, at high pressures, the amount of H_2 adsorbed is very highly correlated with the free volume. Practically, this is a setback because this correlation suggests that the only way to store any helpful amount of H_2 is to force it to adsorb into a MOF at very high pressures (>120 bar) or at high temperatures.[6]

Much of the research done in the realm of gas storage involves linear molecules such as N_2, H_2, and I_2, but not strictly diatomic molecules, as storage of the linear CO_2 has been explored as well.[2,4,5,8,10] Storage of I_2 is particularly useful, considering that one of iodine's isotopes, ^{129}I, a radioactive byproduct of the fission of uranium in nuclear reactors, also exists as I_2 when it is formed. This particular isotope of iodine exhibits beta decay radiation and has a half-life of nearly 16 million years.[9] This poses a problem to human health as iodine is readily absorbed by the thyroid gland. It is this health hazard that has inspired so much research into storage of iodine gas. Historically, gaseous I_2 has been stored in secondary forms such as concrete or glass incorporated with silver because of silver's low solubility salt with iodine.[9] One group's successful storage of iodine—up to 225 weight %—through use of aerogels, another class of highly porous materials, inspired other groups to design metal-organic frameworks to follow suit. One attempt to solve the problem of I_2 storage was through the use of a MOF composed of linking molecules derived from benzoic acid (4-(pyrimidin-5-yl)benzoic acid, to be exact). In this paper, Wang, et al. reported a maximum uptake of iodine of 0.5 I_2 per formula unit of their

reported MOF.[8] By no means is this a large amount of adsorbed material comparatively per

formula unit. For example, Eddaoudi, et al. reported up to 22.87 N_2 molecules per formula unit

in a then-novel MOF.[2]   Still further attempts have been made to synthesize a MOF that can store

I_2 effectively. Yao, et al. successfully created an NbO-net MOF that encompassed 47 I_2

molecules per unit cell. Considering each unit cell in NbO consists of three formula units (based

on basic principles of crystals), we can extrapolate that $\frac{47}{3}$, or 15.666... I_2 molecules were present

per formula unit. This 47 I_2 molecules per unit cell is actually is a higher number than was

predicted through the reported GCMC calculations for this MOF.
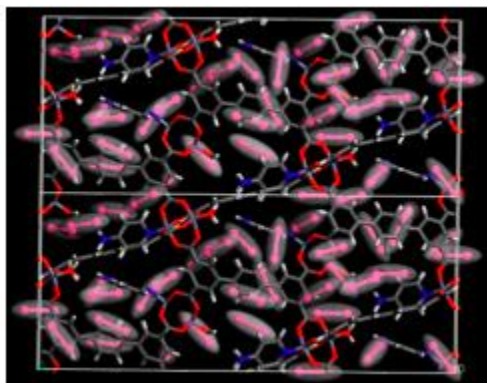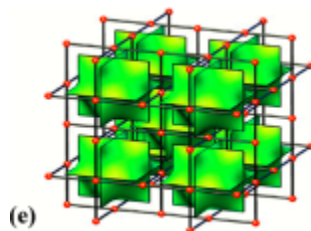
(top): Figure (e) the NbO-net reported by Yao; bottom: the GCMC-calculated placement of I_2

showing the 40 molecules per unit cell.[10]

In fact, the GCMC calculation predicted only 40 I_2 molecules would adsorb per unit cell.[10] The

GCMC calculation simply ran with too many approximations and was therefore unable to predict

the correct number of I_2 molecules adsorbed into the framework. This is a minor setback

because this suggests that we cannot fully trust GCMC calculations for such large frameworks as

reported in Yao's paper. Yao recognized this was a potential setback but carried on with the use of GCMC because standard *ab initio* calculations on such a high molecular-weight compound would be basically impossible even with computers. This particular MOF in question shows a staggering 216 weight % I_2 adsorption, just under the reported 225 weight % I_2 adsorption of the aerogel which initially inspired this synthesis. Interestingly, this adsorption was up to 80% reversible.[10]

As mentioned above, gas storage is not limited to diatomic molecules, but is still more easily carried out on linear molecules. One particular linear molecule at the top of the list of troublesome gases is CO_2. CO_2 is a prime candidate for storage because it is being produced so rapidly and is a major emission into the atmosphere.[5] Historically, CO_2 has been removed from the exhaust of industrial plants by remarkably inefficient and costly methods. Because of this, many scientists have attempted to synthesize porous materials for just this purpose: to trap CO_2 on the conditions that 1) uptake of the gas is reversible and 2) molecular-level fine-tuning is possible. Fortunately, MOFs fulfill both of these roles. Millward and Yaghi studied a variety of MOFs to find their ability to uptake CO_2. They found that under ambient pressures, the amount of CO_2 that could be adsorbed was not very high, but under intermediate pressures (~42 bar), the adsorption was very high. In fact, volumetrically, the uptake of CO_2 was 325cm^3/cm^3 of MOF-177, a very high-surface-area MOF.[5] Interestingly, even though this is an entirely different gas from H_2, this measurement aligns well with what Frost, et al. found regarding adsorption capability of H_2 in the IRMOFs studied: that there is a correlation between the adsorption capability and surface area at intermediate pressures.[6] Unfortunately, there does not seem to be a useful avenue for storage of CO_2 at ambient pressures at present, but this discovery of a high-CO_2-affinity MOF is promising, despite the inconveniently high required pressures to store it

effectively.

Chemical Sensing

Among the many uses of metal-organic frameworks is their ability to act as reasonable chemical sensors.[10–19] As explained earlier, it is possible to tune the size of the pores to fit a specific amount desired, but so too is it possible to tune the chemical environment within the pores to allow for chemical interactions to happen that will allow for both qualitative and quantitative analysis. Mostly, the plausibility of chemical sensing has not been effectively realized among MOFs, but in recent years, much of the research into MOFs has been in this area. Even since before the first viable MOF was reported in 1999, this class of materials has been theorized to serve as a chemical sensor.[1] This is because most theorized MOFs include compounds that have conjugated π electron systems. As expected, MOFs with these π electron systems typically exhibit absorbance in the ultraviolet range of the electromagnetic spectrum. Additionally, they usually exhibit some sort of visible fluorescence upon relaxation from the excited state—fluorescence which can be measured easily. Because of the luminescent effects of π electron-rich areas in these MOFs, it is possible to combine this attribute with the high tunability of pore size in order to design MOFs with remarkably selective excitation and fluorescence patterns.[14]

One particular class of detectable compounds through this excitation and fluorescence method is nitroaromatic explosives.[10,12,19] Mukherjee, et al. designed a MOF with incredibly particular selectivity to trinitrophenol, or TNP, which has a very similar structure to that of TNT. The research group designed an experiment using photoluminescence spectroscopy to test for the quenching efficiency, in other words, the fluorescence disruption, of various nitroaromatic analytes in the aqueous-phase with the MOF they created. Note that the term quenching

efficiency is given in percentages; these percentages are the percent of light that is no longer present. What they found was that even trace amounts of TNP were able to disrupt the fluorescence of the MOF almost entirely, whereas other nitroaromatic compounds they used did not quench the fluorescence in any marked way. The results were quite remarkable because the structural difference between TNP and TNT, two of the tested analytes, is so small (the replacement of one –OH group with one –CH$_3$ group), but nevertheless resulted in a vast quenching efficiency difference—TNP exhibited a quenching efficiency of >95%, whereas TNT showed a quenching efficiency of <10%.[19] The interesting part here is that the fluorescence is supplied by the π-electron rich section of the MOF itself, and that the quenching is in part realized by the π-π interactions between the analytes and the MOF as well as the hydrogen-bonding interactions between the constituents of the analytes and the nearby tertiary aliphatic amino groups on the MOF.


Figure 4. Response of Ur-MOF aqueous dispersions (1 mg in 2 mL water) toward the additions of various nitro analyte aqueous solutions (200 μL each) under UV light ($λ_{max}$ = 365 nm) (a = TNT, b = NM, c = RDX, d = 2,4-DNT, e = 2,6-DNT, f = NB, g = DMNB, h = TNP).

Beyond the π electron interactions and the hydrogen bonding, there is another important thing to note of TNP: its absorbance spectrum is very much in line with the MOF's emission spectrum, so while the MOF absorbs the UV light, it emits visible light in wavelengths that are in line with the wavelengths that TNP absorbs. In the picture taken directly from the paper, it is easy to see the quenching in the luminescence with the use of TNP.[19] Simply put, the other compounds

tested did exhibit the hydrogen-bonding interactions and π-π electron interactions, but they did not share the absorption profile with TNP, and so were not able to quench the fluorescence as efficiently.

Other spectrophotometric measurements show that the presence of an analyte can actually enhance the fluorescence observed.[12] Pramanik, et al. found that the detection of nitroaromatic compounds strictly have a quenching effect on the fluorescence of the MOF and that aromatic compounds without nitro groups actually showed a strict enhancement effect on the fluorescence of the MOF they studied, [$Zn_2(oba)_2(bpy)$]·DMA, where $H_2oba=$ 4,4'-oxybis(benzoic acid), bpy = 4,4'-bipyridine, and DMA = N,N'-dimethylacetamide. This reported MOF has a particularly narrow conduction band, which helps explain the electron transfer mechanism. The electrons in this conduction band are quite mobile and are also responsible for the emission of photons upon excitation.
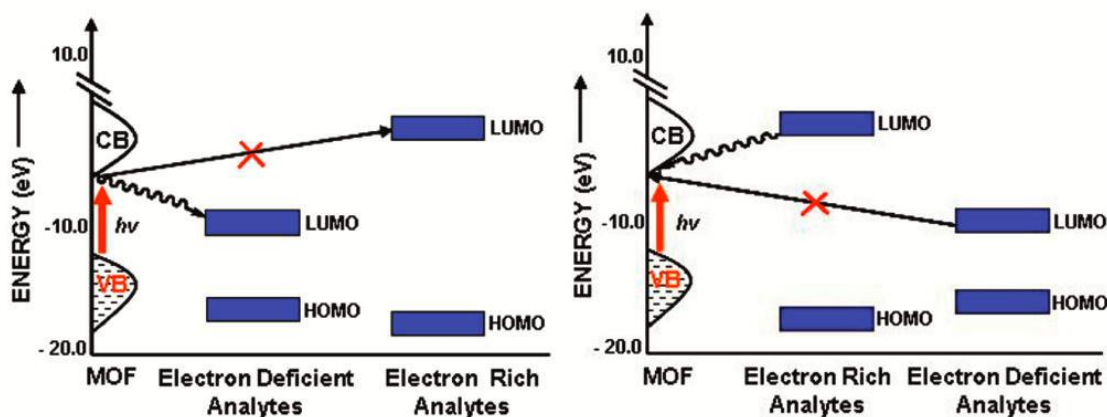
Above: a diagram showing the energy transfer of the electrons (left) into the LUMO of the nitro group and (right) into the conduction band from the excited π* antibonding state in the LUMO of the regular aromatic compound.[12]

In the case of the presence of nitroaromatics, the LUMO of the nitro group actually accepted the electrons that were in the conduction band upon excitation, effectively quenching the emission

light by the MOF. Conversely, in the case of the regular aromatic compounds, upon excitation the π electrons were excited into a π^* antibonding state in the LUMO of the compound and then transferred into the conduction band of the MOF, thereby increasing its emission.[12]

The compounds need not be aromatic or nitroaromatic to affect the emission of light of the MOF in question.[11,16,17] Chen, et al. reported a MOF that was incredibly selective to anions—particularly fluoride ions.[11] The method of testing was similar to the one shown previously with the nitroaromatics, but differed slightly: the MOF was placed in dissolved salt solutions. Their reported MOF-76b was evacuated of its original solvent and dissolved in a solution of a sodium salt in methanol. Tested salts were NaF, NaCl, NaBr, Na_2CO_3, and Na_2SO_4. The MOF took up the anions of the salts into its pores as it adsorbed the methanol. Interestingly, the fluoride-incorporated MOF showed the highest increase in photoluminescence compared to the non-anion-incorporated MOF photoluminescence profile. This was attributed to the apparent hydrogen bonding in between the fluoride ions and the methanol. Hydrogen bonding was confirmed by calculation of the distance between the F^- and the methanol by x-ray diffraction data—the apparent distance was in line with the hydrogen-bonding distance of H and F.[11] Still another group was able to create a method for sensing cations.[17] Tang, et al. through similar photoluminescence testing as above, were able to quantify the quenching and enhancing capabilities of a range of metal ions. Unlike the energy transfers observed previously, energy transfers between this reported MOF and the guest molecules are not simple π electron interactions or hydrogen-bonding interactions. These interactions, rather, exhibit ligand-to-metal energy transfer. The MOF was constructed to have multiple Lewis basic sites which allowed for metal complexes to be formed as metal ions flowed into the framework. Expectedly, the different metal ions had different effects on the luminescence of the MOF. For example, Zn^{2+}

enhanced the emission of the MOF while Fe^{3+} had a remarkable quenching effect. Almost instantly with the addition of Fe^{3+} ions there was a quenching of the light. The sensitivity to Fe^{3+} was quite extraordinary—a concentration of Fe^{3+} of just 0.01 M was enough to quench the emission almost maximally.[17]

Not all spectrophotometric methods involve measuring the quenching or enhancement of a particular wavelength. In some cases, we observe a fluorescence shift in the visible light range.[16] Shustova, et al. reported two ammonia-sensing MOFs that demonstrated a shift in emitted wavelength upon the uptake of ammonia based on temperature. In one of their reported MOFs, an increase in the temperature caused a longer wavelength of light to emit, but in the other reported ammonia-sensing MOF, the opposite effect occurred. Determining the cause of this wavelength shift was difficult, but the proposed mechanism of the wavelength shift is through direct binding of the ammonia to the exposed metal sites within the framework, similar to the ligand-to-metal energy transfer mechanism reported in Tang's paper.[16,17]

A downside to the reported chemical sensing powers of MOFs is that using these chemical sensing powers is unlike other wet chemical methods: it is merely qualitative. It is easy to see this quenching or wavelength shift even to the naked eye, so it is by no means useless as a qualitative analytical tool in a situation where instruments are unavailable, but if the need to quantify anything by the use of MOFs arises, instrumentation must be employed. A positive to this is, however, that the instrumentation and methods used in conjunction with MOFs are widely accessible and well-known. This combined with the current limits of detection of basic spectrophotometry means that quantifying the difference in intensity of a simple emission is actually quite easy. MOFs are clearly useful in this area of qualitative chemical sensing and instrument-assisted quantitative analysis as well as gas adsorption, but advancements in the

discovery of drug delivery has been slow to gain ground; however, some work has indeed been carried out to explore employing MOFs as drug carriers for deliberate delivery of medicine.

Drug Delivery

It has been well-established in the literature that MOFs work well as chemical sensors that are highly sensitive and incredibly selective, and it is also clear that MOFs are excellent at storing gases reversibly, but a new area being explored in the use of these compounds is drug delivery; many have speculated that the reversibility of adsorption could be useful in finding new ways to deliver drugs in the body. In 2007, for the first time ever, a MOF was reported that exhibited promising uses in a controlled drug delivery.[20] Among the many reported MOFs, some have been flexible; their pore sizes adjust slightly upon the uptake of a guest. Horcajada, et al. studied this effect and aspired to use it for advantageous ibuprofen delivery. Depending on the polarity of the solvent used, ibuprofen uptake was strongly affected within the framework. A final 3:1 by weight ibuprofen-to-material ratio was achieved with hexane, which happened to correspond to the maximum solubility of ibuprofen in hexane.[20] Horcajada, et al. also report an optimal adsorption time of 3 days to achieve any kind of reasonable adsorption amount. The experimental section mimicking the delivery of a drug into the human body was quite simple. They placed the fully adsorbed ibuprofen-incorporated MOF in a simulated body fluid, whose composition was similar to that of human blood plasma, at 37° C, stirring continuously. They reported a delivery time of three weeks and found the total concentration of ibuprofen delivered by HPLC methods.[20] The amount of ibuprofen in the MOF was known, as was the amount of the simulated body fluid, so the amount of ibuprofen released was easily calculated from the HPLC data, and the concentration of the stopping point was also found by simple calculation of the maximum ibuprofen concentration possible in that system, which is simply the moles of

ibuprofen adsorbed by the MOF divided by the volume of the simulated body fluid. The calculated kinetics of the delivery of the ibuprofen into the simulated body fluid was zero-order, which is unusual for drug delivery, but shows potential for great amounts of control and increased patient comfort.[20]

Opinion Section

Upon reading through much of the literature on the subject of metal-organic frameworks, I predict that in the next decade, the growth of knowledge of these compounds will lead to some fairly helpful scientific discoveries, potentially groundbreaking ones. What I hope for, mainly, is the synthesis of an MOF that will store CO_2 and H_2 in large amounts, but whose adsorption conditions will not be so extreme. Presently, we have found good MOF candidates for storage of both of these compounds, but we have yet to find anything that is feasible to apply industrially or commercially due to the enormous pressures required to make the most of the free volume of these frameworks. Overcoming the obstacle of the enormous pressures required to maximize the adsorption would be beneficial because we are releasing too much CO_2 into the atmosphere currently, so finding a way to trap the CO_2 reversibly on an industrial scale could legitimately reduce emissions of CO_2 without much additional effort required on the part of the factories involved. If we could create a MOF that can reversibly adsorb CO_2 with great fervor at ambient temperatures and pressures, the synthesis of that MOF would be considered groundbreaking in my eyes since CO_2 emission is such an issue. Unfortunately, it seems unlikely that this will be achieved. In the realm of MOF-based chemical sensing, I anticipate no slowing down. Most of the articles referenced in this paper were in this realm of MOF uses. This is likely because the types of detectable compounds by these MOFs are either toxic, explosive, or both. I do not predict that there will be groundbreaking discoveries in this realm; though great selectivity and

sensitivity has been demonstrated, there is not much more that can be done with the sensing of small molecules. Finally, regarding drug delivery, I did not delve deeply into papers reporting the capabilities of MOFs, but recently I have seen some articles that do involve MOF drug delivery appear on the internet. I anticipate that this aspect of MOFs will continue to be studied and eventually a helpful catalogue of viable drug delivery candidates will be created based on the family of drugs needing delivered, but considering the apparent slow drug delivery reported, I expect that there will be a particularly narrow use of MOFs in medicine.

Conclusion

Metal-organic frameworks certainly exhibit a wide range of uses and can exhibit high selectivity for the guests they hold and the materials which they sense. Based on the data from the articles cited in this paper, it is clear to see that the selectivity of the material largely depends on the linking molecules involved due to the electron environment they create.[13,19] In general, chemical sensor MOFs are effective because of their conjugated π-electron-rich systems which provide the necessary absorbance and emission profiles to allow for easily quantifiable luminescence.[10–15,19] MOFs also clearly demonstrate high gas adsorption capabilities, but show less selectivity for adsorption of compounds than for the sensing of compounds, as several of the reported MOFs were able to trap different gases with similar effectiveness.[1,3–8,10] More specificity is required to create any form of a chemical sensor, but that is not to say that deliberate choice of linker molecules cannot greatly affect the adsorption properties of a MOF, since these properties largely depend on the surface area which is greatly influenced by, but not necessarily directly related to, the chosen linking molecule of the MOF. Of course, the size of the pore and electron environment can allow for larger molecules, as well, such as ibuprofen to be adsorbed into the molecule, rather than just small gas molecules.[20]

There are, indeed, limits to all these areas of MOF usage. Particularly apparent are the limits to gas storage in MOFs. These limits are related to the trends observed on the adsorption of H_2 by Frost's group.[6] Presently, there simply is no compound with a high enough heat of adsorption to adsorb any useful amount of gas at ambient pressures and temperatures, and it is likely that such a compound may never be discovered, so for now, further research must be carried out to take advantage of the capabilities of gas adsorption at intermediate pressures by synthesizing MOFs with even higher apparent surface areas. Regarding the limits of the chemical sensing powers of these frameworks, there is not much to discuss. MOFs have shown a wide range of chemical sensing power with a particular niche in the detection of aromatic compounds including explosives.[10–12,14,18] A potential downside to this is that not all chemical sensing discovered will be entirely practical for explosive detection based on the necessary methods to test for the detectable compounds; it is not the first thing on someone's mind to perform a complex adsorption procedure for a potentially life-threatening compound, only to be able to qualify and quantify the material after a long period of time, which is currently what would be required in the event of a legitimate MOF-based chemical test for a nitroexplosive compound, for example. Finally, a downside to the drug delivery capabilities shown by MOFs is that there has yet to be a great discovery in published articles in this realm. However, the reported information on the uptake and release of ibuprofen is promising to show meaningful advancements in slow-paced drug delivery.[20]

Overall, MOFs provide a plethora of uses. With the wide range of possible MOFs and the possible variations on structure, it is clear that this is a special class of highly porous material that will prove useful in the future. Because of the possible applications to gas storage, chemical sensing, and drug delivery, MOFs have several different avenues to improve the lives of many

potentially through removal of harmful gases such as CO_2 from the air we breathe to sensing

qualitatively the presence of potentially dangerous chemicals in a lab setting to delivering hard-

to-incorporate medicines in a slow, controlled manner to those who need them.

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