Synthesis and Characterization of Metal-Organic Frameworks for Gas Storage and Separations

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Prof. Jeffrey R. Long

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To the giants who

lifted me on their shoulders

to see through the crowd
Contents

1 Introduction 1

2 Synthesis and Characterization of Cu[Ni(pdt)$_2$] 4
   2.1 Experimental .............................................. 5
   2.2 Results and Discussion .................................. 5

3 Synthesis and Characterization of Mg$_2$(doabpdc) 12
   3.1 Experimental .............................................. 13
   3.2 Results and Discussion .................................. 15

4 Synthesis and Characterization of a Zr(alkoxy-tpdc) framework series 16
   4.1 Experimental .............................................. 17
   4.2 Results and Discussion .................................. 18

5 Conclusion 20

6 Acknowledgements 21

References 22

Appendix A Supporting Information: Cu[Ni(pdt)$_2$] Synthesis 23
   A.1 Scheme: Synthesis of Na[Ni(pdt)$_2$]·2H$_2$O Metalloligand .............. 23
   A.3 Powder X-ray Diffraction Data for Cu[Ni(pdt)$_2$] ....................... 24
   A.4 Photoconductivity Data for Cu[Ni(pdt)$_2$] ............................... 25

Appendix B Supporting Information: Mg$_2$(doabpdc) Synthesis 27
   B.1 Scheme: Synthesis of H$_4$(doabpdc) Ligand .............................. 27
   B.2 Scheme: Synthesis of Mg$_2$(doabpdc) Framework ........................ 27
   B.3 Thermogravimetric Analysis of Mg$_2$(doabpdc) ........................ 28

Appendix C Supporting Information: Zr(alkoxy-tpdc) Series Synthesis 29
   C.1 Scheme: Synthesis of H$_2$(alkoxy-tpdc) Ligand Series .................. 29
   C.2 Scheme: Synthesis of Zr(alkoxy-tpdc) Framework Series ................. 29
   C.3 Powder X-ray Diffraction Data for Zr(alkoxy-tpdc) Series ............. 30
List of Figures

1. MOF structure breakdown ........................................ 1
2. Fe$_2$(bdp)$_3$ framework structure .......................... 2
3. Gas binding in M$_2$(dobdc) .................................... 3
4. Cu[Ni(pdt)$_2$] framework and linker structure .......... 4
5. Cu[Ni(pdt)$_2$] PXRD pattern ................................... 6
6. Cu[Ni(pdt)$_2$] isotherms for ethylene/ethane and propylene/propane ... 7
7. Cu[Ni(pdt)$_2$] selectivities for ethylene/ethane and propylene/propane ... 8
8. Cu[Ni(pdt)$_2$] isosteric heats of adsorption for ethylene/ethane ... 9
9. IV curve of Cu[Ni(pdt)$_2$] ..................................... 10
10. Photoconductivity in Cu[Ni(pdt)$_2$]thin films and pellets ... 11
11. Cu[Ni(pdt)$_2$]PXRD patterns after triiodide aging ........ 12
12. H$_4$(doabpdc) linker structure comparison ............... 13
13. Mg$_2$(doabpdc)-Mg$_2$(dotpdc) PXRD comparison .......... 15
14. Mg$_2$(doabpdc)-Mg$_2$(dotpdc) TGA comparison .......... 16
15. Zr(alkoxy-tpdc) series PXRD comparison ............... 19
16. Methane capacities for the Zr(alkoxy-tpdc) series ...... 20
17. Synthesis of Na[Ni(pdt)$_2$] · 2H$_2$O metalloligand ......... 23
19. Powder x-ray diffraction data of the air-free Cu[Ni(pdt)$_2$] framework, with Miller planes labeled ............... 24
20. Light/dark voltammetry of Cu[Ni(pdt)$_2$] .................. 25
22. Temperature change in Cu[Ni(pdt)$_2$]under illumination .... 26
23. Synthesis of H$_4$(doabpdc) linker ............................ 27
24. Synthesis of Mg$_2$(doabpdc) framework ................... 27
25. Temperature-mass loss curves for Mg$_2$(doabpdc) and Mg$_2$(dotpdc) .... 28
27. Synthesis of a series of alkylated Zr-UiO-68 frameworks .... 29
28. Zr(methoxy-tpdc) PXRD pattern ............................ 30
29. Zr(ethoxy-tpdc) PXRD pattern ............................. 30
30. Zr(propoxy-tpdc) PXRD pattern ............................ 31
31. Zr(butoxy-tpdc) PXRD pattern ............................. 31
32. Zr(hexoxy-tpdc) PXRD pattern ............................. 32
33. Zr(tpdc) PXRD pattern ...................................... 32
1 Introduction

Metal-organic frameworks (MOFs) are highly crystalline compounds that consist of repeating metal ions bridged by coordinating organic linkers in order to form three-dimensional structures with high thermal and chemical stability\(^1\) (Figure 1). Their microporous nature leads to a high surface area which can enable reversible physisorption of gases, especially for frameworks with large amounts of coordinatively unsaturated metal sites which can interact strongly with guest molecules such as CH\(_4\) or H\(_2\)\(^2, 3, 4\). The nature of MOF formation provides a wealth of synthetic handles with which to tune the properties of the resulting framework, by modulating metal sites, linker structure, or the frameworks fundamental connectivity and topology. Taken together, these properties make MOFs ideal candidates for applications such as gas storage, CO\(_2\) capture, hydrocarbon separations, catalysis, and as porous conductors. Because of the incredible variety of potential framework morphologies that exist, each with unique metal ions and organic linkers open to functionalization, MOFs are amenable to targeted syntheses for particular properties, both by virtue of the huge number of potential MOFs that can be made and the option for procedural iteration on existing frameworks in order to optimize their values for targeted properties.

Figure 1: MOFs consist of a crystalline lattice of metal ions joined by organic linkers.

An example of the versatile nature of metal-organic frameworks can be found in the framework Fe\(_2\)(bdp)\(_3\) (bdp\(^2^-\) = 1,4-benzenedipyrazolate) (Figure 2a), whose triangular channels are able to effect separation in mixtures hexane isomers commensurate with the ability of the isomers to wedge into the corners of the triangular channels\(^5\). Completely orthogonal to this capability of the framework, recent work by Wiers, et. al. shows
that Fe$_2$(bdp)$_3$ also displays electrical conductivity at room temperature upon chemical reduction with potassium naphthalenide, due to the presence of one-dimensional chains of Fe$^{3+}$ ions bridged by bipyrazolate ligands (Figure 2b).

Figure 2: One-dimensional chains of pyrazolate-linked Fe$^{3+}$ ions (2b, lower) run along the a direction of the Fe$_2$(bdp)$_3$ (2a, upper) structure, enabling electronic conductivity upon chemical reduction.

While the study of conductive MOFs is intellectually fascinating and has, in fact, shown much promise$^{[6, 7, 8, 9]}$, by far the bulk of research on metal-organic frameworks has centered upon their ability to bind, reversibly adsorb, separate, or otherwise physically interact with gas particles$^{[3, 10]}$. A flagship group of frameworks for this type of work has been the MOF-74 structure class, prototypically M$_2$(dobdc) (dobdc$^{4-} = 2,5$-dioxido-1,4-benzenedicarboxylate) but spanning a variety of linkers including an regioisomeric variant M$_2$(m-dobdc) (m-dobdc$^{4-} = 4,6$-dioxido-1,3-benzenedicarboxylate)$^{[4]}$ and a series of isoreticular frameworks, ranging from an expansion of the typical M$_2$(dobdc) structure to a biphenyl molecule to produce M$_2$(dobpdc) (dobpdc$^{4-} = 4,4'$-dioxidobiphenyl-3,3'-
dicarboxylate) all the way up to an eleven-phenylene ring system, affording pore apertures as high as 98 Å\(^{[11, 12]}\); the framework detailed in Section 3 is an example of another isoreticular MOF in this series. Because this framework offers great potential for gas physisorption due to its unique structure, whose square pyramidally-coordinated metal centers have open coordination sites pointing into the pores of the framework (Figure 3), it is a fertile starting ground for utilizing rational design principles to optimize MOFs for particular characteristics.

**Figure 3:** When heated in solution with a metal source, \(H_4(\text{dobdc})\) (3a) crystallizes into a structure with one-dimensional hexagonal pores in a ‘honeycomb’ arrangement, its square pyramidally-coordinated metal centers having an open metal site pointing into the pore (3b). The open metal site can then easily coordinate a variety of gas molecules (3c, 3d).

Herein, we report a number of novel metal-organic frameworks or novel syntheses for existing frameworks, with the goal of characterizing these frameworks via a variety of analytical techniques and determining their viability for applications such as automotive natural gas storage, industrial hydrocarbon separations, porous conductivity or photoconductivity, and more.
2 Synthesis and Characterization of Cu[Ni(pdt)₂]

Figure 4: The Cu[Ni(pdt)₂] structure (4a) was originally targeted for synthesis because its redox-active metallolinker (4b) bears much similarity to a known nickel dithiolate system for olefin separations (4c).

Cu[Ni(pdt)₂] (pdt²⁻ = pyrazine-2,3-dithiolate) is a relatively unusual metal-organic framework, due to its structure of redox-active nickel bis(dithiolate) metalloligands bridged by square planar copper tetrapyrazine centers. The redox sensitivity of the ligand enables conductivities of approximately 1×10⁻⁴ S/cm at room temperature following partial oxidation with I₂, and bears more than a passing resemblance to another known nickel dithiolate system for olefin separations (Figure 4c). We devised an alternative air-free preparation of the framework from the literature procedure, resulting in a higher-quality sample which we evaluated for conductive and gas separation ability.

The original synthesis for the Cu[Ni(pdt)₂] framework was presented by Kobayashi, et. al. [15], itself adapted from a 2004 paper on a series of Cu³⁺ pyrazine-2,3-dichalcogen complexes [17]. In both, sodium salts of the precursor metalloligand (Figure 4b) – with either a Ni³⁺ or a Cu³⁺ center – are prepared with the use of an oxidizing agent. When a
solution of Cu\(^{+}\) ions is mixed with the dissolved metalloligand, the framework (Figure 4a) is formed rapidly at room temperature, at a rate that renders the reaction easily scalable and even amenable to spin-coating processes to produce thin films of the material. By altering the literature preparation to mix the two precursor solutions air-free, we were able to substantially improve the purity (Table 1) and crystal structure (Figure 5) of the resultant framework. We then calculated the IAST selectivities of the framework for a variety of industrially-useful hydrocarbon separations (including ethylene/ethane and propylene/propane, though the framework shows promise for numerous other hydrocarbon separations), as well as assessed its photoconductive properties using a custom-built photoconductivity cell.

2.1 Experimental

**Modified air-free synthesis of Cu[Ni(pdt)\(_2\)].** A flask, initially containing 270mL of acetonitrile, was sparged with N\(_2\) for half an hour, following which Na[Ni(pdt)\(_2\)]·2H\(_2\)O (0.630 g, 1.62 mmol) was added. Concurrently, a separate flask, initially containing 75mL of acetonitrile, was also sparged with N\(_2\) for half an hour, upon which CuI (0.309 g, 1.62 mmol) was added. While under N\(_2\), the solution of CuI was then slowly added to the solution of Na[Ni(pdt)\(_2\)]·2H\(_2\)O via a syringe, rapidly precipitating Cu[Ni(pdt)\(_2\)]. The solid was filtered out on 0.22m nylon filter paper and activated overnight at 90\(^\circ\)C under vacuum, yielding 0.453 g of the framework (68.8%) as a black powder. Elemental Analysis for Cu[Ni(pdt)\(_2\)] (calculated): C, 23.63%; H, 0.99%; N, 13.78%; S, 31.54%. Found: C, 22.92%; H, 1.05%; N, 13.74%; S, 30.43%.

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*Table 1:* Elemental analysis data for Cu[Ni(pdt)\(_2\)]. Included for comparison are values obtained from samples prepared by literature methods\(^{[15, 17]}\).*
As evidenced by the elemental analysis data in Table 1 and the comparative PXRD patterns in Figure 5, the Cu[Ni(pdt)$_2$] synthesized from air-free precursors via the methodology outlined in this work is both substantially purer and has of greater crystallinity than samples produced by literature methods.

![Figure 5: Powder x-ray diffractometry establishes that while the air-free (top) and oxidized (bottom) versions of the framework are isostructural, the air-free framework is more crystalline.](image)

2.2.1 Gas Separations

Using our improved Cu[Ni(pdt)$_2$] sample, we calculated ethane/ethylene and propane/propylene gas adsorption isotherms (Figure 6) and used these isotherms to create selectivity plots using Ideal Adsorbed Solution Theory (IAST) (Figure 7). Our framework is moderately selective for ethylene gas over ethane, with some temperature variation, though its propylene/propane selectivity is minimal. We also determined the framework’s high selectivity for some other industrially-important gas separations (paper in preparation).
Figure 6: Gas adsorption isotherms for Cu[Ni(pdt)$_2$] framework showcase different adsorption patterns for ethylene and ethane (6a) and a lesser distinction between propylene and propane (6b).
(a) IAST selectivities for the Cu[Ni(pdt)$_2$] framework for ethylene/ethane separations

(b) IAST selectivities for the Cu[Ni(pdt)$_2$] framework for propylene/propane separations

Figure 7: Ideal Adsorbed Solution Theory (IAST) selectivity plots for Cu[Ni(pdt)$_2$] show potential for ethylene/ethane separations (7a), though propylene/propane selectivity is near unity (7b).
Figure 8: Isosteric heats of adsorption for Cu[Ni(pdt)$_2$] show a high binding enthalpy for ethylene and a slightly lesser one for ethane.

2.2.2 Photoconductivity

The photoconductive ability of Cu[Ni(pdt)$_2$], along with that of its isostructural framework Cu[Cu(pdt)$_2$], was evaluated with help from Dr. Aravind Kumar. It was reasoned that the framework might have exceptional photoconductive properties due to potential interactions with its redox-active metallolinker. Using a custom-built photoconductivity cell, we constructed IV plots at various optical flux values and determined that the resistance of bulk Cu[Ni(pdt)$_2$] falls off sharply with increasing incident light intensity (Figure 9).
Figure 9: A simple IV curve of Cu[Ni(pdt)_2] shows a direct dependence between the optical flux upon the material and the conductivity of the material.

We conducted further tests, both on bulk pelletized Cu[Ni(pdt)_2] and electrophoretically-deposited thin films, and were able to receive photoconductivities as high as 0.18μS/cm on a thin film, the first measured value for photoconductivity in a metal-organic framework (Figure 10). We suspect that further doping of the linker may also allow for even greater photoconductivity values.
Figure 10: Photoconductivity measurements display light-activated conductivities as high as $0.18\mu S/cm$ for an electrophoretically-deposited thin film, the first measured value for photoconductivity in a metal-organic framework.

Because thin films of the material could potentially be produced rapidly via a spin-coating process and having determined its preliminary photoconductive properties, we decided to test its stability to iodine/triiodide, a common redox shuttle found in dye-sensitized solar cells\textsuperscript{[19]}. As seen in Figure 11, the framework experiences no substantial loss of crystallinity upon aging in iodine/triiodide, warranting further investigation into the viability of incorporating such a framework into a dye-sensitized solar cell.
Aging Cu\[Ni(pdt)\]$_2$ in iodine/triiodide, a common redox shuttle in dye-sensitized solar cells, shows no significant degradation of the framework’s crystal structure by powder x-ray diffractometry.

3 Synthesis and Characterization of Mg$_2$(doabpdc)

Mg$_2$(doabpdc) (doabpdc$^4^-$ = 4',4''-dioxidoanthracene-9,10-biphenyl-3',3''-dicarboxylate) is a framework in the MOF-74 structure class, a variation upon the Mg$_2$(dotpdc) (dotpdc$^4^-$ = 4,4''-dioxidoterphenyl-3,3''-dicarboxylate) expanded linker\cite{11} which substitutes the central benzene ring for an anthracene system (Figure 12). This framework was originally targeted for synthesis because it was hoped that the Mg$_2$(doabpdc) structure would be stable at higher temperatures than comparable Mg$_2$(dotpdc) due to additional π-stacking effects from the central anthracene ring. This increased thermal stability would increase the viability of Mg$_2$(doabpdc) and similar anthracene-based frameworks for use in hydrocarbon separations during the catalytic cracking of oil, during which outflow streams of raw hydrocarbons are ejected at high temperatures\cite{14}. Gas separations at temperature using metal-organic frameworks like Mg$_2$(doabpdc) could provide an alternative to current cryogenic distillation techniques, which are energetically expensive.
3.1 Experimental

3.1.1 Synthesis of $H_4$(doabpdc) linker

**Methylation of 5-bromosalicylic acid.** A flask containing 180mL of DMF was charged with 5-bromosalicylic acid (20 g, 92.16 mmol) and potassium carbonate (50.94 g, 368.6 mmol). Methyl iodide (17.2mL, 276.5 mmol) was injected into the flask, which was left to stir overnight at room temperature. The reaction mixture was quenched with 150mL of water, and the quenched mixture was extracted with diethyl ether, which was rotovapped down to yield the methylated product (17.93 g, 79.38%).

**Borylation of protected bromosalicylic acid.** Methylated 5-bromosalicylic acid (10.0 g, 40.8 mmol), bis(pinacolato)diboron (11.4 g, 44.9 mmol), Pd(dppf)Cl$_2$ (0.716 g, 1.02 mmol), and dry potassium acetate (16.0 g, 163.22 mmol) were added to a dry Schlenk flask, following which 250mL of anhydrous dioxane was cannulated in. The reaction was then heated at 100°C under positive N$_2$ pressure for 16 hours, following which the reaction mixture was filtered to remove excess palladium and the filtrate evaporated to produce the borylated product (7.478 g, 62.1%).
Suzuki coupling to Me<sub>4</sub>(doabpdc) protected linker. 9,10-dibromoanthracene (1.246 g, 3.707 mmol), methylated 5-(pinacolboryl)salicylic acid (2.2743 g, 7.785 mmol), potassium carbonate (10.80 g, 71.18 mmol), and Sphos Pd G2 (0.1337 g, 0.1854 mmol) were added to a Schlenk flask containing 240mL of THF and 60mL of water. The reaction mixture was heated at 65°C for 2 days under positive N<sub>2</sub> pressure, following which it was quenched with 500mL of water and let to stir for 10 minutes. The quenched mixture was then filtered off to obtain 1.4344 g of the Me<sub>4</sub>(doabpdc) product (76.4%).

Deprotection of Me<sub>4</sub>(doabpdc) to H<sub>4</sub>(doabpdc). A dry Schlenk flask was charged with Me<sub>4</sub>(doabpdc) (1.4344 g, 2.834 mmol) and 50mL of anhydrous methylene chloride, then cooled to -78°C in a dry ice/isopropanol bath. A 1M solution of BBr<sub>3</sub> in methylene chloride (14.17mL, 14.17 mmol) was injected into this mixture and let to stir for 10 minutes. The reaction mixture was then slowly poured over ice water, filtered, and washed with water to yield 1.2 g of H<sub>4</sub>(doabpdc) (81.4%).

3.1.2 Synthesis of Mg<sub>2</sub>(doabpdc) framework

Solvothermal synthesis of Mg<sub>2</sub>(doabpdc). H<sub>4</sub>(doabpdc) (0.045 g, 0.10 mmol) and Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (.064 g, 0.25 mmol) were weighed into a 20mL scintillation vial, and dissolved in a mixture of 4.5mL DMF and 5.5mL methanol with the aid of ultrasonication. The vial was tightly sealed with a teflon cap and heated at 120°C for 8 hours. The vial was allowed to cool to room temperature before 0.035 g of solid product was filtered off and washed with hot methanol.

Activation of Mg<sub>2</sub>(doabpdc) framework. The sample underwent numerous solvent exchanges (2× DMF at 120°C for 8 hours each, 4× MeOH at 80°C for 12 hours each). Following solvent exchanges, Mg<sub>2</sub>(doabpdc) was heated at 150°C in a Schlenk flask for 24 hours under flowing N<sub>2</sub>, followed by heating at 150°C under vacuum for another 24 hours.
3.2 Results and Discussion

Ultimately, the anthracene-functionalized framework was shown to form and was identified to be isostructural with the unfunctionalized terphenyl-based Mg$_2$(dotpdc) framework (Figure 12). In fact, the Mg$_2$(dotpdc) framework in particular is so finicky and difficult to form that the anthracene-based Mg$_2$(doabpdc) can actually be formed in a substantially more crystalline form, as evidenced by a direct comparison between the two crystal diffraction patterns (Figure 13).

![Figure 13: Powder x-ray diffractometry patterns for both the Mg$_2$(doabpdc) and the unfunctionalized Mg$_2$(dotpdc) framework show that not only is the anthracene-based ligand isostructural with the terphenyl-expanded MOF-74 structure, it is also substantially more crystalline.](image)

Contrary to our initial hypothesis that $\pi$-stacking interactions would increase the thermal stability of the Mg$_2$(doabpdc) framework above that of the Mg$_2$(dotpdc) framework, thermogravimetric analysis (Figure 14) shows that neither framework displays substantially more or less temperature stability than the other at temperatures up to 500°C.
Figure 14: Thermogravimetric analysis of Mg$_2$(doabpdc) and Mg$_2$(dotpdc) in the region from 25° C to 500° C shows that neither is significantly more stable than the other.

4 Synthesis and Characterization of a Zr(alkoxy-tpdc) framework series

An isostructural series of Zr(alkoxy-tpdc) (alkoxy-tpdc$^{2-}$ = terphenyl-2',5'-di-(R-methyl-ether)-4,4''-dicarboxylate; $R =$ methyl, ethyl, $n$-propyl, $n$-butyl, $n$-hexyl) frameworks was synthesized, with alkyl chains of increasing length extending into the pores of the frameworks. These frameworks would be isostructural with the unsubstituted Zr(tpdc) framework (also known as UiO-68), but retain alkyl moieties filling the tetrahedral holes in the framework. It was hoped that these alkyl moieties would create a semiliquid pore environment in the pore of the framework, and as the chain length of the alkyl substituents increased the pore environment would become increasingly liquid, and thereby more capable of storing gaseous methane via nonpolar solvation effects$^{[13]}$. 

16
4.1 Experimental

4.1.1 Synthesis of H$_2$(alkoxy-tpdc) linker

Radical bromination of 1,4-dibromo-2,5-dimethylbenzene. 1,4-dibromo-2,5-dimethylbenzene (10.00 g, 37.88 mmol), N-bromosuccinimide (14.16 g, 79.56 mmol), and azobisisobutyronitrile (0.75 g, 4.6 mmol) were dissolved in a round-bottom flask containing 150 mL of benzene and refluxed overnight at 95°C. The reaction mixture was cooled to room temperature to precipitate 5.606 g (41%) of 1,4-dibromo-2,5-bis(bromomethyl)benzene product as a tan solid.

Alcohol S$_N$2 of 1,4-dibromo-2,5-bis(bromomethyl)benzene. A reaction flask was charged with 1,4-dibromo-2,5-bis(bromomethyl)benzene (2.803 g, 6.65 mmol) and 50 mL of alcohol (methanol: 1230 mmol; ethanol: 856 mmol; n-propanol: 669 mmol; n-butanol: 546 mmol; n-pentanol: 460 mmol; n-hexanol: 398 mmol) and refluxed overnight (methanol: 64.7°C; ethanol: 78°C; n-propanol: 97°C; n-butanol: 118°C; n-pentanol: 138°C; n-hexanol: 157°C). The reaction mixture was then cooled to -20°C in a freezer, precipitating a white solid which was subsequently filtered off to give the product (methanol: 2.301 g, 91%; ethanol: 2.114 g, 85%; n-propanol: 2.531 g, 91%; n-butanol: 1.922 g, 83%; n-pentanol: 0.216 g, 14%; n-hexanol: 2.971 g, 75%).

Suzuki coupling to protected Me$_2$(alkoxy-tpdc) linker. 1,4-dibromo-2,5-bis(alkoxymethyl)benzene (methoxy: 2.413 g, 6.12 mmol; ethoxy: 2.498 g, 6.12 mmol; n-propoxy: 2.584 g, 6.12 mmol; n-butoxy: 2.670 g, 6.12 mmol; n-hexoxy: 2.841 g, 6.12 mmol), 4-methoxycarbonylphenylboronic acid (2.313 g, 12.85 mmol), potassium carbonate (8.46 g, 6.12 mmol), and Sphos Pd G2 (0.220 g, 0.306 mmol) were mixed in a three-neck flask which was flushed with N$_2$ gas. A mixture of tetrahydrofuran (200 mL) and water (25 mL) was sparged with N$_2$ and cannulated into the reaction flask while stirring. The reaction vessel was then heated to 60°C and stirred overnight under positive N$_2$ pressure. The following morning, the reaction mixture was filtered out, and the product was recrystallized from hexanes at 60°C to yield the Me$_2$(alkoxy-tpdc) product (methoxy:
1.522 g, 40%; ethoxy: 1.102 g, 21%; n-propoxy: 0.435 g, 11%; n-butoxy: 2.312 g, 42%; n-hexoxy: 3.131 g, 55%).

**Deprotection to H$_2$(alkoxy-tpdc) linker.** Dissolve protected Me$_2$(alkoxy-tpdc) in a 50:50 mixture of tetrahydrofuran and 1M aqueous NaOH and heat overnight at 80°C. Upon cooling, rotovap off THF layer and acidify solution to pH 0 with concentrated HCl, precipitating out H$_2$(alkoxy-tpdc) as a white solid (methoxy: 1.384 g, 93%; ethoxy: 1.030 g, 90%; n-propoxy: 0.401 g, 96%; n-butoxy: 2.113 g, 92%; n-hexoxy: 2.993 g, 88%).

### 4.1.2 Synthesis of Zr(alkoxy-tpdc) framework

**Solvothermal synthesis of Zr(alkoxy-tpdc) framework.** A dry Schlenk flask was flushed with N$_2$ gas and charged with H$_2$(alkoxy-tpdc) (3.726 mmol), anhydrous ZrCl$_4$ (0.620 g, 2.661 mmol), and concentrated HCl (5 mL). 150 mL of dry DMF was then cannulated into the Schlenk flask, which was stirred for 36 hours at 80°C under positive N$_2$ pressure, precipitating Zr(alkoxy-tpdc) as an off-white solid.

**Activation of Zr(alkoxy-tpdc) framework.** While still within the Schlenk and under N$_2$, the stirring was stopped and the product was allowed to settle to the bottom of the flask. The supernatant was cannulated off and replaced with dry DMF and the reaction mixture was allowed to stir for another 8 hours. This procedure was then repeated three more times with dry THF. Following this, the flask was sealed and transferred into a glovebox, where the final Zr(alkoxy-tpdc) product was filtered off.

### 4.2 Results and Discussion

As predicted, the alkyl-functionalized frameworks were determined to form largely isostructurally to the unfunctionalized framework, suggesting that they share the $F\overline{4}3m$ space group \cite{18}; these results were validated by powder x-ray diffraction patterns (Figure 15) showing nearly-identical patterns for all frameworks regardless of alkyl chain length. This also corroborated the prediction that the alkyl chains would form an isotropic
and semiliquid environment within the pores that could potentially solvate methane molecules.

Figure 15: PXRD patterns comparing the structures of the Zr(alkoxy-tpdc) frameworks, along with the unsubstituted Zr(tpdc) framework, establish that the entire series is isostructural.

Ultimately, the Zr(alkoxy-tpdc) series failed to increase methane capacities past that of the unsubstituted Zr(tpdc) framework (Figure 16), suggesting that blind alkyl functionalization without fine-tuning is not a viable strategy for increasing methane binding in metal-organic frameworks. This caveat noted, however, the methane uptake of the frameworks does not decrease unilaterally with increasing alkyl chain length (and hence decreasing pore space in the framework), as the Zr(propoxy-tpdc) framework has a higher uptake than the Zr(ethoxy-tpdc) framework, and the Zr(hexoxy-tpdc) framework similarly outperforms the Zr(butoxy-tpdc) framework. This abnormality suggests that while the functionalized frameworks are incapable of capturing as much methane as an empty-
pored equivalent, some degree of nonpolar methane solvation is indeed occurring within the pores of the framework.

![Figure 16: Methane storage capacities for the Zr(alkoxy-tpdc) series. Of note, the Zr(propoxy-tpdc) and Zr(hexoxy-tpdc) frameworks have higher uptakes than the Zr(ethoxy-tpdc) and Zr(butoxy-tpdc) frameworks, respectively, indicating that a degree of methane solvation or coordination within the pores is occurring.](image)

5 Conclusion

Via a variety of novel organic and inorganic syntheses, we have synthesized or created improved routes to a number of metal-organic frameworks of substantial theoretical interest. We provided a substantially improved preparation for Cu[Ni(pdt)$_2$] than the established literature preparation, and determined our improved framework to have significant potential applications in gas separations and photoconductivity. We provided a viable synthetic route to the MOF-74 analogue Mg$_2$(doabpdc), a previously-unreported framework of great theoretical interest due to the potential for π-stacking electronic interactions between linkers. Though the framework did not prove to have enhanced thermal sta-
bility over an unfunctionalized version, we were able to crystallize the anthracene-based 
Mg$_2$ in a substantially more crystalline form than we were capable of creating unfunc-
tionalized Mg$_2$(dotpdc). Finally, we synthesized a series of alkylated UiO-68 frameworks 
that, while they failed to create a nonpolar semiliquid environment within the pores of 
the framework that could successfully dissolve and bind methane more effective than an 
unsubstituted framework, did demonstrate the existence of methane-alkyl interactions be-
tween the framework and the gas. These intellectually-valuable results may help serve as 
foundational work for further analytical studies upon similar metal-organic frameworks.

6 Acknowledgements

The first two years of my undergraduate degree here at UC Berkeley were spent fumbling 
through classes and labwork without really knowing what I was doing. It is therefore a 
testament to the transformative character of the Long Group that the latter two years of 
my time at Cal were not characterized by stumbling blindly from task to task, but rather 
by stumbling blindly and drunkenly from task to task.

For this exceptional feat I must commend above all others my friend and mentor, 
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References


## Appendices

### A Supporting Information: Cu[Ni(pdt)$_2$] Synthesis

#### A.1 Scheme: Synthesis of Na[Ni(pdt)$_2$]$\cdot$2H$_2$O Metalloligand

![Scheme](image)

*Figure 17: Synthesis route to the Na[Ni(pdt)$_2$]$\cdot$2H$_2$O metalloligand used in the synthesis of Cu[Ni(pdt)$_2$].*

Procedure adapted from Kobayashi, et. al.$^{[15]}$ Alternative oxidizing agents, including ferrocenium tetrafluoroborate, hypervalent iodine, and exposure to air were also tested as alternatives to diiodine, and found to produce similar products.
A.2 Scheme: Synthesis of Cu[Ni(pdt)$_2$] Framework

\[
\text{Na[Ni(pdt)$_2$] + Cu} \quad \text{fast} \quad \rightarrow \text{Cu[Ni(pdt)$_2$]}
\]

**Figure 18:** The Cu[Ni(pdt)$_2$] framework forms swiftly at room temperature when the two precursors are mixed together in solution. The rapidity and ease of this synthesis makes scaleup easy and opens the doors to methods like spin-coating to create thin films of the framework.

A.3 Powder X-ray Diffraction Data for Cu[Ni(pdt)$_2$]

**Figure 19:** Powder x-ray diffraction data of the air-free Cu[Ni(pdt)$_2$] framework, with Miller planes labeled. Space group: P4$_2$/mmc (tetragonal).
A.4 Photoconductivity Data for Cu[Ni(pdt)$_2$]

Figure 20: The maximum current density of Cu[Ni(pdt)$_2$] increases nearly threefold under light (20b) than in the dark (20a).
Figure 21: Conductivity as a function of optical flux in Cu[Ni(pdt)$_2$] shows a linear relation between optical intensity and conductivity.

Figure 22: Under an illumination of 111.3 mW/cm$^2$, Cu[Ni(pdt)$_2$] increases in temperature by about 1°C in 30 seconds.
B Supporting Information: Mg$_2$(doabpdc) Synthesis

B.1 Scheme: Synthesis of H$_4$(doabpdc) Ligand

![Scheme of H$_4$(doabpdc) Ligand Synthesis]

**Figure 23:** Synthesis route to the H$_4$(doabpdc) linker used in the synthesis of the Mg$_2$(doabpdc) framework.

B.2 Scheme: Synthesis of Mg$_2$(doabpdc) Framework

\[
\text{H}_4\text{(doabpdc)} + \text{Mg(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \xrightarrow{120^\circ\text{C}, 8\text{h}} \frac{1}{2} \text{Mg}_2\text{(doabpdc) + 4.5H}_2\text{O} + \text{4HNO}_3
\]

**Figure 24:** Solvothermal synthesis of the Mg$_2$(doabpdc) framework.
B.3 Thermogravimetric Analysis of Mg$_2$(doabpdc)

(a) Thermogravimetric analysis of Mg$_2$(doabpdc) in the region from 25° C to 475° C.

(b) Thermogravimetric analysis of Mg$_2$(dotpdc) in the region from 60° C to 525° C.

Figure 25: Temperature-mass loss curves for Mg$_2$(doabpdc) and Mg$_2$(dotpdc)
C Supporting Information: Zr(alkoxy-tpdc) Series Synthesis

C.1 Scheme: Synthesis of H₂(alkoxy-tpdc) Ligand Series

**Figure 26:** A series of isostructural functionalized UiO-68 linkers (alkoxy-tpdc)²⁻ were synthesized by alcohol S_N₂ to produce alkyl chains ranging from one carbon to six carbons long, followed by cross-coupling to produce the full three-ring terphenyl linker.

C.2 Scheme: Synthesis of Zr(alkoxy-tpdc) Framework Series

\[
H₂(\text{alkoxy-tpdc}) + \text{ZrCl}_4 \xrightarrow{80^\circ \text{C}, 36h \text{ DMF, conc. HCl}} \text{Zr}(\text{alkoxy-tpdc})
\]

**Figure 27:** The Zr(alkoxy-tpdc) frameworks were synthesized by solvothermal conditions analogous to the synthesis conditions of Zr(tpdc), also known as UiO-68.
C.3 Powder X-ray Diffraction Data for Zr(alkoxy-tpdc) Series

*Figure 28:* Zr(methoxy-tpdc) PXRD pattern

*Figure 29:* Zr(ethoxy-tpdc) PXRD pattern
Figure 30: Zr(propoxy-tpdc) PXRD pattern

Figure 31: Zr(butoxy-tpdc) PXRD pattern
Figure 32: Zr(hexoxy-tpdc) PXRD pattern

Figure 33: Zr(tpdc) PXRD pattern