Title
Covalent Organic Frameworks for the Catalytic Reduction of Carbon Dioxide

Permalink
https://escholarship.org/uc/item/7319x8qd

Author
Diercks, Christian Simon

Publication Date
2018

Peer reviewed|Thesis/dissertation
Covalent Organic Frameworks for the Catalytic Reduction of Carbon Dioxide

by

Christian S. Diercks

A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Omar M. Yaghi, Chair
Professor Matthew B. Francis
Professor Christopher J. Chang
Professor Kristin A. Persson

Fall 2018
Covalent Organic Frameworks for the Catalytic Reduction of Carbon Dioxide

by

Christian S. Diercks

Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Omar M. Yaghi, Chair

Chapter 1: Introduction to the fundamentals of the reticular synthesis of covalent organic frameworks (COFs). The historical development of COFs, general design considerations, crystallization techniques, and framework functionalization are discussed.

Chapter 2: In this chapter I describe modular optimization of covalent organic frameworks, in which the building units are cobalt porphyrin catalysts linked by organic struts through imine bonds, to prepare a catalytic material for aqueous electrochemical reduction of CO\textsubscript{2} to CO. Catalyst optimization by reticular tuning of the structure metrics and by a building block heterogeneity approach are described. The materials exhibit high Faradaic efficiency (90%) and turnover numbers (up to 290,000 with initial turnover frequency 9,400 h\textsuperscript{-1}) at pH 7 with an overpotential of 550 mV, equivalent to a 60-fold improvement in activity compared to the molecular cobalt complex, with no degradation over 24 h. X-ray absorption data reveal the influence of the COF environment on the electronic structure of the catalytic cobalt centers.

Chapter 3: The electronic character of porphyrin active sites for electrocatalytic reduction of CO\textsubscript{2} to CO in a two-dimensional covalent organic framework is optimized by covalent functionalization of its reticular structure. Efficient charge transport along the COF backbone promotes electronic connectivity between remote functional groups and the active sites and enables the modulation of the catalytic properties of the system. X-ray absorption measurements on the cobalt L-edge for the modified COFs enable correlations between the inductive effects of the appended functionality and the electronic character of the reticulated molecular active sites. Directly growing the COFs as oriented thin films onto the electrode significantly improves electrochemical accessibility and enhances their current density to up to 65 mA/mg — a performance well beyond related molecular catalysts and the first generation of COFs for CO\textsubscript{2} reduction. The catalysts are stable for over 12 hours without any loss in reactivity.

Chapter 4: Further development of COF electrocatalysts requires a better understanding of their electronic structure. The synthesis of a single-layer COF with spatially modulated internal potentials provides new opportunities for manipulating and studying the electronic structure of these molecularly defined materials. In this chapter I discuss the fabrication and electronic characterization of COF-420, a single-layer porphyrin-based square lattice COF containing a periodic array of oriented, type II electronic heterojunctions. In contrast to previous donor-acceptor COFs, COF-420 is constructed from building blocks that yield identical cores upon reticulation, but that are bridged by electrically asymmetric linkers supporting oriented electronic dipoles.
Scanning tunneling spectroscopy reveals staggered gap (type II) band alignment between adjacent molecular cores in COF-420, in agreement with first-principles calculations. Hirshfeld charge analysis indicates that dipole fields from oriented imine linkages within COF-420 are the main cause of the staggered electronic structure in this square grid of atomically-precise heterojunctions.

**Chapter 5:** The problem with current state-of-the-art catalysts for CO$_2$ photo- or electro-reduction is rooted in the notion that no single system can independently control, and thus, optimize the interplay between activity, selectivity, and efficiency. In this chapter I give an outlook on how reticular chemistry of metal-organic frameworks (MOFs) and COFs can be utilized to optimize all of these properties independently; the molecular building blocks that are in a reticular chemist’s toolbox are chosen in such a way that the structures are rationally designed, framework chemistry is performed to integrate catalytically active components, and the manner in which these building blocks are connected endows the material with the desired optoelectronic properties.
Covalent Organic Frameworks for the Catalytic Reduction of Carbon Dioxide

Table of Contents

Table of Contents ........................................................................................................................... i
Acknowledgements ....................................................................................................................... v
Dedication ..................................................................................................................................... vi

Chapter 1. Reticular Synthesis of Covalent Organic Frameworks ................................................. 1
  1.1 Introduction .......................................................................................................................... 2
  1.2 A Chronology of Chemistry Beyond Molecules ................................................................. 2
  1.3 Conceptual Basis of Covalent Organic Frameworks .......................................................... 5
  1.4 Framework Reactions and Properties .............................................................................. 9
  1.5 Future Prospects ............................................................................................................. 12
  1.6 Supporting Information ................................................................................................. 14
  1.7 References .................................................................................................................... 26

Chapter 2. Covalent Organic Frameworks Comprising Cobalt Porphyrins for the
Electrocatalytic Reduction of Carbon Dioxide .............................................................................. 31
  2.1 Introduction ...................................................................................................................... 32
  2.2 Results and Discussion ................................................................................................. 32
    2.2.1 Synthesis of Covalent Organic Frameworks ............................................................... 32
    2.2.2 Electrochemical Characterization ............................................................................. 34
    2.2.3 Reticular Tuning of Structure Metrics ..................................................................... 35
    2.2.4 Reticular Tuning Through Building Block Heterogeneity ........................................ 35
    2.2.5 Spectroelectrochemical Characterization ................................................................. 36
    2.2.6 Mechanism Elucidation ............................................................................................ 37
  2.3 Conclusion ....................................................................................................................... 38
  2.4 Supporting Information .................................................................................................... 40
    2.4.1 Material Synthesis and Characterization ................................................................. 40
    2.4.2 Synthesis .................................................................................................................. 40
    2.4.3 Thermogravimetric Analysis .................................................................................... 43
    2.4.4 Ultraviolet-Visible Spectroscopy ............................................................................. 44
    2.4.5 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy ............... 45
2.4.6 Solid-State Nuclear Magnetic Resonance Spectroscopy ........................................ 52
2.4.7 Scanning Electron Microscopy ............................................................................. 54
2.4.8 Powder X-ray Diffraction Analysis ........................................................................ 57
2.4.9 Structural Modeling ............................................................................................... 61
2.4.10 Porosity and Specific Surface Area Analysis ......................................................... 67
2.4.11 Grazing Incidence Wide-Angle X-ray Scattering of Thin-Film COFs ................... 78
2.4.12 Cross-Sectional Scanning Electron Microscopy of Thin-Film COFs ..................... 80
2.4.13 Electrochemistry .................................................................................................. 81
2.4.14 Cyclic Voltammetry ............................................................................................. 83
2.4.15 GC Calibration ..................................................................................................... 86
2.4.16 Electrolysis at Different Applied Potentials .......................................................... 87
2.4.17 Long-Term Electrolysis of COF-366-Co and COF-367-Co .................................. 91
2.4.18 Characterization of COF-366-Co After Long-Term Electrolysis ........................... 95
2.4.19 Reusability ............................................................................................................ 96
2.4.20 Control Experiments ........................................................................................... 97
2.4.21 Electrolysis with Bimetallic COFs ........................................................................ 100
2.4.22 Spectroelectrochemistry of Thin-Film COF-366-Co on FTO .............................. 104
2.4.23 Direct Current Conductivity Measurement of COF-366-Co on Silicon Oxide .... 108
2.4.24 Reactivity of Thin-Film COF-366-Co .................................................................. 109
2.4.25 Kinetic Data .......................................................................................................... 110
2.4.26 List of Some Existing Electrocatalysts for CO₂ Reduction ................................. 113
2.4.27 X-ray Absorption Spectroscopy .......................................................................... 116
2.5 References .................................................................................................................. 121

Chapter 3. Reticular Electronic Tuning of Porphyrin Active Sites in Covalent Organic Frameworks for Electrocatalytic Carbon Dioxide Reduction .............................................................................. 127

3.1 Introduction .................................................................................................................. 128
3.2 Results and Discussion ............................................................................................... 129
3.2.1 Oriented Thin Films of COF-366-Co. .................................................................. 129
3.2.2 Covalent Functionalization of COF-366-Co......................................................... 131
3.2.3 X-ray Absorption Spectroscopy .......................................................................... 132
3.2.4 Electrochemical Characterization ...................................................................... 133
3.3 Conclusion .................................................................................................................. 134
3.4 Supporting Information ............................................................................................ 135
3.4.1 COF Synthesis ...................................................................................................... 135
3.4.2 Proposed Mechanism of CO₂ Reduction ............................................................ 135
Chapter 4. Local Electronic Structure of Molecular Heterojunctions in a Single-Layer 2D Covalent Organic Framework ................................................................. 174

4.1 Introduction .................................................................................................................. 175

4.2 Results and Discussion ............................................................................................... 175

4.2.1 Synthesis of COF-420 ........................................................................................... 175

4.2.2 Scanning Tunneling Microscopy Studies ............................................................. 176

4.2.3 Scanning Tunneling Spectroscopy ........................................................................ 177

4.2.4 DFT Calculations .................................................................................................. 178

4.3 Conclusion .................................................................................................................... 181

4.4 Supporting Information ............................................................................................... 183

4.4.1 COF Synthesis on Au(111) ................................................................................... 183

4.4.2 Electronic Structure Calculations. ........................................................................ 183

4.4.3 COF-420 Monolayer on Au(111): Partial Charge Density Plots for the VB, CB, VB-1 and CB+1 States.......................................................... 184

4.4.4 Electronic Structure of a Free-Standing COF-420 Monolayer ............................. 184

4.4.5 Justification of the Assignment of Core A from TAPP and Core B from TFPP .. 186

4.4.6 Synthesis of Starting Materials ............................................................................. 188

4.5 References .................................................................................................................... 191

Chapter 5. Is Reticular Chemistry the Answer to the Next Generation of CO_2 Reduction Catalysts? ................................................................................................ 194

5.1 Introduction ................................................................................................................... 195

5.2 MOF photocatalysts for CO_2 reduction .................................................................... 197

5.2.1 First generation: Selectivity and activity. ......................................................... 197

5.2.2 Second generation: Optical efficiency. ............................................................. 198

5.2.3 Third generation: Electronic efficiency. ........................................................... 199

5.2.4 Fourth generation: Future systems................................................................. 200

5.3 MOF and COF electrocatalysts for CO_2 reduction .................................................. 202
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3.1</td>
<td>First generation: Selectivity and activity.</td>
<td>202</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Second generation: Efficiency.</td>
<td>203</td>
</tr>
<tr>
<td>5.4</td>
<td>Outlook</td>
<td>205</td>
</tr>
<tr>
<td>5.5</td>
<td>References</td>
<td>207</td>
</tr>
</tbody>
</table>
Acknowledgements

I want to thank Prof. Omar M. Yaghi for his guidance and support throughout the course of my doctorate. He has provided me with the necessary infrastructure, resources, and freedom to explore my ideas and has encouraged me to do innovative and creative research. The discussions we have had about my research and about the discipline of chemistry in general have had a profound impact on my development as a scientist. I am grateful for his continued mentorship and I will try to adhere to his high standards for challenging and novel research in my future career.

I also want to express my gratitude to Prof. Christopher J. Chang for his support in our collaborations. Access to his equipment and the expertise of him and his group were instrumental for the success of my research. His career advice and recommendations have helped me a lot in achieving my goals.

Furthermore, I want to thank the remaining members of my dissertation committee, Prof. Matthew B. Francis and Prof. Kristin A. Persson, for challenging and thought provoking questions, as well as helpful discussions. Many of my projects were inspired by their recommendations and suggestions.

I want to thank my two undergraduate advisors, Sir Prof. J. Fraser Stoddart and Prof. Jean-Pierre Sauvage. My time in their groups has shaped me as a scientist and as a person. They have taught me to be curious, to aim high, and to think deeply about my results. During the time in their groups I have learned more than in the remainder of my undergraduate studies and I am deeply grateful for their continued guidance.

Additionally, I want to thank all the people whose mentorship and collaboration has helped me throughout my graduate studies: Prof. Song Lin, Prof. Yuebiao Zhang, Prof. Peidong Yang, Prof. Mike Crommie, Prof. Jean-Luc Brédas, Prof. Alexander Schoedel, Dr. Markus J. Kalmutzki, Dr. Eugene A. Kapustin, Peter J. Waller, and Trinity Joshi. I also want to thank the rest of the Yaghi group for helpful discussions and a good atmosphere at work.

This work would not have been possible without the help of Ms. Karen Wong who has helped me stay on top of things and has helped me out when I was not. Without her, my life would have been much more difficult.

Finally, I want to acknowledge my parents, family, and friends: My father, who has sparked my interest in chemistry during long conversations on family hikes as a child. My mother who has supported and helped me in all of my endeavors even when I am overseas. My brothers who are always there for me and whose visits have made living abroad more bearable. Dr. Yuzhong Liu who has not only helped me grow as a scientist but who has also provided emotional support during more difficult times in graduate school. Last but not least, my friends who have encouraged and supported me throughout all these years.

Thank you very much!
To my family
Chapter 1
Reticular Synthesis of Covalent Organic Frameworks

Portions of this chapter have been published in:
1.1 Introduction

Gilbert N. Lewis’s seminal work on chemical bonding, “The Atom and the Molecule,” introduced the concept of what would become known as the covalent bond. He outlined a conceptual approach for addressing the fundamental question of how atoms can be joined to make molecules, and how to describe the bonding of the atoms within these molecules and its impact on reactivity and molecular properties. Chemists have since exploited these concepts in their efforts to master the craft of synthesizing specific molecules of varying structure and complexity, which has led to the art and science of total synthesis. Today, the precision with which organic molecules can be functionalized and their geometry controlled has matured to the point of rational synthesis. However, in contrast, an aspect that molecular chemistry could not control is how to link molecules together by covalent bonds to design extended structures. It is a necessary requirement that this reticulation process be carried out under synthetic conditions that maintain the integrity of the molecule, while allowing for microscopic reversibility in order to afford ordered, crystalline products. The chemistry of such extended organic solids remained largely undeveloped throughout the twentieth century, most likely because reticulating molecules formed through covalent bonds were amorphous materials, thus precluding their structural characterization by x-ray crystallography. This was especially true for two-dimensional (2D) and 3D covalent organic solids as highlighted by an article published in 1993: “Organic chemists are masterful at exercising control in zero dimension. One subculture of organic chemists has learned to exercise control in one dimension. These are polymer chemists, the chain builders… But in two or three dimensions, it is a synthetic wasteland.4

The challenge of making 2D and 3D covalent organic solids was addressed in the discovery and development of covalent organic frameworks (COFs), where extended structures are made by stitching organic molecules together through strong covalent bonds in a process termed reticular synthesis. The molecular units used in reticulation possess the functionality necessary to form specific linkages in a chemically and geometrically defined fashion to construct the framework. In the synthesis of crystalline COFs and the application of precision organic chemistry to their structures without losing crystallinity, covalent bonds create robustness and directionality (necessary to control spatial orientation of the building blocks), achieve well-defined crystalline solids, and ultimately introduce variations and complexity. Considering Lewis’ original work, COFs become the natural extension of the molecule. In a manner akin to how molecules are geometric constructs of atoms, COFs are geometric constructs of molecules linked by covalent bonds. Furthermore, just as the molecule positions atoms, COFs position molecules in a specific spatial orientation to encompass space into which the reactivity of the atom and the molecule are revealed and used in ways not possible in discrete molecules. Here, I highlight the theoretical basis for designing the framework and show how the covalent backbone allows for organic chemistry to be exercised beyond the molecule.

1.2 A Chronology of Chemistry Beyond Molecules

Since Lewis’ conceptual paper on the covalent bond, the systematic development of synthetic organic methodologies has led to several important advances in chemistry, a few of which are depicted in the timeline in Figure 1.1 The discovery of large macromolecular structures (1D polymers) opened up the field of organic performance materials. Another major milestone was the retrosynthesis of complex organic natural products and their use in the pharmaceutical
Improvements in synthetic methodology resulted in the realization of elaborate molecules, but the problem remained of how to get these molecules to assemble in a regular fashion into more complex, functional systems. One solution was supramolecular chemistry, in which noncovalent interactions guide molecular recognition processes, such as selective binding in the original crown ethers and cryptands. Molecular recognition proved useful not only for selective binding of guest molecules, but also as a means of templating the synthesis of molecular macrocycles and cages, and led to the templated synthesis of catenanes — molecules held together by mechanical interlocking of molecular rings. The manner in which mechanical bonds are introduced into frameworks is an aspect that will be discussed further below.

The knowledge of specific interactions can furthermore be used for the design of systems that undergo self-organization, i.e., well-defined extended supramolecular architectures produced by virtue of having selective weak interactions built into their molecular components. However, such supramolecular assemblies are difficult to modify without losing their structure because: (i) Modification of the building blocks will alter the interactions between the constituents and thus lead to different assemblies; (ii) performing chemistry on these assemblies is difficult without destroying their structural integrity; and (iii) the thermal and chemical robustness of their structure puts a limit on their applications. Although nature uses self-organization to assemble complex architectures like enzymes or DNA, these assemblies generally have a 1D covalent backbone that plays a crucial role in maintaining their overall structural integrity. Thus, it is essential to develop strategies that align molecular building blocks not by weak interactions, but rather by those based on strong covalent interactions in a geometrically well-defined manner. When this goal is achieved, it becomes possible to introduce functionalities and complexity within the backbone of such covalent frameworks.

Inspired by the underlying dynamic processes that form the basis for supramolecular chemistry, extensive research has been devoted to the formation of covalent bonds under thermodynamic control. This area has received widespread attention during the past decade as it facilitates the formation of complex molecular architectures, such as interlocking molecules and shape-persistent organic cage compounds. In 2005, the strategy of forming covalent bonds reversibly, which provides for error correction, was used to reticulate molecular building blocks into extended, crystalline covalent organic frameworks. The advantages of reticular synthesis were apparent as the strong bonding allowed for the removal of residual solvent molecules from these organic solids, resulting in highly porous, crystalline 2D and 3D frameworks (Figure 1.1). The architectural and chemical robustness of these COFs meant that precision organic and inorganic chemistry could be carried out on the framework without losing its crystallinity and thus commencing the development of the chemistry of the framework. The same chemistry used to make the COF backbone can be deployed along with metal-ion templates, to make metallated COFs, which upon demetallation yield woven framework structures with unusual elasticity (Figure 1.1). The maintenance of the crystallinity of COFs and the definitiveness of their structure, upon carrying out reactions with the precision of molecular chemistry, makes them a true extension of the covalent bond beyond the molecule. Although we focus on the transition from molecular chemistry to the framework and illustrate the latter by discussion of covalent organic frameworks, the concepts that will be introduced in going from the atom and the molecule to the framework are also applicable to other extended structures such as metal-organic frameworks.
Figure 1.1. Historical Development of Covalent Organic Frameworks. Chronology of advances from Lewis’ original concept of the covalent bond to organic molecules and to linking molecules into frameworks. Important advances in synthetic organic chemistry that have led to the development of 2D, 3D covalent organic frameworks (COFs), and more recently weaving frameworks.
1.3 Conceptual Basis of Covalent Organic Frameworks

Organic chemistry offers an extensive library of molecules that can be synthesized to serve as building blocks in the construction of COFs. A framework, whether a COF or any other covalent extended structure, is composed entirely of two distinct components — linkers (building units), and linkages (bonds formed between those units upon reticulation). Thus, the organic synthesis of COFs starts with the synthesis of the building blocks and ends with the reticulation of these building blocks by stitching them together in a designed way into an extended framework. The general approach for the reticular synthesis of COFs is illustrated in Figure 1.2. In step 1, a target network topology is identified and deconstructed into its fundamental geometric units. In step 2, these constituents are evaluated based on their points of extension (connectivity) and their geometry (i.e., tetrahedral vs. square planar for the connectivity of four). In step 3, equivalents of these geometric units are found in molecules and then deployed as linkers. Linkers are often large molecules as this allows for rigidity and predisposition of linking functionalities, and helps create porous structures with accessible space, low density, and high internal surface area. Furthermore, these properties play a critical role in providing access and space to address the molecules that are now locked in position at precise locations throughout the framework. Specific parts of these molecules can function as the sites of reactivity in catalytic transformations, binding of gases for applications in storage and separations, and modulation of electronic properties affecting the entire framework.

In terms of the underlying net, the geometry of the molecular building block is represented as a vertex figure to be linked into what is described as the augmented net. A question arises concerning the number of possibilities that may result from linking a building block of specific geometry. For example, linking of tetrahedra may result in one or more structures from a large number of possible ones (several million). Among this vast structure space, which will form? It has been the thesis of reticular synthesis that the most symmetric structures are the most likely to form when high-symmetry building blocks are used. Indeed, this has been found to be the case for a large majority of reported structures. The judicious choice of building blocks and the design of angles between the building blocks’ points of extension is a way to direct the synthesis to a target structure that may not be the most symmetric possibility. In order to construct a COF based on a desired topology, it is preferable to use rigid and well-defined building blocks that remain unaltered throughout the construction process. In step 4, the COF is produced through the formation of strong covalent bonds between the linkers. Typically, synthetic conditions must first be identified for crystalline products to be obtained. By balancing the thermodynamics (microscopic reversibility of the linkages between the building units) and the kinetics (appropriate rate of the reaction) of the COF forming reaction, crystalline 2D and 3D frameworks can be made. Finally, in step 5, if the product is single crystalline in nature, the material is characterized by x-ray or electron diffraction techniques. When suitable single crystals cannot be achieved, powder x-ray diffraction (PXRD) is used to evaluate whether the targeted structure has been successfully obtained. Indeed, it is often the practice that a PXRD pattern is calculated for the expected structure and compared to the experimentally acquired data. Such comparison, which facilitates the determination of the structure, would not be possible without knowledge of the targeted framework, so COFs are illustrative examples of true design in making solid-state materials.
Figure 1.2. Topological design and reticular synthesis of COFs. The steps involved in choosing the topology, deconstructing it into its fundamental geometric units, finding the equivalents of these in molecules and eventually reticulating them into the desired COF.

At present, there are >100 COF structures reported, with at least double that number in derivatives. All of these structures were prepared following the concepts outlined above and illustrated in Figure 1.2. Table 1.1 summarizes the connectivity, vertex figure, resulting topology, and the first reported COF examples. Thus far, all known COFs are based on a total of eight
common topologies. In the case of 2D COFs, there are five possible topologies for which the vertices are connected by one kind of edge (Figure S1.1). All of these have already been made as COFs (Table 1.1, Figure S1.2 to S1.6). For 3D topologies, there are many more possibilities, but only four of these have been reported in COFs (Table 1.1, Fig. S1.7 to S1.11).

COFs of varying linker connectivity and size, and character of the linkages, have been reported (Figure 1.3). In general, the reactions that are used in the formation of COFs can be divided in terms of the linkages they form. These are: (i) B-O (boroxine, boronate ester, borosilicate, and spiroborate), (ii) C=N (imine, hydrazone, and squaraine), (iii) C=N (aromatic) (triazine and phenazine), (iv) C-N (β-ketoenamine, imide, and amide), and (v) B=N (borazine); N=N (diazaoxy); and (vi) C=C (alkene) (Figure S1.12). The chemical stability of the resulting linkages follows the expected corresponding trends known in molecular organic chemistry; for example, the phenazine- and β-ketoenamine-based COFs maintain their structure and porosity in strong acids and bases. Molecular reactions for selected linkages are shown in Figure 1.3 to highlight the importance of carrying out the reaction under reversible conditions, which is generally achieved by solvothermal synthesis at elevated temperatures, typically up to 200°C with acid or base catalysts. In molecular organic chemistry most reactions are kinetically controlled and thus prone to errors, which require post-synthetic purification. This procedure is not possible in framework chemistry because the products of the reaction are insoluble. In essence, the challenge that was overcome by reticulating building blocks through covalent bonds to make COFs, is that the formation of the product as both phase-pure and crystalline were achieved in one step.
Figure 1.3. Linkages, linkers, and framework structures. COFs are composed of two main components — linkages and linkers. Here, examples of various linkages and linkers that have been used for the synthesis of COFs are shown, along with the combination of building units used to make COF structures. Color code: Color Code: H, white; B, orange; C, gray; O, red.
Table 1.1. Important nets in the chemistry of covalent organic frameworks. CN refers to the coordination number of the vertices. If there are $p$ kinds of vertex, $q$ kinds of edge (link), $r$ kinds of ring (faces), and $s$ kind of tile, the transitivity is defined as $pqrs$.

<table>
<thead>
<tr>
<th>CN</th>
<th>Net symbol</th>
<th>Vertex figure</th>
<th>Transitivity</th>
<th>First report (ref.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D topologies</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>hcb</td>
<td>triangle</td>
<td>111</td>
<td>2005$^6$</td>
</tr>
<tr>
<td>4</td>
<td>sql</td>
<td>square</td>
<td>111</td>
<td>2011$^{27}$</td>
</tr>
<tr>
<td>4</td>
<td>kgm</td>
<td>square</td>
<td>112</td>
<td>2014$^{28}$</td>
</tr>
<tr>
<td>6</td>
<td>hxl</td>
<td>hexagon</td>
<td>111</td>
<td>2015$^{29}$</td>
</tr>
<tr>
<td>3,6</td>
<td>kgd</td>
<td>triangle, hexagon</td>
<td>211</td>
<td>2017$^{30}$</td>
</tr>
<tr>
<td>3D topologies</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>dia</td>
<td>tetrahedron</td>
<td>1111</td>
<td>2009$^{31}$</td>
</tr>
<tr>
<td>3,4</td>
<td>ctn</td>
<td>triangle, tetrahedron</td>
<td>2122</td>
<td>2007$^7$</td>
</tr>
<tr>
<td>3,4</td>
<td>bor</td>
<td>triangle, tetrahedron</td>
<td>2122</td>
<td>2007$^7$</td>
</tr>
<tr>
<td>4,4</td>
<td>pts</td>
<td>square, tetrahedron</td>
<td>2122</td>
<td>2016$^{32}$</td>
</tr>
</tbody>
</table>

1.4 Framework Reactions and Properties

In order to design materials tailored for specific properties (Table 1.2), specific functionalities need to be present in the COF backbone. Functionalization of COFs can be carried out (i) pre-synthetically by functionalizing the molecular building blocks$^{45}$ or (ii) through post-synthetic modification of the preformed framework itself.$^{46,47}$ The question of whether a functionality should be introduced pre- or post-synthetically depends on whether this functional group is compatible with the COF forming reaction. Not all chemical functionalities can be used in COF formation — for example, the covalent bonds may be too strong to be sufficiently reversible — so some functionalities must be added into existing frameworks. Fortunately, the open and accessible pores of the organic backbone allow for precise functionalization of the structures’ interior space. One example that illustrates the versatility and the scope of the functionalization of COFs is COF-366 and it is the focus of this section (Figure 1.4).$^{48}$ Initially, this layered, 2D material received much attention because of its high charge-carrier mobility. By both, pre- as well as post-synthetic modification, COF-366 was tuned for vastly different applications (Table 1.2). Pore functionalization of COF-366 was carried out for the optimization of its CO$_2$ uptake. In this context, the pore was decorated with varying amounts of hydroxyl- or carboxyl groups to increase the interactions of the framework with CO$_2$.$^{49}$ Because COF-366 is reticulated by the formation of imine bond linkages, the hydroxyl groups are tolerated during the framework formation and can thus be pre-synthetically installed on the organic building blocks. However, carboxyl groups were integrated post-synthetically by ring-opening reactions of hydroxyl groups on the linker with maleic anhydride. This synthetic strategy was essential, as pre-synthetic installation of carboxyl group would interfere with the reaction conditions used to make the COF. A different strategy for the introduction of functional groups onto the COF-366 backbone is the use of the copper(I)
catalyzed click reaction. Azides were installed on the linker and then post-synthetically reacted with alkynes bearing hydroxyl, carboxyl, or amino functional groups. Both strategies resulted in substantially improved CO₂ uptake capacities.

COF-366 has also been used in enantioselective catalysis, where copper(I)-catalyzed click chemistry was applied to covalently incorporate chiral proline moieties within the framework’s pores. The resulting material showed high activity in catalytic enantioselective Michael additions. Interestingly, immobilizing catalytic units on this well-defined COF made this transformation amenable to continuous flow conditions. In this thesis I will show how, metallation of the porphyrin building block resulted in a cobalt-functionalized derivative, COF-366-Co. This framework and other derivatives showed high activity and selectivity for the electrocatalytic reduction of CO₂ to CO in water with improved performance (26 fold increase in activity) over the molecular catalyst. In sum, modification of COFs with a large number of different functionalities has been used to adjust pore metrics, stabilize the framework itself, improve interactions with gases, for applications in energy storage, and for a manifold of catalytic transformations as summarized in Table 2. These modifications of COFs can be done without losing crystallinity or porosity, giving credence to the notion of frameworks being used in chemical transformations as molecules.
Figure 1.4. Precise introduction of functionality onto the COF backbone. Organic and inorganic functionalization of COFs by pre-synthetic and post-synthetic modification, as exemplified for COF-366 can lead to materials with tailored properties for applications in areas such as CO₂ capture, enantioselective catalysis and electrocatalysis.
Table 1.2. Selected properties of covalent organic frameworks. Lowest and highest reported values for the indicated property are listed. $S_A^{BET}$ refers to the Brunauer-Emmet-Teller surface area. PSM refers to post-synthetic modification.

<table>
<thead>
<tr>
<th>Property</th>
<th>Compound</th>
<th>Achieved value or year of report</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lowest reported value</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>COF-108</td>
<td>0.17 g cm$^{-3}$</td>
<td>6</td>
</tr>
<tr>
<td><strong>Highest reported value</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore aperture</td>
<td>HHTP-DPB COF</td>
<td>59</td>
<td>37</td>
</tr>
<tr>
<td>$S_A^{BET}$ for 3D COFs</td>
<td>COF-103</td>
<td>4210 m$^2$ g$^{-1}$</td>
<td>7</td>
</tr>
<tr>
<td>$S_A^{BET}$ for 2D COFs</td>
<td>TPB-DMTP-COF</td>
<td>2015 m$^2$ g$^{-1}$</td>
<td>60</td>
</tr>
<tr>
<td>Excess CO$_2$ uptake (273 K)</td>
<td>[HO]$_{50%}$-H$_2$P-COF</td>
<td>174 mg g$^{-1}$</td>
<td>50</td>
</tr>
<tr>
<td>Proton conductivity (373 K)</td>
<td>TPB-DMTP-COF</td>
<td>7.0 $10^{-4}$ S</td>
<td>61</td>
</tr>
<tr>
<td>Charge mobility</td>
<td>COF-366</td>
<td>8.1 cm$^2$ V$^{-1}$ s$^{-1}$</td>
<td>48</td>
</tr>
<tr>
<td><strong>Earliest report</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capacitance</td>
<td>DAAQ-TPF COF</td>
<td>2013</td>
<td>39</td>
</tr>
<tr>
<td>Heterogeneous catalysis</td>
<td>Pd/COF-LZU1</td>
<td>2011</td>
<td>47</td>
</tr>
<tr>
<td>Electrocatalysis</td>
<td>COF-366-Co</td>
<td>2015</td>
<td>52</td>
</tr>
<tr>
<td>Photocatalysis</td>
<td>TFPT-COF</td>
<td>2014</td>
<td>57</td>
</tr>
<tr>
<td>PSM</td>
<td>COF-LZU1</td>
<td>2011</td>
<td>47</td>
</tr>
<tr>
<td>Oriented thin films</td>
<td>COF-5</td>
<td>2011</td>
<td>62</td>
</tr>
<tr>
<td>Photoluminescence</td>
<td>TP-COF</td>
<td>2008</td>
<td>63</td>
</tr>
<tr>
<td>Photoconduction</td>
<td>TP-COF</td>
<td>2009</td>
<td>64</td>
</tr>
</tbody>
</table>

1.5 Future Prospects

Reticular synthesis of covalent organic frameworks is still at an early stage of its development. Currently, the field is mostly driven by potential future applications and often at the expense of developing the basic chemistry of the framework or its design principles. However, there is no doubt that the ability to build frameworks by covalently stitching together organic molecules will continue to be important because of the precision of this process and the control being exercised in placing molecules in specific geometric and spatial arrangements. The power of this practice is already leading to unusual materials and properties with a wide range of applications in catalysis, gas storage and separations, and electronics. It is anticipated that this will continue to be important well into the future because historically, the field of chemistry has flourished as our skills to control matter on the atomic and molecular level advanced. In the present context, the progression from atoms and molecules to assemblies and, more recently, to frameworks is an intellectually engaging and rewarding endeavor. At this juncture, the question is how these exquisite designs combined with our well-honed synthetic skills will bring new understanding of problems in chemistry. It is possible to provide a glimpse into the impact that the chemistry of the framework will make on various challenging topics such as interfaces, molecular complexity, and hierarchical structures, to mention a few. Here, I examine interfaces and use this subject as an illustrative example.
First, the chemistry of the framework gives precise definition to the underlying atomic arrangement of the structure. I think of interfaces as boundaries between different phases of matter or materials. In the framework, the interface is the boundary defining the framework-substrate interaction, which, unlike many other interfaces, is well defined and can be altered nearly at will without changing the integrity of the backbone structure. This provides flexibility to craft the boundary between the substrate molecule and the framework to affect a highly specific process. For example, one can envision functionalizing the boundary so that it mimics the active site of an enzyme for chemical transformations to be carried out in a stable framework, thus forgoing the fragility of the enzyme.

Second, the framework intrinsically imparts complexity within order to the geometry of the internal surface. Not only is the composition of the binding sites being controlled, but this is also accomplished in the confines of a well-defined, ordered geometry and with precise metrics describing where the binding sites are located on the internal surface of the framework. Because the backbone remains unchanged when substrates bind, the distance between these binding sites is fixed, and it is possible to dial in and apportion the active sites in the exact amount and distribution necessary.

Third, the traditional view of the surface as being 2D, which means that it can be approached freely by an incoming substrate to produce an interface, is no longer true in the framework. Here, the surface can be 2D but, more importantly, it can also assume various different 3D surface geometries each of which may have a hierarchical arrangement of pores capable of confining the substrates to interacting with binding sites of a specific size and geometry. The ability to have a network interface within a 3D framework construct that can be chemically modified, its pore-shape and -size systematically varied, and the electronic and steric character of the designed binding sites crafted to promote a specific binding, constitutes the emergence of shape, size, and electronically selective surfaces and interfaces. In this thesis I highlight how covalent organic frameworks grown on interfaces can be reticcularly tuned to function as electrocatalysts for complex chemical transformations or as intrinsic two-dimensional heterojunctions.
1.6 Supporting Information

Figure S1.1. List of the five edge-transitive 2D topologies represented as their respective augmented nets. Linking triangles with one kind of edge yields a hcb net of transitivity 111. Linking of squares can yield the default sql topology (111) or a kgm layer (112). hxl nets are formed when hexagons are linked (111), and the combination of triangles and hexagons yields a kgd topology (211). Color code: Polygons, blue and orange.
Figure S1.2. Covalent organic frameworks of hcb topology. Synthetic scheme for the formation of COF-1 and COF-5, both of hcb topology. Self-condensation of the linear ditopic BDBA linker through trigonal tritopic boroxin linkages affords COF-1 with layers stacking in a staggered conformation. Cross-condensation of trigonal tritopic HTTP with linear ditopic BDBA yields COF-5 having an eclipsed stacking motif. Color code: H, white; B, orange; C, gray; O, red.
Figure S1. Covalent organic frameworks of sql topology. Synthetic scheme for NiPC-COF and COF-366-Co, both of sql topology. NiPC-COF is constructed from D$_{4h}$ symmetry square shaped tetratopic (OH)$_4$PeNi building units which are reticulated by linear ditopic BDBA struts. COF-366-Co is formed by reticulation of the D$_{4h}$ square-shaped tetratipic (Co)TAP with linear ditopic BDA. Color code: H, white; B, orange; C, gray; N, blue; M (Ni, Co), pink.
Fig. S1.3. Covalent organic frameworks of kgm topology. Synthetic scheme for the formation of [(ETTA)(BDA)₂]_{imine} and SiOC-COF-1, both of kgm topology. Reticulation of ETTA with BDA yields [(ETTA)(BDA)₂]_{imine} with two distinct kinds of pore, triangular micropores and hexagonal mesopores. Reacting ETTA with both BDA and BPDA yields SiOC-COF-1 with three distinct kinds of pore, two different trigonal micropores and a hexagonal mesopore. Color code: H, white; C, gray; N, blue.
Figure S1.5. Covalent organic frameworks of hxl topology. Synthetic scheme for [(HBC)(BDA)$_3$]$_{imine}$ of hxl topology. [(HBC)(BDA)$_3$]$_{imine}$ is formed by reticulation$^{17c}$
Figure S1.6. Covalent organic frameworks of kgd topology. Synthetic scheme for the formation of [(HAT)(NTBA)2]amine and [(HAT)(NTBCA)2]amine, both of kgd topology. Reticulation of hexatopic HAT with trigonal tritopic NTBA or NTBCA yields [(HAT)(NTBA)2]amine and [(HAT)(NTBCA)2]amine, respectively. The structures feature trapezoidal channels of 9.5 and 12.7 Å, respectively, which propagate along the crystallographic c-axes of the frameworks. Color code: H, white; C, gray; N, blue.
Figure S1.7. 3D topologies accessed in COFs represented as augmented nets. All 3D topologies realized in COF chemistry rely on the use of tetrahedral building units. The default topology for linking of tetrahedra is dia. Combination of tetrahedral and trigonal nodes afford ctn and bor nets. The use of tetrahedral and square planar building units yields a pts net. Color code: Polyhedra, blue; polygons, orange.
Fig. S1.8. Covalent organic frameworks of dia topology. Synthetic scheme for the first COF with dia topology, COF-300. All hydrogen atoms are omitted for clarity. Color Code: C, gray; tetrahedral C, blue tetrahedral; N, blue.
Fig. S1.9. Covalent organic frameworks of bor topology. Synthetic scheme for the formation of COF-108 of bor topology. Reticulation of TBPM with HHTP yields COF-108. All hydrogen atoms are omitted for clarity. Tetrahedral carbon and silicon, blue; core of the tritopic linker, orange polygons. Color Code: B, orange; C, gray; O, red.
**Fig. S1.10. Covalent organic frameworks of ctn topology.** Covalent organic frameworks of ctn topology. Synthetic scheme for the first COF with ctn topology, COF-102. Tetrahedral carbon and silicon, blue; core of the tritopic linker, orange polygons. All hydrogen atoms are omitted for clarity. Color Code: B, orange; C, gray; O, red.
Fig S4. Covalent organic frameworks of pts topology. Synthetic scheme for the first COF with pts topology, 3D-Py-COF. All hydrogen atoms are omitted for clarity. Color Code: C, gray; tetrahedral C, blue tetrahedral; N, blue.
Figure S52. Linkages that have been used to reticulate building blocks into COF structures. The linkages have been divided into B-O, C=N, C=N(Arom), C-N, B=N, N=N, and C=C bond forming reactions.
1.7 References


Chapter 2
Covalent Organic Frameworks Comprising Cobalt Porphyrins for the Electrocatalytic Reduction of Carbon Dioxide

Portions of this chapter have been published in:
2.1 Introduction

Global energy demands and climate change underpin broad interest in the sustainable reductive transformation of carbon dioxide (CO₂) in water to value-added carbon products like carbon monoxide (CO), while avoiding the competitive and often kinetically favored off-pathway reduction of water to hydrogen.¹,² In this context, molecular catalysts for electrochemical CO₂ conversions can be systematically tuned to achieve high activity and selectivity over proton reduction,³⁻¹³ but typically require organic media to achieve optimal selectivity and/or stability. In contrast, heterogeneous catalysts are often stable in water, but optimizing their activity through structural changes at a molecular level remains a substantial challenge.¹⁴⁻¹⁹ Against this backdrop, I sought to investigate crystalline porous frameworks, specifically covalent organic frameworks (COFs),²⁰⁻²² as tunable materials for electrocatalysis. I reasoned that such materials could potentially combine advantages of both molecular and heterogeneous catalysts: (i) construction with molecular building blocks would enable precise manipulation of the spatial arrangement of catalytic centers within predetermined COF lattices;²³ (ii) the frameworks could be expanded and functionalized without changing the underlying topology of the structure;²⁴⁻²⁵ (iii) the conserved pore environment around the active sites within the COF could be tuned electronically and sterically²⁶ while providing ready access for the substrate.²⁷⁻³² (Figure 2.1). Moreover, multivariate synthesis in which topologically identical and yet functionally unlike building blocks are introduced to replace part of the catalytic units, might give rise to emergent properties that are greater than the sum of the individual molecular parts.³³ Here I show that incorporation of catalytic cobalt porphyrin³⁴ units into COFs, along with multivariate synthesis of frameworks bearing catalytic cobalt and structural copper units, gives highly active, stable, and selective catalysts for electrochemical reduction of carbon dioxide to carbon monoxide in water. A member of the COF series studied exhibits 60-fold increase in activity compared to the parent molecular precursor and, in many respects, outperforms state-of-the-art molecular and solid-state catalysts, with broad opportunities for further improvement through modular synthesis using appropriate combinations of building units and struts. X-ray absorption measurements reveal that the COF framework can directly influence the electronic structure of the catalytic cobalt centers, in a manner akin to redox non-innocent ligand behavior observed in molecular systems,³⁵ thereby contributing to the observed gains in reaction selectivity and activity beyond the steric effects of surface area and site isolation.

2.2 Results and Discussion

2.2.1 Synthesis of Covalent Organic Frameworks

I focused my initial electrocatalysis studies on COFs, as I sought to exploit the charge-carrier mobility of these materials derived from π conjugation and π–π stacking³⁶⁻³⁸ and stability from reticular network assembly with strong covalent bonds. A model framework COF-366-Co was synthesized by the imine condensation of 5,10,15,20-tetrakis(4-aminophenyl)porphinato]cobalt [Co(TAP)] with 1,4-benzenedicarboxaldehyde (BDA) (Figure 2.1). The porous COF material was evacuated by activation with supercritical carbon dioxide and heating to 100 °C for 18 hours. The retention of cobalt in the coordinating porphyrin units within the framework and was confirmed by elemental analysis (Section S2.1), thermogravimetric analysis (TGA) (Figure S2.1 and S2.2) and solid-state UV-Vis spectroscopy (Figure S2.3). The formation of the imine linkages in the COF was confirmed/monitored by attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR), which showed the characteristic imine stretching vibration band at 1621 cm⁻¹ and the absence of the aldehyde stretching vibration band at 1684 cm⁻¹ (Figure S2.10).
The morphologies of the activated COF samples were examined by scanning electron microscopy (SEM), which showed aggregation of only one kind of crystallites of rectangular rods morphology (ca. 50 nm; Figure 2.2a). Powder X-ray diffraction (PXRD) patterns (Figure 2.2b) showed intense peaks in the expected low-angle range with no residual peaks characteristic of the starting materials. To elucidate the constitution of the framework, I constructed a structural model (Figure 2.1) using Materials Studio 7.0 in an orthorhombic Cmmm space group to allow the lattice distortion from regular square nets. Pawley refinements of the PXRD patterns were carried out for full profile fitting against the proposed models resulting in a good agreement factor ($R_{wp} = 2.59\%$ and $R_p = 1.38\%$ after convergence) and reasonable profile differences. These refinements revealed one-dimensional channels running along the c-axis 21 Å in width, with a distance between the stacking two-dimensional sheets of 4.4 Å. The porosity and specific surface area were characterized by nitrogen adsorption isotherms at 77 K (Figure 2.2c). The BET surface area was determined as 1360 m$^2$/g. DFT fitting of the adsorption branches showed relatively narrow pore size distributions (10 to 18 Å) in agreement with that of the proposed model.

Figure 2.1. Design and synthesis of metallorporphyrin-derived two-dimensional covalent organic frameworks. The space-filling structural models of COF-366-M and COF-367-M were obtained using Materials Studio 7.0.
2.2.2 Electrochemical Characterization

For electrochemical experiments, the activated microcrystalline COF powders were deposited on porous, conductive carbon fabric. Cyclic voltammetry (CV) measurements on COF-366-Co were conducted in pH 7 aqueous phosphate buffer (Figure 2.3a). Under a nitrogen atmosphere, the voltammogram trace shows a departure from the electrode background at about -0.45 V vs. reversible hydrogen electrode (RHE), and a broad reduction wave at about -0.67 V, which was assigned to the CoII/CoI redox couple. The surface concentration of electrochemically active cobalt porphyrin sites was measured by integration of the reduction wave to be $1 \times 10^{-8}$ mol/cm$^2$, corresponding to activity at 4% of the cobalt porphyrin sites in the material. The observed continuous current increase at potentials more negative than -0.67 V likely arises from Co(I)-catalyzed proton reduction activity. After the solution was saturated with carbon dioxide, a significant current enhancement was observed (catalytic current/noncatalytic current ratio $i_{\text{cat}}/i_{\text{p}} = 1.8$ at -0.67 V), with a catalytic onset potential at -0.42 V, indicating a prominent catalytic effect of COF-366-Co on the reduction of carbon dioxide in neutral aqueous solution. In contrast, the carbon fabric electrode alone showed minimal current enhancement under a carbon dioxide or nitrogen atmosphere (Figure S2.56).

In controlled potential electrolyses performed in carbon dioxide-saturated aqueous bicarbonate buffer (pH = 7.3) under applied potentials between -0.57 V and -0.97 V (vs. RHE), carbon monoxide was observed as the major reduction product (Figure 2.3b) with no other detectable carbon-based products; at -0.67 V, which represents a -0.55 V overpotential, the catalyst displayed optimal performance (Figure S2.63-2.64). More positive potentials lead to sluggish carbon dioxide reactivity, whereas more negative potentials promoted off-pathway water reduction. At -0.67 V, COF-366-Co promoted carbon monoxide evolution at an initial current...
density of 5 mA/mg catalyst (ca. 80 mA/mg cobalt) with high selectivity over competing proton reduction (Faradaic efficiency for carbon monoxide, \( \text{FE}_{\text{CO}} = 90\% \)). Catalytic cobalt porphyrin centers embedded within the COF showed greater than 10% enhancement in carbon dioxide to proton selectivity over the molecular cobalt porphyrin unit alone (Figure 2.3b). The catalytic activity of the COF could be maintained for 24 h, accumulating more than 36 mL carbon monoxide (STP) per mg COF, corresponding to a turnover number (TON) of 1,352 (TON per electroactive cobalt based on the measurements described above, \( \text{TION}_{\text{EA}} \approx 34,000 \)), with an initial turnover frequency (TOF) of 98 h\(^{-1}\) (TOF per electroactive cobalt, \( \text{TOF}_{\text{EA}} \approx 2,500 \)). This result represents a significant improvement over the molecular Co(TAP), which showed an initial TOF of 36 h\(^{-1}\) (TOF \( \approx 360 \)) and a TON of 794 (TON \( \approx 8,300 \)) after 24 h of reaction (surface coverage of electroactive sites on Co(TAP)-modified electrode constitutes ca. 10% of the total cobalt). PXRD (Figure S2.73) and SEM (Figure S2.74) measurements on the COF catalyst after electrolysis showed neither marked changes in crystallinity and microscopic morphology nor evidence of cobalt nanoparticle formation. By incorporating this molecular unit into a COF scaffold, the resulting hybrid catalyst could be recovered from the electrolysis mixture and reused at least five times without decrease in activity and selectivity (Table S2.8). Control experiments with COFs containing either free-base or copper-metallated porphyrin units, a physical mixture of cobalt nanoparticles and COF, as well as Co\(_3\)O\(_4\) and related cobalt salts that could be formed as impurities during COF synthesis, did not give appreciable carbon dioxide reduction (Figure S2.75).

### 2.2.3 Reticular Tuning of Structure Metrics

To optimize this carbon dioxide catalyst platform by a modular reticular approach, I prepared the expanded COF-367-Co analog using biphenyl-4,4’-dicarboxaldehyde (BPDA) as the strut in place of BDA (Figure 2.1). I reasoned that a larger pore size would allow for higher capacity of carbon dioxide adsorption inside the framework as well as higher accessibility of the catalytic cobalt porphyrin active sites. COF-367-Co was obtained as a dark purple powder comprising rectangular rod-shaped crystallite aggregates (ca. 100 nm; Figure 2.2d). The structural model based on PXRD data and DFT fitting indicated that the constitution and topology of COF-367-Co is analogous to that of COF-366-Co, with the former showing an increased channel width (24 Å) and interlayer distance (4.8 Å) (Figure 2.2e). The BET surface area was determined by nitrogen adsorption isotherm (Figure 2.2f) as 1470 m\(^2\)/g with pore size distribution consistent with the model (12 to 23 Å). Cyclic voltammetry studies with COF-367-Co on a carbon fabric electrode in bicarbonate buffer indicated that this extended organic framework exhibits an improved surface concentration of active cobalt porphyrin sites over COF-366-Co of \( 2 \times 10^{-9} \) mol/cm\(^2\), corresponding to accessibility of 8% of the cobalt sites in the bulk material. When the solution was saturated with CO\(_2\), a catalytic current was evident with an onset potential at -0.40 V and a 2.2-fold enhancement at -0.67 V, indicating a prominent effect of COF-367-Co in the catalysis of CO\(_2\) reduction at these potentials (Figure 2.2a). As predicted, electrolysis under the same conditions described above revealed that this expanded COF displays improved catalytic efficiency in comparison to COF-366-Co. At an applied potential of -0.67 V, COF-367-Co produced more than 100 mL carbon monoxide (STP) per mg COF during a 24 h period (TON = 3,901, TON\( \text{EA} \approx 48,000 \)) with high Faradaic efficiency (91%).

### 2.2.4 Reticular Tuning Through Building Block Heterogeneity

In addition to framework expansion, I also sought to optimize catalyst performance by introducing building-block heterogeneity through a multivariate strategy, as I hypothesized that not all cobalt porphyrin sites in the bulk material fully participated in electrocatalysis owing to the
low aqueous solubility of carbon dioxide. Specifically, I reasoned that diluting electroactive cobalt porphyrin active sites within the extended lattice with isostructural copper porphyrin units that are catalytically inactive (Figure S2.75) for carbon dioxide reduction could improve the proportion of the active sites exposed to the reactant and thereby increase the turnover frequency on a per cobalt basis. The resulting bimetallic COF-367 derivatives, termed COF-367-Co(10%) and COF-367-Co(1%), were prepared with the number in the parenthesis indicating the proportion of cobalt in all metal sites (Figure 2.1). Indeed, ICP analyses confirmed that the final chemical composition of the COFs obtained reflected the initial ratio of the two metalloporphyrin starting materials used (Section S2.1.1). The turnover frequency (TOF) per electroactive cobalt site for carbon monoxide production in these multivariate Co/Cu COF-367 catalysts showed a significant improvement with each 10-fold dilution of cobalt loading. The average TOF per active cobalt for the first 4 h of reaction was measured to be: COF-367-Co: 165 h⁻¹ (TOFEA ≈ 1,900), COF-367-Co(10%): 360 h⁻¹ (TOFEA ≈ 4,400), and COF-367-Co(1%): 764 h⁻¹ (TOFEA ≈ 9,400) (Figure 2.3c). The TOF values were roughly estimated assuming that all three frameworks had comparable percentages of electroactive sites (8%); although the low cobalt concentration in COF-367-Co(10%) and COF-367-Co(1%) hampered the accurate determination of the surface concentration of electrochemically accessible cobalt sites by CV, the fact that the bimetallic frameworks had nearly identical pore sizes, interlayer distances and surface areas to the parent COF-367-Co on the basis of PXRD and nitrogen adsorption measurements (Figure S2.25, 2.32-2.43) suggested that such an assumption may be valid. Owing to the moderate proton reduction ability of the copper porphyrin sites in the hybrid organic framework, the TOF increased as the Co/Cu ratio decreased at the expense of Faradaic efficiency for carbon monoxide production [FE CO = 70% for COF-367-Co(10%) and 40% for COF-367-Co(1%)]. In a long-term electrolysis experiment (Figure 2.3d), COF-367-Co(1%) displayed a TON of over 24,000 (TONEA ≈ 296,000), constituting one of the most active electrochemical carbon dioxide reduction catalysts reported to date (3,4). The observed activity enhancements for the bimetallic COFs are due to their unique multivariate nature; indeed, the analogous physical mixture of COF-367-Co and COF-367-Cu in a 1:9 ratio gave far less carbon dioxide reduction activity compared to COF-367-Co(10%) (Table S17).

2.2.5 Spectroelectrochemical Characterization

As only a small portion (4 to 8%) of the cobalt centers in the COF material deposited in this manner proved electroactive, presumably on account of the limited electrochemical contact between the COF powder and the electrode,41 I explored the possibility of growing COF directly onto the surface of an electrode substrate in the form of oriented thin films.42-44 Layers of COF sheets could be successfully synthesized directly on glassy carbon, fluorine-doped tin oxide (FTO) and silicon oxide. Grazing incidence wide-angle X-ray diffraction patterns showed the formation of highly crystalline COF thin films (Figure S2.48-2.51).45 The concentration of COF on the substrate surface was determined using ICP to be 1.3 × 10⁻⁵ mmol Co per cm², corresponding to a thickness of ~350 nm, which is consistent with images obtained via cross-sectional SEM (Figure S2.54-2.55). The charge transport through the COF-366-Co thin films was characterized using spectroelectrochemistry. Under an applied potential more negative than -0.37 V in nitrogen- or carbon dioxide-saturated pH 7 aqueous buffer, the UV-Vis spectrum of the FTO-supported COF underwent changes attributable to Co(II)/Co(I) reduction (Figure 2.3g, S2.78-2.82). Using the steady-state spectroscopic response to the reducing potentials in combination with the Nernst equation, the redox potential (\(E_{1/2}\)) could be estimated to be more negative than -0.52 V (Figure S2.82), in agreement with the CV measurements (\(E_{1/2} \approx -0.67 V\)).46 The time-dependence of the UV-Vis response of a COF-coated FTO electrode to an applied potential of -0.57 V was studied
in a CO$_2$-saturated KHCO$_3$ solution (Figure 2.3g), and a fit of the data to a modified Cottrell equation afforded an apparent diffusion coefficient of $2 \times 10^{-12}$ cm$^2$/s (Figure S2.80), a value substantially higher than that obtained with analogous metal-organic framework (MOF) thin films bearing cobalt porphyrin units.\textsuperscript{47} The direct current conductivity of COF-366-Co was also measured using the silicon oxide-hosted sample to be about $10^{-6}$ S/cm, also higher than that of the MOF (Figure S2.83-2.84). The favorable charge transport properties in addition to a presumably increased portion of electroactive cobalt sites lead to a higher catalytic efficiency. Under the same electrolysis conditions, COF-366-Co thin films on glassy carbon exhibited a TOF of 665 h$^{-1}$, a value seven times as high as that of the same material deposited on a carbon fabric, with a high current density of 45 mA/mg and a Faradaic efficiency of 86%.

### 2.2.6 Mechanism Elucidation

Electrokinetics experiments indicated that embedding cobalt porphyrin active sites within a COF influences the mechanistic pathways for carbon dioxide reduction. For the systems employing COF-366-Co, COF-367-Co and COF-367-Co(10%), Tafel plots of logarithm of current density [log($j_{CO}$)] vs. overpotential ($\eta$) display comparable slopes between 470 mV/dec and 550 mV/dec in the linear, lower current density regime (-0.57 to -0.87 V), which differ significantly from what is observed for the molecular Co(TAP) analog (270 mV/dec) (Figures 2.3e, S2.65-2.68). This difference suggests that, when embedded in a structurally and electronically extended framework, cobalt porphyrin catalyzes carbon dioxide reduction by a different mechanism than pertains with the simple molecular analog. In addition, both the COF and Co(TAP) catalysts showed a first-order rate-dependence on the partial pressure of carbon dioxide (Figure S2.86) and no rate-dependence on the pH (Figures S2.87-2.88), indicating that the rate-limiting chemical step involves the participation of one molecule of carbon dioxide and no proton.

Finally, I applied X-ray absorption spectroscopy (XAS) as a probe to evaluate how the surrounding COF influenced the electronic structures of embedded catalytic cobalt porphyrin units and in turn the associated carbon dioxide reduction mechanism.\textsuperscript{47} Comparison of the cobalt K-edge XAS spectra of Co(TAP), COF-367-Co and COF-367-Co(10%) (Figure 2.3f) reveals a similar line size and shape, consistent with a formal cobalt (II) oxidation state for all samples. When a reducing potential was applied (-0.67 V) to COF-367-Co under a carbon dioxide atmosphere, the K-edge revealed a line shape change consistent with the reduction of Co(II) to Co(I) (Figure S2.95). The two COF catalysts also exhibited a new pre-edge feature absent in the molecular Co(TAP) analog (Figure 2.3f inset); this difference shows indeed that the COF environment can directly modulate the electronic properties of molecular centers coupled into the extended lattice. This COF-unique feature was also observed when the catalysts were subjected to open-circuit or electrolysis (-0.67 V) potentials in bicarbonate buffer (Figure S2.91–S2.94). I tentatively assign this pre-edge feature to a dipole-forbidden 1s-3d electronic transition,\textsuperscript{48} which can occur when the d-orbitals exhibit some degree of hybridization and take on p-orbital character. The communication between the metal and COF lattice furnishes a cobalt center with a more delocalized electronic structure, a network-solid analogue to non-innocent ligand behavior in molecular systems.\textsuperscript{35}
Embedding tunable molecular units within an extended COF thus gives rise to electrocatalysts that display advantageous features of both molecular and heterogeneous systems and promote carbon dioxide reduction to carbon monoxide with exceptionally high activity and selectivity compared to existing systems (Table S2.21). I anticipate these hybrid molecular-material platforms will be applicable to a broad range of catalytic applications, particularly those that require sustainable electrical and/or solar input and aqueous compatibility.

2.3 Conclusion

The findings of this study illustrate the promise of covalent organic frameworks as an emerging class of materials for supporting catalysis with molecular-level control of both physical and electronic structure. I demonstrated that optimizing the morphology of COFs and growing them as oriented thin films significantly improves the catalytic activity of the material compared to bulk samples. More importantly, reticular electronic tuning of the catalytically active cobalt sites was used to optimize the material for high activity and selectivity by facile functionalization of the reticular parent structure with electron-withdrawing groups. In this regard, x-ray absorption spectroscopy on the metal L-edge has proved a useful tool for the direct observation of the effect of framework functionalization on the metal center. The importance of the spectroscopic evidence is highlighted by the fact that the differences in the electronic character of the active sites do not follow the expected trend according to basic inductive effect considerations. I anticipate the modularity of COF systems through reticular synthesis, combined with the ability to engender electronic communication between reticulated active sites and the surrounding framework, will
promote further opportunities for a broad array of catalytic transformations and related applications.
2.4 Supporting Information

2.4.1 Material Synthesis and Characterization

Commercial reagents and solvents were purchased from Sigma Aldrich, Alfa Aesar or Fisher Scientific and used as received. 5,10,15,20-Tetra(4-aminophenyl)porphyrin [H₂(TAP)] was purchased from Frontier Scientific.

Solution ¹H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AMX-300 (300 MHz) spectrometer operating with an Avance electronics console.

2.4.2 Synthesis

Synthesis of 5,10,15,20-tetrakis(4-aminophenyl)porphinato)cobalt(II) [Co(TAP)].

Following a modified procedure from reference.⁴⁹ To a suspension of H₂(TAP) (200 mg, 0.30 mmol) and NaOAc (108 mg, 1.3 mmol) in chlorobenzene (27 mL) and DMF (19 mL) was added Co(OAc)₂·4H₂O (147 mg, 0.59 mmol). After equipping with a Soxhelt apparatus with a paper thimble containing K₂CO₃ (1.1 g, 8.0 mmol), the reaction mixture was stirred under nitrogen at reflux for 24 h. Upon cooling, the Soxhlet apparatus was replaced with a distillation setup, and the solvent was removed under vacuum. The resulting dark solid was suspended in CHCl₃ (100 mL) and transferred to a Buchner funnel with a glass frit, and the solvent was removed through vacuum filtration. The crude product was then washed thoroughly with water (3 × 20 mL), saturate NaHCO₃ solution (1 × 20 mL), and then water again (3 × 20 mL). The resulting dark purple microcrystalline powder was dried under high vacuum overnight before being subjected to COF synthesis. UV-Vis (in DMF) 450, 550, 600 nm. FT-IR (solid) 1606, 1508, 1351, 1279, 1181, 1003, 796 cm⁻¹.

Synthesis of 5,10,15,20-tetrakis(4-aminophenyl)porphinato)copper(II) [Cu(TAP)].

Following a modified procedure from reference.⁵⁰ To a suspension of H₂(TAP) (198 mg, 0.30 mmol) and Cu(OAc)₂ (218 mg, 1.20 mmol) in methanol (20 mL) was added chloroform (90 mL) and DMF (30 mL). The dark red/brown solution was stirred under nitrogen at reflux for 24 h. Upon cooling, the solution was transferred into a separatory funnel and washed with water (3 × 100 mL). The organic layer was collected and dried over Na₂SO₄. The solvent was removed under vacuum. The resulting dark purple solid (172 mg, 80% yield) was dried under high vacuum overnight before being subjected to COF synthesis. UV-Vis (in DMF) 432, 548, 592 nm. FT-IR (solid) 3325, 1662, 1606, 1501, 1343, 1281, 1259, 1176, 1093, 995, 799 cm⁻¹.
**Synthesis of COF-366-Co:**

A Pyrex tube measuring 10 × 8 mm (o.d × i.d) was charged with Co(TAP) (18 mg, 0.025 mmol), BDA (10 mg, 0.075 mmol), 1,2-dichlorobenzene (1 mL), butanol (1 mL), and 6 M aqueous acetic acid (0.25 mL). After sonication for 15 minutes the tube was flash frozen at 77 K (liquid N₂ bath). After one freeze-pump-thaw cycle the system was evacuated to an internal pressure of 50 mtorr and flame sealed. Upon sealing, the length of the tube was reduced to approximately 18–20 cm. The reaction was heated at 120 ºC for 48 hours yielding a dark purple precipitate at the bottom of the tube, which was isolated by filtration. The wet sample was then transferred to a Soxhlet extractor and thoroughly washed with dioxane (24 hours) and acetone (24 hours). Following that, the product was washed five times with liquid CO₂. The system was then heated up to 45 ºC to bring about the supercritical state of CO₂ and slowly bled to ambient pressure. Finally the product was evacuated at 100 ºC for 18 hours at 10⁻² mtorr to yield activated sample. Yield: 24.18 mg, 92% based on Co(TAP). EA for the activated sample of COF-366-Co: Calcd for \([C₆₀H₃₆N₈Co]∙(H₂O)₃\): C, 73.39; H, 4.31; N, 11.42%. Found C, 73.42; H, 4.02; N, 11.76%.

**Synthesis of COF-367-Co:**

A Pyrex tube measuring 10 × 8 mm (o.d × i.d) was charged with Co(TAP) (18 mg, 0.025 mmol), BPDA (15.6 mg, 0.075 mmol), 1,2-dichlorobenzene (0.9 mL), butanol (0.8 mL), and 6 M aqueous acetic acid (0.213 mL). After sonication for 15 minutes the tube was flash frozen at 77 K (liquid N₂ bath). After one freeze-pump-thaw cycle the system was evacuated to an internal pressure of 50 mtorr and flame sealed. Upon sealing, the length of the tube was reduced to approximately 18–20 cm. The reaction was heated at 120 ºC for 48 hours yielding a dark purple precipitate at the bottom of the tube, which was isolated by filtration. The wet sample was then transferred to a Soxhlet extractor and thoroughly washed with dioxane (24 hours) and acetone (24 hours). Following that, the product was washed five times with liquid CO₂. The system was then heated up to 45 ºC to bring about the supercritical state of CO₂ and slowly bled to ambient pressure. Finally the product was evacuated at 100 ºC for 18 hours at 10⁻² mtorr to yield activated sample. Yield: 17.64 mg, 63% based on Co(TAP). EA for activated COF-367-Co: Calcd. for \([C₇₂H₄₄N₈Co]∙(H₂O)\): C, 78.75; H, 4.22; N, 10.20%. Found C, 78.31; H, 4.17; N, 9.90%.

**Synthesis of COF-367-Cu:**

The synthesis of COF-367-Cu was carried out following the same protocol as for COF-367-Co, by replacing the Co(TAP) with Cu(TAP) (18 mg, 0.025 mmol). Yield: 25.41 mg, 91% based on Cu(TAP). EA for the activated sample of COF-367-Cu: Calcd. for \([C₇₂H₄₄N₈Cu]∙(H₂O)\): C, 78.42; H, 4.20; N, 10.16%. Found C, 78.31; H, 4.17; N, 9.90%.

**Synthesis of COF-367-Co(10%):**

The synthesis of COF-367-Co(10%) was carried out following the same protocol as for COF-367-Co, by replacing the Co(TAP) with Cu(TAP) (16.2 mg, 0.0225 mmol) and Co(TAP) (1.8 mg, 0.0025 mmol). Yield: 24.22 mg, 87% based on Co(TAP). EA for the activated sample of COF-367-Co(10%): Calcd. for \([C₇₂H₄₄N₈Cu₀.₉Co₀.₁]∙(H₂O)\): C, 78.45; H, 4.21; N, 10.17%. Found C, 77.60; H, 3.66; N, 9.98%. ICP: Co/(Co + Cu) ratio Calcd. 0.100; Found 0.108.

**Synthesis of COF-367-Co(1%):**

The synthesis of COF-367-Co(1%) was carried out following the same protocol as for COF-367-Co, by replacing the Co(TAP) with Cu(TAP) (17.82 mg, 0.02475 mmol) and Co(TAP) (0.18 mg, 0.0025 mmol). Yield: 25.61 mg, 91% based on Co(TAP). EA for the activated sample of COF-
367-Co(1%): Calcd. for [C_{72}H_{44}N_{8}Cu_{0.99}Co_{0.1}](H_{2}O): C, 78.01; H, 4.18; N, 10.11%. Found C, 77.07; H, 3.54; N, 9.98%. ICP: Co/(Co + Cu) ratio Calcd. 0.0100; Found 0.0086.

**Synthesis of COF-366-Co on glassy carbon, FTO, or silicon oxide:**

A Pyrex tube measuring 10 × 8 mm (o.d × i.d) was charged with a 4 × 3 × 7 mm glassy carbon (Tokai Carbon Co., Ltd, polished with alumina), Co(TAP) (18 mg, 0.025 mmol), BDA (10 mg, 0.075 mmol), 1,2-dichlorobenzene (1 mL), butanol (1 mL), and 6 M aqueous acetic acid (0.25 mL). After sonication for 15 minutes the tube was flash frozen at 77 K (liquid N2 bath). After one freeze-pump-thaw cycle the system was evacuated to an internal pressure of 50 mtorr and flame sealed. Upon sealing, the length of the tube was reduced to approximately 18~20 cm. The reaction was heated at 120 °C for 48 hours. The glassy carbon was retrieved from the reaction mixture, immersed in acetone, and sonicated for 20-30 minutes. The electrode was stored in acetone and dried in air prior to use.
2.4.3 Thermogravimetric Analysis

Thermogrammetric analysis (TGA) traces for the activated COF samples were collected on a TA Instruments Q-500 series thermal gravimetric analyzer with the sample held in a platinum pan under air atmosphere with the flow rate of 40 ml/min. Temperature was controlled by the furnace heating from 25 °C up to 900 °C with a ramp rate of 5 °C/ min.

Figure S2.1. TGA trace for the activated sample of COF-366-Co under air atmosphere.

Figure S2.2. TGA trace for the activated sample of COF-367-Co under air atmosphere.
2.4.4 Ultraviolet-Visible Spectroscopy

Solid-state UV-Vis spectra of starting materials and COF samples were recorded on a diffuse reflectance spectrometer.

Figure S2.3. Solid-state UV-Vis spectrum of COF-366-Co.

Figure S2.4. The band gap calculation from the UV-Vis spectrum of COF-366-Co.
2.4.5 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of starting materials and COF samples were recorded in-house on a Bruker ALPHA ATR-FTIR spectrometer.

Figure S2.5. ATR-FTIR spectrum of the activated sample of COF-366-Co.

Figure S2.6. ATR-FTIR spectrum of the activated sample of COF-367-Co.
Figure S2.7. ATR-FTIR spectrum of the activated sample of COF-367-Co(10%).

Figure S2.8. ATR-FTIR spectrum of the activated sample of COF-367-Co(1%).
Figure S2.9. ATR-FTIR spectrum of the activated sample of COF-367-Cu.
Figure S2.10. Stack plot of the ATR-FTIR spectra of the activated sample of COF-366-Co compared with his starting materials, Co(TAP) and BDA.
Figure S2.11. Stack plot of the ATR-FTIR spectra of the activated sample of COF-367-Co compared with its starting materials, Co(TAP) and BPDA.
Figure S2.12. Stack plot of the ATR-FTIR spectra of the activated sample of COF-367-Cu compared with its starting materials, Cu(TAP) and BPDA.
Figure S2.13. Stack plot of the ATR-FTIR spectra of activated samples of COF-367-Co, COF-367-Co(10%), COF-367-Co(1%), and COF-367-Cu for comparison.
2.4.6 Solid-State Nuclear Magnetic Resonance Spectroscopy

Solid-state nuclear magnetic resonance (SSNMR) spectra were collected on a Bruker AV-500 NMR spectrometer using a standard Bruker magic angle-spinning (MAS) probe with 4-mm (o.d.) zirconia rotors. The magic angle was adjusted by maximizing the number and amplitudes of the signals of the rotational echoes observed in the $^{79}$Br MAS FID signal from KBr. The transmitter frequency of $^{13}$C NMR is 125.80 MHz. The solid-state $^{13}$C NMR spectra were acquired using cross-polarization (CP) MAS technique with the ninety degree pulse of $^1$H with 4.2 μs pulse width. The CP contact time was 5 ms. High power two-pulse phase modulation (TPPM) $^1$H decoupling was applied during data acquisition. The decoupling frequency corresponded to 32 kHz. The MAS sample spinning rates were 13 kHz. Recycle delays between scans were varied from 0.1 to 0.5 s. The $^{13}$C chemical shifts are given relative to neat tetramethylsilane as zero ppm, calibrated using the methylene carbon signal of adamantane assigned to 38.48 ppm as secondary reference.

Figure S2.14. $^{13}$C CP/MAS solid-state NMR spectrum for the activated sample of COF-366-Co. Chemical shifts are expressed in ppm (vs. tetramethylsilane). Spinning side bands are marked with asterisks.
Figure S2.15. $^{13}$C CP/MAS solid-state NMR spectrum for the starting material Co(TAP). Chemical shifts are expressed in ppm (vs. tetramethylsilane). Spinning side bands are marked with asterisks.
2.4.7 Scanning Electron Microscopy

Samples of COF samples were measured by dispersing the materials onto silica wafers attached to a flat aluminum sample holder, which were further coated with gold. Samples were analyzed on a JEOL JSM 6340F field-emission SEM operating at 5 kV.

Figure S2.16. SEM image showing the morphology of activated sample of COF-366-Co.

Figure S2.17. SEM image showing the morphology of activated sample of COF-367-Co.
Figure S2.18. SEM image showing the morphology of activated sample of COF-367-Co(10%).

Figure S2.19. SEM image showing the morphology of activated sample of COF-367-Co(1%).
Figure S2.20. SEM image showing the morphology of activated sample of COF-367-Cu.
2.4.8 Powder X-ray Diffraction Analysis

Powder X-ray diffraction data were collected using a Bruker D8 Advance \( \theta-\theta \) diffractometer in parallel beam geometry employing Cu K\( \alpha \) line focused radiation (\( \lambda = 1.54056 \) Å) at 1600 W (40 kV, 40 mA) power and equipped with a position sensitive LYNXEYE detector with at 1.0 mm radiation entrance slit. Samples were mounted on zero background sample holders by dropping powders from a wide-blade spatula and then leveling the sample with a razor blade. Diffraction intensity data for \( 2\theta \) from 2 ~ 60° were collected at the scanning speed of 1 sec/step with \( 2\theta \) step increment of 0.02°.

The Pawley PXRD refinements were performed using the Reflex module in the Materials Studio 7.0, in which the Thompson-Cox-Hastings profile function were used for the profile fitting (peak broadening, peak asymmetry and zero shift error were taken into account). Unit cell and sample parameter were refine at the meantime.
Figure S2.21. Stack plot of PXRD patterns of COF-366-Co compared with its starting materials, Co(TAP) and BDA.

Figure S2.22. Pawley refinement of the PXRD patterns of activated samples of COF-366-Co.

- Simulated
- Experimental
- Difference
- Bragg position

$R_w = 2.59\%$
$R_p = 1.38\%$
Figure S2.23. Stack plot of PXRD patterns of COF-367-Co compared with its starting materials, Co(TAP) and BPDA.

Figure S2.24. Pawley Refinement of the PXRD patterns of activated samples of COF-367-Co.
Figure S2.25. PXRD patterns of activated samples of COF-366-Co, COF-367-Co(10%), COF-367-Co(1%), and COF-367-Cu.
2.4.9 Structural Modeling

Modeling of crystal structures for target COFs were performed using the Materials Studio 7.0 software package (Accelrys Software Inc.). Geometry optimization in the Forcite module was applied to optimize the unit cell and the geometry of the molecular fragment.

Figure S2.26. Crystal structure model of COF-366-Co.
Table S2.1. Fractional atomic coordinates for crystal structure model of COF-366-Co with eclipsed arrangement.

**COF-367-Co**

Formula: C₆₀H₃₆N₈Co

Crystal system: Orthorhombic

Space group: Cmmm (No. 65)

\[ a = 31.13020 \, \text{Å}; \quad b = 40.20970 \, \text{Å}; \quad c = 6.68370 \, \text{Å} \]

\[ \alpha = \beta = \gamma = 90^\circ \]

\[ V = 8366.229 \, \text{Å}^3 \]

\[ Z = 2 \]

\[ d = 0.316 \, \text{g/cm}^3 \]

\[ Void = 81.8\% \]

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co1</td>
<td>0.50000</td>
<td>0.50000</td>
<td>0</td>
<td>0.125</td>
</tr>
<tr>
<td>N2</td>
<td>0.50000</td>
<td>0.45796</td>
<td>0</td>
<td>0.25</td>
</tr>
<tr>
<td>N3</td>
<td>0.44691</td>
<td>0.50000</td>
<td>0</td>
<td>0.25</td>
</tr>
<tr>
<td>N4</td>
<td>0.33419</td>
<td>0.33400</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C5</td>
<td>0.48162</td>
<td>0.41157</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>H5</td>
<td>0.46617</td>
<td>0.39038</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C6</td>
<td>0.47095</td>
<td>0.44006</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C7</td>
<td>0.43481</td>
<td>0.44837</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C8</td>
<td>0.42431</td>
<td>0.47700</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C9</td>
<td>0.38833</td>
<td>0.48545</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>H9</td>
<td>0.36157</td>
<td>0.47321</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C10</td>
<td>0.40635</td>
<td>0.42583</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C11</td>
<td>0.39288</td>
<td>0.41513</td>
<td>-0.18054</td>
<td>1</td>
</tr>
<tr>
<td>H11</td>
<td>0.40376</td>
<td>0.42381</td>
<td>-0.32758</td>
<td>1</td>
</tr>
<tr>
<td>C12</td>
<td>0.36616</td>
<td>0.39385</td>
<td>-0.18047</td>
<td>1</td>
</tr>
<tr>
<td>H12</td>
<td>0.35526</td>
<td>0.38523</td>
<td>-0.32763</td>
<td>1</td>
</tr>
</tbody>
</table>

62
<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C13</td>
<td>0.35278</td>
<td>0.38313</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C14</td>
<td>0.32481</td>
<td>0.36086</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>H14</td>
<td>0.29495</td>
<td>0.36713</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C15</td>
<td>0.30941</td>
<td>0.31027</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C16</td>
<td>0.32338</td>
<td>0.28238</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>H16</td>
<td>0.35396</td>
<td>0.27883</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C17</td>
<td>0.30010</td>
<td>0.25873</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>H17</td>
<td>0.31171</td>
<td>0.23605</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C18</td>
<td>0.26234</td>
<td>0.26255</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C19</td>
<td>0.24841</td>
<td>0.29060</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>H19</td>
<td>0.21781</td>
<td>0.29398</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C20</td>
<td>0.27169</td>
<td>0.31425</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>H20</td>
<td>0.25991</td>
<td>0.33687</td>
<td>0</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Figure S2.27. Crystal structure model of COF-367-Co.
Table S2.2. Fractional atomic coordinates for crystal structure model of COF-367-Co with eclipsed arrangement.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co1</td>
<td>0.50000</td>
<td>0.50000</td>
<td>0.000</td>
<td>0.125</td>
</tr>
<tr>
<td>N2</td>
<td>0.50000</td>
<td>0.45035</td>
<td>0.000</td>
<td>0.25</td>
</tr>
<tr>
<td>N3</td>
<td>0.43596</td>
<td>0.50000</td>
<td>0.000</td>
<td>0.25</td>
</tr>
<tr>
<td>N4</td>
<td>0.30339</td>
<td>0.30723</td>
<td>0.000</td>
<td>0.5</td>
</tr>
<tr>
<td>C5</td>
<td>0.47818</td>
<td>0.39703</td>
<td>0.000</td>
<td>0.5</td>
</tr>
<tr>
<td>H5</td>
<td>0.45840</td>
<td>0.37503</td>
<td>0.000</td>
<td>0.5</td>
</tr>
<tr>
<td>C6</td>
<td>0.46445</td>
<td>0.42965</td>
<td>0.000</td>
<td>0.5</td>
</tr>
<tr>
<td>C7</td>
<td>0.42157</td>
<td>0.43919</td>
<td>0.000</td>
<td>0.5</td>
</tr>
<tr>
<td>C8</td>
<td>0.40925</td>
<td>0.47243</td>
<td>0.000</td>
<td>0.5</td>
</tr>
<tr>
<td>C9</td>
<td>0.36718</td>
<td>0.48308</td>
<td>0.000</td>
<td>0.5</td>
</tr>
<tr>
<td>H9</td>
<td>0.33880</td>
<td>0.46775</td>
<td>0.000</td>
<td>0.5</td>
</tr>
<tr>
<td>C10</td>
<td>0.38811</td>
<td>0.41324</td>
<td>0.000</td>
<td>0.5</td>
</tr>
<tr>
<td>C11</td>
<td>0.37224</td>
<td>0.40088</td>
<td>0.18040</td>
<td>1</td>
</tr>
<tr>
<td>H11</td>
<td>0.38431</td>
<td>0.41029</td>
<td>0.32027</td>
<td>1</td>
</tr>
<tr>
<td>C12</td>
<td>0.34077</td>
<td>0.37631</td>
<td>0.18035</td>
<td>1</td>
</tr>
<tr>
<td>H12</td>
<td>0.32873</td>
<td>0.36690</td>
<td>0.32030</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>------</td>
<td>------</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C13</td>
<td>0.32502</td>
<td>0.36393</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C14</td>
<td>0.29211</td>
<td>0.33818</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>H14</td>
<td>0.25905</td>
<td>0.34579</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C15</td>
<td>0.29444</td>
<td>0.24736</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>H15</td>
<td>0.32892</td>
<td>0.24504</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C16</td>
<td>0.27562</td>
<td>0.27882</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>C17</td>
<td>0.23070</td>
<td>0.28126</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>H17</td>
<td>0.21455</td>
<td>0.30488</td>
<td>0</td>
<td>0.5</td>
</tr>
</tbody>
</table>
2.4.10 Porosity and Specific Surface Area Analysis

The N\textsubscript{2} adsorption isotherms were conducted on a QuadraSorb SI automated surface area & pore size analyzer (Quantachrome Instruments). Ultrahigh purity N\textsubscript{2} and He compressed gas cylinders (Praxair, Purity > 99.999%) were used for the gas sorption measurement. Liquid N\textsubscript{2} bath was used for temperature control at 77 K.

The BET and Langmuir surface area were estimated according to established procedures. The pore size distribution (PSD) was evaluated using the DFT method in the QuadraWin software using the QSDFT model.

Table S2.3. Porosity data of COF materials studied in this work

<table>
<thead>
<tr>
<th>Materials</th>
<th>( S_{\text{BET}} ) (m\textsuperscript{2}/g)</th>
<th>( S_{\text{Langmuir}} ) (m\textsuperscript{2}/g)</th>
<th>( V_p ) (cm\textsuperscript{3}/g)</th>
<th>PSD (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COF-366-Co</td>
<td>1360</td>
<td>1700</td>
<td>0.63</td>
<td>10–18</td>
</tr>
<tr>
<td>COF-367-Co</td>
<td>1470</td>
<td>2325</td>
<td>0.81</td>
<td>10–22</td>
</tr>
<tr>
<td>COF-367-10%Co</td>
<td>1740</td>
<td>2577</td>
<td>0.96</td>
<td>10–22</td>
</tr>
<tr>
<td>COF-367-1%Co</td>
<td>1480</td>
<td>2372</td>
<td>0.85</td>
<td>10–22</td>
</tr>
<tr>
<td>COF-367-Cu</td>
<td>2055</td>
<td>2684</td>
<td>1.0</td>
<td>10–22</td>
</tr>
</tbody>
</table>
Figure S2.28. \( \text{N}_2 \) sorption isotherm of COF-366-Co at 77 K.

Figure S2.29. Pore size distribution histogram of COF-366-Co. Calculated from DFT fitting of the adsorption branch of the \( \text{N}_2 \) adsorption isotherm at 77 K (inset) with the fitting error of 0.976% using slit/cylindr./sphere pores QSDFT model.
Figure S2.30. Multiple point BET plot of COF-366-Co giving a specific surface area of 1360 m$^2$/g.

Figure S2.31. Langmuir plot of COF-366-Co giving a specific surface area of 1700 m$^2$/g.
Figure S2.32. N\textsubscript{2} sorption isotherm of COF-367-Co at 77 K.

Figure S2.33. Pore size distribution histogram of COF-367-Co. Calculated from DFT fitting of the adsorption branch of the N\textsubscript{2} adsorption isotherm at 77 K (inset) with the fitting error of 1.088\% using slit/cylindr./sphere pores QSDFT model.
Figure S2.34. Multiple point BET plot of COF-367-Co giving a specific surface area of 1470 m²/g.

Figure S2.35. Langmuir plot of COF-367-Co giving a specific surface area of 2325 m²/g.
Figure S2.36. $N_2$ sorption isotherm of COF-367-Co(10%) at 77 K.

Figure S2.37. Pore size distribution histogram of COF-367-Co(10%). Calculated from DFT fitting of the adsorption branch of the $N_2$ adsorption isotherm at 77 K (inset) with the fitting error of 0.930% using slit/cylindr./sphere pores QSDFT model.
Figure S2.38. Multiple point BET plot of COF-367-Co(10%) giving a specific surface area of 1740 m²/g.

Figure S2.39. Langmuir plot of COF-367-Co(10%) giving a specific surface area of 2577 m²/g.
Figure S2.40. N$_2$ sorption isotherm of COF-367-Co(1%) at 77 K.

Figure S2.41. Pore size distribution histogram of COF-367-Co(1%). Calculated from DFT/Monte-Carlo fitting of the adsorption branch of the N$_2$ adsorption isotherm at 77 K (inset) with the fitting error of 0.944% using slit/cylindr./sphere pores QSDFT model.
Figure S2.42. Multiple point BET plot of COF-367-Co(1%) giving a specific surface area of 1480 m²/g.

Figure S2.43. Langmuir plot of COF-367-Co(1%) giving a specific surface area of 2372 m²/g.
Figure S2.44. N$_2$ sorption isotherm of COF-367-Cu at 77 K.

Figure S2.45. Pore size distribution histogram of COF-367-Cu. Calculated from DFT/Monte-Carlo fitting of the adsorption branch of the N$_2$ adsorption isotherm at 77 K (inset) with the fitting error of 1.009% using slit/cylindr./sphere pores QSDFT model.
Figure S2.46. Multiple point BET plot of COF-367-Cu giving a specific surface area of 1470 m²/g.

Figure S2.47. Langmuir plot of COF-367-Cu giving a specific surface area of 2325 m²/g.
2.4.11 Grazing Incidence Wide-Angle X-ray Scattering of Thin-Film COFs

Grazing incidence wide angle X-ray scattering (GIWAXS) measurements were performed at the Advanced Light Source (ALS) at Lawrence Berkeley National Lab (LBNL).

Figure S2.48. 2-D GIWAXS of COF-366-Co on FTO.

Figure S2.50. 2-D GIWAXS of COF-366-Co on silicon oxide.
Figure S2.53. 2-D GIWAXS of glassy carbon (background).
2.4.12 Cross-Sectional Scanning Electron Microscopy of Thin-Film COFs

Samples were analyzed on a JEOL JSM 6340F field-emission SEM operating at 5 kV. Glassy carbon-based samples cannot be imaged with cross-sectional SEM because the surface of glassy carbon is uneven on the micrometer/nanometer scales. The cross-sectional SEM of COF-coated glassy carbon cannot lead to meaningful measurements because the substrate surface is not even and smooth enough.

Figure S2.54. Cross-sectional SEM image of COF-366-Co on FTO.

Figure S2.55. Cross-sectional SEM image of COF-366-Co on silicon oxide.
2.4.13 Electrochemistry

General Information:

Electrolysis experiments were performed using a BASi EC Epsilon potentiostat/galvanostat with a glass cell custom made by Adams & Chittenden Scientific Glass. Carbon fabric (99.5% carbon) was purchased from Fuel Cell Earth LLC. The fabric was cut into 1 x 2.5 cm² pieces, treated with 6 M HCl overnight to remove trace metal impurity, rinsed thoroughly with Milli-Q water, and dried in air before use. Graphite planchets (1 inch diameter, impurity < 2 ppm) were purchased from Ted Pell, Inc. Graphite rods (99.9995% trace metal basis, 6.15 mm diameter x 152 mm length) were purchased from Alfa Aesar. Ag/AgCl reference electrodes were obtained from BASi and stored in saturated NaCl solution before use. Nafion cation-exchange membrane and silver wire (99.9% trace metal basis, 0.5 mm diameter) were obtained from Sigma Aldrich. Carbon dioxide (99.995%), carbon monoxide (99.99%), hydrogen (99.999%) and ethylene (99.90%) were purchased from Praxair. House nitrogen (N₂) was used as the nitrogen source. Gas production was measured on an SRI gas chromatography instrument (model #8610C) equipped with a Haysep D column (1/8” × 6’) and a 13X Mol Sieve column (1/8” × 6’), with ethylene (C₂H₄) as the internal standard; carbon monoxide (CO) was quantified using flame ionization detector (FID) and hydrogen (H₂) using thermal conductivity detector (TCD).

General Procedures:

Preparation of the working electrode: A freshly prepared carbon fabric electrode (1 x 2.5 cm²) was placed on a clean piece of glass. A 6 cm long silver wire was threaded through the top 1 x 0.5 cm² area of the carbon fabric electrode for connecting the working electrode to the potentiostat. The electrochemical contact was confirmed using an ohmmeter. COF catalyst was weighed out on a microbalance, suspended in 80 μL DMF in a 2 dr vial, and sonicated for 20 minutes. The resulting mixture was deposited evenly on the bottom 1 x 2 cm² area of the carbon fabric, and left in air overnight to dry.

Preparation of the electrolyte solution: KHCO₃ (100 g) was dissolved in 2000 mL of Milli-Q water in a 4 L Erlenmeyer flask equipped with a 6 cm long stir bar. Two graphite rods were bound together with a copper wire and used as the cathode and another graphite rod was used as the anode, all of which were connected to a potentiostat using copper wires. A constant stream of CO₂ gas was gently passed through the electrolyte solution, which was maintained during the entire course of the electrolysis treatment. The solution was electrolyzed at a constant current of 150 μA for ~16 h. After removal of the graphite rods, the electrolyte was passed through a vacuum filter with polyethersulfone membrane (0.22 micron), and stored in glass containers before use.

Electrochemistry setup: Controlled-potential electrolysis was conducted using a custom-made, three-piece glass cell, including a working compartment body, a working compartment lid, and a counter compartment body. The main bodies of the two compartments were assembled together using an O-ring and a Teflon clamp, and were separated by a Nafion cation-exchange membrane. The body of the working compartment was charged with a 3 cm long Teflon-coated stir bar and 150 mL of electrolyte solution (0.5 M aqueous KHCO₃, unless otherwise noted), and the lid was fitted with a carbon fabric working electrode (1 x 2.5 cm², fixed onto a ~6 cm long silver wire) with pre-deposited COF catalyst and a Ag/AgCl reference electrode. Both electrodes were connected to the outside through a stainless steel rod (1/16 inch diameter x 2 inch length, connected to the carbon fabric through the silver wire and the reference electrode through a two-
way metal socket). The lid was also equipped with a Teflon sparging line that would extend into
the electrolyte solution and a gas outlet that would connect to the headspace of the cell. Both of
the gas ports were connected to a two-way Swagelok valve, and the valve at the gas outlet was
also fitted with a Swagelok female miniature quick-connect. During sample analysis, this quick-
connect was adapted to a male miniature quick-connect on the injection line of the GC. The lid
and the main body of the working compartment were assembled using an O-ring and a Teflon
clamp, and the position of the working electrode was adjusted so that only the area covered with
the COF (bottom 1 x 2 cm²) was immersed in the solution while the silver wire was not. The
resulting working compartment has a headspace volume of ~100 mL. The counter compartment
was filled with 50 mL of electrolyte solution (0.5 M aqueous KHCO₃, unless otherwise noted),
and equipped with a Teflon cap with a septum, as well as a graphite auxiliary electrode connected
to the outside with a stainless steel alligator clip and a silver wire.

Electrolysis: After the electrochemical cell was assembled, the electrolyte solution in the
working compartment was sparged for 10 minutes with CO₂. Then, 1 mL ethylene was injected
into the headspace as the internal standard for GC analysis. The solutions were electrolyzed at a
constant potential (-1.30 V vs. Ag/AgCl, equivalent to -0.67 V vs. RHE, unless otherwise noted)
for a given amount of time. In the end of the electrolysis, the headspace of the cell was analyzed
with the GC. Since a significant amount (~10 mL) of gas in the headspace was injected into the
GC, the pressure in headspace of the working compartment was decreased after the analysis. If
electrolysis needed to be continued using the same setup, in order to obtain accurate data, the
working side of the cell was re-sparged with CO₂ again for 5-10 minutes and injected with 1 mL
ethylene.

Cyclic voltammetry: Using the same electrochemical setup, the electrolyte solution in the
working compartment was sparged for 10 minutes with N₂ or CO₂. Electrolysis was first conducted
at -1.30 V vs. Ag/AgCl for 10 minutes to active the surface of the carbon fabric electrode. CV
scans were then taken from 0 to -1.50 V vs. Ag/AgCl with 100 mV/s scan rate (or from 25 to 500
mV/s scan rates when studying the scan rate-dependence of the current). The electrolytes used in
Figure 2.3A and Figure S2.56 are as follows: under N₂ – 0.2 M potassium phosphate buffer at pH
7.2 with 0.5 M NaClO₄; under CO₂ – 0.2 M potassium phosphate buffer at pH 7.2 with 0.5 M
KHCO₃. The electrolyte used in Figures S2.57-2.61 is as follows: under N₂ or CO₂ – 0.5 M
KHCO₃.

Determination of surface concentration of electroactive cobalt porphyrin: The surface
concentration of electroactive cobalt sites were determined by cyclic voltammetry method.
Integration of the peak area under the Co(II)/Co(I) reduction wave leads to the charge that passed
to reduce Co(II) to Co(I), \( Q_{\text{CV}} \). The surface concentration, \( \Gamma \), is then calculated using the following
equation: \( \Gamma = \frac{Q_{\text{CV}}}{nFA} \). Here, \( n \) is the number electrons transferred for the redox couple \((n = 1)\),
\( F \) is the Faraday constant, and \( A \) is the surface area of the electrode.\(^{51}\)
2.4.14 Cyclic Voltammetry

Figure S2.56. Cyclic voltammogram of bare carbon fabric electrode in 0.2 M aq. phosphate buffer (pH 7.2) saturated with N₂ or CO₂ at scan rate of 100 mV/s. Under CO₂, 0.5 M KHCO₃ was added to balance the pH. Under N₂, 0.5 M NaClO₄ was added to match the ionic strength.

Figure S2.57. Cyclic voltammogram of COF-366-Co in 0.5 M aq. KHCO₃ saturated with N₂ or CO₂ at scan rate of 100 mV/s.
Figure S2.58. Cyclic voltammogram of COF-367-Co in 0.5 M aq. KHCO₃ saturated with N₂ or CO₂ at scan rate of 100 mV/s.

Figure S2.59. Cyclic voltammogram of Co(TAP) in 0.5 M aq. KHCO₃ saturated with N₂ or CO₂ at scan rate of 100 mV/s.
Figure S2.60. Scan rate dependence of cyclic voltammetry response of COF-367-Co (from 25 mV/s to 500 mV/s).

Figure S2.61. Peak current of the cyclic voltammogram of COF-367-Co as a function of scan rate. The peak current shows a linear dependence on the scan rate between 25 to 200 mV/s. At high scan rate, the current deviates from the linear correlation likely as a result of mass transport limitation. Regression of the linear regime between 25 and 200 mV/s with equation: \( i_p = \frac{FST}{4RT} \) gives surface concentration of electroactive Co porphyrin: \( I = 1.9 \times 10^{-8} \) mol/cm\(^2\), consistent with the peak area measurements described in the general procedure section.\(^{53} \)
2.4.15 GC Calibration

Following the general procedures described above with the following alterations: in addition to ethylene injection, a given amount of CO and H2 was also injected to the headspace; the resulting gas mixture was directly analyzed with the GC without conducting the controlled potential electrolysis. The amount of CO and H2 were plotted against the area ratio between these gas analytes and the internal standard, ethylene.

Figure S2.62. GC calibration curves for CO and H2.
2.4.16 Electrolysis at Different Applied Potentials

General information:

Following the general procedures. Since at high overpotential, the COF was only stable for ~ 1 h under electrolysis conditions and showed compromised reactivity in the second hour reaction, the Tafel plot was constructed only using data from the first hour experiment.

Table S2.4. Electrolysis with COF-366-Co at different potentials

<table>
<thead>
<tr>
<th>Potential vs. RHE (V)</th>
<th>Overpotential (mV)</th>
<th>Volume CO (mL) COF-366-Co</th>
<th>COF-367-Co</th>
<th>Co(TAP)</th>
<th>COF-367-Co(10%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 h</td>
<td>2 h</td>
<td></td>
<td>Run 1</td>
</tr>
<tr>
<td>-0.56</td>
<td>450</td>
<td>0.41</td>
<td>0.66</td>
<td>0.62</td>
<td>0.10</td>
</tr>
<tr>
<td>-0.61</td>
<td>500</td>
<td></td>
<td></td>
<td></td>
<td>0.164</td>
</tr>
<tr>
<td>-0.66</td>
<td>550</td>
<td>0.93</td>
<td>1.73</td>
<td>1.46</td>
<td>0.40</td>
</tr>
<tr>
<td>-0.71</td>
<td>600</td>
<td></td>
<td></td>
<td></td>
<td>0.304</td>
</tr>
<tr>
<td>-0.76</td>
<td>650</td>
<td>1.12</td>
<td>2.01</td>
<td>2.10</td>
<td>0.85</td>
</tr>
<tr>
<td>-0.81</td>
<td>700</td>
<td></td>
<td></td>
<td></td>
<td>0.307</td>
</tr>
<tr>
<td>-0.86</td>
<td>750</td>
<td>1.57</td>
<td>1.79</td>
<td>2.64</td>
<td>1.24</td>
</tr>
<tr>
<td>-0.96</td>
<td>850</td>
<td>1.79</td>
<td>2.63</td>
<td></td>
<td>1.17</td>
</tr>
</tbody>
</table>

Note: Grey-colored cells – data not obtained. For COF-367-Co(10%), due to relatively large error bars associated with the measurements, which are likely as a result of non-uniformity in distribution of Co/Cu sites, multiple data points were taken and the Tafel plot was derived from all data points between 450 and 750 mV overpotential (Figure S59).
Figure S2.63. Current density as a function of applied potential with COF-366-Co in the 1st and 2nd hour electrolysis.

Figure S2.64. Faradaic efficiency of COF-366-Co catalyzed CO$_2$ reduction as a function of applied potential.

The graph shows that potentials less negative than -0.66 V are ideal for COF-366-Co catalyzed CO$_2$ reduction in terms of the stability of the material. At potentials higher than -0.76 V, a significant decrease of rate of CO evolution is observed in the 2nd-hour electrolysis compared to the 1st-hour, which is accompanied by an increase of the amount H$_2$ produced. This observation indicates the decomposition, presumably through demetallation of the porphyrin sites, during electrolysis under these potentials.

88
Figure S2.65. Tafel plot of COF-367-Co catalyzed CO$_2$ reduction. Tafel slope = 47 mV/dec.

Figure S2.66. Tafel plot of COF-366-Co catalyzed CO$_2$ reduction. Tafel slope = 54 mV/dec. Upward Tafel slope curvature at high overpotential (> 0.8 V) likely reflects mass transport limitations in this regime.
Figure S2.67. Tafel plot of Co(TAP) catalyzed CO₂ reduction. Tafel slope = 27 mV/dec. Upward Tafel slope curvature at high overpotential (> 0.8 V) likely reflects mass transport limitations in this regime.

Figure S2.68. Tafel plot of COF-367-Co(10%) catalyzed CO₂ reduction. Tafel slope = 55 mV/dec.
2.4.17 Long-Term Electrolysis of COF-366-Co and COF-367-Co

Table S2.5. COF-366-Co (0.50 mg, 0.49 μmol Co)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Total Charge (C)</th>
<th>Volume CO (mL)</th>
<th>FE CO (%)</th>
<th>Volume H₂ (mL)</th>
<th>FE H₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>39.8</td>
<td>4.51</td>
<td>89</td>
<td>0.72</td>
<td>14</td>
</tr>
<tr>
<td>8</td>
<td>74.3</td>
<td>8.01</td>
<td>85</td>
<td>1.39</td>
<td>14</td>
</tr>
<tr>
<td>12</td>
<td>103</td>
<td>11.0</td>
<td>84</td>
<td>1.99</td>
<td>15</td>
</tr>
<tr>
<td>16</td>
<td>125</td>
<td>14.0</td>
<td>88</td>
<td>2.58</td>
<td>16</td>
</tr>
<tr>
<td>20</td>
<td>145</td>
<td>16.2</td>
<td>89</td>
<td>3.26</td>
<td>17</td>
</tr>
<tr>
<td>24</td>
<td>160</td>
<td>18.2</td>
<td>90</td>
<td>3.40</td>
<td>16</td>
</tr>
</tbody>
</table>

Note: The TCD channel of the GC has high detection limit for H₂ and internal standard C₂H₄, thus leading to large uncertainty in the quantification of H₂. As a result, the Faradaic efficiency for H₂ and the overall Faradaic efficiency has an error of ± 10%. However, the CO quantification by GC (FID) is accurate and so is the corresponding Faradaic efficiency. This applies to the following data as well.

Figure S2.69. Representative chronoamperogram of COF-366-Co catalyzed CO₂ reduction in the first 2h electrolysis.
Figure S2.70. Chronocoulomogram of COF-366-Co catalyzed CO\textsubscript{2} reduction over 24 h.
Table S2.6. COF-367-Co (0.60 mg, 0.55 μmol Co)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Total Charge (C)</th>
<th>Volume CO (mL)</th>
<th>FE CO (%)</th>
<th>Volume H₂ (mL)</th>
<th>H₂</th>
<th>FE H₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>92.2</td>
<td>10.7</td>
<td>91</td>
<td>2.43</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>170</td>
<td>18.8</td>
<td>87</td>
<td>4.82</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>263</td>
<td>28.0</td>
<td>84</td>
<td>7.53</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>348</td>
<td>36.8</td>
<td>83</td>
<td>10.2</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>429</td>
<td>45.8</td>
<td>84</td>
<td>12.9</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>494</td>
<td>52.5</td>
<td>83</td>
<td>15.0</td>
<td>23</td>
<td></td>
</tr>
</tbody>
</table>

Figure S2.71. Representative chronoamperogram of COF-367-Co catalyzed CO₂ reduction in the first 4 h electrolysis.
Figure S2.72. Chronocoulomogram of COF-367-Co catalyzed CO$_2$ reduction over 24 h.

Table S2.7. Co(TAP) (0.44 mg, 0.61 μmol Co)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Total Charge (C)</th>
<th>Volume CO (mL)</th>
<th>FE CO (%)</th>
<th>Volume H$_2$ (mL)</th>
<th>FE CO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>20.1</td>
<td>1.91</td>
<td>75</td>
<td>0.57</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>41.0</td>
<td>4.27</td>
<td>82</td>
<td>1.23</td>
<td>23</td>
</tr>
<tr>
<td>12</td>
<td>58.5</td>
<td>6.03</td>
<td>81</td>
<td>1.87</td>
<td>25</td>
</tr>
<tr>
<td>16</td>
<td>75.1</td>
<td>7.78</td>
<td>81</td>
<td>2.44</td>
<td>25</td>
</tr>
<tr>
<td>20</td>
<td>89.7</td>
<td>9.23</td>
<td>81</td>
<td>2.98</td>
<td>26</td>
</tr>
<tr>
<td>24</td>
<td>102</td>
<td>10.5</td>
<td>80</td>
<td>3.49</td>
<td>26</td>
</tr>
</tbody>
</table>
2.4.18 Characterization of COF-366-Co After Long-Term Electrolysis

Figure S2.73. PXRD of COF-366-Co post-electrolysis.

Figure S2.74. SEM of COF-366-Co pre-electrolysis (left) and post-electrolysis (right).
2.4.19 Reusability

General information: Following the general procedures using 0.24 mg COF-366-Co deposited on a 1 x 1 cm$^2$ area of a 1 x 1.5 cm$^2$ carbon fabric electrode. After GC analysis, the electrode was removed from the current electrolyte solution and subjected to a new batch of fresh electrolyte solution before electrolysis was continued.

Table S2.8. COF-366-Co (0.24 mg, 0.23 μmol Co)

<table>
<thead>
<tr>
<th>Reuse #</th>
<th>Volume CO (mL)</th>
<th>Volume H$_2$ (mL)</th>
<th>Charge (C)</th>
<th>FE CO (%)</th>
<th>FE H$_2$ (%)</th>
<th>CO/H$_2$ Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.62</td>
<td>0.11</td>
<td>6.4</td>
<td>85</td>
<td>14</td>
<td>5.5</td>
</tr>
<tr>
<td>1</td>
<td>0.57</td>
<td>0.14</td>
<td>7.2</td>
<td>79</td>
<td>14</td>
<td>5.7</td>
</tr>
<tr>
<td>2</td>
<td>0.52</td>
<td>0.14</td>
<td>6.4</td>
<td>77</td>
<td>15</td>
<td>5.3</td>
</tr>
<tr>
<td>3</td>
<td>0.53</td>
<td>0.15</td>
<td>6.9</td>
<td>74</td>
<td>15</td>
<td>5.0</td>
</tr>
<tr>
<td>4</td>
<td>0.70</td>
<td>0.19</td>
<td>5.8</td>
<td>77</td>
<td>16</td>
<td>4.7</td>
</tr>
</tbody>
</table>
2.4.20 Control Experiments

Table S2.9. COF-366-Co (Run 1: 0.52 mg, 0.51 μmol Co; Run 2: 0.53 mg, 0.52 μmol Co; Run 3: 0.54 mg, 0.53 μmol Co)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Run 1</th>
<th></th>
<th></th>
<th>Run 2</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume CO (mL)</td>
<td>FE CO (%)</td>
<td>Volume H₂ (mL)</td>
<td>FE H₂ (%)</td>
<td>Charge (C)</td>
<td>Volume CO (mL)</td>
<td>FE CO (%)</td>
</tr>
<tr>
<td>1</td>
<td>1.02</td>
<td>59</td>
<td>0.21</td>
<td>12</td>
<td>13.5</td>
<td>1.17</td>
</tr>
<tr>
<td>2</td>
<td>2.52</td>
<td>73</td>
<td>0.40</td>
<td>12</td>
<td>27.1</td>
<td>2.25</td>
</tr>
<tr>
<td>3</td>
<td>4.21</td>
<td>82</td>
<td>0.75</td>
<td>14</td>
<td>40.7</td>
<td>3.64</td>
</tr>
<tr>
<td>4</td>
<td>4.95</td>
<td>78</td>
<td>0.98</td>
<td>15</td>
<td>49.9</td>
<td>4.76</td>
</tr>
</tbody>
</table>

Table S2.10. Co(TAP) (Run 1: 0.38 mg, 0.54 μmol Co; Run 2: 0.38 mg, 0.54 μmol Co)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Run 1</th>
<th></th>
<th></th>
<th>Run 2</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume CO (mL)</td>
<td>FE CO (%)</td>
<td>Volume H₂ (mL)</td>
<td>FE H₂ (%)</td>
<td>Charge (C)</td>
<td>Volume CO (mL)</td>
<td>FE CO (%)</td>
</tr>
<tr>
<td>1</td>
<td>0.97</td>
<td>60</td>
<td>0.23</td>
<td>14</td>
<td>12.8</td>
<td>ND</td>
</tr>
<tr>
<td>2</td>
<td>2.07</td>
<td>64</td>
<td>0.55</td>
<td>17</td>
<td>25.6</td>
<td>1.13</td>
</tr>
<tr>
<td>3</td>
<td>3.74</td>
<td>78</td>
<td>0.82</td>
<td>17</td>
<td>37.9</td>
<td>1.40</td>
</tr>
<tr>
<td>4</td>
<td>5.26</td>
<td>84</td>
<td>0.99</td>
<td>15</td>
<td>49.7</td>
<td>1.73</td>
</tr>
</tbody>
</table>

ND = not determined (time point not taken)
Table S2.11. COF-366 (Run 1: 0.49 mg, 0.56 μmol porphyrin; Run 2: 0.48 mg, 0.55 μmol porphyrin)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Run 1</th>
<th></th>
<th></th>
<th>Run 2</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
<td>FE CO</td>
<td></td>
<td>H2</td>
<td>FE H2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Volume (mL)</td>
<td>FE CO (%)</td>
<td>Volume (mL)</td>
<td>FE H2 (%)</td>
<td>Charge (C)</td>
<td>Volume (mL)</td>
</tr>
<tr>
<td>1</td>
<td>0.008</td>
<td>8.5</td>
<td>0.02</td>
<td>23</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.013</td>
<td>6.6</td>
<td>0.07</td>
<td>35</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.021</td>
<td>6.5</td>
<td>0.15</td>
<td>47</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.027</td>
<td>6.2</td>
<td>0.27</td>
<td>63</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ND</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ND</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ND</td>
<td>ND</td>
<td></td>
</tr>
</tbody>
</table>

ND = not determined (time point not taken)

Table S2.12. Co₃O₄ (0.088 mg, 1.10 μmol Co)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Volume CO (mL)</th>
<th>FE CO (%)</th>
<th>Volume H₂ (mL)</th>
<th>FE H₂ (%)</th>
<th>Charge (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0018</td>
<td>0.05</td>
<td>4.58</td>
<td>119</td>
<td>30.2</td>
</tr>
<tr>
<td>2</td>
<td>0.0019</td>
<td>0.02</td>
<td>10.6</td>
<td>106</td>
<td>78.8</td>
</tr>
</tbody>
</table>

Table S2.13. Background: bare carbon fabric

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Volume CO (mL)</th>
<th>FE CO (%)</th>
<th>Volume H₂ (mL)</th>
<th>FE H₂ (%)</th>
<th>Charge (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.002</td>
<td>0.5</td>
<td>0.39</td>
<td>96</td>
<td>3.2</td>
</tr>
<tr>
<td>4</td>
<td>0.003</td>
<td>0.5</td>
<td>0.73</td>
<td>103</td>
<td>5.6</td>
</tr>
</tbody>
</table>
Table S2.14. Co nanoparticles (~10 nm) + COF-366 (0.49 mg, 0.56 μmol porphyrin)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Volume CO (mL)</th>
<th>FE CO (%)</th>
<th>Volume H₂ (mL)</th>
<th>FE H₂ (%)</th>
<th>Charge (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0011</td>
<td>0.02</td>
<td>4.84</td>
<td>103</td>
<td>36.8</td>
</tr>
</tbody>
</table>

Figure S2.75. Performance of various control molecular and materials catalysts in CO evolution.
2.4.21 Electrolysis with Bimetallic COFs

Table S2.15. COF-367-Co(10%) (Run 1: 0.58 mg, 0.58 μmol Co; Run 2: 0.62 mg, 0.62 μmol Co)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Run 1</th>
<th>Run 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volume CO (mL)</td>
<td>FE CO (%)</td>
</tr>
<tr>
<td>1</td>
<td>0.49</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>0.91</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>1.42</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>1.83</td>
<td>66</td>
</tr>
</tbody>
</table>

Table S2.16. COF-367-Co(1%) (Run 1: 0.58 mg, 0.57 μmol Co; Run 2: 0.62 mg, 0.61 μmol Co)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Run 1</th>
<th>Run 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volume CO (mL)</td>
<td>FE CO (%)</td>
</tr>
<tr>
<td>1</td>
<td>0.10</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>38</td>
</tr>
<tr>
<td>3</td>
<td>0.33</td>
<td>46</td>
</tr>
<tr>
<td>4</td>
<td>0.41</td>
<td>46</td>
</tr>
</tbody>
</table>
Table S2.17. COF-367-Cu (Run 1: 0.60 mg, 0.56 μmol Cu; Run 2: 0.57 mg, 0.53 μmol Cu)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Run 1</th>
<th></th>
<th></th>
<th></th>
<th>Run 2</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volume CO (mL)</td>
<td>FE CO (%)</td>
<td>Volume H₂ (mL)</td>
<td>FE H₂ (%)</td>
<td>Charge (C)</td>
<td>Volume CO (mL)</td>
<td>FE CO (%)</td>
<td>Volume H₂ (mL)</td>
</tr>
<tr>
<td>1</td>
<td>0.008</td>
<td>3.9</td>
<td>0.16</td>
<td>75</td>
<td>1.6</td>
<td>0.007</td>
<td>3.2</td>
<td>0.16</td>
</tr>
<tr>
<td>2</td>
<td>0.014</td>
<td>3.8</td>
<td>0.30</td>
<td>82</td>
<td>2.9</td>
<td>0.017</td>
<td>4.0</td>
<td>0.36</td>
</tr>
<tr>
<td>3</td>
<td>0.021</td>
<td>4.1</td>
<td>0.44</td>
<td>86</td>
<td>4.0</td>
<td>0.023</td>
<td>4.2</td>
<td>0.48</td>
</tr>
<tr>
<td>4</td>
<td>0.029</td>
<td>4.6</td>
<td>0.54</td>
<td>86</td>
<td>4.9</td>
<td>0.031</td>
<td>3.6</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Table S2.18. Mixture of COF-367-Co and COF-367-Cu (1:9) (0.066 mg COF-367-Co, 0.061 μmol Co, and 0.524 mg COF-367-Cu, 0.49 μmol Cu)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Volume CO (mL)</th>
<th>FE CO (%)</th>
<th>Volume H₂ (mL)</th>
<th>FE H₂ (%)</th>
<th>Charge (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.32</td>
<td>59</td>
<td>0.095</td>
<td>21</td>
<td>3.6</td>
</tr>
<tr>
<td>2</td>
<td>0.53</td>
<td>56</td>
<td>0.18</td>
<td>22</td>
<td>6.7</td>
</tr>
<tr>
<td>3</td>
<td>0.74</td>
<td>57</td>
<td>0.26</td>
<td>22</td>
<td>9.4</td>
</tr>
<tr>
<td>4</td>
<td>0.97</td>
<td>66</td>
<td>0.35</td>
<td>23</td>
<td>12.2</td>
</tr>
</tbody>
</table>
Table S2.19. COF-367-Co(1%) long-term (0.60 mg, 0.59 µmol Co)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Charge (C)</th>
<th>Volume CO (mL)</th>
<th>FE CO (%)</th>
<th>Volume H₂ (mL)</th>
<th>FE H₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>20.0</td>
<td>1.35</td>
<td>53</td>
<td>1.59</td>
<td>62</td>
</tr>
<tr>
<td>16</td>
<td>33.8</td>
<td>2.11</td>
<td>49</td>
<td>2.36</td>
<td>55</td>
</tr>
<tr>
<td>24</td>
<td>45.0</td>
<td>2.59</td>
<td>45</td>
<td>3.03</td>
<td>53</td>
</tr>
<tr>
<td>32</td>
<td>55.6</td>
<td>2.87</td>
<td>40</td>
<td>3.67</td>
<td>52</td>
</tr>
<tr>
<td>40</td>
<td>64.4</td>
<td>3.08</td>
<td>37</td>
<td>4.32</td>
<td>53</td>
</tr>
<tr>
<td>48</td>
<td>72.3</td>
<td>3.25</td>
<td>35</td>
<td>5.11</td>
<td>56</td>
</tr>
<tr>
<td>56</td>
<td>80.3</td>
<td>3.38</td>
<td>33</td>
<td>5.76</td>
<td>57</td>
</tr>
<tr>
<td>72</td>
<td>88.1</td>
<td>3.56</td>
<td>31</td>
<td>7.10</td>
<td>58</td>
</tr>
<tr>
<td>88</td>
<td>97.4</td>
<td>3.71</td>
<td>29</td>
<td>8.85</td>
<td>58</td>
</tr>
<tr>
<td>112</td>
<td>104</td>
<td>3.82</td>
<td>28</td>
<td>10.3</td>
<td>61</td>
</tr>
<tr>
<td>136</td>
<td>110</td>
<td>3.95</td>
<td>27</td>
<td>12.8</td>
<td>64</td>
</tr>
</tbody>
</table>
Figure S2.76. Representative chronoamperogram of COF-367-Co(1%) catalyzed CO\textsubscript{2} reduction in the first 8 h electrolysis.

Figure S2.77. Chronocoulomogram of COF-367-Co(1%) catalyzed CO\textsubscript{2} reduction over 24 h.
2.4.22 Spectroelectrochemistry of Thin-Film COF-366-Co on FTO

General information: All absorption spectra were acquired with a Shimadzu 3101 PC UV-Vis-NIR spectrometer fitted with an integrating sphere. Fluorine-doped tin oxide (FTO) on glass was used as a working electrode and Ag/AgCl and titanium foil were used as reference and counter electrodes, respectively. A Gamry Reference 600 mobile potentiostat was used for electrochemical measurements. A 5 mL quartz cuvette filled with 0.5 M KHCO₃ electrolyte, saturated with carbon dioxide was used as a one-compartment electrochemical cell. A carbon dioxide atmosphere was maintained throughout the course of the measurements. Prior to spectral acquisition, the COF-coated FTO working electrode was held at the desired potential for 3 minutes to attain a steady state. Each spectral acquisition took approximately 2 minutes.

Figure S2.78. UV-Vis spectra of COF-366-Co thin films on FTO in 0.5 M KHCO₃ saturated with CO₂ under different applied potentials. Following the direction of the arrows: 0.33, 0.23, 0.13, 0.03, -0.07, -0.17, -0.27, -0.32, -0.37, -0.42, -0.47, -0.52, -0.57 V.
Figure S2.79. UV-Vis absorbance of COF-366-Co thin films on FTO in 0.5 M KHCO₃ saturated with CO₂ under different applied potentials relative to that under 0.33 V. Following the direction of the arrows: 0.23, 0.13, 0.03, -0.07, -0.17, -0.27, -0.32, -0.37, -0.42, -0.47, -0.52, -0.57 V.

Figure S2.80. Time-dependence of the UV-Vis absorbance of COF-366-Co thin films on FTO at 630 nm at -0.60 V vs RHE only showing the linear regime (4-16 sec, for full scale, see Figure 2.3g in the main text). Linear regression gives the slope needed for the calculation of the apparent diffusion coefficient ($D_{app}$) according to a modified Cotrell equation: 

$$\Delta A = \frac{2A_{max} \delta_{app}^{1/2}}{d n^{1/2}} t^{1/2}$$

Here, $A_{max}$ is the maximum absorption of the thin films at 640 nm, $d$ is the overall thickness of the thin films.
Figure S2.81. UV-Vis absorbance of COF-366-Co thin films on FTO in pH 7.2 phosphate buffer (nitrogen saturated) under different applied potentials relative to that under 0.33 V. Following the direction of the arrows: 0.33, 0.23, 0.13, 0.03, -0.07, -0.17, -0.27, -0.32, -0.37, -0.42, -0.47, -0.52 V.

Figure S2.82. UV-Vis absorbance of COF-366-Co thin films on FTO in pH 7.2 phosphate buffer (nitrogen saturated) under different applied potentials relative to that under 0.33 V at 640 nm, showing that when more negative potentials (up to -0.52 V) are applied, the ratio of Co(I)/Co(II) keeps increasing. The inset shows the first derivative of a polynomial fit of the absorbance vs. potential data. Based on the Nernst equation, the Co(II)/Co(I) redox potential ($E_{1/2}$) is where half of the Co(II) is reduced to Co(I). Therefore, it is the potential of the inflection point on Δ absorbance vs. potential curve or the maximum point on the first derivative of Δ absorbance vs. potential curve. However, as shown in the inset of Figure. S2.82, the potential of the maximum point is more negative than -0.52 V. Due to decomposition of FTO at potentials more negative than -0.57 V, we cannot further determine $E_{1/2}$.
2.4.23 Direct Current Conductivity Measurement of COF-366-Co on Silicon Oxide

The direct current (DC) electrical transport studies were conducted with a probe station at room temperature (25 °C) under ambient conditions with a computer-controlled analogue-to-digital converter. Gold contact pads were thermally deposited on a Si/SiO₂ substrate with a thermal oxide layer. In the blank sample, the gold contact pads were directly in contact with the thermal oxide, while in case with COF, the gold contact pads were in contact with the thin films of COF-366-Co directly grown on the oxide surface (Figure S2.83).

Figure S2.83. Graphic representation of the direct current conductivity of COF-366-Co on thermal oxide.

![Diagram](image)

Figure S2.84. $I-V$ profile of a COF-366-Co-coated silicon oxide (blue) and a bare silicon oxide (black).
2.4.24 Reactivity of Thin-Film COF-366-Co

Table S2.20. COF-366-Co thin films on glassy carbon long-term (ICP analysis shows that there is $9.1 \times 10^{-6}$ mmol Co on the electrode surface that is covered by the electrolyte during electrolysis, corresponding to 8.4 μg COF-366-Co)

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Charge (C)</th>
<th>Volume CO (mL)</th>
<th>FE CO (%)</th>
<th>Volume H₂ (mL)</th>
<th>FE H₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.4</td>
<td>0.15</td>
<td>86</td>
<td>0.035</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>3.8</td>
<td>0.40</td>
<td>84</td>
<td>0.11</td>
<td>22</td>
</tr>
<tr>
<td>18</td>
<td>6.9</td>
<td>0.68</td>
<td>78</td>
<td>0.23</td>
<td>26</td>
</tr>
<tr>
<td>24</td>
<td>8.1</td>
<td>0.79</td>
<td>76</td>
<td>0.28</td>
<td>27</td>
</tr>
</tbody>
</table>

Figure S2.85. Reactivity of COF-366-Co thin films catalyzed CO₂ reduction.
2.4.25 Kinetic Data

General information: Following the general procedures using 0.2 mg COF-366-Co deposited on a 1 x 1 cm$^2$ area of a 1 x 1.5 cm$^2$ carbon fabric electrode. Each electrolysis was performed over 30 minutes at -0.67 V vs. RHE.

Figure S2.86. Rate dependence on partial CO$_2$ pressure.

Figure S2.87. Rate dependence on pH.
Figure S2.88. Rate dependence on pH with Co(TAP).

\[
y = 0.0019x + 0.2714
\]

Figure S2.89. Possible elementary steps for a metal-catalyzed hydrogen evolution reaction (HER).\textsuperscript{54}

1-Volmer: \[ \text{H}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}} \]

2-Heyrovsky: \[ \text{H}_{\text{ads}} + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2 \]

3-Tafel: \[ \text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2 \]

Possible Mechanistic Scenarios for a Metal-Catalyzed HER and Corresponding Tafel Slopes:

- When Tafel slope = 40 mV/dec, HER undergoes Volmer–Heyrovsky mechanism, where a fast 1e\textsuperscript{-} transfer (Volmer step) is followed by a rate-limiting H\textsubscript{2} production that also involve a 1e\textsuperscript{-} transfer (Heyrovsky step);
- When Tafel slope = 30 mV/dec, HER undergoes Volmer-Tafel mechanism, where two fast 1e\textsuperscript{-} transfers (Volmer steps) are followed by a rate-limiting recombination of adsorbed H atoms (Tafel step);
- When Tafel slope = 120 mV/dec, HER starts with a rate-limiting Tafel step with a 1e\textsuperscript{-} transfer, which can be followed by various different post-rate-limiting pathways.
Tafel slope = 120 mV/dec

Figure S2.90. Possible mechanistic scenarios for a gold-catalyzed CO2 reduction (adopted from ref. 55)

Mechanism A: (Tafel slope = 59 mV/dec)

\[
\begin{align*}
\text{Co(II)-L} & \quad \overset{e^-}{\longrightarrow} \quad \text{Co(I)-L} \\
\text{CO2} & \quad \overset{\text{rate-limiting}}{\longrightarrow} \quad \text{O2C-Co(I)-L} \\
\text{H+} & \quad \overset{e^-}{\longrightarrow} \quad \text{HO2C-Co(I)-L} \\
& \quad \overset{\text{rate-limiting}}{\longrightarrow} \quad \text{CO} + \text{H2O} + \text{Co(II)-L}
\end{align*}
\]

Mechanism B: (Tafel slope = 40 mV/dec)

\[
\begin{align*}
\text{Co(II)-L} & \quad \overset{e^-}{\longrightarrow} \quad \text{Co(I)-L} \\
\text{CO2} & \quad \overset{\text{rate-limiting}}{\longrightarrow} \quad \text{O2C-Co(I)-L} \\
\text{H+} & \quad \overset{e^-}{\longrightarrow} \quad \text{HO2C-Co(I)-L} \\
& \quad \overset{\text{rate-limiting}}{\longrightarrow} \quad \text{CO} + \text{H2O} + \text{Co(II)-L}
\end{align*}
\]

Mechanism C: (Tafel slope = 30 mV/dec)

\[
\begin{align*}
\text{Co(II)-L} & \quad \overset{e^-}{\longrightarrow} \quad \text{Co(I)-L} \\
\text{CO2} & \quad \overset{\text{rate-limiting}}{\longrightarrow} \quad \text{O2C-Co(I)-L} \\
& \quad \overset{2e^-}{\longrightarrow} \quad \text{CO} + \text{H2O} + \text{Co(II)-L}
\end{align*}
\]

Figure S2.91. Possible mechanistic scenarios for COF- or Co(TAP)-catalyzed CO2 reduction. L represents the porphyrin ligand. In Mechanism A, the Co(II) porphyrin gets reduced by a fast 1e\(^-\) transfer to form Co(I) porphyrin, then participates in CO2 sequestration to form the Co(I)-CO2 complex, which is the rate-limiting step. This draws analogy from the second scenario from Figure S2.88, with necessary modifications based on the nature of the catalyst and the kinetic data. In Mechanism B, Co(II) porphyrin gets reduced via a fast 1e\(^-\) transfer to form Co(I) porphyrin, then participates in CO2 sequestration concomitant with another 1e\(^-\) transfer to form the Co(I)-CO2 complex. The second step is rate-limiting. This mechanism is analogous to the Volmer–Heyrovsky mechanism in an HER (Figure S2.87). In Mechanism C, the reaction undergoes two consecutive 1e\(^-\) transfers followed by the rate-limiting CO2 binding to form Co(I)-CO2\(^-\) complex. The second step from Co(I)-L to Co(I)-L\(^-\) represents a ligand-based 1e\(^-\) reduction, which is frequently observed with metalloporphyrins. This mechanism is analogous to a Volmer-Tafel mechanism of an HER, again with necessary revisions based on the nature of the system.
## 2.4.26 List of Some Existing Electrocatalysts for CO₂ Reduction

### Table S2.21. Performance of a selection of existing CO₂ reduction catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Product</th>
<th>Time ( \text{a,b} ) (h)</th>
<th>TON ( \text{a,b} )</th>
<th>TOF (h(^{-1}))</th>
<th>Medium and Cathode Material</th>
<th>Current Density (mA/cm(^2))</th>
<th>Current Density (mA/mg)</th>
<th>Potential ( \alpha ) overpot.</th>
<th>Faradaic Effic.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{26})</td>
<td>CO</td>
<td>2 h</td>
<td>70</td>
<td>35</td>
<td>DMF + CF₃CH₂OH (1.37 M); mercury pool</td>
<td>3.3</td>
<td>N/A</td>
<td>-1.46 V [770 mV] ( E^0 = -0.69 )</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>2(^{27})</td>
<td>CO</td>
<td>3 h</td>
<td>n.r.</td>
<td>19</td>
<td>DMF + PhOH (3 M); carbon crucible</td>
<td>0.5</td>
<td>N/A</td>
<td>-1.08 V [390 mV] ( E^0 = -0.69 )</td>
<td>100%</td>
</tr>
<tr>
<td>3(^{28})</td>
<td>CO</td>
<td>n.r.</td>
<td>n.r.</td>
<td>11</td>
<td>DMF + H₂O (2 M); carbon crucible</td>
<td>0.31</td>
<td>N/A</td>
<td>-1.16 V [470 mV] ( E^0 = -0.69 )</td>
<td>94%</td>
</tr>
<tr>
<td>4(^{29})</td>
<td>CO</td>
<td>14 h</td>
<td>300</td>
<td>22</td>
<td>DMF/H₂O (9:1); glassy carbon</td>
<td>0.51</td>
<td>N/A</td>
<td>-1.25 V [560 mV] ( E^0 = -0.69 )</td>
<td>98%</td>
</tr>
<tr>
<td>5(^{30})</td>
<td>CO</td>
<td>5 h</td>
<td>240</td>
<td>48</td>
<td>MeCN; glassy carbon</td>
<td>1</td>
<td>N/A</td>
<td>-1.61 V [960 mV] ( E^0 = -0.69 )</td>
<td>99%</td>
</tr>
<tr>
<td>6(^{31})</td>
<td>CO</td>
<td>22 h</td>
<td>~26</td>
<td>3.3</td>
<td>MeCN/H₂O (19:1); glassy carbon</td>
<td>0.2</td>
<td>N/A</td>
<td>-1.50 V [850 mV] ( E^0 = -0.69 )</td>
<td>quant.</td>
</tr>
<tr>
<td>7(^{32})</td>
<td>CO</td>
<td>25 h</td>
<td>~60</td>
<td>3.4</td>
<td>MeCN + CF₃CH₂OH (0.3 M); glassy carbon</td>
<td>3.5 (1.5 after 25 h)</td>
<td>N/A</td>
<td>-1.60 V [950 mV] ( E^0 = -0.69 )</td>
<td>98%</td>
</tr>
<tr>
<td>8(^{33})</td>
<td>CO</td>
<td>8 h</td>
<td>8,000</td>
<td>1,000</td>
<td>Aq. KClO₄ (0.1 M, pH 4.1); mercury cathode</td>
<td>0.23</td>
<td>N/A</td>
<td>-1.00 V [640 mV] ( E^0 = -0.36 )</td>
<td>up to 99%</td>
</tr>
<tr>
<td>9(^{34})</td>
<td>CO</td>
<td>3.5 h</td>
<td>4</td>
<td>1.1</td>
<td>MeCN/H₂O (4:1); glassy carbon</td>
<td>1.8</td>
<td>N/A</td>
<td>-1.21 V [560 mV]</td>
<td>90%</td>
</tr>
<tr>
<td>Entry</td>
<td>Reagents</td>
<td>Conditions</td>
<td>Products</td>
<td>Potential</td>
<td>Current Efficiency</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>----------</td>
<td>------------</td>
<td>----------</td>
<td>-----------</td>
<td>--------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>CO</td>
<td>1 h</td>
<td>228</td>
<td>Aq. NaClO₃ (0.1 M, pH 5); mercury pool</td>
<td>4</td>
<td>N/A</td>
<td>E° = -0.56</td>
<td>88%</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>CO</td>
<td>8 h</td>
<td>35</td>
<td>MeCN; glassy carbon</td>
<td>4–6</td>
<td>N/A</td>
<td>E° = -0.96 V [550 mV]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>CO</td>
<td>15 h</td>
<td>190</td>
<td>DMF + HBF₄ (0.1 M); glassy carbon</td>
<td>n.r.</td>
<td>N/A</td>
<td>E° = -1.05 V [740 mV]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>CO</td>
<td>24 h</td>
<td>&gt; 48</td>
<td>MeCN; Pt gauze</td>
<td>n.r.</td>
<td>N/A</td>
<td>E° = -1.50 V [940 mV]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>HCO₂H</td>
<td>24 h</td>
<td>400</td>
<td>Aq. NaHCO₃ (0.1 M, pH 6.6) + MeCN (1% v/v); glassy carbon</td>
<td>0.6</td>
<td>N/A</td>
<td>E° = -1.41 V [900 mV]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>CO</td>
<td>40 min</td>
<td>4.1</td>
<td>MeCN + H₂O (10 M); glassy carbon</td>
<td>3</td>
<td>N/A</td>
<td>E° = -1.73 V [1080 mV]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>oxide-derived copper</td>
<td>7 h</td>
<td>N/A</td>
<td>Aq. KHCO₃ (0.5 M, pH 7.3); copper electrode</td>
<td>2.7</td>
<td>1.4</td>
<td>E° = -0.93 V [380 mV]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>copper nanoparticles</td>
<td>10 min</td>
<td>N/A</td>
<td>Aq. KHCO₃ (0.1 M, pH 6.6); glassy carbon</td>
<td>47</td>
<td>n. r.</td>
<td>E° = -1.49 V [980 mV]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>oxidized-derived gold nanoparticles</td>
<td>8 h</td>
<td>N/A</td>
<td>Aq. KHCO₃ (0.5 M, pH 7.3); gold electrode</td>
<td>10 (6 after 8 h)</td>
<td>5.8</td>
<td>E° = -0.83 V [280 mV]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>gold nanoparticles</td>
<td>0.5 h</td>
<td>6</td>
<td>Aq. KHCO₃ (0.5 M, pH 7.3); graphitized porous carbon support</td>
<td>n.r.</td>
<td>3</td>
<td>E° = -0.95 V [400 mV]</td>
<td>97%</td>
<td></td>
</tr>
<tr>
<td>ID</td>
<td>Material/Methodology</td>
<td>HCO₂H</td>
<td>Time</td>
<td>Temperature</td>
<td>Electrolyte</td>
<td>Potential</td>
<td>Current</td>
<td>Efficiency</td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>----------------------</td>
<td>-------</td>
<td>------</td>
<td>-------------</td>
<td>-------------</td>
<td>-----------</td>
<td>---------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>polyethylenimine-coated N-doped carbon nanotubes</td>
<td>HCO₂H</td>
<td>24 h</td>
<td>N/A</td>
<td>N/A</td>
<td>Aq. KHCO₃ (0.1 M, pH 6.6); glassy carbon</td>
<td>9.5</td>
<td>2.7</td>
<td>-1.56 V [1050 mV] $E^0 = -0.51$</td>
</tr>
<tr>
<td>21</td>
<td>SnO₂/graphene</td>
<td>HCO₂H</td>
<td>18 h</td>
<td>N/A</td>
<td>N/A</td>
<td>Aq. NaHCO₃ (0.1 M, pH 6.6); glassy carbon</td>
<td>10.2</td>
<td>6.8</td>
<td>-1.56 V [1050 mV] $E^0 = -0.51$</td>
</tr>
<tr>
<td>22</td>
<td>tin thin film</td>
<td>CO</td>
<td>10 h</td>
<td>N/A</td>
<td>N/A</td>
<td>Aq. KHCO₃ (0.1 M, pH 6.6); glassy carbon</td>
<td>1.8</td>
<td>1.5</td>
<td>-1.13 V [580 mV] $E^0 = -0.55$</td>
</tr>
<tr>
<td>23</td>
<td>bismuth</td>
<td>CO</td>
<td>40 min</td>
<td>N/A</td>
<td>N/A</td>
<td>Aq. KHCO₃ (0.1 M, pH 6.6); Ti electrode</td>
<td>31</td>
<td>14.8</td>
<td>-1.76 V [170 mV] $E^0 = -1.59$</td>
</tr>
<tr>
<td>24</td>
<td>N-based silver catalyst</td>
<td>CO</td>
<td>330 s</td>
<td>ca. 200 e</td>
<td>ca. 2,000 e</td>
<td>Aq. KOH (1 M); carbon</td>
<td>90</td>
<td>90</td>
<td>-1.60 V $E^0 = -0.51$</td>
</tr>
<tr>
<td>25</td>
<td>silver nanoparticles</td>
<td>CO</td>
<td>7 h</td>
<td>ca. 200 e</td>
<td>ca. 2,000 e</td>
<td>Aq. KOH (1 M); carbon</td>
<td>1.9</td>
<td>0.3</td>
<td>-0.90 V [490 mV] $E^0 = -0.41$</td>
</tr>
<tr>
<td>26</td>
<td>gold/copper alloy nanoparticles</td>
<td>CO</td>
<td>1 h</td>
<td>N/A</td>
<td>N/A</td>
<td>Aq. KHCO₃ (0.1 M, pH 6.6); glassy carbon</td>
<td>3</td>
<td>30</td>
<td>-1.13 V [620 mV] $E^0 = -0.51$</td>
</tr>
<tr>
<td>27</td>
<td>Co(TAP)</td>
<td>CO</td>
<td>24 h</td>
<td>794</td>
<td>36 e</td>
<td>Aq. KHCO₃ (0.5 M, pH 7.3); carbon fabric</td>
<td>0.7</td>
<td>3</td>
<td>-1.10 V [550 mV] $E^0 = -0.55$</td>
</tr>
<tr>
<td>28</td>
<td>COF-366-Co</td>
<td>CO</td>
<td>24 h</td>
<td>1,352</td>
<td>98 e</td>
<td>Aq. KHCO₃ (0.5 M, pH 7.3); carbon fabric</td>
<td>1.8</td>
<td>7</td>
<td>-1.10 V [550 mV] $E^0 = -0.55$</td>
</tr>
<tr>
<td>29</td>
<td>COF-367-Co</td>
<td>CO</td>
<td>24 h</td>
<td>3,901</td>
<td>165 e</td>
<td>Aq. KHCO₃ (0.5 M, pH 7.3); carbon fabric</td>
<td>3.3</td>
<td>13</td>
<td>-1.10 V [550 mV] $E^0 = -0.55$</td>
</tr>
<tr>
<td>29</td>
<td>COF-367-Co(10%)</td>
<td>CO</td>
<td>4 h</td>
<td>1,440</td>
<td>360 e</td>
<td>Aq. KHCO₃ (0.5 M, pH 7.3); carbon fabric</td>
<td>0.8</td>
<td>3</td>
<td>-1.10 V [550 mV] $E^0 = -0.55$</td>
</tr>
<tr>
<td></td>
<td>COF-367-Co(1%)</td>
<td>CO</td>
<td>136 h</td>
<td>24,00</td>
<td>764</td>
<td>Aq. KHCO$_3$ (0.5 M, pH 7.3); carbon fabric</td>
<td>0.4</td>
<td>1.2</td>
<td>-1.10 V [550 mV]</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>30</td>
<td>COF-366-Co thin films on glassy carbon</td>
<td>CO</td>
<td>24 h</td>
<td>3,542</td>
<td>665</td>
<td>Aq. KHCO$_3$ (0.5 M, pH 7.3); glassy carbon</td>
<td>0.7</td>
<td>45</td>
<td>-1.10 V [550 mV]</td>
</tr>
</tbody>
</table>

Notes:  

$^a$ Time of electrolysis reported in the referenced work. The turnover number (TON) is the value obtained during this time.

$^b$ TON is defined as the total moles of carbon product formed ($n_{\text{prod}}$) divided by total moles of catalyst employed in the electrolysis ($n_{\text{cat}}$). TON = $n_{\text{prod}}/n_{\text{cat}}$. Values in parentheses are the time in which the corresponding TONs are achieved. In a few systems, the catalyst remains active after this period of time. Turnover frequency (TOF) is defined as TON per unit time: TOF = TON/$t$ = $n_{\text{prod}}/(n_{\text{cat}} t)$, where $t$ is the electrolysis time. When TON is not reported or cannot be calculated directly using the reactivity data in the reference, the following equation is used to estimate TOF: TOF = $QE_i/(tNFn_{\text{cat}})$ = $iE_i/(NFn_{\text{cat}})$, where $Q$ is the total charge passed in time $t$, $i$ is the current, $E_i$ is the Faradaic efficiency for the desired product, $N$ is the number of electrons in the half reaction ($N = 2$ for CO$_2$ to CO or HCO$_2$H conversion), and $F$ is the Faraday constant ($F = 96485 \text{ C/mol electrons}$). When catalyst decomposition is evident, the TOF is calculated on the basis of the initial catalytic activity. For TON/TOF values based on electroactive catalytic sites using various different methods, please see the corresponding reference.

$^c$ Current density based on total mass of the electrocatalytic material. In cases when the catalytically active material is generated in situ, only the surface-active material was taken into account in the calculation of the current density. Surface area is given.

$^d$ Applied potential vs. SHE, with overpotential in square brackets. $E^0$ = thermodynamic potential for CO$_2$ to CO reduction under reported conditions. $E^0$ is calculated using methods reported in reference 50.

$^e$ Overpotential not calculated because the pH of the electrolysis medium was not reported.

$^f$ Assuming pH = 5.0.

$^h$ Average TOF in the first 4 h of electrolysis.

$^i$ Average TOF in the first hour of electrolysis.

$^j$ Abbreviations: N/A – not applicable; n.r. – not reported or not calculated due to limited data reported.

$^k$ Systems where more reduced products, such as methanol and methane, are produced are not listed in this table, as the thermodynamic potentials of reaction are substantially different and direct comparison would be meaningless.
2.4.27 X-ray Absorption Spectroscopy

General information:

X-ray absorption measurements were conducted at beamline 10.3.2. at the Advanced Light Source (ALS) at Lawrence Berkeley National Lab with an electron energy of 1.9 GeV and average current of 500 mA. Incident X-ray photons were monochromated with a Si(111) two-crystal, constant-exit monochromator with a resolving power of 7000. Fluorescence spectra were recorded using a seven-element Ge solid state detector. Energy calibration was performed with a cobalt foil standard and shifting all spectra to a glitch in the incident intensity, I₀. XANES data reduction and normalization was performed with the Athena software package based on the IFEFFIT library of numerical and XAS algorithms.

To acquire ex-situ and in-situ XANES spectra, a home-built single compartment spectroelectrochemical cell was utilized. This cell contains inlets for working, counter, and references electrodes as well as gas inlets and outlets. The material of interest was drop cast on a carbon fabric electrode and allowed to dry overnight. The sample-containing electrode was pressed between the electrolyte compartments of the cell and a 6 micron thick mylar film to seal the cell. For in-situ measurements, the cell was subsequently filled with electrolyte (0.5 M aq. KHCO₃). Ag/AgCl and Pt were used as a reference and counter electrode, respectively.

XANES spectra were recorded for COF-367-Co, COF-367-Co(10%) and Co(TAP) under ex-situ (dry sample) and in-situ conditions (in electrolyte solution, either under open-circuit potential or applied potential of -0.67 V vs. RHE).
Figure S2.92. Ex-situ X-ray absorption spectra of COF-367-Co, COF-367-Co(10%), and Co(TAP).

Figure S2.93. Pre-edge region of the ex-situ X-ray absorption spectra of COF-367-Co, COF-367-Co(10%), and Co(TAP).
Figure S2.94. *In-situ* X-ray absorption spectra of COF-367-Co, COF-367-Co(10%), and Co(TAP) under open circuit potential.

Figure S2.95. Pre-edge region of the *in-situ* X-ray absorption spectra of COF-367-Co, COF-367-Co(10%), and Co(TAP) under open circuit potential.
Figure S2.96. *In-situ* X-ray absorption spectra of COF-367-Co, COF-367-Co(10%), and Co(TAP) under reduced potential of -0.67 V.

Figure S2.97. Pre-edge region of the *in-situ* X-ray absorption spectra of COF-367-Co, COF-367-Co(10%), and Co(TAP) under reduced potential of -0.67 V.
Figure S2.98. Near-edge X-ray absorption spectra of COF-367-Co under ex-situ conditions, or in-situ conditions with open-circuit potential or a reducing potential of -0.67 V.
2.5 References


[39] In pH 7.2 phosphate buffer, electrolyses at potentials equal to or more negative than -0.67 V result in moderate hydrogen evolution reactivity. This activity is however largely suppressed when the solution is saturated with carbon dioxide (*vide infra*).

[40] The intrinsic $i_{\text{cat}}/i_{\text{p}}$ value is likely higher as under carbon dioxide atmosphere, the current resulting from proton reduction is inhibited.


The COF-coated glassy carbon shows an ill-defined GIWAXS pattern due to high background scattering (Figures S2.52-2.53). Because the synthetic conditions are identical to those used with FTO and silicon oxide, we assume that the COF grown on glassy carbon also forms a crystalline thin film.

$E_{1/2}$ cannot be accurately measured using this method due to decomposition of FTO at potentials more negative than -0.57 V.


Chapter 3
Reticular Electronic Tuning of Active Sites in Covalent Organic Frameworks for Electrocatalytic Carbon Dioxide Reduction

Portions of this chapter have been published in:
3.1 Introduction

Covalent organic frameworks (COFs) are composed of covalently linked organic molecules, which are held together in specific geometric and spatial arrangements.\textsuperscript{1-5} Research efforts have largely focused on varying the size and shape of the molecular building blocks to design the structural properties of COFs such as porosity.\textsuperscript{5-15} In this report, we show how these building blocks can also be tuned electronically such that remote functionalization of linker units has a significant impact on the electronic character of molecular active sites embedded within the reticular superstructure and consequently, their accompanying reactivity. Within this context, we and others have recently identified COFs and their related MOF congeners as promising materials platforms for supporting molecular catalysts for the electrochemical conversion of carbon dioxide to carbon monoxide.\textsuperscript{16-18} Indeed, extensive research has been devoted to the design of molecular catalysts that facilitate this chemical transformation, and while electrolytic approaches benefit from using water as a reaction medium that facilitates proton and electron transfer, its use also requires good selectivity of the catalyst over the competitive off-pathway reduction of water itself to hydrogen.\textsuperscript{19-29} Consequently, systems used for this transformation must be tuned for both high reactivity and selectivity.\textsuperscript{24,30-36} Molecular CO\textsubscript{2} reduction catalysts have been optimized in terms of activity and selectivity by functionalization of the organic ligands on the catalytically active metal center, as illustrated by extensive work on metalloporphyrin systems as a prime example.\textsuperscript{37-43} Indeed, the direct functionalization of the porphyrin building block is synthetically challenging through such a pure molecular approach. We reasoned, however, that the high charge carrier mobility of COF-366-Co would allow for electronic communication throughout the whole framework of the material and thus hypothesized that we can therefore circumvent the direct modification of the porphyrin building-block and instead functionalize the organic strut that is used to reticulate it into the extended framework. It is worthy of note that the potential for remote functionalization is advantageous in the context of the rational optimization of CO\textsubscript{2} electroreduction catalysts because it reduces the influence of the introduced functionality to electronic effects and potentially circumvents undesirable interference in the reaction via steric hindrance or through non-covalent interactions.

As a first step we synthesized a series of COFs with different electron withdrawing groups on their respective struts termed COF-366-Co, COF-366-(OMe)-Co, COF-366-F-Co and COF-366-(F)\textsubscript{4}-Co (Figure 3.1; SI, Section S3.1). In order to make a comparison between the aforementioned materials in terms of reactivity, two critical points had to be addressed. First and foremost, when deposited on the electrode as a microcrystalline powder, only a small amount of the COF is electrochemically accessible.\textsuperscript{44} As such, to better compare the reactivity of the different samples, we prepared thin films of the materials to ensure that the majority of the metal centers in the framework are electrochemically active. Second, to rationally design a catalyst it is important to monitor the effect of the functionalization on the electronic structure of the active site. Because the orbitals that are primarily relevant to the catalytic activity of the cobalt centers are its 3d orbitals, we decided to investigate the cobalt L-edge x-ray absorption spectroscopy (XAS) data of the functionalized COFs to assess inductive effects of the reticular structure. These transitions consist of excitation of 2p core electrons into empty 3d-orbitals. Indeed, we observe that functionalization of the struts with electronegative elements directly translates into an electron withdrawing effect on the cobalt center and the extent of this effect is proportional to the electronegativity, as well as the amount of functional groups that are installed. The observed differences in electronics significantly alter the reactivity of the molecular active sites in the
Reticular material, which can be rationalized based on the proposed mechanism for the electrocatalytic reduction of CO$_2$ to CO using cobalt porphyrin derived catalysts. This report represents a study of direct electronic structure-function relationships of COF electrocatalysts.$^4$

**Figure 3.1. Design and synthesis of cobalt-porphyrin derived covalent organic frameworks.** The molecular nature of the COF backbone allows for systematic modulation of the electronic structure of the catalytically active cobalt center. Due to the porosity of the framework diffusion of the reactants to the active sites is facilitated.

3.2 Results and Discussion

3.2.1 Oriented Thin Films of COF-366-Co.

Our initial efforts were directed towards the optimization of the electrochemical accessibility of the COF catalyst by controlling the morphology of the system. One major drawback of our initial system was that only a small portion, 4-8%, of the cobalt sites were in fact electrochemically accessible which we attributed to the poor contact of the sample with the electrode surface and sluggish transportation between individual COF crystallites.$^{16}$ As such, we chose to move from depositing the microcrystalline COF powder onto porous carbon fabric towards directly growing thin films of COF onto the electrode surface. In our first attempt we tried to grow COF-366-Co on glassy carbon. While these films showed improved activity on a per cobalt basis the material had poor interactions with the substrate, resulting in detachment of the COF films over time. We reasoned that this challenge could be overcome by growing oriented thin films of COFs on a more ordered surface. In addition to an improved interaction with the electrode surface, oriented thin films have also been shown to facilitate redox processes in COF materials.$^{44}$ Accordingly we chose highly ordered pyrolytic graphite (HOPG) as our electrode material. Oriented thin films were grown by adding the substrate to the reaction mixture containing $[5,10,15,20$-tetrakis(4-aminophenyl)porphinato]cobalt, Co(TAP), and 1,4-benzenedicarboxaldehyde (BDA) (Figure 3.2). The crystallinity and preferred orientation of the films in respect to the substrate were confirmed.
by grazing incidence wide angle x-ray scattering (GIWAXS) (Figure 3.2a). The diffraction pattern of the oriented thin films of COF-366-Co confirmed the formation of the expected structure (Figure 3.2d). Contrary to our expectations, the COF layers did not grow coplanar to the electrode surface but orient perpendicular to the graphite layers (Figure 3.2c). Scanning electron microscopy showed films of uniform thickness of ~250nm (Figure 3.2b).

Electrochemical experiments were carried out in 0.5M potassium bicarbonate aqueous buffer at pH 7.2 and controlled potential electrolysis was performed under an applied potential of -0.67 (vs. RHE). The oriented thin films of COF-366-Co exhibited significantly improved catalytic performance on a per cobalt basis with current densities for the formation of CO of 45 mA/mg cobalt with a faradaic efficiency of 87% which constitutes a 9-fold improvement over the microcrystalline COF powders. While the reactivity of the films grown on glassy carbon initially showed a similar performance, the oriented films show a significantly improved long-term stability for more than 12 hours (Figure 3.2e). With the optimized morphology at hand, we chose to advance a step further and utilize the unique features of our catalyst system: (i) the high degree of electronic communication throughout the whole framework and (ii) the organic backbone of the structure which allows for chemical modification. The proposed mechanism for CO$_2$ reduction with cobalt porphyrin suggests that in a first step cobalt(II) gets reduced to cobalt(I) (SI, Section S3.2). In order to facilitate this step we decided to introduce electron withdrawing functional groups onto the linker of the COF to take away electron density from the cobalt center and make it more prone to reduction.
Figure 3.2. Optimizing the morphology of the COF catalyst. Grazing incidence wide angle x-ray scattering (GIWAXS) of the COF film on HOPG shows preferred orientation of the material (a). The COF forms uniform films of 250 nm in thickness as shown by SEM (b). The data suggest that the COF layers are oriented in a 90° angle with respect to the substrate (c). The 2D line-profile of the GIWAXS data is in good agreement with the expected diffraction pattern (d). The oriented thin films of COF-366-Co outperform deposited COF on porous carbon fabric and films without preferred orientation obtained on glassy carbon (e).

3.2.2 Covalent Functionalization of COF-366-Co.

We thus set out to make a series of COFs with systematically incorporated functionality, namely COF-366-Co, COF-366(OMe)2-Co, COF-366-F-Co and COF-366-(F)4-Co (Figure 3.1), to determine the COF with the optimal amount of electron withdrawing groups to maximize the reactivity at a given overpotential. The synthesis of these frameworks was carried out analogous to the synthesis of the parent framework COF-366-Co. Powder x-ray diffraction confirmed that the space group and the metrics of the structures remained essentially unaltered (SI, Section S3.3 and S3.4). The films of all COFs were crystalline and the grazing incidence wide angle x-ray scattering of all structures confirmed the same orientation with respect to the substrate as described above for COF-366-Co (SI, Section S3.3 and S3.4). To confirm that the effects that we measure in the COFs are due to differences in electronic nature and not to different affinities of the framework itself for CO2 we carried out CO2 sorption on all of the studied materials. The materials all displayed a comparable uptake of CO2 at 295 K (23.5 – 27.4 cm³ cm⁻¹). To confirm that the affinity for CO2 of the different frameworks is also similar we measured CO2 sorption at different temperatures to derive isosteric heat of adsorption ($Q_{st}$) values for all frameworks which turned
out to be the same for all measured materials (24.6 – 24.1 KJ mol⁻¹) (Table 1; SI, Section S5 and S8).

**Table 3.1.** Pore size distribution (PSD), BET surface area (A_BET), CO₂ uptake and isosteric heat of adsorption (Q_{st}) values for the binding of CO₂ for the COF catalysts.

<table>
<thead>
<tr>
<th>Material</th>
<th>PSD [Å]ᵃ</th>
<th>A_BET [m² g⁻¹]ᵇ</th>
<th>CO₂ Uptake [cm³ cm⁻³]ᶜ</th>
<th>Q_{st} [KJ mol⁻¹]ᵈ</th>
</tr>
</thead>
<tbody>
<tr>
<td>COF-366-Co</td>
<td>10-18</td>
<td>1700</td>
<td>23.4</td>
<td>24.6</td>
</tr>
<tr>
<td>COF-366-(OMe)₂-Co</td>
<td>8-18</td>
<td>867</td>
<td>24.2</td>
<td>24.4</td>
</tr>
<tr>
<td>COF-366-F-Co</td>
<td>10-18</td>
<td>1901</td>
<td>27.0</td>
<td>24.2</td>
</tr>
<tr>
<td>COF-366-(F)₄-Co</td>
<td>8-16</td>
<td>832</td>
<td>27.4</td>
<td>24.1</td>
</tr>
</tbody>
</table>

ᵃ Determined by fitting of the adsorption branch using quenched solid state density functional theory (QSDFT) cylindrical/slit pore model on the absorption branch of the isotherm. ᵇ Calculated using the BET method from the nitrogen sorption data of the activated samples at 77 K. ᶜ Uptake at 800 Torr and 298 K, the conditions under which we carry out the catalysis. ᵈ Calculated from pure component isotherms using Henry's law.

### 3.2.3 X-ray Absorption Spectroscopy.

In order to further probe the effect of the introduced groups on the catalytically active cobalt site we turned to x-ray absorption spectroscopy (XAS) on the cobalt L-edge. Such a measurement would directly determine whether or not modification does indeed cause a change in the electronic structure of the metal center. The metal L-edge spectra feature transitions from 2p core electrons into unoccupied 3d-states.⁵²⁻⁵⁴ The resulting spectrum imparts information regarding the formal oxidation state, symmetry, and extent of electronic delocalization of the probed element.⁵⁵⁻⁵⁷ Considering the fact that the d-orbitals are the orbitals that are principally relevant to the catalytic activity of the porphyrin metal center, L-edge absorption measurements yield direct information on the effect of the substituents on the electronic structure of the catalyst. The L₃-edge spectra of the different COFs and a series of molecular porphyrin model systems {Co(TIP) = [5,10,15,20-tetrakis(1-N-benzylideneaniline)porphinato]cobalt, Co(THP) = [5,10,15,20-tetrakis(4-hydroxyphenyl)porphinato]cobalt, Co(TCPP) = [5,10,15,20-tetrakis(4-carboxyphenyl)porphinato]cobalt, Co(TAP)} are illustrated in Figure 3a and 3b, respectively. Immediately noticeable is the increasing intensity of peaks at 777 and 779 eV for the porphyrin model with increasing electron withdrawing character of the functional groups. The XAS spectra of the COFs also change depending on the functional group that is present on the linker. Comparison of the data to theoretically modeled spectra by introducing inductive effects from a hypothetical square planar ligand field confirmed an increasing electron withdrawing effect of the linker on the cobalt site in the order: COF-366-Co, COF-366-(OMe)₂-Co, COF-366-(F)₄-Co and COF-366-F-Co (Figure 3.3c-g; SI, Section S3.6). The fact that the differences in electron withdrawing character on the cobalt center do not follow the expected trend according to basic inductive effect considerations is giving credence to the importance of this study for accurate structure-property relationships of the catalysts. Furthermore, it is noteworthy that COF-366-Co itself when compared to the starting material Co(TAP) does in fact have an electron withdrawing
effect on the cobalt center which might be a possible explanation for the significantly lower reactivity of the molecular catalyst in comparison to the COF (Figure 3.3d,f; SI, Section S3.6).

**Figure 3.3. XAS Co L-edge spectroscopy.** Spectra of COF-366-Co and derivatives (a), and of various molecular cobalt porphyrin complexes (b). In both cases the spectra are stacked in order of increasing negative inductive effect. In (c) the changes in the theoretical spectrum of a cobalt(II) ion are shown for a hypothetical increasing electron withdrawing ligand field where the negative inductive effect of the ligand field increases from bottom (blue) to top (red). Obtained XAS cobalt L-edge spectra for COF-366-Co (d), COF-366-(F)₄-Co (e), Co(TAP) (f) and Co(TCPP) (g) are in good agreement with their respective simulated patterns.

### 3.2.4 Electrochemical Characterization.

To verify that the differences in electronic structure translate into modified electrochemical properties, we measured cyclic voltammograms of the different compounds in N,N-dimethylformamide with tetrabutylammonium hexafluorophosphate as the electrolyte, which show that the potential of the cathodic wave does indeed shift from -1.425 V vs. ferrocene/ferrocenium (Fc/Fc⁺) for COF-366-Co up to -1.380 V vs. Fc/Fc⁺ for COF-366-F-Co (Figure 3.4b). The trend here tracks to what is observed in the XAS spectra, which confirms the unexpected order of electron withdrawing effects in the different COF materials. It should be noted that the CVs were obtained from powder samples deposited on a porous carbon cloth as opposed to COF thin films and that the resulting current was not normalized by the weight of the material (Figure 4b). Consequently, we further tested the reactivity of the different COF catalysts to evaluate differences in current at a given potential. Controlled potential electrolyses were carried out in aqueous solution at -0.67 V vs. reversible hydrogen electrode (RHE) and the different catalysts show significant differences in reactivity. As expected, the electron withdrawing character observed by XAS and cyclic voltammetry improves the catalytic behavior of the framework and the current density for CO formation increases from 45 mA mg⁻¹ for COF-366-Co...
to 46 mA mg\(^{-1}\) COF-366-(OMe)\(_2\)-Co up to 65 mA mg\(^{-1}\) for COF-366-F-Co. COF-366-(F)\(_4\)-Co does not perfectly represent the trend as it is the second most electron withdrawing material but displays the lowest reactivity. We attribute this observation to the higher hydrophobicity of the framework and resulting decreased access of electrolyte to the active sites (Figure 3.4c).

Figure 3.4. Electrochemical characterization of the COFs. Illustration of the electrolysis cell and the two respective half reactions (a). Cyclic voltammograms of COF-366-Co, COF-366-(OMe)\(_2\)-Co, COF-366-F-Co, and COF-366-(F)\(_4\)-Co in \(N, N\)-dimethylformamide with tetrabutylammonium hexafluorophosphate as the electrolyte (b). Current densities per milligram of cobalt in the different COF catalysts under an applied potential of -0.67 V vs. RHE in 0.5 M aqueous potassium bicarbonate buffer (c).

3.3 Conclusion

The findings of this study illustrate the promise of covalent organic frameworks as an emerging class of materials for supporting catalysis with molecular-level control of both physical and electronic structure. We demonstrated that optimizing the morphology of COFs and growing them as oriented thin films significantly improves the catalytic activity of the material compared to bulk samples. More importantly, reticular electronic tuning of the catalytically active cobalt sites was used to optimize the material for high activity and selectivity by facile functionalization of the reticular parent structure with electron withdrawing groups. In this regard, x-ray absorption spectroscopy on the metal L-edge has proved a useful tool for the direct observation of the effect of framework functionalization on the metal center. The importance of the spectroscopic evidence is highlighted by the fact that the differences in the electronic character of the active sites do not follow the expected trend according to basic inductive effect considerations. We anticipate the modularity of COF systems through reticular synthesis, combined with the ability to engender electronic communication between reticulated active sites and the surrounding framework, will promote further opportunities for a broad array of catalytic transformations and related applications.
3.4 Supporting Information

3.4.1 COF Synthesis

A Pyrex tube measuring 10 × 8 mm (o.d × i.d) was charged with 5,10,15,20-tetrakis(4-aminophenyl)porphinato)cobalt [Co(TAP)] (18 mg, 0.025 mmol), BDA, 2,5-dimethoxyterephthaldehyde/2-fluoroterephthaldehyde/2,3,5,6-tetrafluoroterephthaldehyde (0.075 mmol), 1,2- dichlorobenzene (1 mL), butanol (1 mL), and 6 M aqueous acetic acid (0.25 mL). After sonication for 15 minutes the tube was flash frozen at 77 K (liquid N2 bath). After one freeze-pump-thaw cycle the system was evacuated to an internal pressure of 50 mtorr and flame sealed. The reaction was heated at 120 ºC for 72 hours yielding a dark purple precipitate at the bottom of the tube, which was isolated by filtration. The wet sample was then transferred to a Soxhlet extractor and thoroughly washed with methanol (24 hours) and acetone (24 hours). Following that, the product was washed five times with liquid CO2. The system was then heated up to 45 ºC to bring about the supercritical state of CO2 and slowly bled to ambient pressure. Finally the product was evacuated at 100 ºC for 18 hours at 10⁻² mtorr to yield activated sample. Yield: 24.18 mg, ~90% based on Co(TAP). For the synthesis of the thin films an HOPG substrate was added to the synthesis conditions described above. Upon completion of the reaction the substrate was separated from the bulk COF, sonicated briefly and washed over two days with acetone and methanol in a 20 mL vial.

3.4.2 Proposed Mechanism of CO2 Reduction

Figure S3.1. Proposed mechanism for electrocatalytic CO2 reduction in COF-366-Co.
3.4.3 Grazing incidence wide angle x-ray scattering analysis

Grazing incidence wide angle x-ray scattering data was obtained by wide angle X-ray scattering (WAXS) using a Pilatus 2M (Dectris) detector on beamline 7.3.3 at the Advanced Light Source, Lawrence Berkeley National Laboratory ($\lambda = 1.24$ Å). The sample-detector distance and beam center were calibrated using silver behenate. 1-D scattering profiles were reduced from the 2-D data using the Nika package for IGOR Pro (Wavemetrics). The 1-D line profiles shown in this material are obtained by converting the WAXS data to 2θ values, assuming $\lambda = 1.5406$ Å (Cu Kα1).

The Pawley PXRD refinements were performed using the Reflex module in Materials Studio 7.0, in which the Thompson-Cox-Hastings profile function were used for the profile fitting (peak broadening, peak asymmetry and zero shift error were taken into account). Unit cell and sample parameters were refined at the meantime.47

![Figure S3.2. Pawley refinement of the PXRD pattern of activated sample of COF-366-Co.](image-url)
Figure S3.3. Pawley refinement of the PXRD pattern of activated sample of COF-366-(OMe)$_2$-Co and GIWAXS pattern of a film of the COF on HOPG.

Figure S3.4. Pawley refinement of the PXRD pattern of activated sample of COF-366-F-Co and GIWAXS pattern of a film of the COF on HOPG.
Figure S3.5. Pawley refinement of the PXRD pattern of activated sample of COF-366-(F)$_n$-Co and GIWAXS pattern of a film of the COF on HOPG.
3.4.4 Structural modeling

Modeling of crystal structures for target COFs were performed using the Materials Studio 7.0 software package (Accelrys Software Inc.). Geometry optimization in the Forcite module was applied to optimize the unit cell and the geometry of the molecular fragment.

Figure S3.6. Crystal structure model of COF-366-Co. (a) View along the crystallographic c-axis. (b) View along the crystallographic b-axis.
Figure S3.7. Crystal structure model of COF-366-(OMe)$_2$-Co. (a) View along the crystallographic c-axis. (b) View along the crystallographic b-axis.

Figure S3.8. Crystal structure model of COF-366-F-Co. (a) View along the crystallographic c-axis. (b) View along the crystallographic b-axis.
Figure S3.9. Crystal structure model of COF-366-F-Co. (a) View along the crystallographic c-axis. (b) View along the crystallographic b-axis.
### 3.4.5 Fractional Atomic Coordinates

Table S3.1. Fractional atomic coordinates for crystal structure model of COF-366-Co with eclipsed arrangement.

<table>
<thead>
<tr>
<th>COF-366-Co</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula: C&lt;sub&gt;120&lt;/sub&gt;H&lt;sub&gt;72&lt;/sub&gt;N&lt;sub&gt;24&lt;/sub&gt;Co&lt;sub&gt;8&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal system: Orthorhombic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Space group: PBAN (No. 50)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a = 41.1020 \text{ Å}; b = 32.4036 \text{ Å}; c = 4.6700 \text{ Å})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha = \beta = \gamma = 90^\circ)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.36479</td>
<td>0.36757</td>
<td>-0.30182</td>
<td>1</td>
</tr>
<tr>
<td>C2</td>
<td>0.39294</td>
<td>0.39285</td>
<td>-0.28911</td>
<td>1</td>
</tr>
<tr>
<td>H3</td>
<td>0.34964</td>
<td>0.36912</td>
<td>-0.49128</td>
<td>1</td>
</tr>
<tr>
<td>H4</td>
<td>0.39808</td>
<td>0.41306</td>
<td>-0.46832</td>
<td>1</td>
</tr>
<tr>
<td>C5</td>
<td>0.87662</td>
<td>0.84086</td>
<td>-0.16694</td>
<td>1</td>
</tr>
<tr>
<td>C6</td>
<td>0.90534</td>
<td>0.86589</td>
<td>-0.17774</td>
<td>1</td>
</tr>
<tr>
<td>H7</td>
<td>0.87112</td>
<td>0.82157</td>
<td>-0.34941</td>
<td>1</td>
</tr>
<tr>
<td>H8</td>
<td>0.92007</td>
<td>0.86523</td>
<td>-0.36991</td>
<td>1</td>
</tr>
<tr>
<td>N9</td>
<td>0.1735</td>
<td>0.18078</td>
<td>0.09669</td>
<td>1</td>
</tr>
<tr>
<td>C10</td>
<td>0.18863</td>
<td>0.20689</td>
<td>-0.096</td>
<td>1</td>
</tr>
<tr>
<td>C11</td>
<td>0.2192</td>
<td>0.22804</td>
<td>-0.04313</td>
<td>1</td>
</tr>
<tr>
<td>C12</td>
<td>0.23675</td>
<td>0.22511</td>
<td>0.21645</td>
<td>1</td>
</tr>
<tr>
<td>C13</td>
<td>0.2333</td>
<td>0.2535</td>
<td>-0.25797</td>
<td>1</td>
</tr>
<tr>
<td>C14</td>
<td>0.47325</td>
<td>0.41255</td>
<td>-0.00567</td>
<td>1</td>
</tr>
<tr>
<td>C15</td>
<td>0.41389</td>
<td>0.39321</td>
<td>-0.04814</td>
<td>1</td>
</tr>
<tr>
<td>C16</td>
<td>0.4399</td>
<td>0.4241</td>
<td>-0.02256</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C17</td>
<td>0.35542</td>
<td>0.34159</td>
<td>-0.0736</td>
<td>1</td>
</tr>
<tr>
<td>C18</td>
<td>0.43125</td>
<td>0.46638</td>
<td>-0.01566</td>
<td>1</td>
</tr>
<tr>
<td>C19</td>
<td>0.48297</td>
<td>0.37167</td>
<td>-0.00508</td>
<td>1</td>
</tr>
<tr>
<td>C20</td>
<td>0.39899</td>
<td>0.47868</td>
<td>-0.00741</td>
<td>1</td>
</tr>
<tr>
<td>H21</td>
<td>0.17732</td>
<td>0.21172</td>
<td>-0.30251</td>
<td>1</td>
</tr>
<tr>
<td>H22</td>
<td>0.22738</td>
<td>0.20629</td>
<td>0.38948</td>
<td>1</td>
</tr>
<tr>
<td>H23</td>
<td>0.22108</td>
<td>0.25695</td>
<td>-0.46213</td>
<td>1</td>
</tr>
<tr>
<td>H24</td>
<td>0.46774</td>
<td>0.34447</td>
<td>-0.01284</td>
<td>1</td>
</tr>
<tr>
<td>N25</td>
<td>0.45171</td>
<td>0.5</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Co26</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>N27</td>
<td>0.5</td>
<td>0.56156</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>
Table S3.2. Fractional atomic coordinates for crystal structure model of COF-366-(OMe)-Co with eclipsed arrangement

**COF-366-(OMe)₂-Co**

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.47489</td>
<td>0.40548</td>
<td>0.49382</td>
<td>1</td>
</tr>
<tr>
<td>C2</td>
<td>0.44326</td>
<td>0.41751</td>
<td>0.47729</td>
<td>1</td>
</tr>
<tr>
<td>C3</td>
<td>0.43626</td>
<td>0.46375</td>
<td>0.4908</td>
<td>1</td>
</tr>
<tr>
<td>C4</td>
<td>0.48458</td>
<td>0.36207</td>
<td>0.49419</td>
<td>1</td>
</tr>
<tr>
<td>C5</td>
<td>0.40692</td>
<td>0.47793</td>
<td>0.50564</td>
<td>1</td>
</tr>
<tr>
<td>H6</td>
<td>0.47075</td>
<td>0.33283</td>
<td>0.48638</td>
<td>1</td>
</tr>
<tr>
<td>H7</td>
<td>0.38661</td>
<td>0.45904</td>
<td>0.52686</td>
<td>1</td>
</tr>
<tr>
<td>C8</td>
<td>0.36563</td>
<td>0.37042</td>
<td>0.23423</td>
<td>1</td>
</tr>
<tr>
<td>C9</td>
<td>0.39404</td>
<td>0.39275</td>
<td>0.23639</td>
<td>1</td>
</tr>
<tr>
<td>C10</td>
<td>0.41721</td>
<td>0.38517</td>
<td>0.44259</td>
<td>1</td>
</tr>
<tr>
<td>C11</td>
<td>0.35766</td>
<td>0.33632</td>
<td>0.42814</td>
<td>1</td>
</tr>
<tr>
<td>C12</td>
<td>0.6186</td>
<td>0.67487</td>
<td>0.62202</td>
<td>1</td>
</tr>
<tr>
<td>C13</td>
<td>0.5899</td>
<td>0.65134</td>
<td>0.6282</td>
<td>1</td>
</tr>
<tr>
<td>H14</td>
<td>0.34938</td>
<td>0.38047</td>
<td>0.07526</td>
<td>1</td>
</tr>
<tr>
<td>H15</td>
<td>0.39738</td>
<td>0.41832</td>
<td>0.07744</td>
<td>1</td>
</tr>
<tr>
<td>H16</td>
<td>0.62228</td>
<td>0.70087</td>
<td>0.77682</td>
<td>1</td>
</tr>
<tr>
<td>H17</td>
<td>0.57405</td>
<td>0.66022</td>
<td>0.79346</td>
<td>1</td>
</tr>
<tr>
<td>N18</td>
<td>0.32833</td>
<td>0.31732</td>
<td>0.41493</td>
<td>1</td>
</tr>
</tbody>
</table>

Formula: C\(_{128}\)N\(_{24}\)H\(_{88}\)O\(_8\)Co\(_8\)

Crystal system: Orthorhombic

Space group: PBAN (No. 50)

\(a = 44.7537\ \text{Å}; b = 30.2937\ \text{Å}; c = 4.6757\ \text{Å}\)

\(\alpha = \beta = \gamma = 90^\circ\)
<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>C19</td>
<td>0.31346</td>
<td>0.28347</td>
<td>0.56625</td>
<td>1</td>
</tr>
<tr>
<td>C20</td>
<td>0.28176</td>
<td>0.2672</td>
<td>0.52899</td>
<td>1</td>
</tr>
<tr>
<td>C21</td>
<td>0.26052</td>
<td>0.28552</td>
<td>0.33645</td>
<td>1</td>
</tr>
<tr>
<td>C22</td>
<td>0.2703</td>
<td>0.23047</td>
<td>0.69303</td>
<td>1</td>
</tr>
<tr>
<td>H23</td>
<td>0.32658</td>
<td>0.26693</td>
<td>0.7284</td>
<td>1</td>
</tr>
<tr>
<td>O24</td>
<td>0.29059</td>
<td>0.21051</td>
<td>0.88538</td>
<td>1</td>
</tr>
<tr>
<td>C25</td>
<td>0.21734</td>
<td>0.6696</td>
<td>1.01643</td>
<td>1</td>
</tr>
<tr>
<td>H26</td>
<td>0.26825</td>
<td>0.31288</td>
<td>0.20823</td>
<td>1</td>
</tr>
<tr>
<td>H27</td>
<td>0.23675</td>
<td>0.67388</td>
<td>1.16143</td>
<td>1</td>
</tr>
<tr>
<td>H28</td>
<td>0.2221</td>
<td>0.64421</td>
<td>0.85086</td>
<td>1</td>
</tr>
<tr>
<td>H29</td>
<td>0.19824</td>
<td>0.65802</td>
<td>1.14784</td>
<td>1</td>
</tr>
<tr>
<td>N30</td>
<td>0.45533</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Co31</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>N32</td>
<td>0.5</td>
<td>0.56665</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>
Table S3.3. Fractional atomic coordinates for crystal structure model of COF-366-F-Co with eclipsed arrangement.

<table>
<thead>
<tr>
<th>COF-366-F-Co</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula: C_{120}N_{24}H_{64}F_{4}Co_{8}</td>
<td></td>
</tr>
<tr>
<td>Crystal system: Orthorhombic</td>
<td></td>
</tr>
<tr>
<td>Space group: PBAN (No. 50)</td>
<td></td>
</tr>
<tr>
<td>$a = 42.4325$ Å; $b = 30.6471$ Å; $c = 4.6597$ Å</td>
<td></td>
</tr>
<tr>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td></td>
</tr>
<tr>
<td><strong>Atom</strong></td>
<td><strong>x</strong></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C1</td>
<td>0.36299</td>
</tr>
<tr>
<td>C2</td>
<td>0.39177</td>
</tr>
<tr>
<td>C3</td>
<td>0.41548</td>
</tr>
<tr>
<td>C4</td>
<td>0.35646</td>
</tr>
<tr>
<td>H5</td>
<td>0.34534</td>
</tr>
<tr>
<td>H6</td>
<td>0.39487</td>
</tr>
<tr>
<td>C7</td>
<td>0.61895</td>
</tr>
<tr>
<td>C8</td>
<td>0.59017</td>
</tr>
<tr>
<td>H9</td>
<td>0.62217</td>
</tr>
<tr>
<td>H10</td>
<td>0.57344</td>
</tr>
<tr>
<td>C11</td>
<td>0.47396</td>
</tr>
<tr>
<td>C12</td>
<td>0.43312</td>
</tr>
<tr>
<td>C13</td>
<td>0.48388</td>
</tr>
<tr>
<td>C14</td>
<td>0.40183</td>
</tr>
<tr>
<td>H15</td>
<td>0.46952</td>
</tr>
<tr>
<td>H16</td>
<td>0.38037</td>
</tr>
<tr>
<td>C17</td>
<td>0.55868</td>
</tr>
<tr>
<td>N18</td>
<td>0.1732</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C19</td>
<td>0.1858</td>
</tr>
<tr>
<td>C20</td>
<td>0.2178</td>
</tr>
<tr>
<td>C21</td>
<td>0.23997</td>
</tr>
<tr>
<td>C22</td>
<td>0.22869</td>
</tr>
<tr>
<td>H23</td>
<td>0.17094</td>
</tr>
<tr>
<td>H24</td>
<td>0.23317</td>
</tr>
<tr>
<td>F25</td>
<td>0.29108</td>
</tr>
<tr>
<td>N26</td>
<td>0.45313</td>
</tr>
<tr>
<td>Co27</td>
<td>0.5</td>
</tr>
<tr>
<td>N28</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Table S3.4. Fractional atomic coordinates for crystal structure model of COF-366-(F)₄-Co with eclipsed arrangement.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.36046</td>
<td>0.37266</td>
<td>0.68167</td>
<td>1</td>
</tr>
<tr>
<td>C2</td>
<td>0.38931</td>
<td>0.39747</td>
<td>0.68862</td>
<td>1</td>
</tr>
<tr>
<td>C3</td>
<td>0.41383</td>
<td>0.39156</td>
<td>0.90328</td>
<td>1</td>
</tr>
<tr>
<td>C4</td>
<td>0.35549</td>
<td>0.33942</td>
<td>0.87855</td>
<td>1</td>
</tr>
<tr>
<td>H5</td>
<td>0.34159</td>
<td>0.37983</td>
<td>0.52203</td>
<td>1</td>
</tr>
<tr>
<td>H6</td>
<td>0.39179</td>
<td>0.42291</td>
<td>0.53211</td>
<td>1</td>
</tr>
<tr>
<td>C7</td>
<td>0.61895</td>
<td>0.6693</td>
<td>1.07902</td>
<td>1</td>
</tr>
<tr>
<td>C8</td>
<td>0.59054</td>
<td>0.64324</td>
<td>1.09344</td>
<td>1</td>
</tr>
<tr>
<td>H9</td>
<td>0.62122</td>
<td>0.69454</td>
<td>1.23602</td>
<td>1</td>
</tr>
<tr>
<td>H10</td>
<td>0.57319</td>
<td>0.64871</td>
<td>1.26843</td>
<td>1</td>
</tr>
<tr>
<td>F11</td>
<td>0.26542</td>
<td>0.68138</td>
<td>1.34626</td>
<td>1</td>
</tr>
<tr>
<td>N12</td>
<td>0.17427</td>
<td>0.81834</td>
<td>0.8717</td>
<td>1</td>
</tr>
<tr>
<td>C13</td>
<td>0.18492</td>
<td>0.78544</td>
<td>1.0403</td>
<td>1</td>
</tr>
<tr>
<td>C14</td>
<td>0.21737</td>
<td>0.76809</td>
<td>1.01617</td>
<td>1</td>
</tr>
<tr>
<td>C15</td>
<td>0.24153</td>
<td>0.78484</td>
<td>0.82611</td>
<td>1</td>
</tr>
<tr>
<td>C16</td>
<td>0.22651</td>
<td>0.73295</td>
<td>1.18926</td>
<td>1</td>
</tr>
<tr>
<td>H17</td>
<td>0.16831</td>
<td>0.77185</td>
<td>1.1988</td>
<td>1</td>
</tr>
<tr>
<td>F18</td>
<td>0.20436</td>
<td>0.71546</td>
<td>1.37614</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C19</td>
<td>0.47327</td>
<td>0.41068</td>
<td>0.97246</td>
<td>1</td>
</tr>
<tr>
<td>C20</td>
<td>0.43975</td>
<td>0.4228</td>
<td>0.94392</td>
<td>1</td>
</tr>
<tr>
<td>C21</td>
<td>0.43068</td>
<td>0.46588</td>
<td>0.97092</td>
<td>1</td>
</tr>
<tr>
<td>C22</td>
<td>0.48349</td>
<td>0.36873</td>
<td>0.97471</td>
<td>1</td>
</tr>
<tr>
<td>C23</td>
<td>0.39793</td>
<td>0.47877</td>
<td>0.98937</td>
<td>1</td>
</tr>
<tr>
<td>H24</td>
<td>0.46902</td>
<td>0.34027</td>
<td>0.94433</td>
<td>1</td>
</tr>
<tr>
<td>H25</td>
<td>0.37557</td>
<td>0.45998</td>
<td>0.99332</td>
<td>1</td>
</tr>
<tr>
<td>N26</td>
<td>0.45141</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Co27</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>N28</td>
<td>0.5</td>
<td>0.56273</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
3.4.6 Porosity and specific surface area analysis

The N\textsubscript{2} adsorption isotherms were conducted on a QuadraSorb SI automated surface area & pore size analyzer (Quantachrome Instruments). Ultrahigh purity N\textsubscript{2} and He compressed gas cylinders (Praxair, Purity > 99.999\%) were used for the gas sorption measurement. Liquid N\textsubscript{2} was used for temperature control at 77 K.

The BET and Langmuir surface area were estimated according to established procedures. The pore size distribution (PSD) was evaluated using the DFT method in the QuadraWin software using a carbon slit/cylindr./sphere pore QSDFT model on the adsorption branch of the isotherm.

Table S3.5. Porosity data of COF materials studied in this work.

<table>
<thead>
<tr>
<th>Material</th>
<th>(S\textsubscript{BET} (m^2/g))</th>
<th>(S\textsubscript{Langmuir} (m^2/g))</th>
<th>PSD (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COF-366-Co</td>
<td>1360</td>
<td>1700</td>
<td>10–18</td>
</tr>
<tr>
<td>COF-366-Co-2F</td>
<td>1511</td>
<td>1901</td>
<td>10–18</td>
</tr>
<tr>
<td>COF-366-Co-4F</td>
<td>666</td>
<td>867</td>
<td>8–16</td>
</tr>
<tr>
<td>COF-366-Co-(OMe)\textsubscript{2}</td>
<td>651</td>
<td>832</td>
<td>8-18</td>
</tr>
</tbody>
</table>

Table S3.5. Porosity data of COF materials studied in this work.
Figure S3.10. $N_2$ sorption isotherm of COF-366-Co-2F at 77 K.

Figure S3.11. Pore size distribution histogram of COF-366-Co-2F. Calculated from a DFT fitting of the adsorption branch of the $N_2$ adsorption isotherm at 77 K with a fitting error of 0.853% using the slit/cylindr./sphere pores QSDFT model.
Figure S3.12. Multiple point BET plot of COF-366-Co-2F giving a specific surface area of 1511 m²/g.

Figure S3.13. Langmuir plot of COF-366-(F)₄ giving a specific surface area of 1901 m²/g.
Figure S3.14. N\textsubscript{2} sorption isotherm of COF-366-(F)\textsubscript{4} at 77 K.

Figure S3.15. Pore size distribution histogram of COF-366-(F)\textsubscript{4}. Calculated from a DFT fitting of the adsorption branch of the N\textsubscript{2} adsorption isotherm at 77 K with a fitting error of 0.097\% using the slit/cylindr./sphere pores QSDFT model.
Figure S3.16. Multiple point BET plot of COF-366-(F)₄-Co giving a specific surface area of 666 m²/g.

Figure S3.17. Langmuir plot of COF-366-(F)₄-Co giving a specific surface area of 867 m²/g.
Figure S3.18. N$_2$ sorption isotherm of COF-366-(OMe)$_2$-Co at 77 K.

Figure S3.19. Pore size distribution histogram of COF-366-(OMe)$_2$-Co. Calculated from a DFT/Monte-Carlo fitting of the adsorption branch of the N$_2$ adsorption isotherm at 77 K with a fitting error of 0.331% using the slit/cylindr./sphere pores QSDFT model.
Figure S3.20. Multiple point BET plot of COF-366-(OMe)-Co giving a specific surface area of 651 m²/g.

Figure S3.21. Langmuir plot of COF-366-(OMe)₂-Co giving a specific surface area of 832 m²/g.
### 3.4.7 X-ray absorption spectroscopy

XAS data was acquired at beamline 6.3.1 at the Advanced Light Source in Lawrence Berkeley National Lab. Samples were prepared for measurement by lightly pressing a thin film of the desired sample onto a conductive copper or carbon substrate prior to loading into the measurement chamber. The X-ray source was 1.9 GeV with a current of 500 mA. L-edge energy calibration was performed with a metallic cobalt foil standard. All samples were measured in an ultra-high vacuum (UHV) environment of $10^{-9}$ Torr and 300 K. The monochromater slit width was decreased to the smallest possible value to simultaneously decrease photon flux incident on the sample of interest and to obtain the highest possible energy resolution. For our chosen parameters, the resulting energy resolution was measured to be 0.6 eV. X-ray induced damage was carefully monitored for.

Each spectrum experimental spectrum consists of >6 individual spectra taken at different spots of the sample on the stage. Before each individual high-resolution spectrum was taken, a fast survey scan was also taken on the same sample spot. The high-resolution and survey spectra were closely compared to determine that the X-ray beam did not damage the COF and change the resulting spectrum.

Cobalt L-edge spectra were simulated with CTM4XAS software\textsuperscript{55} A reasonable set of starting parameters was obtained through a survey of the literature. D4h symmetry, Co$^{2+}$ formal oxidation state, 1.6 eV 10Dq, 300oK, 0.95 spin orbital coupling, 0.2 eV Lorentzian broadening, and 0.2 eV Gaussian broadening parameters were consistent for simulations across all samples. The effects of electron withdrawing and donating groups were simulated through the variation of the Slater integral parameters from 0.6 to 1.1.

![Figure S3.22. Comparison of experimental and simulated spectrum of COF-366-Co.](image-url)
Figure S3.23. Comparison of experimental and simulated spectrum of COF-366-(OMe)2-Co.

Figure S3.24. Comparison of experimental and simulated spectrum of COF-366-F-Co.
Figure S3.25. Comparison of experimental and simulated spectrum of COF-366-(F)₄-Co.

Figure S3.26. Comparison of experimental and simulated spectrum of CoTAP.
Figure S3.27. Comparison of experimental and simulated spectrum of CoTCPP.

Figure S3.28. Comparison of experimental and simulated spectrum of CoTHP.
Figure S3.29. Comparison of experimental and simulated spectrum of CoTIP.

Figure S3.30. Relative amplitudes of peaks at 777, 779 / peak at 780 for COF-366-Co (brown), COF-366-(OMe)2-Co (red), COF-366-F-Co (blue) and COF-366-(F)4-Co (pink).
Figure S3.31. Relative amplitudes of peaks at 777, 779 / peak at 780 for CoTAP (green), CoTCPP (purple), CoTHP (yellow) and CoTIP (blue).
3.4.8 Electrochemistry

**General information:**

Electrolysis experiments were performed using a BASi EC Epsilon potentiostat/galvanostat with a glass cell custom made by Adams & Chittenden Scientific Glass. Carbon fabric (99.5% carbon) was purchased from Fuel Cell Earth LLC. HOPG (Grade 2) was purchased from Structure Probe Inc. The substrate (carbon fabric or HOPG) was treated with 6 M HCl overnight to remove trace metal impurities, rinsed thoroughly with Milli-Q water, and dried in air before use. Graphite planchets (1 inch diameter, impurity < 2 ppm) were purchased from Ted Pella, Inc. Graphite rods (99.9995% trace metal basis, 6.15 mm diameter x 152 mm length) were purchased from Alfa Aesar. Ag/AgCl reference electrodes were obtained from BASi and stored in saturated NaCl solution before use. Nafion cation-exchange membrane and silver wire (99.9% trace metal basis, 0.5 mm diameter) were obtained from Sigma Aldrich. Carbon dioxide (99.995%) and ethylene (99.90%) were purchased from Praxair. House nitrogen (N2) was used as the nitrogen source. Gas production was measured on an SRI gas chromatography instrument (model #8610C) equipped with a Haysep D column (1/8” × 6’) and a 13X Mol Sieve column (1/8” × 6’), with ethylene (C2H4) as the internal standard; carbon monoxide (CO) was quantified using a flame ionization detector (FID) and hydrogen (H2) using a thermal conductivity detector (TCD).

**Preparation of the electrolyte solutions:**

0.5 M aqueous KHCO3: KHCO3 (100 g) was dissolved in 2000 mL of Milli-Q water in a 4 L Erlenmeyer flask equipped with a 6 cm long stir bar. Two graphite rods were bound together with a copper wire and used as the cathode and another graphite rod was used as the anode, all of which were connected to a potentiostat using copper wires. A constant stream of CO2 gas was gently passed through the electrolyte solution, which was maintained during the entire course of the electrolysis treatment. The solution was electrolyzed at a constant current of 150 μA for 12 h. After removal of the graphite rods, the electrolyte was passed through a vacuum filter with polyethersulfone membrane (0.22 micron), and stored in glass containers before use.

**Electrochemistry setup**

Controlled-potential electrolysis was carried out in a custom-made, three-piece glass cell, including a working compartment body, a working compartment lid, and a counter compartment body. The main bodies of the two compartments were assembled using an O-ring and a Teflon clamp, and were separated by a Nafion cation-exchange membrane. The body of the working compartment was charged with a 3 cm long Teflon-coated stir bar and 150 mL of electrolyte solution (0.5 M aqueous KHCO3), and the lid was fitted with a HOPG working electrode modified with the thin film COF catalyst and a Ag/AgCl reference electrode. Both electrodes were connected to the outside through a stainless steel rod (1/16 inch diameter x 2 inch length, connected to the working electrode through a stainless steel alligator clip and the reference electrode through a two-way metal socket). The lid was also equipped with a Teflon sparging line that would extend into the electrolyte solution and a gas outlet that would connect to the headspace of the cell. Both of the gas ports were connected to a two-way Swagelok valve, and the valve at the gas outlet was also fitted with
A Swagelok female miniature quick-connect. During sample analysis, this quick-connect was adapted to a male miniature quick-connect on the injection line of the GC. The lid and the main body of the working compartment were assembled using an O-ring and a Teflon clamp, and the position of the working electrode was adjusted so that only the alligator clip was not immersed in the solution. The resulting working compartment has a headspace volume of ~100 mL. The counter compartment was filled with 50 mL of electrolyte solution (0.5 M aqueous KHCO₃), and equipped with a Teflon cap with a septum, as well as a graphite auxiliary electrode connected to the outside with a stainless steel alligator clip and a silver wire.

**Electrolysis:**

After the electrochemical cell was assembled, the electrolyte solution in the working compartment was sparged for 20 minutes with CO₂. Then, 1 mL ethylene was injected into the headspace as the internal standard for GC analysis. The solutions were electrolyzed at a constant potential (-1.30 V vs. Ag/AgCl) for a given amount of time. In the end of the electrolysis, the headspace of the cell was analyzed with the GC. Since a significant amount (~10 mL) of gas in the headspace was injected into the GC, the pressure in headspace of the working compartment was decreased after the analysis. If electrolysis needed to be continued using the same setup, in order to obtain accurate data, the working side of the cell was re-sparged with CO₂ again for 5-10 minutes and injected with 1 mL ethylene.
3.4.9 Carbon Dioxide Uptake

The CO₂ binding affinity is calculated by Henry's Law. A virial-type equation was applied for the estimation of Henry's constant:

\[
\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i
\]

Where \( P \) is pressure, \( N \) is the adsorbed amount, \( T \) is temperature, \( a_i \) and \( b_i \) are virial coefficients and \( m \) and \( n \) are the number of virial coefficients required for adequate fitting of the isotherms. As a result, Henry's constant \( (K_H) \) at the temperature \( T \) can be calculated according to:

\[
K_H = \exp(-b_0) \cdot \exp\left(-\frac{a_0}{T}\right)
\]
Figure S3.32. CO₂ adsorption isotherm for COF-366-Co at 273 (circle), 283 (triangle), and 298 K (square).

Figure S3.33. CO₂ adsorption isotherm for COF-366-(OMe)₂-Co at 273 (circle), 283 (triangle), and 298 K (square).
Figure S3.34. CO$_2$ adsorption isotherm for COF-366-F-Co at 273 (circle), 283 (triangle), and 298 K (square).

Figure S3.35. CO$_2$ adsorption isotherm for COF-366-(F)$_4$-Co at 273 (circle), 283 (triangle), and 298 K (square).
Figure S3.36. The isosteric heat of adsorption of CO₂ for COF-366-Co (blue), COF-366-(OMe)₂-Co (green), COF-366-F-Co (orange), and COF-366-(F)₄-Co (red), respectively.
3.5 References


Chapter 4
Local Electronic Structure of Molecular Heterojunctions in a Single-Layer 2D Covalent Organic Framework

Portions of this chapter have been published in:
4.1 Introduction

Covalent organic frameworks (COFs) are 2D or 3D crystalline structures constructed from organic molecular building blocks stitched together through strong covalent bonds. Different electronic and chemical properties can be engineered into COF networks by modifying the molecular properties of the building-blocks. Two-component COFs provide a high degree of electronic tunability since one molecular element can act as a ‘core’ while the second acts as a ‘linker’ between cores, and both can be precisely modified. This approach, for example, has been used to create donor-acceptor COFs that are made by either directly fusing donor/acceptor molecules into core/linker arrangements or by introducing either donor or acceptor guests into the pores of COFs to yield ordered arrays of molecular charge-transfer pairs, with potential applications in optoelectronics and catalysis. Such electrically modulated COFs, however, have up to now been fabricated using techniques that do not allow synthesis of a single-layer structure, and no local probe measurements have been performed to verify the effects of local charge-transfer. Here I discuss a new technique for fabricating COFs that exhibit internal electronic heterojunctions with staggered potential offsets. The core of the COF is tuned independently from charge-transfer elements that are placed between adjacent cores. This is accomplished through directed Schiff-base condensation reactions that allow oriented dipoles to be placed between core elements in an alternating arrangement, thus causing adjacent cores to experience a relative potential offset. The surface compatibility of this chemistry allows bottom-up fabrication of single-layer COF-420 whose local electronic structure was characterized at the atomic scale using scanned probe microscopy.

4.2 Results and Discussion

4.2.1 Synthesis of COF-420

The new COF was fabricated by first synthesizing two square planar tetratopic building blocks (5,10,15,20-tetrakis(4-aminophenyl)porphyrin (TAPP) and 5,10,15,20-tetrakis(4-formylphenyl)porphyrin (TFPP)) as shown in Figure 4.1. Upon reticulation at a surface these precursors yield cores that have identical chemical composition but are rendered electrically asymmetric by the relative orientation of the imine linkages connecting them. Charge-transfer functionality thus resides in the linker and is separated from the core electronic properties. This unique COF is termed COF-420 (((TAPP)(TFPP))imine) and exhibits a square lattice (sql) topology. Due to the asymmetrical configuration of the linkage (Figure 4.1a), each 5,10,15,20-tetraphenyl porphyrin core in COF-420 experiences a different chemical environment than its four nearest neighbor porphyrin cores. For example, if one denotes cores arising from TAPP as ‘core A’ and cores arising from TFPP as ‘core B’, then the nitrogen atom of the imine linkage is the first atom encountered as one moves outward from core A, whereas for core B the first atom encountered is carbon. Scanning tunneling microscopy (STM) was used to experimentally verify that this asymmetrical bonding scheme results in the spatial separation of the conduction band (CB) and the valence band (VB) onto different porphyrin cores (i.e., different sublattices), thus forming a grid of molecular type II heterojunctions within COF-420. Hirshfeld charge analysis performed using density functional theory (DFT) suggests that these molecular heterojunctions arise from dipole fields generated within the imine linkages of the COF.

The synthesis of single-layer COF-420 was carried out on a Au(111) surface in ultrahigh vacuum (UHV). TFPP molecules were first deposited onto the surface via thermal evaporation, followed by deposition of TAPP molecules (see Figure S6 for the electronic structure of the
constituent molecules before reticulation into COF-420). The adsorbed precursors were then gradually annealed to 180 °C and held at that temperature for 45 minutes to induce the condensation reaction that results in imine bond formation (Figure 4.1a). Figure 1b shows an STM topographic image of the resulting single-layer COF-420. Square lattice patches are observed that exhibit a ‘checker board’ pattern, indicating an alternating array of two electrically distinct porphyrin cores (a small fraction of cores near the edge of the COF do not exhibit the checkerboard pattern, possibly due to metalation of core B)[16].[Adatoms underneath Single Porphyrin Molecules on Au(111).] The unit cell determined via STM imaging has equal sides of length $a = b = 27±1.6$ Å. Figure 1c shows a zoomed-in image of COF-420, with a superimposed line drawing of the chemical structure in the top right corner. It is possible to unambiguously identify the darker porphyrin cores as core A (originating from TAPP) and the brighter porphyrin cores as core B (originating from TFPP) through the use of subsidiary reaction with 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (DMA) test molecules (see SI, Section 4.3 for details).

Figure 1. Bottom-up fabrication of COF-420. (a) Schematic representation of the synthesis of COF-420 from molecular precursors TAPP and TFPP. (b) Representative large-scale STM topographic image of COF-420 on Au(111) (sample bias $V_s= 0.8$ V, tunnel current $I_t=10$ pA). (c) Close-up STM image of COF-420 with the chemical structure overlaid in top-right corner ($V_s=0.8$ V, $I_t=10$ pA).

4.2.2 Scanning Tunneling Microscopy Studies

The local electronic structure of COF-420 was characterized by STM $dI/dV$ point spectroscopy performed at different positions on the single-layer COF as shown in Figure 4.2 (point spectroscopy positions are shown in Figure 4.2a). The black curve in Figure 4.2b shows a reference spectrum taken at a nearby bare Au(111) region (the sharp drop at -0.5V corresponds to a Shockley surface state band edge[17]). The blue curve shows a typical $dI/dV$ point spectrum recorded on core A within the COF, whereas the red curve shows a typical $dI/dV$ point spectrum recorded on the neighboring core B. Both cores exhibit two well-defined resonances that arise from bands composed of porphyrin molecular orbitals. The bands localized on core A, however, are shifted up in energy by ~0.25 eV relative to the bands whose weight lies on core B (i.e., the bands are localized on different sublattices). This causes the valence band (VB) to lie on core A while the conduction band (CB) lies on core B. Similarly, the outlying VB-1 and CB+1 bands are located on core B and core A respectively. The resulting experimental bandgap for COF-420 is $1.92 ± 0.06$ eV (i.e., the difference in energy between the CB and VB peaks).
Figure 4.2. Electronic structure of COF-420. (a) Close-up STM image of COF-420 ($V_s = 0.8$ V, $I_t = 10$ pA). Red and blue x’s indicate the positions where $dI/dV$ spectra were recorded. (b) $dI/dV$ spectra taken at location of core B (red curve) and core A (blue curve) shown in panel a, as well as spectrum from bare Au(111) surface for reference (black curve). Each curve is normalized by the value at $V_s = -1.28$V and the red (blue) curve is upshifted by 4 a.u. (1.75 a.u.) for clarity (open feedback set point parameters: $V_s = 0.8$V, $I_t = 20$ pA for all the curves; modulation voltage $V_{rms} = 10$mV). Experimental $dI/dV$ maps for (c) the COF CB at 0.72V, (d) the COF VB at -1.09V, (e) the COF CB+1 at 0.98V and (f) the COF VB-1 at -1.35V ($dI/dV$ map parameters: $I_t = 20$pA; modulation voltage $V_{rms} = 10$mV).

4.2.3 Scanning Tunneling Spectroscopy

The spatial localization of the COF-420 bands onto different sublattices is better seen in the $dI/dV$ maps of Figure 4.2c-f, obtained at the different peak energies in the same COF region as imaged in Figure 4.2a. Figure 4.2c shows the $dI/dV$ map obtained at the CB energy, where the local density of states (LDOS) lights up (i.e., has highest intensity) on core B sites. The CB LDOS pattern at each core exhibits a nearly 4-fold symmetric structure with two orthogonal nodal lines crossing through the center of the porphyrin core. The LDOS intensity at the VB energy is shown in Figure 4.2d, and is found to be shifted from core B sites to core A sites. The VB LDOS symmetry is also quite different than the CB LDOS in that it is ‘dumbbell’ shaped and 2-fold symmetric rather than 4-fold symmetric. The difference between the VB and CB LDOS shapes reflects the difference in symmetry between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for isolated porphyrin molecules and their derivatives. Unlike the CB states seen on the core B sublattice, some of the core A sites do not show LDOS intensity at the VB energy. This is caused by small, spatially inhomogeneous shifts in the energy
of the VB peak, likely due to surface defects and conformational changes within the COF (including the number of complete nearest neighbor bonds). The VB peak has the narrowest width and so slight shifts in energy for molecules on the core A sublattice causes dramatic reductions in VB intensity in constant bias dI/dV maps. Figure 4.2e-f show that the CB+1 and VB-1 LDOS also reside separately at core A and core B sites, respectively, thus separating onto different sublattices just as seen for the VB and CB states. The COF-420 spectroscopy shows all of the hallmarks of type II heterojunctions, including a staggered band structure and spatial localization of VB and CB states at different physical locations. Unlike a conventional type II heterojunction which has only a single interface, COF-420 exhibits a periodic array of heterojunctions that exist between each adjacent molecular core.

### 4.2.4 DFT Calculations

In order to identify the underlying cause of the staggered band structure and wavefunction localization observed in our experiments, first-principles calculations of COF-420 using density functional theory (DFT) were performed at the generalized gradient approximation (GGA) level. These efforts were aimed at answering three fundamental questions. The first question is simply whether DFT-based simulations are able to reproduce the experimental phenomena observed in order to confirm that it is consistent with the physical system. The second is whether this behavior is intrinsic to the COF, or rather a byproduct of the interaction between the COF and the Au(111) substrate. The third question is what microscopic mechanism causes type II heterojunction behavior to arise between the sublattices of COF-420.

The first question was addressed by modeling the behavior of COF-420 on Au(111) using the unit cell sketched in Figure 3a. The STM dI/dV spectra were simulated by separately calculating the projected density of states of this system onto core A and core B, as shown in Figure 3b. The core A sublattice (blue curve) shows two prominent peaks corresponding to the VB and CB+1 bands whereas core B (red curve) shows two peaks shifted down in energy with respect to core A (corresponding to the VB-1 and CB bands). The resulting bandgap is 1.10 eV, approximately 0.82 eV smaller than the experimental value, which is due to the known behavior of GGA-DFT calculations to underestimate quasiparticle bandgaps. Other than the gap, however, the calculation reproduces the experimental results closely. For example, the VB and CB are seen to localize on different sublattice cores, precisely as seen in the experiment (Figure S1). Also, the energy differences between VB and VB-1 as well as between CB and CB+1 have an average magnitude of 0.31 eV, very close to the average experimental value of 0.25 eV (these differences do not suffer the known GGA-DFT tendency to underestimate bandgaps). The simulated electronic structure thus yields a robust network of molecular type II heterojunctions in agreement with the experiment.
Figure 3. Theoretical electronic structure of COF-420. (a) Optimized geometry of COF-420 on a Au(111) surface resulting from density functional theory (DFT) calculation (unit cell marked by dashed lines). (b) Theoretical projected density of states (PDOS) calculated for COF-420 on Au(111) (i.e., DOS projected separately onto the two cores). The red curve represents the PDOS of core B whereas the blue curve represents the PDOS of core A.

The behavior of freestanding COF-420 layers was also calculated in order to check that the staggered electronic structure of COF-420 is an intrinsic property and not the result of substrate interactions. The behavior of freestanding COF-420 was found to be nearly identical to COF-420 on Au(111). This can be seen in the PDOS plots of Figure S3 as well as in Figure 4a and b which show that the VB and CB wavefunctions of freestanding COF-420 are separately localized on core A and core B, just as observed experimentally and in the COF-420/Au(111) simulation. The bandgap calculated for freestanding COF-420 is 1.38 eV (Figure S3), slightly larger than the energy gap calculated for COF-420 on Au(111) (1.10 eV). This difference is expected to be due to the enhanced screening experienced by COF-420 when it is in contact with Au. The band offset obtained from the average energy difference of the VB and VB-1 bands as well as the CB and CB+1 bands for freestanding COF-420 is 0.31 eV, almost identical to the average band offset calculated for COF-420 on Au(111) (0.31 eV), as well as the average experimental offset (0.25 eV).

To understand the microscopic mechanism driving the formation of a periodic array of type II heterojunctions in COF-420, a closer look was taken at the simulated charge distribution within the COF network. This suggests that the staggered band structure originates from the dipole field generated by the oriented imine bonds linking the porphyrin cores. The charge distribution was calculated for a freestanding COF-420 single-layer using the Hirshfeld charge analysis as implemented by the Tkatchenko-Scheffler method in VASP (see Methodology). This technique allows evaluation of the difference in charge density that arises in the vicinity of each atom due to the formation of surrounding chemical bonds and has been used to analyze other extended molecular systems. A Hirshfeld population plot of the freestanding COF-420 is shown in Figure 4c. While significant charge redistribution can be seen throughout the COF, the distributed net charge on core A is very similar to the distributed charge on core B (the dashed circles enclose the identical porphyrin macrocycles of core A and core B). The formation of dipoles can be seen
between the porphyrin macrocycles that are generated by charge accumulation on the nitrogen
atom (blue, qN = -0.128 |e|) as well as the carbon and hydrogen atoms (red, qCH = 0.075 |e|) within
the imine bonds. The lower energy of core B relative to core A arises because the positive end of
the imine dipole always points toward core B, whereas the negative end always points toward core
A.

To further test this idea a rough estimate of the inter-sublattice electrostatic energy offset
arising from the dipole field of the oriented imine bonds using the simplified geometry of Figure
4d was performed. For an electron placed at the center of core A, the energy increase arising from
the four nearest imine dipoles is

\[ \Delta E_A = \frac{1}{4\pi\varepsilon_0} \times \frac{4|e|p}{r^2-d^2/4} \]  

Here p is the strength of the imine dipole, d is the length of the dipole, and r is the distance from
the dipole center to the core center. The strength of the imine dipole is where qN is the charge on
the nitrogen atom and qCH is the charge on the CH group. From symmetry it is seen that \( \Delta E_B = - \Delta E_A \), and so the energy difference arising from the dipole field for an electron on core A compared
to an electron on core B is \( \Delta E_T = 2\Delta E_A \). When the values qN = -0.128 |e| and qCH = 0.075 |e|
fmarshfeld analysis, r = 9.53 Å from the molecular geometry, and d = 1.29 Å (the length
of a double bond) are used it is observed that \( \Delta E_T = 0.16 \) eV, in reasonable agreement (given the
degree of approximation) with the observed experimental band offset of 0.25 eV.
4.3 Conclusion

In conclusion, a porphyrin-based imine-linked square-lattice single-layer COF was synthesized with atomically-precise type II heterojunctions distributed throughout the entire lattice. Characterization of the COF by STM/STS measurements and ab initio simulations reveals that an asymmetrical chemical environment of the adjacent porphyrin cores causes localization of the CB and VB onto distinct COF sublattices. Hirshfeld charge analysis implies that the origin of the
heterojunction behavior is the asymmetrical dipole field that arises from oriented imine linkages within the COF. This COF is expected to exhibit novel optoelectronic properties since exciton formation should lead to the generation of electron and hole quasiparticles localized on different COF sublattices.
4.4 Supporting Information

4.4.1 COF Synthesis on Au(111)

**Surface growth:** Standard Ar+ sputtering/annealing cycles were applied to a polished Au(111) crystal to yield an atomically clean surface. Molecular precursors for COF-420 were deposited onto the clean Au(111) surface held at room temperature in an ultrahigh vacuum environment (base pressure ~2x10^{-10} Torr) using a home-built Knudsen-type dual-cell evaporator. The temperature of evaporator for TAPP and TFPP precursors were 330°C and 340°C respectively. The mixed adlayer was then gradually annealed to 180°C and held at that temperature for 45 minutes to induce the Schiff-base condensation reaction to form the COF. All STM and STS measurements were performed at T = 7K in a home-built cryogenic STM. A Pt/Ir tip was used for all STM measurements. The tip microstructure was changed repeatedly for STM imaging and spectroscopy to rule out tip-based artifacts.

4.4.2 Electronic Structure Calculations.

Geometry optimization and electronic structure calculations for freestanding COF monolayers were performed using the projector-augmented wave (PAW) method with the Perdew-Burke-Ernzerhof (PBE) functional (dispersion interactions were taken into account using the Tkatchenko-Scheffler (TS) method). The plane-wave cutoff was set at 400 eV. A Gamma-point-only k-sampling was adopted for geometry optimizations and a 6 × 6 × 1 k-mesh generated by the Monkhorst-Pack scheme for the Brillouin zone was used for electronic structure analysis. An energy convergence criterion of 10^{-6} eV was used for self-consistent calculations while atomic positions were relaxed until the maximal force on each atom was smaller than 0.01 eV Å^{-1}. A 15 Å vacuum layer was placed between periodic images of the COF monolayer to ensure decoupling between neighboring monolayers. Charge transfer values were obtained by the Hirshfeld charge density analysis.

The COF-420/Au(111) system was modeled using a repeated slab approach that included a vacuum region of more than 18 Å along the z-direction and four Au layers. The bottom two layers of Au were fixed in their bulk positions (primitive lattice constant = 4.17 Å) while all other atoms in the slab were relaxed to obtain the optimized structure. Dispersion interactions were taken into account using the Tkatchenko-Scheffler vdw\textsuperscript{surf} correction (DFT-vdw\textsuperscript{surf}) which has been known to yield accurate absorption heights and binding energies for a variety of atoms and molecules adsorbed on metal surfaces. The convergence of the Helmann-Feymann force was set at 0.02 eV Å^{-1}. To compensate for long-range dipole–dipole interactions among the asymmetric slabs, a dipole sheet was introduced in the middle of the vacuum gap; this procedure leads to zero electric field in the vacuum region, allowing a reliable evaluation of the surface potential.

All quantum-chemical calculations were performed with the Vienna Ab Initio Simulation Package (VASP).

183
4.4.3 COF-420 Monolayer on Au(111): Partial Charge Density Plots for the VB, CB, VB-1 and CB+1 States.

The partial charge density plot for the COF-420 VB and VB-1 state (Figure S1a, c) exhibits two-fold symmetric intensity on core A and core B respectively. The partial charge density plot for the COF-420 CB and CB+1 state (Figure S1b, d) exhibits a 4-fold symmetric distribution on core B and core A respectively.

**Figure S4.1.** Partial charge density plot for a COF-420 monolayer on the Au(111) surface: (a) VB state (-0.46 eV < E < -0.33 eV), (b) CB state (0.64 eV < E < 0.84 eV), (c) VB-1 state (-0.79 eV < E < -0.67 eV) and (d) CB+1 state (0.91 eV < E < 1.05 eV). The iso-surface is 0.0008 e (bohr)$^3$.

4.4.4 Electronic Structure of a Free-Standing COF-420 Monolayer

The optimized structure of a free-standing COF-420 monolayer (lattice constant = 27.1 Å) calculated at the PBE-TS level under periodic boundary conditions is shown in Figure S2. Unlike the saddle-like deformation of the porphyrin macrocycle observed for COF-420 adsorbed on the Au(111) surface, the four pyrrole rings of the porphyrin macrocycle are co-planar in the freestanding COF-420 monolayer.
Figure S4.2. Structure model of COF-420. 2x2 unit cell of the optimized structure of a free-standing COF-420 monolayer.

The projected densities of states (PDOS) for core A (originating from TAPP) and core B (originating from TFPP) are shown in Figure S3. Similar to the PDOS calculated for COF-420 on Au(111), core A (blue curve) exhibits two pronounced peaks corresponding to the VB and CB+1 states. On the other hand, core B (red curve) exhibits two pronounced peaks corresponding to the VB-1 and CB states. In other words, core A orbitals are shifted up in energy compared to core B orbitals, corroborating both the theoretical results on Au(111) as well as the experimental results, and confirming the formation of type-II heterojunctions between the two cores within the COF.
4.4.5 Justification of the Assignment of Core A from TAPP and Core B from TFPP

Core A (originating from TAPP) and core B (originating from TFPP) are structurally identical upon reticulation and differ only in their local chemical environment due to the imine linkage. Although a checkerboard pattern for COF-420 in STM topographic scans was observed, careful consideration was made in order to assign darker (brighter) cores to core A (core B). It was chosen to structurally identify these cores by co-depositing a small amount of 2,5-dimethoxybenzene-1,4-dicarboxaldehyde linker molecules (DMA) onto the same surface (Figure S4a). After annealing only core A (from TAPP) was expected to undergo a Schiff-base condensation reaction with the DMA, thus forming a covalent bond with it (Figure S4a). To accomplish this, TAPP, TFPP and DMA were co-deposited onto a Au(111) surface and the sample was annealed to ~150°C to induce the Schiff-base condensation reaction. Figure S4 shows an STM topographic image of a sample prepared in this way. As shown in the blue box in the figure, the porphyrin cores with lower intensity were the ones that covalently bonded with DMA linkers. Thus the porphyrin core with the lower intensity is assigned as core A (originating from TAPP) and the porphyrin core with the higher intensity as core B (originating from TFPP).
Figure S4.4. STM investigations on COF-420. (a) Sketch of COF-420 in the presence of DMA linker. DMA can undergo a condensation reaction only with core A. (b) STM topograph of a Au(111) surface obtained by annealing adsorbed TAPP, TFPP and DMA molecules (sample bias $V_s = 0.8$ V, tunneling current $I_t = 10$ pA). The blue box shows that only porphyrin cores with lower intensity form covalent bonds with the DMA linker, thus justifying the identification of these porphyrin cores as core A (originating from TAPP).
4.4.6 Synthesis of Starting Materials

General Information
All starting materials and solvents, unless otherwise specified, were obtained from Aldrich Chemical Co. and used without further purification. 5,10,15,20-Tetrakis(4-aminophenyl)-21H,23H-porphine was obtained from Combi-Blocks (QC-4722, 96% purity). Elemental microanalyses were performed at the University of California, Berkeley, College of Chemistry. Solution 1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVQ-400 (400 MHz) spectrometer operating with an Avance electronics console.

Synthesis of meso-Tetra(p-formylphenyl)porphyrin (TFPP):

The synthesis of TFPP was carried out according to a literature protocol (Section S4). In a first step, 4-bromobenzaldehyde was protected using neopentyl glycol to yield 2-(4-bromophenyl)-5,5-dimethyl-1,3-dioxane (90%). In a second step, lithiation at -78 °C followed by formylation with 1-formyl piperidine yielded 4-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde (91%). In a third step, reaction with pyrrole catalyzed by trifluoroacetic acid yielded tetrakis[4-(1,3-dioxo-5,5-dimethylcyclohex-2-yl)phenyl]porphyrin (3%). Finally, deprotection of the 5,5-dimethyl-1,3-dioxane protecting groups yielded meso-Tetra(p-formylphenyl)porphyrin which was purified by column chromatography (dichloromethane) and isolated as a dark violet solid (78%).
Scheme 4.1. Synthesis of meso-tetra(\(\rho\)-formylphenyl)porphyrin.
Figure S4.5. $^1$H NMR spectrum of meso-tetra($\rho$-formylphenyl)porphyrin. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 10.4 (s, 4H), 8.83 (s, 8H), 8.41 (d, $J = 9$ Hz, 8H), 8.31 (d, $J = 6$ Hz, 8H), -2.79 (s, 2H).
4.5 References


Chapter 5
Is Reticular Chemistry the Answer to the Next Generation of CO$_2$ Reduction Catalysts?

Portions of this chapter have been published in:
5.1 Introduction

The grand challenge in photo- and electrocatalytic carbon dioxide reduction to value-added carbon products lies in the fact that a singular catalytic system must control the interplay between efficiency, activity, and selectivity (Figure 5.1). In this context, the efficiency governs the energy cost of the process and is defined by a material’s optical (photocatalytic systems) and/or electronic (photo- and electrocatalytic systems) properties. When considering the optical properties, one must engineer the material’s band gap to enhance the photon efficiency whereas the electronic properties are related to the inherent charge carrier mobility, both of which impact the quantum and Faradaic efficiencies, respectively. The activity provides the turnover and yield and is related to the number of and the diffusion to the active sites. These directly correlate to the surface area and metrics of the catalyst structure. Finally, the selectivity dictates the desired product and purity thereof and is directly linked to the chemical nature of the catalyst with both the binding affinity to CO₂ and the redox behavior of the active site playing pivotal roles. Thus far, a number of different catalytic systems have been discovered, albeit to a certain extent serendipitously, for effectively catalyzing the reduction of CO₂; however, there remains a noticeable absence of a consummate solution that combines all of these properties together in one material.

Much of what has been done synthetically has been inspired from what is accomplished in natural photosynthesis.¹⁻³ Nature has evolved catalysts with perfected activity and selectivity for CO₂ reduction, however, the efficiency of the system is not very high. The fact that efficiency is low appears counterintuitive at first, but can be understood when considering the conditions under which the reaction takes place. Due to the low concentration of CO₂ in the atmosphere, relative to this process, the rate-determining step is carbon fixation. The problem then lies with the fact that there are more photons absorbed than can be used for affecting carbon conversion, with the remaining energy dissipated to feed other processes. Simply put, nature affords a highly active and selective system, but one lacking optimal efficiency for carbon conversion (Figure 5.1).

The first class of synthetic materials developed, metals and metal oxides (heterogeneous catalysts),⁴⁻⁵ were targeted for their optoelectronic properties, which held promise for improving the efficiency problem inherent to nature. Not only were these materials able to achieve superior efficiency, but their activity was also demonstrated as being amenable to fine-tuning through nanostructuring synthetic approaches (i.e. controlling the size and morphology) (Figure 5.1).⁶⁻⁷ It is noted that by nanostructuring, materials increase their surface, thus effectively improving their activity, while at the same time altering their optoelectronic properties. It would be preferable to control each of these independently. Another aspect of heterogeneous inorganic catalysis that must be put forth is the fact that these materials are difficult to rationally control on the molecular level and the most active systems rely mainly on the use of precious metals.⁸ Although such drawbacks are obvious, inorganic materials remain at the forefront in terms of performance for both photo- and electrocatalytic CO₂ reduction.⁶⁻⁹ The next class of synthetic materials, molecular (homogeneous) catalysts,¹⁰⁻¹² by virtue of the nature of the organic ligand, can be tailored towards enhanced selectivity and, to a certain extent, efficiency (Figure 5.1). Although the molecular nature of this class of materials provides a handle over these two characteristics it also often comes at the expense of activity. This is primarily due to catalyst deactivation (e.g. dimerization) and limitations with respect to solubility of the catalyst as well as the substrate. Furthermore, activity is hindered in molecular systems because they require multiple components that are at the mercy of randomness in solution. In order to address these activity issues, one must be able to effectively orient the multiple components in an ordered manner such that they operate synergistically. The
question then arises: how do we combine the advantages of each class of material within one system? Ideally, this system must be an extended (heterogeneous) structure with an ordered and metrically-defined organic backbone capable of being tailored to achieve the appropriate optoelectronic properties. In this way, the material can achieve optimal efficiency, activity, and selectivity in a way that they are not mutually exclusive, but rather mutually beneficial.13

Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) — reticular materials — represent ideal platforms for realizing this in one system.14,15 In terms of selectivity, these materials are constructed from molecular building units, which allow for the integration of well-defined, highly selective molecular catalysts within the backbone of the architecture.16,17 With respect to activity, both are well-known for their high surface areas and tunable pore metrics, thus allowing for facile diffusion of substrates to the active sites.18,19 Finally, in the context of efficiency, great strides have been made in engineering the band gaps and/or intrinsic charge carrier mobility of different MOF/COF structures.20,21 The important aspect to remember here is that one is not limited by structure type — the right framework can be chosen in terms of chemical composition, pore metrics, and optoelectronic properties all the while allowing for the addition of the appropriate metal catalyst. The MOF/COF backbone is responsible for activity and efficiency whereas the framework chemistry of the structure is responsible for the selectivity. Indeed, these can all be optimized independently (Figure 5.1). In a sense, these classes of materials can be considered ‘materials on demand’.

In this chapter, I critically assess state-of-the-art research for photo- and electrocatalytic CO2 reduction in the realm of reticular chemistry and provide suggestions for future developments.
Figure 5.1. The grand challenge in developing carbon dioxide reduction catalysts lies in the interplay between selectivity, activity, and efficiency. Selectivity is governed by chemical features, such as binding affinity, redox properties, and acid/base character. Activity is founded upon structural and material properties like surface area, crystallinity, and particle size. Finally, efficiency is defined by the optoelectronic properties (i.e. photonic-, quantum-, and Faradaic efficiencies as well as the morphology). In this context, Nature provides highly active and selective catalysts, but lacks optimal efficiency. On the contrary, inorganic catalysts, such as metals and metal oxides, display high efficiency and activity. However, tuning the selectivity on the molecular level remains absent. Homogeneous molecular catalysts are capable of achieving high selectivity and efficiency, but are inherently limited with regard to activity. The prospect of realizing all three aspects in a singular system can only be achieved by reticular chemistry.

5.2 MOF photocatalysts for CO₂ reduction

5.2.1 First generation: Selectivity and activity.

Molecular CO₂ reduction catalysts are highly selective, but lack the efficiency and activity necessary for practical use.²² A strategy to take advantage of their selectivity, while at the same time enhancing their activity, is to spatially isolate them to prevent catalyst poisoning by dimerization. To accomplish this, molecular catalysts can be grafted onto a well-defined solid support, and MOFs are the ideal platform in this context for three reasons: (i) They are often transparent single crystals, which allows for light to penetrate through the whole material in contrast to amorphous solids or powders, which suffer from light scattering; (ii) the high surface area of MOFs and related materials is an advantage over other solid supports as it maximizes the density of active sites; and (iii) the fact that MOFs can be considered as pores without walls allows for easy access of the substrate to those active sites.

Site isolation: The first MOF, a modified version of UiO-67, capable of reducing CO₂ was reported in 2011.²³ The synthetic strategy for developing this MOF was to integrate a well-known molecular catalyst into the backbone of the framework. ReI(bpy)(CO)₃Cl (bpy = 2,2’-bipyridine) has been extensively studied as a molecular CO₂ reduction catalyst in homogeneous systems.²⁴,²⁵ While this molecular catalyst is initially very selective and active, it quickly degrades due to off-pathway dimerization. By employing ReI(dcbpy)(CO)₃Cl (dcbpy = 2,2’-bipyridine-5,5’-dicarboxylic acid) as an organic linker in an isoreticular functionalized UiO-67 framework, the catalytic centers become site-isolated, which prevents degradation by dimerization.²³,²⁶ The ReI(dcbpy)(CO)₃Cl functionalized UiO-67 photocatalyzes CO₂ reduction towards CO in an acetonitrile solution with trimethylamine serving as a sacrificial reducing agent. The resulting turnover number (TON) was 10.9 over the course of 20 h — a result that is almost three-fold higher than that of the homogeneous ReI(dcbpy)(CO)₃Cl linker. It is noted however, that the recovered functionalized UiO-67 solid was inactive for further CO generation. This is attributed to carbonyl moieties detaching from the rhenium center on the MOF backbone during the catalytic cycle as evidenced by the loss of CO stretching vibrations in the material.

Open metal sites. There are considerable synthetic challenges associated with integrating homogeneous molecular photocatalysts within a MOF framework. To overcome this challenge and still maintain the high selectivity previously achieved, attention turned to exploring MOFs that are composed of redox active metals and available coordination sites within their secondary building units (SBUs). MIL-101(Fe) represents a viable material in this regard.²⁷ The MOF’s Fe₃O SBUs have up to three possible open coordination sites (terminal water ligands cap the clusters) that are capable of effectively adsorbing and subsequently reducing CO₂. Under visible light irradiation and with triethanolamine (TEOA) as a sacrificial agent, MIL-101(Fe) was shown to reduce CO₂ exclusively to formate with a TON of 1.2 over 24 h. Electron spin resonance spectroscopy studies
revealed that photogenerated Fe(II) was directly involved in the reduction process. Furthermore, MIL-101(Fe) was shown to significantly outperform other Fe-based MOFs, MIL-53(Fe) and MIL-88B(Fe),\textsuperscript{28,29} which was credited to the fact that open coordination sites were only available in MIL-101(Fe).

### 5.2.2 Second generation: Optical efficiency.

Generally, the catalytic sites do not absorb light in the visible region; a requirement for maximizing photonic efficiency. The band gap can be engineered through tailoring the MOF backbone to ensure that the frameworks’ optical properties match the proper range of light absorption. The efficiency of MOFs can be optimized in the following ways: (i) Organic functionalization aimed at integrating chromophoric antennae into the framework;\textsuperscript{30,31} (ii) inorganic modification through the judicious choice of metal character and cluster size of the SBUs.\textsuperscript{32} It is noted here that the SBU can be considered as discrete metal oxide nanoparticles linked together through organic linkers; and (iii) incident light can be intensified locally by wrapping MOF structures around plasmonic nanoparticles.

**Band gap engineering.** Titanium(IV)-based MOFs combine the photocatalytic activity of titanium oxide with the light absorption properties of organic linkers. This combination affords materials that are photocatalytically active under UV-visible light.\textsuperscript{33} MIL-125(Ti) has an absorption band edge at 350 nm allowing for photocatalysis to take place in the UV region. Using sunlight to reduce CO\textsubscript{2} directly would be ideal, however, the majority of sunlight is in the visible range, which is too low in energy to induce photoreduction within such systems. Toward this end, an isoreticular functionalized analogue, termed NH\textsubscript{2}-MIL-125(Ti), was synthesized bearing amino functionalities on the linker.\textsuperscript{34,35} The resulting MOF adsorbed visible light with the band edge extending to \textasciitilde 550 nm. The photocatalytic reduction of CO\textsubscript{2} was then performed in acetonitrile with TEOA as the sacrificial agent under visible light irradiation. The inactivity of the parent MIL-125(Ti) under otherwise similar conditions confirms that the visible light photocatalytic activity of NH\textsubscript{2}-MIL-125(Ti) was induced by the amino functionality. A temporal concentration change of formate as a function of the irradiation time shows that the amount of formate reached 8.14 μmol in 10 h. Given the pronounced effect of linker substitution on the catalytic activity, an isoreticular series of MOFs was designed where the amino functionality of the original NH\textsubscript{2}-MIL-125(Ti) was replaced with N-alkyl groups of varying connectivity (primary and secondary N-alkyl amines) and chain length.\textsuperscript{36} This series exhibits reduced optical band gaps, which are directly related to the inductive donor ability of the alkyl substituents. In addition, the secondary N-alkyl functionalized MOFs feature larger apparent quantum yields than the primary N-alkyl derivatives, owing to an increase in their excited-state lifetime. The efficiency of the most promising member of this series, NH\textsubscript{Cyp}-MIL-125(Ti) (Cyp = cyclopentyl), is substantially enhanced due to a smaller band gap, a longer excited-state lifetime, and a resulting improved apparent quantum yield (E\textsubscript{g} = 2.30 eV, τ = 68.8 ns, Φ\textsubscript{app} = 1.80%) as compared to the parent NH\textsubscript{2}-MIL-125(Ti) (E\textsubscript{g} = 2.56 eV, τ = 12.8 ns, Φ\textsubscript{app} = 0.31%).

**Plasmonic enhancement.** For most MOF photocatalysts, a second component, either a photosensitizer or a co-catalyst, is needed to achieve a significant TON for CO\textsubscript{2} reduction. In these cases, slow mass transport through MOF channels and inefficient electron transfer between the MOF and the homogeneous component will greatly affect the performance and decrease the activity. Therefore, better designs are needed to integrate different components within a single system to obtain a more active catalyst.\textsuperscript{37,38} Re\textsubscript{3}-MOF (UiO-67, 3 Re centers per SBU incorporated
on the linker) was coated onto Ag nanocubes (Ag⊂Re₃-MOF), which spatially confines photoactive Re centers to their intensified near-surface electric fields. This composite material resulted in a 7-fold enhancement of CO₂-to-CO conversion (as compared to the molecular catalyst) under visible light with long-term stability maintained up to 48 h (TON = 2.9).³⁹

5.2.3 Third generation: Electronic efficiency.

A standing challenge for increasing efficiency lies in the fact that not every photon absorbed by the system is productively used for the catalytic process. Upon absorption of light, photons can be either emitted or excited electrons are transferred to the substrate. Therefore, it is necessary to consider how a material’s electronic properties can be designed in such a way to ensure that the lifetime of charge-separated states is long enough for electrons to be transferred to the CO₂ substrate to affect the chemical transformation. Two approaches have been utilized in MOF photocatalysts: (i) Introducing a molecular photosensitizer within the MOF system (not grafted). For this, the photosensitizer is a molecular complex that has visible light absorption, inherent high quantum efficiency, and acts as a mediator to prolong the charge-separated state lifetime; and (ii) altering the electronic character of the inorganic SBU. In this scenario, by changing the nature of the metal, the excited-state lifetime can be extended. A longer lifetime leads to a higher quantum efficiency and higher catalytic activity.

Photosensitizer. An important factor for the low efficiency of the aforementioned catalysts is the low apparent quantum yield of these systems. To address this shortcoming a manganese bipyridine complex, Mn(dcbpy)(CO)₃Br, was incorporated into UiO-67 and the reaction carried out in conjunction with [Ru(dmb)₃]²⁺ (dmb = 4,4′-dimethyl-2,2′-bipyridine) as a photosensitizer.⁴⁰,⁴¹ Indeed, in N,N'-dimethylformamide (DMF)/TEOA and in the presence of 1-benzyl-1,4-dihydronicotinamide as a sacrificial donor, this system efficiently catalyzes CO₂ reduction to formate under visible light irradiation. Over the course of 18 h the catalyst reaches a TON of 110. More importantly, owing to the use of the photosensitizer, the high quantum yield of Φformate = 13.8% in the visible region of the spectrum is far superior to those of previously reported MOF systems. The catalyst can be reused over several cycles, although its photochemical performance does decrease due to a loss of the photosensitizer after prolonged irradiation to visible light.

Electronic character of the SBU. Photosensitizers have a problem of reusability and they function as an added component to the catalytic system. In this regard, altering the electronic character of the SBU of a MOF catalyst is seen as a viable alternative approach. One such example is that of post-synthetically modifying the Zr₆O₄(OH)₄ SBU of UiO-66 with catalytically active Ti(IV).⁴² On its own, the SBU of UiO-66 cannot accept electrons from the linker due to a mismatch in the redox potential energy levels of the SBU and the linker. However, by doping the SBU of UiO-66 with Ti(IV) ions, in conjunction with tuning the light absorption properties of the linker, a new material was created. Through a combination of diffuse reflectance UV-Vis, photoluminescence, and UV light photo-electron spectroscopy measurements this material was shown to: (i) Supply an added light absorption route; (ii) generate electron-hole pairs; (iii) effectively slow the recombination rate of those photogenerated electron-hole pairs; and (iv) improve charge separation. The photocatalytic reduction of CO₂ to formic acid was performed under visible light in an acetonitrile, TEOA (sacrificial base), and 1-benzyl-1,4-dihydronicotinamide (sacrificial reductant) suspension. The mixed-metal MOF achieved an
Taking stock of these advances, the fourth generation MOF photocatalyst quickly takes shape (Figure 2.2). In this future system, a high density of open metal sites, functioning as the active sites, are needed. The metals must be chosen judiciously (e.g. Fe, Co, Cu) in order to allow for efficient electron transfer to adsorbed CO₂ substrates. Indeed, this takes care of the activity and selectivity challenges. To also ensure high optical efficiency, the MOF backbone must be appropriately conjugated and functionalized to absorb visible light. The MOF backbone must also have high charge carrier mobility by choosing coordinating groups that ensure proper frontier orbital overlap and redox matching between the organic linker and SBU (e.g. metal-semiquinoid, metal-dithiolene, and diiminobenzosemiquinonate).⁴³⁻⁴⁵ Strategies to achieve this have focused on incorporating linker and metal mixed valency to increase the charge density.⁴⁶ For future systems development, not all of these components are equal in terms of importance. In practice, the rate-limiting structural feature, which has plagued other photocatalytic systems, remains charge carrier recombination.⁴⁷ In the context of photocatalytic CO₂ reduction by MOFs, these last two aspects have yet to be fully addressed.⁴⁸,⁴⁹
Figure 5.2. The design of MOFs as CO\(_2\) reduction photocatalysts. The modular nature of metal-organic frameworks allows for the precise control over and installation and tuning of various chemical and structural features with respect to enhancing selectivity, activity and efficiency. (a) The first generation of MOF photocatalysts focused on developing selectivity through site isolation (discrete nanoparticle metal oxide SBUs, site isolated molecular catalysts) and enhanced their activity by tailoring the pore metrics and surface area. (b) In the second generation, the photonic efficiency was optimized by altering the nature of the linker (band gap engineering through functionalization...
and conjugation of the linker) and by integration of plasmonic nanoparticles to expose the catalyst to their intensified near surface electric field. (c) The third generation targeted the optimization of the electronic efficiency of MOF catalysts by using molecular photosensitizers to improve the apparent quantum yield of the system or by tuning the electronic character of the SBU to improve charge separation and slow down the recombination rate of photo-generated electron-hole pairs. (d) Looking forward to the fourth generation, future systems need to further enhance the electronic efficiency by improving the charge-carrier mobility. This will lead to a higher quantum efficiency of the catalyst. (e) Taking stock of all of the achievements, the ideal system must build upon and combine the success of the previous generations.

5.3 MOF and COF electrocatalysts for CO₂ reduction

In order to operate, photocatalytic processes are inherently at the mercy of sunlight (i.e. quantum efficiency). This means that the sunlight dictates the voltage that can be used to affect CO₂ reduction. With too little sunlight, efficiency significantly drops. Furthermore photo-generated electron flux is generally significantly lower than electron flux provided by an external electrical source under an applied potential. Additionally, due to the fact that sunlight contains photons of multiple wavelengths, varying potentials are generated. This is disadvantageous since the applied potential exponentially correlates to the current density of product formation and thus varying potentials lead to decreased figures of merit. In order to avoid this, electrocatalysis is an attractive alternative process because one does not have to rely on the constant presence of sunlight as an energy source and one can dial in the exact voltage needed to ensure that the selectivity towards a desired product is optimized.

5.3.1 First generation: Selectivity and activity.

Homogeneous catalysts have been optimized for high selectivity toward CO₂ reduction, however they lack sufficient activity. The three key considerations for ensuring that an electrocatalyst maintains the high selectivity observed in homogeneous catalysts, but also achieves high activity are: (i) Incorporate homogeneous catalysts within the backbone of an extended framework; (ii) the reaction must take place in an aqueous media because at room temperature CO₂ has a higher solubility than in organic solvents. Furthermore, water as a reaction medium is beneficial as it facilitates necessary proton and electron transfer processes (i.e. increases the activity); and (iii) there needs to be a controlled interface between the catalyst and the electrode. The reason for this comes down to the idea of a 3-component versus 2-component system (FIG. 3a,b). If no permanent interface exists then the catalyst, CO₂, and the electrode must come together at the exact same time to carry out the reaction. When the catalyst is interfaced with the electrode, one effectively removes a variable from this equation.

Maximizing areal density. MOF-525(Fe) is comprised of metalloporphyrin linkers, which serve as active sites. Thin films of this MOF were electrophoretically deposited on an electrode in order to maximize the areal density of the active sites while achieving the necessary electronic contact with the electrode. Electrolysis at an overpotential of ~650 mV was carried out in a tetrabutylammonium hexafluorophosphate/DMF electrolyte solution resulting in 15.3 μmol cm⁻² and 14.9 μmol cm⁻² of CO and H₂, respectively. When taking into account the amount of electronically accessible catalyst, these values translate into a turnover frequency (TOF) for CO formation of 64 h⁻¹ and a TON of 272. The addition of a weak Bronsted acid, 2,2,2-trifluoroethanol, increased the CO production by 7-fold with the TON reaching 1520 after 3.2 h. Mechanistic studies with regard to the catalytic activity of MOF-525(Fe) showed that in this system the turnover is limited by electron transport.
5.3.2 Second generation: Efficiency.

Thin films of MOFs allow for the necessary electronic contact of the catalytic material with the electrode. The first generation of MOF catalysts is, however, limited in regard to their charge-carrier mobility properties. It is, therefore, necessary to further assess the impact of the mass transport in the system. The reason that one must assess the mass transport for solving the problem of low intrinsic charge carrier mobility is rooted in the fact that to improve efficiency one must balance both mass and electron transport (FIG. 3c). This makes it such that a system does not have to solely rely on one property over the other.

In the realm of porous materials, the diffusion of CO\textsubscript{2} to the catalytic sites causes the local concentration of CO\textsubscript{2} close to the electrode to decrease with increasing film thickness. Consequently, the number of active sites that are exposed to a high concentration of CO\textsubscript{2} is limited. There are two tunable parameters for maximizing the efficiency of such systems: (i) fine-tuning of the thickness to the point, in which the interplay between mass- and electron transport is optimized; and (ii) enhancing the charge carrier mobility of the material to allow for efficient electron transport to active sites further away from the electrode. In this context, the first point is related to engineering the morphology of the catalyst and the second point entails modifying the inherent electronic properties of the material.

Matching electron- and mass transport. An aluminum porphyrin-based MOF\textsuperscript{55} Al\textsubscript{2}(OH)\textsubscript{2}TCPP-Co \textsuperscript{[TCPP-H\textsubscript{2} = 4,4',4'',4'''-(porphyrin-5,10,15,20-tetrayl)tetrabenzoate]}, comprising cobalt porphyrin active sites was employed for the electrocatalytic reduction of CO\textsubscript{2} to CO\textsuperscript{56}. Here, thin films of the MOF were directly grown on a conductive carbon disk electrode. The synthetic strategy is based on the formation of aluminum oxide thin films, serving as metal precursors, via atomic layer deposition (ALD). Subsequent MOF formation was carried out by reacting the coated electrode with the linker under solvothermal conditions. This strategy holds great promise for balancing electron and mass transport as the thickness of the precursor can easily be controlled by the number of ALD cycles, which was found to be proportional to the thickness of the resulting MOF thin films. As such, the thickness of the aluminum oxide precursor was varied by changing the number of ALD cycles from 5 to 100 resulting in aluminum oxide films of 0.5 to ~10 nm. The performance of the resulting MOF catalyst initially improves with increasing film thickness until reaching a maximum of ~2.8 mA cm\textsuperscript{-2} at 50 ALD cycles. This translates to a MOF thickness of ~30-70 nm. The fact that the performance decreases at a higher thin film thickness demonstrates that the optimal thickness was achieved. The optimized catalyst thickness exhibited a Faradaic efficiency for CO production of up to 76% and, within 7 h, reached a turnover number of 1400.
Figure 5.3. Conceptual principles for developing MOFs/COFs as electrochemical CO$_2$ reduction catalyst.

(a) In the context of electrocatalytic CO$_2$ reduction, the activity of homogeneous molecular catalysts is intrinsically limited by the necessity for concurrent migration of both CO$_2$ and the catalyst to the electrode in order to affect transformation. As such, the reaction is at the mercy of randomness of molecular fluctuations in solution. (b) In contrast, heterogeneous catalysts can effectively be interfaced with the electrode material, and thus the only limiting factor for turnover is the diffusion of CO$_2$ to the active sites. (c) With respect to efficiency, electrocatalysts need to balance the interplay between electron and mass transport. A given material has an optimal catalyst thickness, which maximizes the reciprocity of these two intrinsic material characteristics.

Enhancing the charge-carrier mobility. In comparison to MOF systems, layered imine-based covalent organic frameworks are attractive due to their superior charge-carrier mobility. In particular, COF-366, another material comprising porphyrin building blocks, was reported to have a high charge-carrier mobility of 8.1 cm$^2$ V$^{-1}$ s$^{-1}$. As a result, a metalated COF-366, termed COF-366-Co, and derivatives thereof were investigated as electrocatalytic CO$_2$ reduction catalysts. COF-366-Co was demonstrated to reduce CO$_2$ in water at an overpotential of -0.55 V, producing 36 mL mg$^{-1}$ of CO over the course of 24 h with a Faradaic efficiency of 90%. Interestingly, increasing the pore size of COF-366-Co, by means of isoreticular expansion (1.8 nm to 2.3 nm), to realize COF-367-Co had a pronounced effect on the performance of the material. This new isoreticular structure produced 100 mL mg$^{-1}$ of CO under identical conditions. In addition to framework expansion, the catalyst performance was further tailored using a building-block
heterogeneity approach. Since it was hypothesized that not all electroactive sites (cobalt porphyrin moieties) in the parent material fully participate in the reaction, owing to the low aqueous solubility of CO$_2$ (CO$_2$ is rate-limiting), a partial replacement of these sites with catalytically inactive copper porphyrin units was examined. Indeed, this catalyst dilution strategy led to materials that achieved TONs of up to 290,000, with an initial turnover frequency of 9400 h$^{-1}$. This corresponded to a 26-fold improvement in performance as compared to the molecular cobalt complex employed for this reaction.

5.4 Outlook

In considering the next generation of CO$_2$ reduction systems,$^{59}$ one has to take account of the advantages and drawbacks of both photo- and electrochemical processes. While photochemical reduction processes benefit from clean solar energy, they are hindered by the necessary evil of sacrificial donors as an electron source. This is even true in the case of MOFs. Furthermore, as it stands now, a worthwhile photochemical reduction MOF catalyst requires a rather complex multicomponent system, which must take advantage of introducing photosensitizers to increase photonic and quantum efficiency, catalytically active sites, and designing an SBU and/or linker with the appropriate band gap (photonic efficiency again). In this regard, a deeper fundamental understanding of the structure-chemistry-property relationship of these complex systems is essential prior to promoting the practicability of reticular chemistry for this purpose.$^{13}$ When turning attention to electrochemical reduction MOF and COF catalytic systems, the ideal overpotential can be determined experimentally such that the current and faradaic efficiency are optimized. This allows for the optimization of the MOF or COF catalyst in a way not possible with a photochemical approach where not all of the absorbed photons can be utilized since they do not necessarily have the necessary potential to affect conversion or due to charge carrier recombination. As a consequence, the figures of merit for efficiency in electrocatalytic systems are considerably higher than those of their photocatalytic counterparts. It is noted that by using reticular chemistry to design catalytic materials, the selectivity and activity criteria can be met for both photo- and electrochemical reduction processes. Hence, the determining factor for developing the next generation must lie in maximizing the efficiency. In this regard, electrochemical processes are far more advanced and represent a viable answer toward this end. In fact, it has been shown that electrocatalytically-driven COF catalysts already meet all criteria for an active, selective, and efficient reduction catalyst. The problem now lies not solely in materials design — albeit there are outstanding materials design challenges that remain (long-term stability and assessing other structure-function parameters for practical use) — but rather in implementing the electrocatalyst within the right system. Our view is that the next step in this progression is one in which a MOF or COF electrochemically reduces CO$_2$, where the energy is derived from sunlight. Such a photoelectrochemical approach combines the desired renewable energy input of photocatalytic systems with the higher efficiency of electrochemical reduction. The need for a sacrificial donor to feed electrons to the system is also removed as these electrons can be generated from water splitting on the counter electrode.
Figure 5.4 Schematic of the proposed photoelectrocatalytic reduction of CO₂ to CO by COF-366(Co) in a hypothetical photoelectrochemical cell. Photoelectrochemical reduction of carbon dioxide combines the advantages of both, photocatalytic and electrocatalytic approaches. Similar to photocatalysis, this setup makes use of sunlight as the energy source and the fact that the reaction is carried out in two half cells, as in the electrocatalytic conversion, the system circumvents the need for the addition of a sacrificial donor because electrons are generated from the oxidation of water on the counter electrode. Atom colors: C, grey; H, white, N, blue; and Co, purple.
5.5 References


208


[59] Note: Although the focus of this chapter was in considering reticular chemistry as the next generation of CO₂ reduction materials, it is important to point out that the economic feasibility of any CO₂ reduction system implemented on a grand scale remains controversial, at best, with widespread doubt being voiced by academics, economists, and policymakers alike. With this point in mind, we direct the readers to the following for further reading: Mac Dowell, N.; Fennell, P. S.; Shah, N.; Maitland, G. C. The role of CO₂ capture and utilization in mitigating climate change. Nature Climate Change 2017, 7, 243-249.