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Covalent Triazine Frameworks Functionalized with N-Heterocyclic Carbenes for CO2 Capture and Device Fabrication

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Covalent Triazine Frameworks Functionalized with N-Heterocyclic Carbenes for CO₂ Capture and Device Fabrication

A thesis submitted in partial fulfillment of the requirements for the degree of Masters of Science in Chemistry

by

Chain Lee

2014
Here I describe the synthesis and characterization of a new Covalent Triazine Framework (CTF) with the potential to coordinatively link organometallic complexes inside the pores for enhanced carbon dioxide (CO$_2$) adsorption and for control of the electronic transport properties of the framework. An N-heterocyclic Carbene (NHC) precursor is synthesized and then used to construct a CTF through the trimerization of 1,3-bis(4-cyanophenyl)-1H-imidazol-3-ium in molten ZnCl$_2$. X-ray Diffraction (XRD) studies and Selective Area Electron Diffraction (SAED) reveal the highly crystalline nature of the resulting framework, and the Brunauer-Emmett-Teller (BET) analysis demonstrates a high specific surface area up to 850 m$^2$/g with high H$_2$ and CO$_2$ uptakes.
The thesis of Chain Lee is approved

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Richard B. Kaner

Xiangfeng Duan, Committee Chair

University of California, Los Angeles
2014
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resource within their reach, saved none for themselves, to help ensure a better future for me.
1. Introduction

1.1. Carbon Capture and Sequestration

Carbon dioxide (CO$_2$) emissions are mainly produced from the combustion of fossil fuels, our main source of energy.$^1$ The concentration of CO$_2$ in the atmosphere is sharply rising, surpassing 400 ppm for the first time in human history. This can lead to undesired effects such as global warming.$^2$ Consequently, carbon capture and sequestration (CCS) technologies represent important solutions to this increasingly challenging problem. CCS implementation is already well developed: they can be placed at stationary emission sources, such as coal and natural gas firing plants, greatly reducing our carbon footprint.$^3$ Once captured, the CO$_2$ can be reused for industry. Underground geological formations such as depleted oil reserves may serve as permanent storage sites for the captured carbon. Furthermore, extensive research has been being put into using CO$_2$ as a feedstock for a variety of industrial products.$^4$ The problem is that no satisfactory CCS material exists that is both reusable and durable under the conditions of factory exhaust.

Current technologies utilize aqueous alkanolamines to capture CO$_2$ in flue gas.$^5$ The problem is that these amines are too selective towards CO$_2$, binding too strongly through their chemisorptive properties. An actual chemical bond is formed, which results in tremendous energy required to regenerate the alkanoamine. Utilizing a reversible physisorption to capture carbon would be significantly more efficient and offer an ease of regeneration. Metal-Organic-Frameworks and Zeolites have shown promising results in this area.$^6$-$^8$ While their performance is strong, this
technology is still in their infancy and there is still great room for improvement. Moreover, as an inorganic compound their improved absorption comes at a price of increased weight due to excess metal centers, which is a potential barrier towards certain applications. CTFs, with their high chemical and thermal stability, may prove to be a potentially interesting material for CO₂ sequestration. CTFs are a new class of crystalline organic polymers. These CTF materials possess a 2-dimensional (2D), highly porous structures, with surface areas ranging from 500-3000 m²/g.⁹ Moreover, CTFs are stable under highly acidic and basic conditions and can withstand high temperatures above 450 °C without decomposition. CTFs are made of cheap, earth abundant materials, making them a suitable material as a permanent sorbent in underground geological reserves for CO₂.

1.2. CTF as a new Layered Material

On another application, 2D materials such as the recently discovered graphene¹⁰ have drawn considerable attention as a potential material for electronic devices. These single-layers of graphite are made of atomically thin crystalline carbon and have demonstrated exceptional performance in terms of electrical carrier mobility and quantum electronic transport.¹¹⁻¹⁴ These discoveries have led to intensive research of other 2D materials, such as metal-dichalcogenides and boron nitride.¹⁵⁻¹⁶ CTFs represents another type of layered material that might be isolated as single or few layers. Many CTFs posses a 2D layered structure of sp²-carbons, along with a myriad of sp²-nitrogen atoms and regular porosity. The extended networks of benzene and triazine rings in CTFs are linked in a completely conjugated planar array resembling graphene. The introduction of porosity,
nitrogen groups and other functional groups into CTFs may open up additional opportunity to tune their electronic properties. Yet, little research has been published on usage of CTFs as materials for devices. We plan to look into the potential of CTF as an alternative electronic material.

1.3. **Synthesis of CTF**

The trimerization of nitriles can be catalyzed using molten ZnCl$_2$ as both solvent and catalyst, in a well-known process called ionothermal synthesis.$^9$ At 400 $^\circ$C, Kuhn et al, has shown three aromatic nitriles on separate molecules may trimerize into a triazine ring. The reaction is reversible enough to create crystalline organic polymers named CTF. When aromatic nitriles with two or more nitrile groups present are reacted in this zinc melt, porous frameworks with high porosities and stability are achieved. These materials are robust, linked together by covalent sigma and pi bonds, giving them a high resistance to acid and base conditions. Using this ionothermal, high-temperature, flux-growth technique produces materials with much lower defects, allowing for better crystallinity and electron transport throughout the framework. Until now, only a few variations of these CTFs exist and even fewer with well-defined structures.$^9,17,18$ At this moment, the functional groups located on the framework backbone are limited to only triazine, pyridine, and thiophene groups. In this work, we seek to broaden the chemical composition of CTFs by introducing an N-heterocyclic carbene into the framework.

N-heterocyclic carbene-metal complexes have attracted increasing interest in organometallic synthesis and catalysis due to their ability to simultaneously
enhance the reactivity to and stability of the NHC-metal complex.\textsuperscript{16,19} These desirable properties of NHCs stem from their strong $\sigma$-donorship to the metal center and $\pi$-acceptor function. The NHC to metal $\sigma$-donation creates a near permanent chelation, along with metal to NHC back-donation into the $\pi^*$ orbital.\textsuperscript{19} This results in a highly stable metal-complex which have been well proven for a variety of usages.

1.4. Overview of the thesis

CTFs represent a versatile new material with significant potential for diverse applications. We hypothesize the strong dipole moment of the non-heterocyclic carbene chelated metal center can be used to enhance CO$_2$ absorption, and tune the electronic properties of the resulting CTFs.\textsuperscript{20} In this study, we demonstrate how to synthesize a new CTF, which contains the NHC functional group with high crystallinity. Since kinetics is the most essential condition for producing materials with good crystalline orientation, we utilize a slow cooling process to maximize reversibility. The NHC functionality will allow us to chemically modify the CTF porous structure post-synthetically—in other words, after the framework has been constructed. We aim to incorporate functional groups, not only by the imidazolium ring, but also its variable counter-ion to allow a great deal of chemical flexibility and tunable properties. Furthermore, the fully conjugated 2D structures of CTFs should act as a suitable material for device fabrication. We plan on using exfoliation techniques to produce single or thin-layers and study its electron transport properties.
2. Materials and Methods

2.1. Materials
Reagent grade 4-aminobenzoic acid, glyoxal (40% aqueous solution), paraformaldehyde, and Zinc Chloride (anhydrous) were purchased from Sigma-Aldrich and used without further purification. Unless stated otherwise, all reactions were done in air. $^1$H NMR spectra were recorded on Bruker Avance spectrometers (400, 500 MHz) and are reported relative to their deuterated solvent signals. The data for $^1$H NMR spectra are reported as follows: chemical shift (δppm), coupling constant (Hz) and integration. PXRD measurements were performed on a Bruker D8 Discover Diffractometer. Absorption measurements were performed on a Micromeritics Tristar II porisometer at their respected temperatures and pressures.

2.2. Synthesis of 1,3-Bis(4-cyanophenyl)imidazolium Chloride. The successful synthesis of the starting monomer for our proposed NHC-CTF is outlined in Scheme 1, using a modified procedure from Sen et al.$^{21}$ The reaction took place in a round bottom flask capped with septum, under reduced pressure and minimal exposure to air. Anhydrous solvents were used to increase yield. The reaction involves the condensation of 4-amino-benzonitrile with glyoxal in methanol to produce the intermediate. The intermediate is recovered through filtration, washed with cold methanol, and then dried in air. Lastly, the intermediate is reacted with paraformaldehyde, which adds the final apical carbon of the imidazole ring. H-NMR and ESI-Mass Spectrometry characterization confirmed our proposed product, NHC-CTF Monomer. Purification of the monomer was performed by recrystallization in acetonitrile at room temperature.
2.3. NHC-CTF Synthesis.

A 1:10 molar ratio of NHC-CTF Monomer : ZnCl₂ was packed into a quartz tube under inert atmosphere. The tube was flame sealed in vacuo and placed into a tube furnace at 400 °C for 40 hrs. The chemical reaction is outlined in Scheme 2. The material was then slow cooled to room temperature at 3° per hour, and subsequently washed with copious amounts of 3M HCl, THF, and acetone to yield the NHC-CTF. The remaining black powder was collected by filtration then dried in vacuum (10⁻³ torr) for 4 hrs. For de-solvation, the material is heated to 120°C under high vacuum (10⁻⁶ torr) overnight. Yield is roughly 90%.
2.4. Exfoliation. Solvent exfoliations of NHC-CTF were obtained using solvents acetonitrile, DMF, or IPA in combination with 3hrs of bath sonication. All the solvents provided similar samples, which are roughly 1000 nm in length and 400 nm in height. Mechanical exfoliations of NHC-CTF were carried out using an agate mortar and pestle. 50 mg of CTF were placed into a 3-inch mortar, with 1-2 drops of methanol added, and the sample was ground for at room temperature for 30 mins. The resulting solid was re-suspended in 100mL of methanol, and centrifuge at 8000 rpm for 5 mins, obtaining a clear solution. For TEM imaging, samples were drop coated onto carbon coated copper grid and dried at room temperature.

3. Results and Discussion
3.1. NMR Studies of the Monomer

$^1$H-NMR confirms the identity of our starting monomer. All protons are aromatic and found in the proper sp$^2$ aromatic region of the spectrum. Furthermore, integrations confirm the proper ratio between imidazolium protons (ImH) and aromatic ring protons (ArH) as shown in Figure 1. $^1$H NMR (400 MHz, DMSO-d6, 25°C: a 10.8 (s, 1H, ImH), b 8.74 (d, 2H, ImH), c 8.26 (d, 4H, ArH), d 8.2 (d, 4H, ArH).

ESI-MS confirms the molecular weight of our desired product in Figure 2. ESI-MS (m/z): 271.1 (100%) Fragmentation products are consistent with our proposed molecule. The spectrum was acquired in the positive region, giving further evidence our starting monomer is positively charged. An anion scan was performed on the monomer through elemental analysis confirming Cl as the counterion to the monomer.
Figure 1. $^1$H-NMR of NHC-CTF Monomer.

Though the synthetic procedure produces monomer in high purity, we observed a direct correlation between crystalline quality of the CTF and the crystallinity of the starting material. To help ensure the highest purity of monomer and pre-align the molecules, we performed recrystallizations in acetonitrile. Higher surface areas, uniform grown, and fewer defects were observed when pre-crystallizing the monomer powder.

![Figure 2 - ESI-MS of NHC-CTF Monomer, positive spectrum](image)

3.2. XRD Studies of the CTF Structure

Powder X-ray Diffraction (PXRD) displays two main reflection peaks at $2\theta = 4.6^\circ$, and $26.2^\circ$. Several 2D confirmations were investigated including AAA stacking.
ABAB stacking. Best-fit simulations using Materials Studio v4.3.0.0 are shown in Figure 3 to reveal peaks corresponding to $[100]$ and $[001]$ reflections in an eclipsed AAAA stacking structure. Unit cell parameters used for simulation were $a = b = 25.4 \, \text{Å}$ and $c = 3.4 \, \text{Å}$, corresponding to anticipated pore size and $\pi - \pi$ interlayer stacking respectively. Peak broadening simulations were also used to account for limited long-range crystalline order in the structure. While it is possible to grow large single crystals with appropriate flux ratios and temperature profiles, we will get much higher surface area and pore access with smaller grain sizes. Our theoretical predictions match well with the calculated d-spacing of the $[100]$ and $[001]$ peaks.

The intensities of the simulated pattern versus the experimental differ greatly, with the $[001]$ interlayer-stacking peak overwhelming the $[100]$ pore peak. This suggests that the crystal preferentially grows along the C-axis instead of along the AB-plane. While this is unusual for a layered structure, this could be a result of the ZnCl$_2$ flux. As the CTF is assembled, the ZnCl$_2$ would be trapped within the pores from chelation with the lone pairs of the nitrogen. This in turn creates a localized abundance of catalyst in a columnar motif, and any further assembly will occur vertically along this column. Another possibility lies with some graphitization from overheating (which would also explain the small peak at 40, corresponding to the graphite $[100]$ peak). However, the presence of a strong $[001]$ pore peak precludes significant graphitization: pores of the CTF cannot coexist with the non-porous graphite. From the powder pattern a crystal structure is simulated with a single pore of NHC-CTF being comprised of four unit cells. The NHC-CTF with its Realeaux triangle pore shape has a smallest expected pore size of $13.9 \, \text{Å}$ and largest expected
pore size of 25.5 Å as obtained through software measurements. A crystal structure representation is shown in figure 4. The blue atoms represent nitrogens, and the gray atoms represent carbons. Hydrogen atoms and chlorine counter ions have been omitted for clarity. Although the quality of the diffraction pattern does not allow us to perform a meaningful full structure Rietvelt refinement, the observed peaks do correspond to the largest d-spacings and their expected 2θ positions. Analysis using SAED help provide further evidence of our proposed structure.

Figure 3. Powder X-Ray Diffraction of NHC-CTF. Experimental represented in red, optimal crystal growth simulations in black, and line-broadening simulations blue.
Figure 4. Four cages of the NHC-CTF displaying a Realeaux triangle pore shape, and stacking orientation. Each cage shares edges with six others. The nitrogen atoms are represented in blue, and carbon atoms are represented in gray. The interlayer d-spacing is calculated to be 3.4 Å

The bent nature of our starting monomer potentially creates a defect-prone building block, as seen in Figure 5. Three possible conformers may occur from each trimerization unit. Isomer A is threefold symmetric, with B and C being non-threefold symmetric resulting in defect units not beneficial towards CTF
crystallization. This may also be a major contributing factor to our peak broadness and limited long-range order in our PXRD patterns.

![Figure 5](image)

**Figure 5.** Three conformers are possible from the trimerization of three monomer units.

### 3.3. Solid State NMR studies of CTF Structure

Further structural evidence of covalent bonding is given through $^{13}$C CP-MAS solid-state NMR (Figure 6). No peaks of residual cyano groups (~85 ppm) could be detected in the spectrum, confirming the compete trimerization of the starting monomer. A simulation on the NHC-CTF unit cell was conducted to show the locations of the possible sp$^2$ carbons in the NMR spectra. These peaks lie within the proper range of our spectrum between $\delta = 110$-150 ppm. As it is well known that high resolutions for solid-state NMR are difficult to obtain, our multiple aromatic carbon atoms with similar peak shifts may account for the spectrums broadness.

With the generation of our CTF-metal complex significant chemical shifts should be observed in the apical carbon of the imidazole ring. These would be attributed to the strong sigma-donarship of electrons from the carbene to the metal center, as well as pi-backbonding of electrons from the metal-center to the carbene ring.
Figure 6. $^{13}$C CP-MAS solid-state NMR, a single broad peak is observed

It should be noted the monomer to zinc salt ratio and reaction cooling rate are crucial to producing our CTF material with crystallinity. The ratio of 1:10 monomer to zinc salt produced materials with highest surface area as observed by Kuhn et al.\textsuperscript{1} Coupling these ratios with a cooling rate of 1.5\textdegree/hr, produced well-defined crystalline compounds when comparing to other organic porous materials. These synthesis conditions were found to be optimal, with deviations from monomer to zinc ratio resulting in a loss of surface area, sometimes as low as 350 m$^2$/g. A comparison is shown in Figure 7. Under non-optimized synthesis procedures the CTFs grow with heavy defects, low crystallinity, and surface area. Their physical appearance can clearly be seen. The roughness of the surface of a
non-optimal growth CTF in comparison to the shiny metallic-like optimized CTF on the right. Materials with black, shiny appearances tend to have conductive behaviors, and we see the same correlation with our material. Upon optimized growth conditions, the sheet resistance is reduced over two orders of magnitude from roughly 25 MΩ to 0.15 MΩ. Rapid cooling of the material post the 40 hr 400 °C synthesis gave amorphous powders with lower surface areas. Elemental analysis of the optimal reaction condition showed just a small deviation from the theoretical C/H/N values. This variation may be due to slight material carbonization of the triazine rings, which as been previously observed in these types of materials. However, the overall material is proven to be robust even after extended heating times of 80 hr at 400 °C.

**Figure 7.** Photo comparison of non-optimally synthesized NHC-CTF on the left, and optimized synthesis on the right.
3.4. IR and Raman studies of CTF Structure

Further bonding studies were conducted on our CTF by utilizing Attenuated-Total-Reflectance IR Spectroscopy (ATR-IR), Figure 8. Our starting monomer is displayed in black, over-laid with two different samples of NHC-CTF in red and blue. The red spectrum displays our optimal CTF, with the absence of a nitrile peak ~2218, indicates successful trimerization of our monomer. It should be mentioned it is extremely difficult to obtain clear IR spectrums from carbonaceous and carbon like materials, due to the high extinction coefficients and substantial transmission losses due to absorbance.\textsuperscript{23-24} Consequently, our current IR spectrums are not conclusive in identifying the presence of the imidazole nitrogen for post-synthesized CTFs. A strong carbonyl peak (~1680) can be seen in our partially oxidized CTF sample. This may have been due to a small leak in the quartz tube during material synthesis.
**Figure 8.** ATR-IR of NHC-Monomer (black), NHC-CTF (red) and NHC-CTF presence of defects and oxidation (blue)

Raman spectroscopy measurements (RSMs) were conducted using 514 nm excitation to help identify the electronic structure of our CTF, as well as structural periodicity. We compared our spectra of CTF to that of graphite (Figure 9). The G peak corresponds to the doubly degenerated zone center E2g mode, which correlates to the motion of atoms in the 2D honeycomb structure. The D peak, typically inactive for perfect graphite, is activated by disorder in the 2D structure. Therefore the D band is associated with defects. This could be attributed to the stress from the high-temperature synthesis, as well as formation of different conformers as outlined in Figure 5, along with the small grain boundaries. Our 2D
peak at \( \sim 2700 \) is historically called the \( G' \) peak. Comparison of the D:G peak intensity ratio suggests our CTF has a much shorter 2-dimensional ordered structure. The existence of a G peak our CTF does help confirm the formation of a 2D honeycomb structure made up of stacked triazine and benzene rings.

**Figure 9.** Raman spectrum of NHC-CTF and graphite.
3.5. Surface area characterization

To investigate the porosity of the NHC-CTF material, N$_2$ adsorption isotherms were performed on the de-solvated materials shown in Figure 11a. Measurements reveal a porosity of 850 m$^2$/g at 760 torr and 77K using BET analysis fits. The values are in line with expected theoretical calculations of ~920 m$^2$/g and other 2D mesoporous COFs. These measurements reveal a true Type I isotherm with no hysteresis. The absence of a mesoporous filling in the N$_2$ isotherm may be attributed to the unique Realeaux Triangle shape of NHC-CTF. Though total pore cavity is near 2.5 nm, the shape of the pore vertices creates steric sites. The result divides each mesopore into four micropore regions. Three micropore regions are located on the edges of the triangle, one located on the center, as can be more clearly seen in Figure 4. Our DFT pore size analysis calculations suggest a pore size distribution of 2.5 nm, further supporting our proposed structure.

In terms of absolute uptakes, NHC-CTF adsorbs 1.1 wt% of H$_2$ at STP as seen in Figure 11b. This is in the moderate range of CTF type materials. The absence of open metal sites for strong interactions and density of a hexagonal structure contributes to the non-optimal H$_2$ uptake.

NHC-CTF adsorbs 68 cm$^3$/g of CO$_2$ at 760 mmHg (1atm) at 273 K as shown in Fig 11c. The highest recorded uptake of CO$_2$ in a CTF absorbing at 15.7 wt%. Though NHC-CTF nearly supersedes the best range of uptake for organic polymers, further improvements are possible. The binding of metal centers has been known to increase gas uptake abilities in various porous materials. This strategy of
decorating the internal framework with strong dipoles may be utilized in the future for enhancing NHC-CTFs CO$_2$ uptake.
**Figure 10.** Nitrogen surface area measurements at 77 K a), hydrogen adsorption measurements taken at 77 K, plotted in w.t% at STP b), and CO$_2$ adsorption measurements taken at 273 K, plotted in volumetric uptake c).

Upon metallation, we expect an even greater increase in binding affinity, $Q_{st}$, for CO$_2$ absorption, and possibly even H$_2$. Using our NHC complex, we can bind virtually any transition metal and also vary its counter-ion. It has been well known that open metal sites are key to increasing gas storage. However, in MOFs they traditionally have excess metal clusters, which are only present for structural support. These excess metal clusters not only add to the overall cost of synthesis but also in excess weight of the material since absorptions are measured in volumetric uptake over grams of material. Usage of an all-organic framework helps alleviate not only the chemical sensitivity of some metal-organic bonds, but also the heavy weight of these metal atoms. Creating tunable pore ligands will employ metal centers only in the sites of need, leaving out unnecessary metal centers only there for structural support.

### 3.6. TEM Studies of the exfoliated CTF nanosheets

The NHC-CTF was exfoliated in IPA to produce thin samples suitable for HR-TEM analysis. Examination of the material by HR-TEM reveals clear hexagonal growth plates with regular porosity in Figure 11a and 11c. The SAED pattern in Figure 11b shows clear diffraction rings, an observation which endorses the crystalline nature of our NHC-CTF. Calculation of the rings’ d-spacing correspond well to peaks: [700], [900], [10 00], [880], [990], [10 10 0] respectively. Additionally, the 2.5 nm pores of the CTF are somewhat visible in the HR-TEM image.
especially through Figure 11d, confirming the AAA stacking. In terms of CTFs, this is not only the first case of hexagonal growth plates being observed, but also the usage of SAED to characterize its structure.

Figure 11. HR-TEM images of roughly 400nm thick films of NHC-CTF. SAED measurements displayed in part b. Vertically oriented pores can be observed in c and d.
Mechanical grinding techniques of exfoliation were performed to produce thin layer samples. This strategy has been shown to be safe, eco-friendly and energy efficient process without the use of harsh solvents.\textsuperscript{26} The process of mechanical grinding helps separate the $\pi$-$\pi$ stacking of AA layers from the stable CTF layers as seen in Figure 12. The layers become thin enough where they are nearly transparent on TEM. If not for the crystal grain boundary the thin layers would be nearly indistinguishable from the carbon coated TEM grid. At the moment, the sheet size of these delaminated CTFs is only $\sim$200 nm. Optimally we would like to produce layers at least 1 micron in length, and minimally stacked.

![Figure 12](image.png)

\textbf{Figure 12.} TEM image of mechanically ground and exfoliated NHC-CTF.
4. Summary, Conclusion, and Future Work

In conclusion, we have successfully synthesized the first ionic CTF, containing NHC moieties throughout its structure. We show the bent monomer is susceptible to synthetic variations and are defect prone building blocks during synthesis. Yet, this is the first CTF to date, which has been crystallized and characterized from a bent shaped starting material. Our characterization methods are unique in that the NHC-CTF is the first CTF able to be characterized by SAED. This is due to high crystallinity from careful synthesis and employment of exfoliation techniques. Moreover, our CTF exhibits high surface area and high uptake of CO$_2$ and H$_2$ gas. These results, in conjunction with the ongoing efforts in exfoliations and post-synthesis modifications, are important steps toward applications that utilize CTFs in electronic devices, gas sorption, and catalysis.

Further investigations for successful formation of poly-triazine networks should be conducted. Additionally, $^{13}$C and $^{15}$N CP-MAS solid-state NMRs utilizing isotopic labeling on the starting monomer will offer well defined peaks to evaluate bonding characteristics of NHC-CTF. TGA will help determine the overall thermal stability of this uniquely ionic CTF with specific functionalization.

A proper method of generating the NHC-Carbene with metal centers needs to be developed. Some strategies include the use of adducts such as chloroform or methoxy groups$^{27}$, as well as employing air and light sensitive reactions involving strong bases or transmetallation strategies$^{28}$. Full characterization of the bound organometallic complex will be required. Characterization methods include CP-MAS
solid state NMR and solid state UV-VIS spectroscopy. Upon successful metal-CTF complex formation, a difference in gas uptake volume is also expected. This effect of generating strong electric dipoles has been observed using metal loaded variants of MOFs.\textsuperscript{23} We expect the same type of behavior, if not better, using NHC-metal-carbene complexes. Using gas adsorption analysis a variety of adsorbents can then be tested for enhanced uptake abilities.

Exfoliation techniques need to be improved to obtain thin-layers of NHC-CTF suitable for device fabrication. Currently, these layers are \~400 nm in height from AFM studies. Suitable samples should be less than 100 nm for field-effect transistor measurements. Lastly, we search for adequate redox partners, which will not harm the crystal structure, yet will help promote full electron transfer.
References

1.) U.S. Environmental Protection Agency:
http://www.epa.gov/climatechange/emissions/co2_human.html


