Second Generation MOFs for Hydrogen Storage:
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ABSTRACT

This final technical report summarizes work exploring strategies to generate second generation metal organic frameworks (MOFs). These strategies were a) the formation of interpenetrated frameworks and b) the generation of coordinatively unsaturated metal centers (open metal sites). In the first phase of the project the effectiveness of these strategies was evaluated experimentally by measuring the saturation hydrogen uptake at high pressure and low temperature of 14 MOFs. The results of these studies demonstrated that surface area is the most useful parameter that correlates with ultimate hydrogen capacity. The strategy of interpenetration has so far failed to produce MOFs with high surface areas and therefore high saturation capacities for hydrogen have not been achieved. The incorporation of coordinatively unsaturated metal centers, however, is a promising strategy that allows higher heats of H_2 adsorption to be realized without compromising surface area. Based on these initial findings, research efforts in phase two have concentrated on the discovery of new ultrahigh surface area materials with metal centers capable of supporting coordinative unsaturation without structural collapse. One approach has been the synthesis of new organic linkers that have more exposed edges, which is a factor that contributes to increasing surface area, at least when considering subunits of graphene sheets. Another strategy has been to synthesize MOFs with reduced symmetry linkers in order to generate structure types that are less likely to interpenetrate. Successful implementation of these strategies has resulted in the synthesis of 7 new compounds one of which is the highest surface area Cu based MOF reported to date.

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EXECUTIVE SUMMARY

Renewable energy in the United States is an important national goal for achieving energy independence and environmentally sustainable technologies. The research program undertaken focuses on the design and production of porous materials that are useful in the storage of hydrogen. In particular, porous metal-organic frameworks (MOFs) are being designed to increase the weight percent of hydrogen held in a material at reasonably safe pressures for use of hydrogen as a fuel.

The specific objectives of the program are centered on increasing the gravimetric uptake capacity of MOFs. The project seeks to discover materials with 9% gravimetric H_2 uptake. At the outset of this project there were a number of strategies put forth to achieve high levels of hydrogen storage in MOFs. These included optimization of pore size and adsorption energy by linker modification, impregnation, catenation, and the inclusion of open metal sites and lighter metals.[1] These criteria were proposed based on either reasonable assumptions or available low pressure cryogenic hydrogen sorption data. During the first project period we have been able to evaluate several of the approaches experimentally using high pressure hydrogen uptake measurements under conditions leading to saturation binding behavior. The results of these studies clearly indicate that results obtained under low pressure hydrogen uptake conditions, conditions which comprise the vast majority of literature reports, often have no relevance for high capacity applications such as hydrogen storage for mobile applications.

In the first phase of this project we investigated the saturation hydrogen uptake of six MOF materials and these data combined with the earlier work on MOF-177 comprise a seminal paper which demonstrates that surface area of a MOF is the most critical parameter in determining ultimate hydrogen uptake.[2] The MOFs chosen represent a subset of well characterized materials that exhibit some of the highest surface areas experimentally determined to date. These materials vary in chemical functionality, metrics of the link, and the nature of the secondary building units (SBU, which is the metal oxide connector that assembles the organic linkers). The MOF structures were derived from noninterpenetrated nets, with the exception of the doubly interpenetrated IRMOF-11, and three distinct SBUs. Crystalline samples of all the MOFs were prepared and activated prior to sorption measurements according to optimized procedures. Prior to H_2 sorption studies, apparent surface areas of the activated materials were calculated from the adsorption branches of the N_2 isotherms obtained at 77 K. These results have completely refocused our efforts on the quest for materials with ultrahigh surface areas to achieve 9 wt% hydrogen storage materials.

In phase II of the project, we implemented two new strategies that would decrease the chances of forming interpenetrated structures which has shown to reduce surface area for H_2 binding. These strategies are the use of reduced symmetry linkers and the use of linkers with more exposed edges. Coupled with the strategy of including open-metal sites, new materials with high surface areas have been synthesized that are not interpenetrated. A mesoporous Cu-based MOF with the highest surface area measured to date has been produced which shows a saturation H_2 uptake of ~ 6 wt%. Such control of the porosity in these materials still remains a significant challenge.

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REPORT DETAILS

Experimental methods:

I. Synthesis and activation of MOFs

Whereas less than a hundred milligrams is sufficient for characterization by X-ray diffraction techniques such as powder XRD, single crystal XRD; spectroscopic methods such as, IR, Raman, and UV/Vis; and thermal methods such as TGA, significantly larger quantities of phase pure materials are needed for obtaining reliable hydrogen adsorption measurements. Initial optimizations of the synthesis conditions were achieved in 20-mL scintillation vials under solvothermal conditions. The solvothermal method is the synthetic method of choice because it is carried out at relatively mild temperatures (typically between 85-125 °C) facilitating the dissolution of sparingly soluble starting materials at room temperature and dramatically increasing the rate of reaction compared to diffusion methods where crystals are typically grown. Scale-up of the reactions were accomplished in 1 L vessels once conditions were identified that produced good to moderate yields of high-quality single crystals. Detailed synthetic procedures for some of the MOFs used in phase one were published in 2006.[3]

Just as important as synthesizing phase pure materials, is the activation procedure of the MOFs which serves to remove all occluded guests from the surface and pore walls of the material. Both physisorbed and chemisorbed species may be present and must be removed to prevent pore blockage while maintaining the integrity of the framework. After screening numerous combinations of solvents and heating conditions, it was found that for a significant number of MOFs, the highest surface area materials were achieved by first allowing the as synthesized materials to soak in chloroform for an extended period of time. This allows the formamide guest molecules that are in the pores, as well as other possible decomposition products formed during the reaction, to be exchanged with chloroform molecules from the bulk solution. After a few iterations, the chloroform can usually be removed under vacuum at room temperature yielding the fully porous material. For other MOFs, depending on the nature of the adsorbed species, a programmed temperature ramp may be necessary to remove more strongly interacting guests. For example, solvent molecules that are chemisorbed to framework metals need to be removed by slowly heating above 100 °C.

II. Characterization of new MOFs

Characterization of new linkers and the corresponding MOFs were carried out using standard techniques. The linkers and intermediates were characterized by solution NMR spectroscopy on a Varian Mercury NMR spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C). Single crystal XRD studies were carried out on a Rigaku R-Axis Spider diffractometer using graphite-monochromatized Cu Kα radiation (λ = 1.54187 Å) equipped with an Oxford Cryosystems Cryostream cooler for low temperature collections. IR absorption spectra were obtained from KBr pellets on a Nicolet Avatar 360 FT-IR spectrometer. Raman spectra were collected on a Renishaw inVia Raman microscope. Thermal analyses were performed on a TA Instruments Q50 instrument from room temperature to 600 °C using a heating rate of 5 °C/min under nitrogen.

III. Sorption Measurements

1. Apparent surface area measurements from N_2 adsorption isotherms

N_2 adsorption/desorption isotherms were measured volumetrically at 77 K in the range $1.00 \times 10^{-3} \leq p/p^o \leq 1.00$ with an Autosorb-1C outfitted with the micropore option by Quantachrome Instruments (Boynton Beach, Florida USA), running version 1.2 of the ASWin software package. Ultra-high purity He (99.999%, for void volume determination) and N_2 (99.999%) were purchased from Cryogenic Gasses and used as received. All N_2 isotherms were measured using samples (typically 8-14 mg) that were activated *ex situ*: that is, other than the initial evacuation of the sample in the sample cell for sorption measurements to commence, no other treatment of the sample was performed. This was done to ensure that the nature of the material used in the surface area measurements was the same as that being used in the high pressure H_2 sorption experiments. Typically, 1 g of the MOF material was activated and thereafter was handled and stored using standard Schlenk techniques. For all the Zn_4O based MOFs, exposure to ambient atmosphere did not degrade the material substantially and thus these materials could be handled in air for short periods of time. However, for both MOF-74 and HKUST-1, considerable decreases in surface were observed after only a few minutes of exposure to air. These samples were thus loaded into sample cells in an inert atmosphere (N_2) glovebox.

Type I isotherms were observed for some of the MOFs as previously described.[4] Strictly speaking, the mechanism of adsorption in microporous materials (pores < 2 nm) is pore-filling as opposed to mono-multi layer adsorption. Therefore, application of the Langmuir or Brunauer, Emmett, Teller (BET) methods only gives rise to apparent surface areas and are reported in order to facilitate comparisons with other materials. The linear region of the N_2 isotherm used for the BET plot was $0.02 \leq p/p^o \leq 0.1$, and for the Langmuir plot the range was $0.02 \leq p/p^o \leq 0.35$.

For purposes of screening and optimization of activation procedures, a Nova 4200e from Quantachrome Instruments capable of analyzing 4-samples simultaneous was used to evaluate surface areas from N_2 adsorption isotherms.

2. High pressure H_2 sorption

Equilibrium H_2 adsorption/desorption isotherms were measured using the static volumetric method in an HPA-100 (High Pressure Analyzer) from the VTI Corporation (Hialeah, FL, USA). The system is equipped with two electronic Bourdon gauge-type transducers (Mensor) that cover the range 0 - 1500 psi (accuracy 0.010% full scale): one is used to measure the pressure in the dosing manifold, while the other monitors the pressure in the sample cell. The working temperature of the manifold is kept at 45 °C by heating the manifold compartment. Vacuum is provided by a TSH 071 E turbomolecular pumping station (Pfeiffer) capable of reaching pressures of $< 1 \times 10^{-6}$ mbar. The sample cell is a 2-piece assembly that consists of a sample chamber (~ 4 mL) and a high pressure bellows valve. The two are connected via ¼" VCR fittings and the materials of construction are all 316 stainless steel. Connection to the system is achieved by a ¼" VCO fitting. Two ports are available: one for outgassing the sample and an analysis port, outfitted to hold either a thermostated recirculating bath or a small cryogenic dewar. Ultra-high purity He (99.999%) and H_2 (99.999%) were purchased from Cryogenic Gasses and used as received. In a typical experiment 300–500 mg of an *ex situ* activated sample was charged into the cell and evacuated at room temperature to 10^{-6} mbar prior to sorption experiments.

WARNING: *A hydrogen safety plan should be put in place prior to performing any experiments with hydrogen under any appreciable pressure. Hydrogen gas is highly flammable even at low concentrations and thus care must be taken when working with H_2 at high pressures. Efficient ventilation of the area where the experiments are carried out is necessary and a hydrogen detector should be employed.*
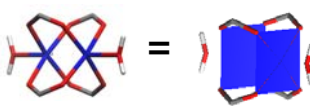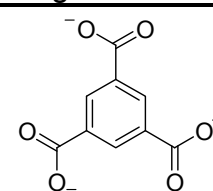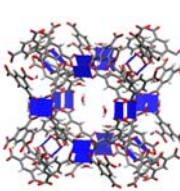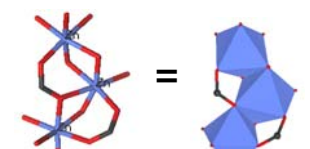
Results and discussion:
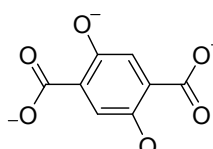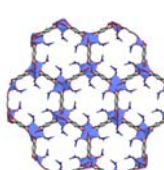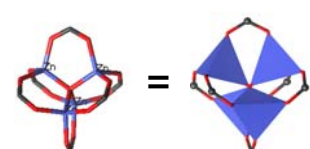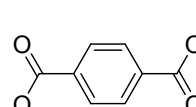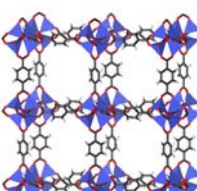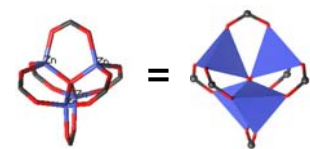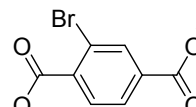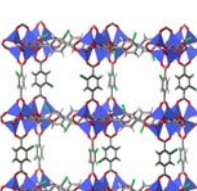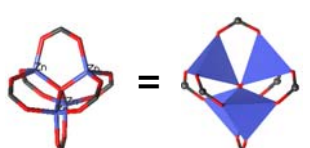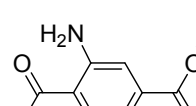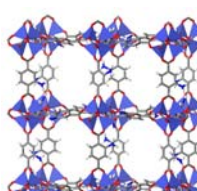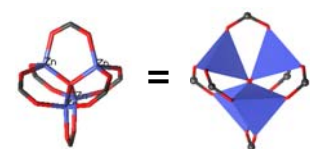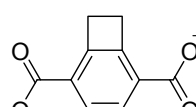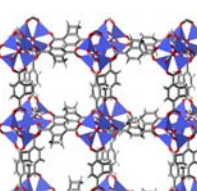
Our proposed approach, which was executed during the first project period, was to exploit existing MOF materials and use readily available hydrogen uptake data collected at cryogenic temperature up to one atmosphere. The strategy of conducting low temperature measurements of hydrogen uptake was employed for several of the types of MOFs we proposed and these results were recently published.[3] The MOFs investigated include HKUST-1, MOF-74, IRMOF-2, IRMOF-3, IRMOF-6, IRMOF-9, IRMOF-13, and IRMOF-20 in addition to IRMOF-1 (also referred to as MOF-5) and are shown in Table 1.
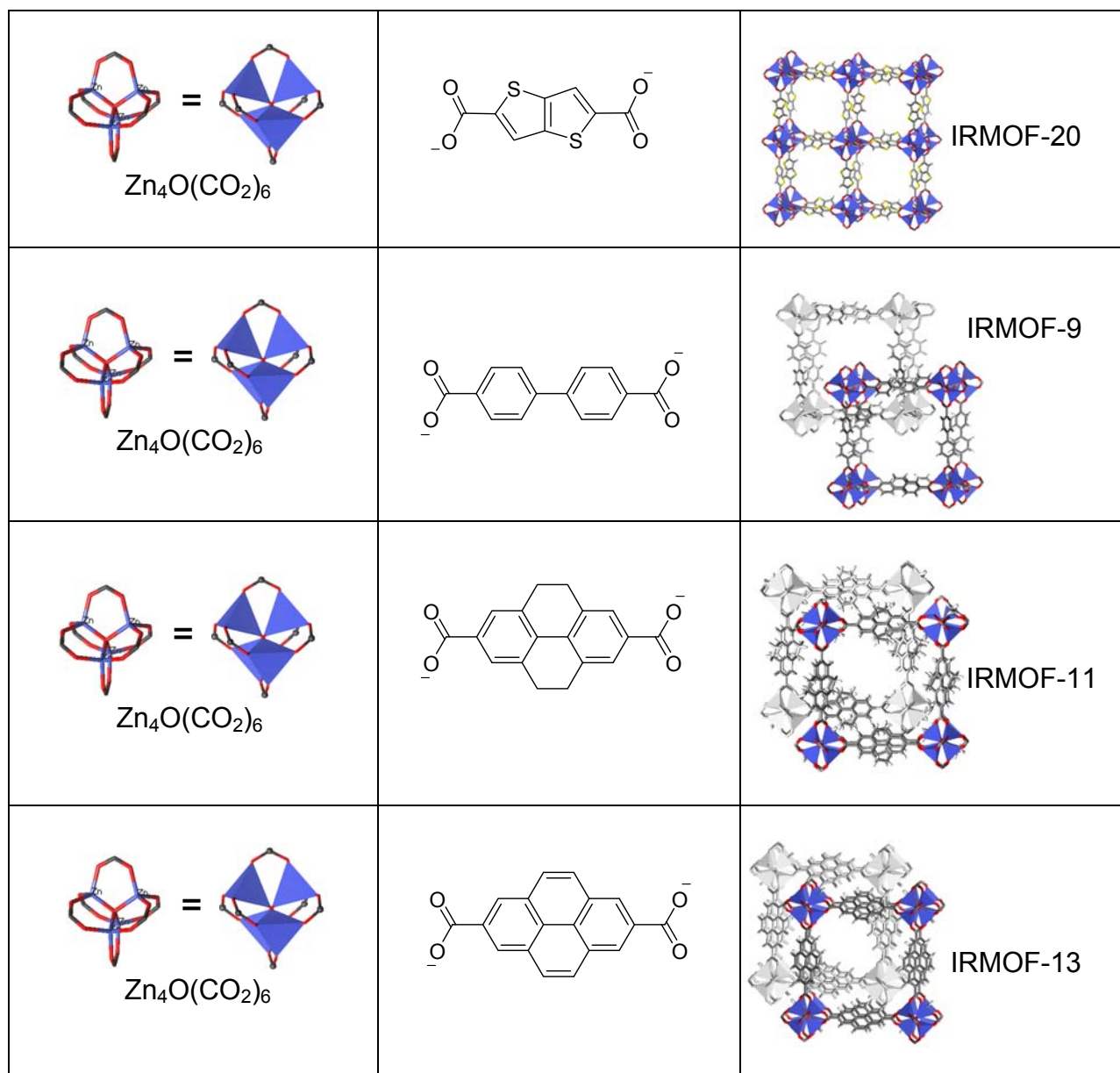
HKUST-1 is a 3-dimensional cubic MOF composed of aquated dinuclear Cu(II) square paddlewheel SBUs that are linked together by benzene-1,3,5-tricarboxylate. The structure is analogous to the rock salt (NaCl) structure where the pores are constructed of mutually perpendicular channels resulting in cavities that are 13 and 11 Å in diameter. The chemical environments of the pores are quite different; the larger pore is lined with the faces of 12 paddlewheel units in which the axial water ligands are pointed into the pore, whereas the smaller pore is lined by the edges of 12 paddlewheels.

MOF-74 is constructed from inorganic SBUs derived from infinite 3_1 (or 3_2) helical rods of composition $Zn_3[(O)_3(CO_2)_3]$ that are bridged by the carboxylate and phenolate oxygens of 2,5-dioxidobenzene-1,4-dicarboxylate. These rods pack in a parallel fashion, forming a hexagonal framework with 1-dimensional hexagonal channels. Removal of the bound solvent molecule (DMF in this case) gives a calculated channel diameter of 10.8 Å.

The IRMOFs-1, 2, 3, 6, and 20 constitute a series of 3-dimensional simple cubic MOFs that are composed of octahedral $Zn_4O(CO_2R)_6$ units that are connected together by linear organic linkers. These MOFs assemble into the same net allowing an evaluation of the influence of the electronic character of the organic linker on hydrogen adsorption. Compared to IRMOF-1, IRMOF-2 is 2-bromo substituted, IRMOF-3 is 2-amino substituted, IRMOF-6 contains a cyclobutenyl ring, while IRMOF-20 is synthesized from thieno[3,2-*b*]thiophene-2,5-dicarboxylate, a sulfur rich heteroaromatic linker. Similarly the IRMOFs-9, 11, and 13 assemble into simple cubic networks, but due to the extended length of the organic unit, two frameworks interpenetrate; that is, the vertices of one framework occupy the void space of another. The consequence of this catenation is the reduction of void space of the pore which should result in a higher binding affinity for hydrogen. In all cases, the crystal structures of these materials show that the catenation in these frameworks can be best described as interwoven, which is seen by the close proximity of one vertex of one framework to the vertex of another. From crystallographic data, pore sizes vary from apertures as small as 7.5 Å (IRMOF-2) to pore diameters as large as 18.6 Å (IRMOF-1).[4]

Table 1. Inorganic SBU, organic linker, and the MOF structure.

Inorganic SBU	Organic Linker	MOF structure[a]
$(Cu_2(CO_2)_4)$		HKUST-1
$Zn_3[(O)_3(CO_2)_3]$		MOF-74
$Zn_4O(CO_2)_6$		IRMOF-1
$Zn_4O(CO_2)_6$	Br	IRMOF-2
$Zn_4O(CO_2)_6$	H_2N	IRMOF-3
$Zn_4O(CO_2)_6$		IRMOF-6

Zn$_4$O(CO$_2$)$_6$		IRMOF-20
Zn$_4$O(CO$_2$)$_6$		IRMOF-9
Zn$_4$O(CO$_2$)$_6$		IRMOF-11
Zn$_4$O(CO$_2$)$_6$		IRMOF-13

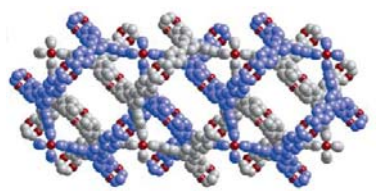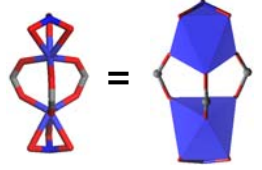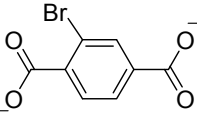[a]All structures have been determined by single crystal X-ray diffraction.
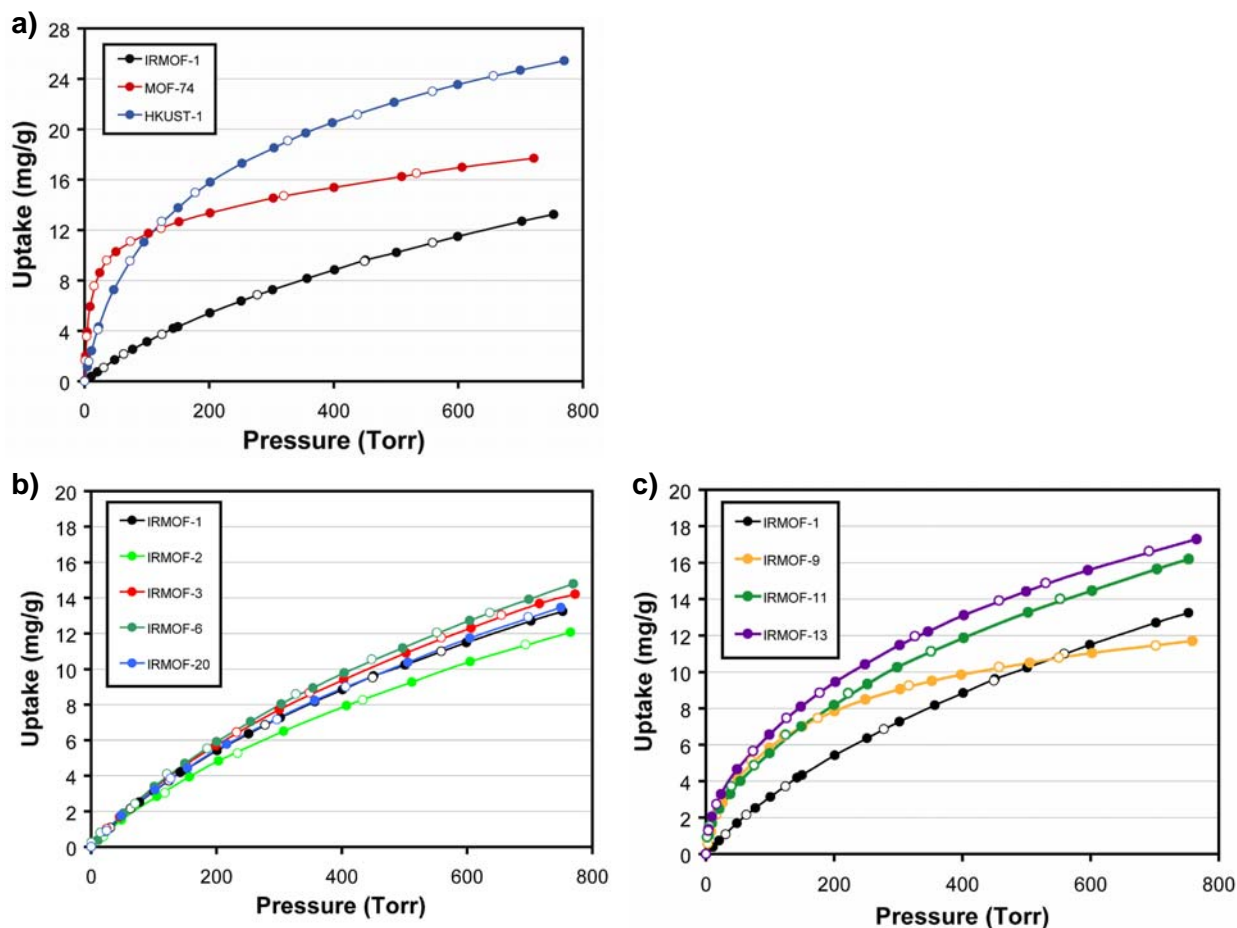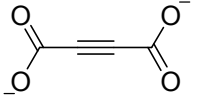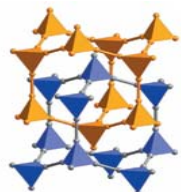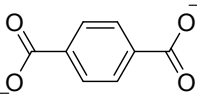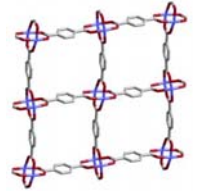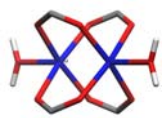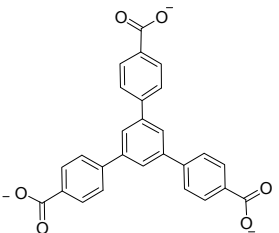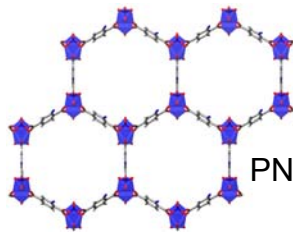
Figure 1.[3] Comparison of H$_2$ gravimetric capacities (mg/g) at 1 bar (760 Torr) and 77 K, categorized according to structure type. For comparison, the isotherm for IRMOF-1 is plotted on all three graphs. (a) MOFs with open metal sites available. (b) Simple cubic MOFs with different fuctionalized backbones. (c) Simple cubic MOFs that are doubly interpenetrated. Lines through the data are not fits to a model, but serve as guides to the eye. Filled circles denote adsorption and open circles desorption.

Figures 1a-c summarize the low pressure hydrogen capacity of the MOFs from Table 1. For comparison the isotherm for IRMOF-1 is plotted on all three graphs. It is clear from these data that H$_2$ saturation uptake capacity has not been achieved for any of the MOFs examined. From these data it can be seen that both MOF-74 and HKUST-1 take up more H$_2$ compared to the IRMOFs (Figure 1a). The very steep initial slopes indicate that there is a strong interaction with H$_2$ compared the IRMOFs, especially for MOF-74 where the slope of the isotherm is rather steep up to 50 Torr. Figure 1b shows that uptake capacity is not so sensitive to the functional group incorporated into the framework as the isotherms are clustered around 12 to 15 mg/g. Catenation, on the other hand, appears to improve uptake in this range (Figure 1c), and has a more dramatic effect on capacity as demonstrated by the steeper rise compared to IRMOF-1 below 500 Torr, but then appears

to plateau whereas IRMOF-1 continues to increase. However both IRMOF-11 and -13 show a steeper initial slope as well a constant increase up to 1 bar.

In addition to these MOFs with published hydrogen uptake data, we have examined MOF-31, MOF-2, MOF-14, and PNMOF-3[5] (Table 2). Taken together with the established materials, these represent a breath of structure types and include MOFs with open metal sites (HKUST-1 and MOF-74), interpenetration (IRMOF-9, IRMOF-11, IRMOF-13, and MOF-31), and acetylenic functionality (MOF-31). Both MOF-31 and PNMOF-3 were determined to be non-porous after solvent removal/activation and were not further examined. The remaining compounds were considered for scaled-up production under Task 2.

Table 2. Inorganic SBU, organic linker, and the MOF structure.

Inorganic SBU	Organic Linker	MOF structure[a]
  ZnO_4		 MOF-31
  ($Zn_2(CO_2)_4$)		 MOF-2
  ($Cu_2(CO_2)_4$)		 MOF-14
  $Zn_2(CO_2)_3(NO_3)_2$		 PNMOF-3

[a]All structures have been determined by single crystal X-ray diffraction.

Ultimately HKUST-1, MOF-74 and IRMOFs -1, 2, 3, 6, 8, 9, 11, 20, and MOF-2 were made on a scale of 1 gram or more. This sample quantity is sufficient to carry out hydrogen

uptake measurements with an uncertainty of less than 1.0 wt%. Activation procedures for each of these materials were optimized in order to obtain the highest N_2 determined surface areas. Each of these compounds was subjected to detailed analysis by volumetric gas sorption at 77 K at pressures sufficiently high to saturate all binding sites. The prediction from the data in Figure 1 was that coordinatively unsaturated metal centers (open metal sites) and catenation should both play a very important role in maximizing hydrogen storage capacities.
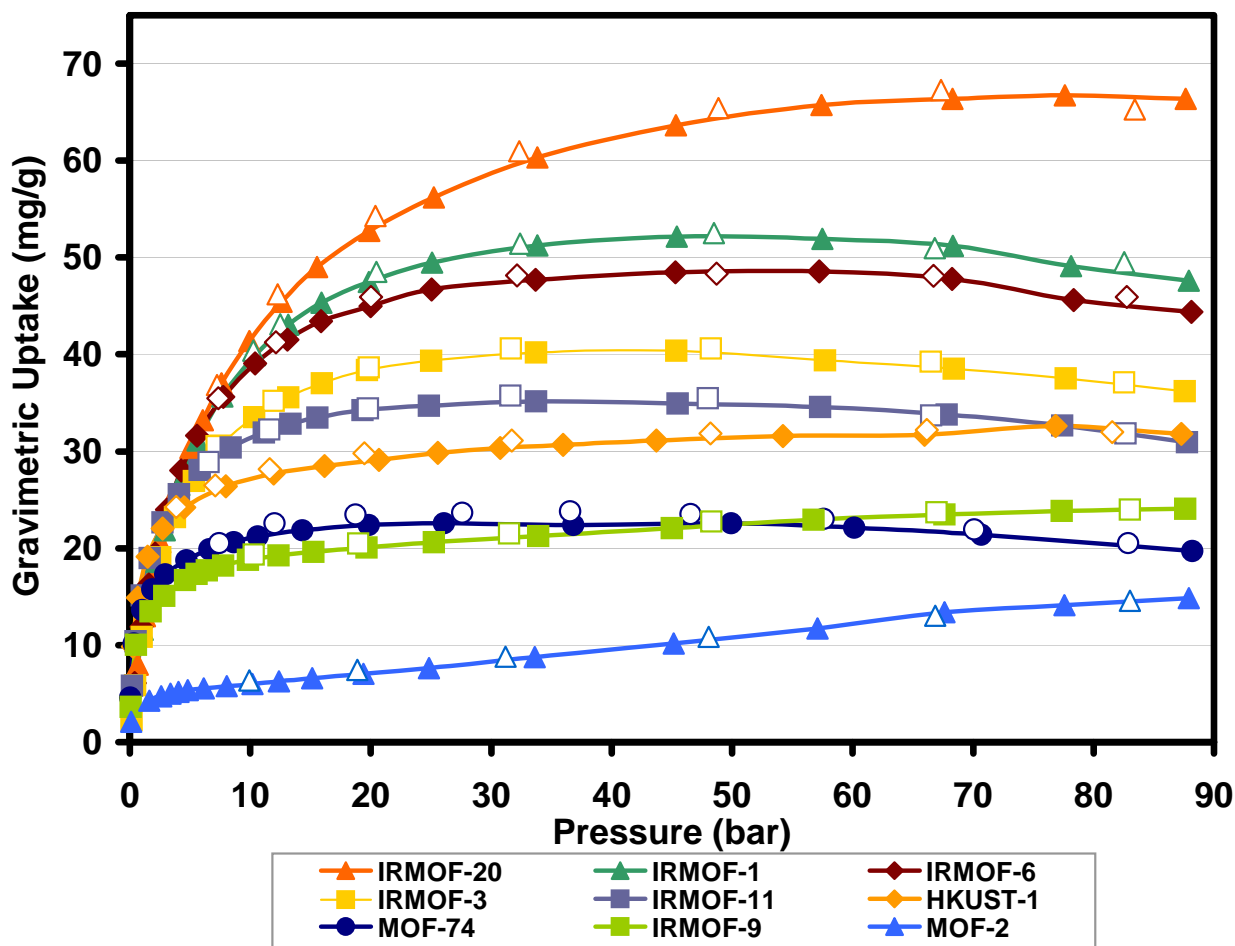
Figure 2. High-pressure H_2 isotherms for selected MOFs at 77 K in gravimetric units (mg/g). Lines through the data are not fits to a model, but serve as guides to the eye. Filled markers denote adsorption and open markers denote desorption.

Figure 2 shows the resulting H_2 sorption isotherms up to 90 bar at 77 K, where saturation binding of H_2 is achieved. The isotherms do not show significant hysteresis, consistent with physisorption of supercritical H_2. The saturation uptakes vary widely: for MOF-2 the uptake at saturation (88 bar) is 1.4 wt % and 3.5 wt % for IRMOF-11 (34 bar), whereas for IRMOF-20 saturation is reached between approximately 70 and 80 bar, giving a H_2 uptake of 6.7 wt %. A plot of gravimetric uptake as a function of apparent surface area, applying either the Langmuir or BET models, reveals a nearly linear correspondence

(Figure 3). This result stands in stark contrast to those obtained at low pressures where MOF-74, HKUST-1 and IRMOFs-11 and -13, the lowest surface area materials, showed maximal uptake. This difference may arise from binding to relatively higher affinity coordinatively unsaturated metal centers (present in MOF-74 and HKUST-1) or to constricted pores in IRMOF-11 and -13. However, once these high affinity sites are occupied, there is no more space for extra H_2 molecules to dock. On the other hand, IRMOFs -1 and -20 show approximately the same affinity for H_2 (their low pressure isotherms almost overlay in Figure 1b), but due to the accessibility of their pores and extremely high surface areas, much more H_2 can be packed into them.
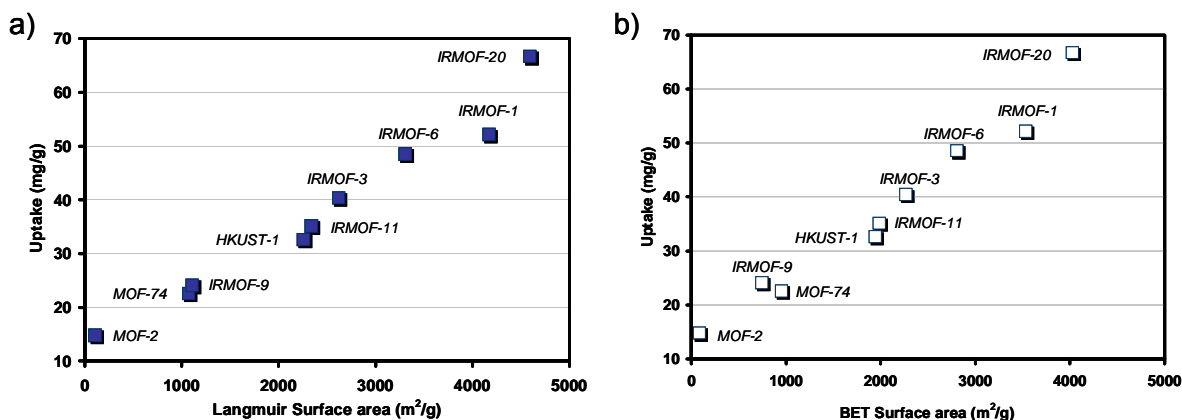
Figure 3. Saturation H_2 uptake plotted against a) apparent Langmuir surface areas, b) apparent BET surface areas.

Based on these findings in the first phase of the program, a strong correlation between surface area of a MOF and saturation hydrogen uptake behavior was established for a set of 9 MOFs. This is a sufficient sample size to strongly suggest that pursuing high surface area materials is the best route to achieve 9 wt% hydrogen storage materials. Moreover, interpenetration should be avoided because it generally leads to lower surface areas. The strategy of using coordinatively unsaturated metal centers, however, is desirable because of the increased interaction between the MOF and hydrogen at low pressures. MOFs are the highest surface area materials currently known and it is likely that their limits are far from being explored. Therefore, efforts in the second phase of this project have been completely refocused to synthesize materials with ultrahigh surface areas that incorporate the structural attributes of the higher affinity MOFs to achieve 9 wt % hydrogen storage capacities.

One strategy that we have developed in the course of this project is the use of reduced symmetry linkers to form MOFs where interpenetration may not be so favored. This concept is illustrated in Figure 4. In Figure 4a the carboxylic acid groups are all related by symmetry and are chemically equivalent, whereas in Figure 4b, though the carboxylic acid groups are all of similar reactivity, one carboxylic acid group cannot be generated by symmetry from the others. A total of four new linkers have been designed and successfully synthesized.
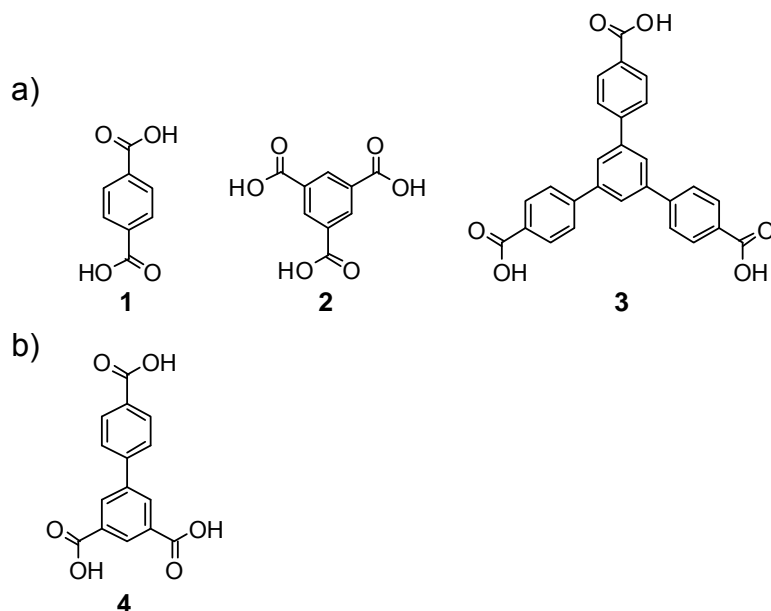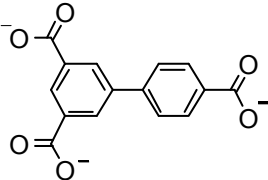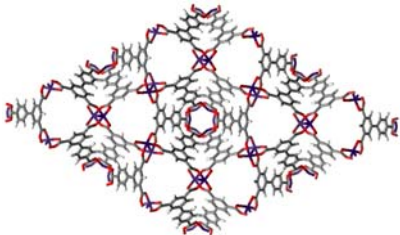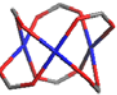
Figure 4. a) High symmetry linkers-- all carboxylic acid groups are equivalent by symmetry. b) A reduced symmetry linkers-- not all carboxylic acid groups are equivalent by symmetry.

Screening a number of different metals identified Cu(II) as the most promising metal ion for MOF formation. Three out of the four linkers produced new materials. Single crystal X-ray studies revealed these structures to be highly porous and are shown in Table 3. In general the expected $Cu_2(CO_2R)_4$, paddlewheel motif is the SBU generated in these reactions. However, this may not always be the case as demonstrated by the structure formed from linker **4**. Here, a new MOF is generated wherein two distinct types of carboxylate clusters are formed, a rare occurrence for linkers where the coordinating functionalities are symmetrically disposed. On the ring containing the meta-carboxylates, Cu(II) paddlewheel clusters are formed whereas on the ring with the single carboxylate, the rare trinuclear $Cu_3(CO_2R)_6$ cluster is formed (Table 3, first entry).[6] With tricarboxylic acid **6**, two different MOFs are generated which differ in the manner in which carboxyphenyl groups come together to assemble the Cu(II) paddlewheel and thus can be considered isomers. In addition, under the appropriate reaction conditions, UMCM-152 transform to UMCM-153 implying that UMCM-153 is the thermodynamic product. Due to the reduced symmetry of linker **6**, new networks are accessed. Importantly, all the new MOFs synthesized to date are non-interpenetrated structures with calculated surfaces areas that range from 3000 to 5000 m^2/g. These new materials have been given the designation UMCM which stands for University of Michigan Crystalline Material.

Table 3. Inorganic SBU, organic linker, and the MOF structure.

Inorganic SBU	Organic Linker	MOF structure
$(Cu_2(CO_2)_4)$ $(Cu_3(CO_2)_6)$		UMCM-150
$(Cu_2(CO_2)_4)$	Linker **5**	UMCM-151
$(Cu_2(CO_2)_4)$	Linker **6**	UMCM-152
$(Cu_2(CO_2)_4)$	Linker **6**	UMCM-153

Another approach for the discovery of new ultrahigh surface area materials has been to synthesize new organic carboxylic acid linkers with more exposed edges. This notion has been tested by calculations on subunits of graphene sheets that show it to be a significant factor that contributes to increasing surface area (Figure 5).[7] A selection of these linkers is shown in Figure 6.
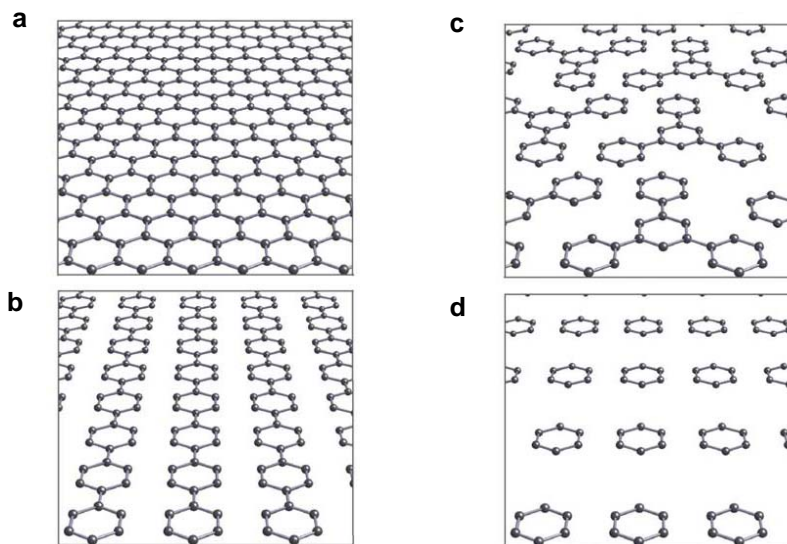
Figure 5.[7] The surface area of graphite fragments. **a**) A graphene sheet extracted from the graphite structure has a Connolly surface area of 2,965 m^2/g when calculated in Cerius2. **b**) A series of poly-p-linked six-membered rings can be extracted from that sheet, thus increasing the surface area to 5,683 m^2/g. **c**), Excision of six-membered rings 1,3,5-linked to a central ring raises the surface area to 6,200 m^2/b. **d**) The surface area reaches a maximum of 7,745 m^2/g when the graphene sheet is fully decomposed into isolated six-membered rings.
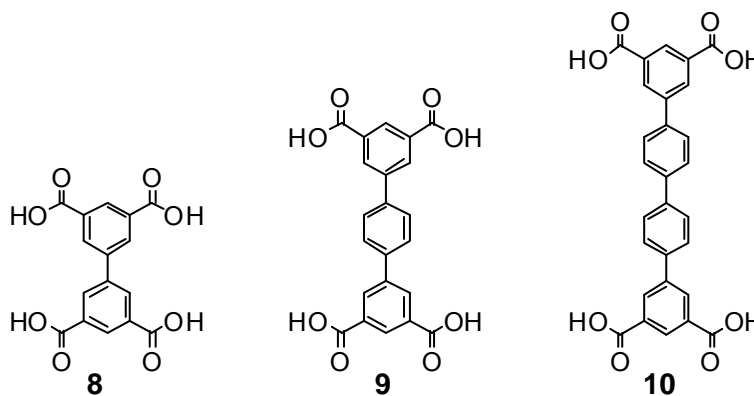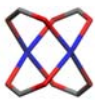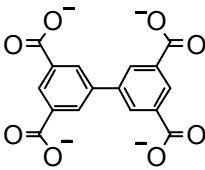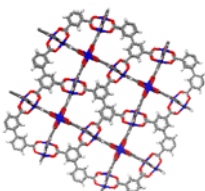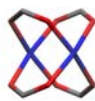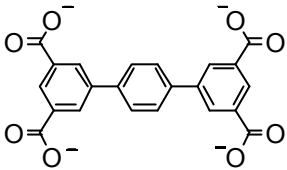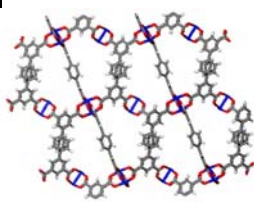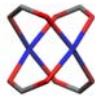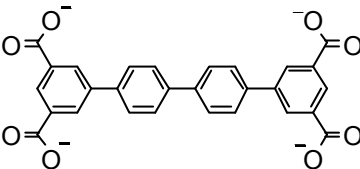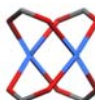

Figure 6. Linkers with more exposed edges.

MOFs derived from these linkers are shown in Table 4. In the presence of Cu(II) tetracarboxylic acids **8**, **9**,and **10** generate an isostructural series of MOFs that all have the same underlying topology, that of the nbo net. Increasing the number of benzene rings between the isophthalate groups leads to an increase in the Langmuir surface areas of these materials ranging from 1830 to 3669 m^2/g. Whereas crystalline MOFs were obtained with **8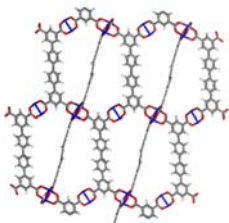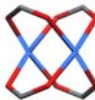**, **9**,and **10** with Cu(II), only crystalline materials were obtained when compounds **11** and **12** were combined with Zn(II) ions. UMCM-101 obtained with **11** is a 2D-sheet structure that was non-porous after activation while UMCM-102 obtained from **12** was a 1D channel

structure that had a surprisingly low surface area of less than 1000 m^2/g. The hexacarboxylic acid **14**, however, yielded the highly porous UMCM-300 in the presence of Cu(II) ions. Its Langmuir surface area is 3900 m^2/g, (3100 m^2/g BET) making it the highest surface area Cu-based MOF to date.

Table 4. Inorganic SBU, organic linker, and the MOF structure.

Inorganic SBU	Organic Linker	MOF structure[a]
$(Cu_2(CO_2)_4)$		MOF-505a
$(Cu_2(CO_2)_4)$		MOF-505b
$(Cu_2(CO_2)_4)$		MOF-505c
$(Zn_2(CO_2)_4)$	Linker **11**	UMCM-101
$(Zn_2(CO_2)_4)$	Linker **12**	UMCM-102
$(Cu_2(CO_2)_4)$	Linker **13**	UMCM-300

After suitable activation procedures were discovered for the MOFs shown in Tables 3 and 4, high pressure H_2 sorption isotherms at 77 K, were collected until saturation binding

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of H_2 was observed. Like the previous MOFs, the isotherms do not show significant hysteresis, consistent with physisorption of supercritical H_2. In Figure 7a is plotted the gravimetric saturation H_2 uptake as a function of apparent Langmuir surface area. An initial examination of the data reveals again that saturation uptake is a function of surface area. However, upon closer examination, a number of observations are worth comment. A number of new MOFs show capacities that appear to deviate from the previously determined trend line (Figure 7b). These compounds are mainly Cu(II) paddlewheel based materials, namely MOF-505a, -505b, and UMCM-150. In addition, UMCM-102, which is a Zn based material can be grouped with these materials since it is built up of Zn(II) paddlewheel SBUs. All these materials, when properly activated, should contain coordinatively unsaturated metal sites (the apical positions of the paddlewheels). Thus, for a given surface area, if a material has coordinatively unsaturated metal centers, a higher saturation uptake can be observed. Unfortunately, this does not explain the lower that expected uptakes observed with MOF-505c and UMCM-300. Both materials have ultra-high surface areas as well as coordinatively unsaturated metal centers. In fact, these materials are much more in-line with previous MOFs (Figure 7b). One feature common to these materials is very large pore size.
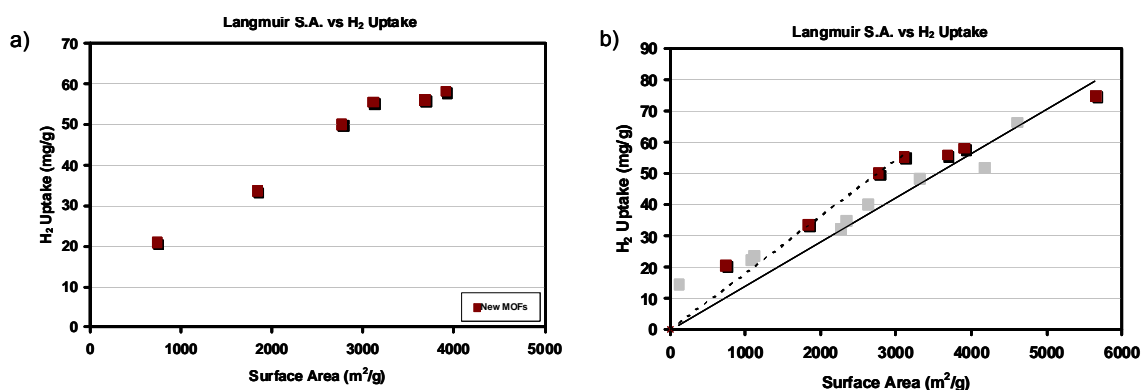

Figure 7. Saturation H_2 uptake plotted against Langmuir surface area, a) new MOFs produced in phase two of the project. b) Overlay of all MOFs measured.

Conclusion:

This work has investigated a number of strategies for achieving high H_2 uptakes. Although surface area is identified as the key parameter to maximize performance, other factors such as coordinately unsaturated metal sites exert considerable influence and likely will be needed in concert with ultrahigh surface area to achieve 9 wt % storage materials. A new strategy of employing reduced symmetry linkers as ligands to copper is promising because it seems to avoid interpenetration while maintaining coordinative unsaturation.

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LIST OF ACRONYMS AND ABBREVIATIONS
MOF = metal-organic framework
IRMOF = Isoreticular metal-organic framework
SBU = secondary building unit
DEF = Diethylformamide
DMF = Dimethylformamide
XRD = x-ray diffraction
IR = Infra-red
UV = ultraviolet
Vis = visible
TGA = thermal gravimetric analysis
BET = Brannaur-Emmett-Teller