Dissertation zur Erlangung des Doktorgrades der Fakultät für Chemie und Pharmazie der Ludwig-Maximilians-Universität München

## **Dynamic Processes in**

## **Covalent Organic Frameworks –**

## From Charge Carrier Diffusion to CO<sub>2</sub> Conversion

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#### Erklärung

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#### Abstract

The development of advanced materials for sustainable energy conversion is becoming increasingly important in today's society. Reticular chemistry, with its ability to create crystalline frameworks with tailored properties, offers a valuable toolbox for designing such materials. Among these, Covalent Organic Frameworks (COFs) have attracted growing interest as promising candidates for applications in gas and energy storage, photo- and electrocatalysis, battery applications, or optoelectronics. A fundamental understanding of the dynamic processes in COFs is essential to unlock their potential for energy conversion applications. This thesis focuses on studying key aspects of optoelectronic processes in COFs and their implications for  $CO_2$  catalysis.

In the first project, the spatiotemporal dynamics of charge carrier diffusion in thin films of a highly crystalline 2D COF, constructed from benzodithiophene-dialdehyde *BDT* and *N*,*N*,*N*',*N*'-tetra(4-aminophenyl)benzene-1,4-diamine *W* (WBDT COF) were investigated. Combining remote-detected time-resolved photoluminescence (RDTR PL) and optical pump terahertz probe (OPTP) measurements with excited state simulations allowed for previously inaccessible insights into this material class. With a direct access to the lateral excited state diffusion, the study identified two diffusive species dominating the process at different timescales: short-lived ultrafast free charge carriers with an almost temperature-independent diffusion coefficient  $D = 10 \text{ cm}^2 \text{ s}^{-1}$ , and a slower species, attributed to excitons. These excitons possess exceptionally high diffusion coefficients ( $D = 4 \text{ cm}^2 \text{ s}^{-1}$  at 200 K) and diffusion lengths ( $L_D = 200 - 800 \text{ nm}$ ), surpassing those in other COFs and organic semiconductors by several orders of magnitude, thereby demonstrating that excitons can traverse grain boundaries in WBDT. A charge transport model describing the temperature-dependent behaviour of exciton transport was developed, underlining the complex role of order and disorder in the diffusion processes in COFs.

On the transition from fundamental studies on dynamic processes towards application of COFbased systems as energy conversion materials, the second project presents the development of a novel COF-based CO<sub>2</sub> photocatalyst. A new dibenzochrysene (DBC)-based COF was synthesized, in which Re<sup>I</sup> centres were incorporated to create a hybrid photocatalyst for CO<sub>2</sub> reduction. The COF retained its high crystallinity upon introduction of Re<sup>I</sup>, enabling the atomistic-level resolution of the metal centre-distribution in the porous framework by employing scanning transmission electron microscopy in high-angle annular dark field mode (STEM-HAADF). The rigid structure of the COF led to extended stability under visible light illumination of at least 72 h, whereas the efficient light-harvesting capability and the strong electronic interactions between the COF and the Re<sup>I</sup> centres led to CO evolution rates of up to  $1.16 \text{ mmol g}^{-1} \text{ h}^{-1}$ .

In the final project, a COF-based catalyst was developed for the electrochemical reduction of  $CO_2$  to CO. The COF's phenanthroline moieties enabled the immobilization of a homogeneous  $Mn^{I}$  catalyst at pre-defined binding sites in the framework. This design effectively suppressed the formation of  $Mn^{0}$ - $Mn^{0}$  dimers, reaction intermediates known to impair catalytic performance. The hybrid Mn-COF catalyst was successfully employed in a catholyte-free membrane-electrode-assembly (MEA) cell, an architecture that allows for direct contact between the catalyst and the  $CO_2$  gas flow, while avoiding interaction with the aqueous electrolyte. The novel catalyst achieved partial CO current densities of 3.6 mA cm<sup>-2</sup> and a turnover frequency of 618 h<sup>-1</sup>, showing significantly increased stability and catalytic activity compared to its homogeneous counterpart, and provides a compelling proof-of-concept for utilizing this class of materials in industry-relevant cell architectures.

## **List of Abbreviations**

2D	Two-dimensional
3D	Three-dimensional
BDT	Benzodithiophene-dialdehyde
bpy	2,2'-Bipyridine-5,5'-dicarbaldehyde
CB	Conduction band
CE	Counter electrode
CO <sub>2</sub> RR	CO <sub>2</sub> reduction reaction
COF	Covalent organic framework
CTF	Covalent triazine framework
CV	Cyclic voltammetry
D-A	Donor-acceptor
DBC	Dibenzo[g,p]chrysenetetraamine
DFT	Density functional theory
FE	Faradaic efficiency
FTIR	Fourier-transform infrared
GDE	Gas diffusion electrode
GIWAXS	Grazing-incidence wide angle X-ray scattering
HER	Hydrogen evolution reaction
НОМО	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
MEA	Membrane-electrode-assembly
MWCNT	Multi-walled carbon nanotubes
NHE	Normal hydrogen electrode
OPTP	Optical-pump terahertz probe spectroscopy
Phen	4,4'-(1,10-Phenanthroline-3,8-diyl)dibenzaldehyde
PL	Photoluminescence
Ру	4,4',4"',4"'-(1,3,6,8-Pyrenetetrayl)tetrakis[benzene-amine]
RDTR-PL	Remote-detected time-resolved photoluminescence
RE	Reference electrode

RHE	Reversible hydrogen electrode
SCE	Standard calomel electrode
SEM	Scanning electron microscopy
SHE	Standard hydrogen electrode
SI	Supporting Information
SSA	Singlet-singlet annihilation
STEM-HAADF	Scanning transmission electron microscopy in high-angle annular
	dark field
ТА	Transient absorption spectroscopy
TAA	Transient absorption anisotropy
TCSPC	Time-correlated single photon counting
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
THz	Terahertz
TOF	Turnover frequency
TON	Turnover number
UV-vis	Ultraviolet-visible
VB	Valence band
W	N,N,N',N'-Tetra(4-aminophenyl)benzene-1,4-diamine
WE	Working electrode
XRD	X-ray diffraction

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# CHAPTER 1

Introduction

#### **1** Introduction

In the context of the increasingly evident consequences of anthropogenic climate change, including the occurrence of extreme weather events such as droughts, floods, heatwaves and cold spells, as well as a geopolitical landscape shaped by tension and complexity, it is imperative that the scientific community plays a leading role in developing innovative technologies for sustainable energy conversion, thereby facilitating the transition towards a carbon-neutral economy. The creation of advanced materials capable of addressing the challenges of renewable energy storage, carbon capture and efficient catalytic processes is central to this effort. Reticular chemistry, with its capacity to design and construct crystalline frameworks from molecular building blocks, offers an ideal platform for the development of such materials. By enabling precise control over chemical composition, porosity and structural functionality, reticular chemistry provides access to a vast library of frameworks with tailored properties, making it a key tool for innovation in energy-related applications.<sup>1-2</sup>

#### 1.1 Covalent Organic Frameworks

Covalent Organic Frameworks (COFs) have attracted significant interest since 2005 following the first reports on their crystalline porous nature, their achievable high chemical stability, and their virtually unlimited structural tunability.<sup>3</sup> Comprised of earth-abundant and light-weight elements (C, B, N, O, etc.), COFs are promising candidates for a large variety of applications, such as gas storage,<sup>4-6</sup> molecular separation,<sup>7-8</sup> energy storage,<sup>9-12</sup> catalysis,<sup>13-15</sup> and optoelectronics.<sup>16-18</sup> Employing the principles of reticular chemistry, COFs are constructed *via* covalent connections of organic building units (often denoted as linkers) yielding highly ordered, periodic networks. The slightly reversible nature of the covalent coupling reactions permits the formation of crystalline structures rather than an amorphous polymer, as it allows for error correction and rearrangement of the network by cleaving and reforming connections within the lattice, the so-called "self-healing".<sup>19</sup>

Planar or nearly planar aromatic molecules promote the formation of layered materials comprising 2D molecular sheets. The predetermined symmetry and connectivity of these linkers leads to a variety of different COF topologies, such as hexagonal, tetragonal, trigonal, rhombic or dual-pore (Figure 1.1a).



Figure 1.1. Different 2D (a) and 3D (b) COF topologies, dictated by the choice of the building block geometry. Adapted with permission.<sup>20</sup> Copyright 2021 Elsevier.

Building units with a 3D spatial character allow for polymerization propagation in all directions, resulting in the formation of 3D networks, often exhibiting an interpenetrated structure (Figure 1.1b). The virtually limitless library of existing and potentially producible organic molecules drives the great structural versatility of COFs, leading to a broad range of structures with various topologies, geometries and functionalities.

The first reported COFs were formed *via* the co-condensation of boronic acids with catechols to form five-membered boronate ester rings as linkages and *via* self-condensation of boronic esters to boroxines.<sup>3</sup> As these linkage types are highly sensitive towards hydrolysis, imine linkages formed by the acid-catalyzed Schiff-base condensation between aldehydes and primary amines were introduced.<sup>21</sup> Imine linked COFs often exhibit extended  $\pi$ -conjugated systems, making them promising for applications in organic (opto)electronics. Coupled with their improved chemical stability and straightforward synthesis under mild solvothermal conditions, these advantageous properties have established the imine linkage motif as the most widely employed in COF design.<sup>22</sup> Ever since, a growing number of novel linkage types in COFs have been reported, such as hydrazone<sup>23</sup>, squaraine<sup>24</sup>, phenazine<sup>25</sup> as well as azine<sup>26</sup>, imide<sup>27</sup> and  $\beta$ -ketoenamine<sup>28</sup> (Figure 1.2). Fully conjugated 2D COF with enhanced stability were obtained *via* the Knoevenagel or aldol condensation, implementing olefin linkages based on sp<sup>2</sup>-hybridized carbon.<sup>29</sup>

#### 1 Introduction



Figure 1.2. Common linkage types for the formation of COFs based on reversible condensation reactions. Adapted with permission.<sup>20</sup> Copyright 2021 Elsevier.

The influence of building block choice, linkage chemistry, interlayer interactions, crystallinity and porosity on the electronic and optical properties of COFs is discussed in detail in chapters 1.3.1.1 - 1.3.1.4 with an additional focus on the implications for their application as CO<sub>2</sub> photocatalysts.

#### **1.2 Charge Carrier Dynamics in Covalent Organic Frameworks**

Excited state dynamics, fundamental properties in semiconductors, define their ability to generate, transport and transfer charge carriers. Linking those properties with a material's molecular structure has been a long-standing goal, paving the way towards more efficient photoactive materials. COFs as modular and easily tunable materials with a well-defined crystalline structure are ideal candidates for studies on structure-property relations.

In recent years, COF have attracted significant attention for their potential use in sustainable energy applications.<sup>13, 30</sup> Organic building blocks with suitable electronic properties can feature strong optical absorption in the visible light range, whereas the crystalline and periodic network can establish a band structure enabling long-range coherent transport.<sup>31-32</sup> Despite the prevalent and well-documented view that COFs can be tailored to suit specific applications, a comprehensive understanding of the correlation between their structures and the properties they exhibit remains elusive. Fundamental questions on the nature (thermally activated hopping *vs.* delocalized band-like transport) or the direction of charge transport (in-plane *vs.* out of plane) persist.

Excited state dynamics in COFs have been investigated both theoretically and experimentally by means of time-resolved techniques, namely transient absorption spectroscopy<sup>33-35</sup>, optical-pump terahertz-probe spectroscopy<sup>36-37</sup>, hall effect measurements<sup>38-39</sup>, microwave conductivity<sup>40</sup> and, more recently, remote-detected photoluminescence. This chapter will focus on factors governing the energy transport phenomena of excited state diffusion, charge carrier mobility and (photo)conductivity in two-dimensional COFs.

#### 1.2.1 Excited state diffusion

Diffusion is the response of mobile "particles", for example atoms, ions, molecules, excited states, to concentration gradients, generally from a region of higher concentration to a region of lower concentration, as illustrated in Figure 1.3. Diffusion of excited states (or charge carriers) is crucial for energy conversion materials, requiring long diffusion lengths and high diffusion coefficients to guarantee the efficient transport of energy or charge carriers from the site of generation to the location where they can be effectively harvested and ultimately utilized.



Figure 1.3. Diffusion of excited states in a periodic network (schematic). (a) An incipient ray of light with the energy hv hits the surface of a material, creating (photo)excited states. (b) Immediately, a region with a high density of carriers emerges, causing the surrounding region to be of low carrier density. (c) The carriers or excited states subsequently diffuse from a region of high density to a region of low density, driven by a gradient in concentration.

Excited state diffusion in COFs has been mostly investigated using transient absorption spectroscopy (TA) on colloidal suspensions. Helweh *et al.* conducted a systematic study on the exciton dynamics of an imine-linked 2D COF (TAPB-DiOMe), its corresponding hexagonal macrocycle (MC) and extended nanotubes comprised of stacked macrocycles (NT) to understand the processes occurring in the plane of covalently connected macromolecules and between the layers of NT and 2D COFs.<sup>41</sup> Spectroscopic studies involving femtosecond-TA revealed that the assembled structures (NT and 2D COF) exhibit a significantly longer excited state lifetime than the isolated MC (< 5 ps *vs.* ~100 ps), underlining the importance of the ordered 2D-layered structure of COFs in stabilizing excited states by inhibiting recombination processes such as internal conversion. Femtosecond-TA anisotropy (fs-TAA) measurements confirmed exciton diffusion along the 2D COF sheets while interlayer energy transport could not be accessed through fs-TAA. Nevertheless, anisotropy measurements on the NT indicate that the interlayer transport direction is relevant in 2D COFs.

Incorporation of a fully conjugated sp<sup>2</sup>-c linkage appears to be an effective method for facilitating energy transport along and across stacks, as excitons can be readily delocalized across multiple building units. Zhang *et al.* studied exciton diffusion and annihilation in colloidal vinylene-linked 2D COFs bearing 1,3,6,8-tetraphenylpyrene (TFPPy) knots and linear phenyl linkers.<sup>34</sup> The diffusion coefficient *D* extracted from a three-dimensional diffusion and collisional annihilation model is on the order of 10<sup>-5</sup> to 10<sup>-3</sup> cm<sup>2</sup> s<sup>-1</sup>. Estimations for the diffusion length  $L_D$  range from ~3 nm to ~50 nm, depending on the initial exciton density. They found that long-range exciton-exciton interactions are the primary trapping pathway for delocalized excited states in the COF. Despite the extended conjugation within the 2D COF sheets, the

exciton distribution has a preferred direction, interestingly along the stacks; orientations that are highly favorable for inter-exciton resonance and annihilation. However, a study by Wang and co-workers compared an imine linked TFPPy COF (imCOF) with its vinylene-linked analogue (viCOF), suggesting that the intralayer energy transfer pathway is preferred in the viCOF.<sup>42</sup> This ambivalence in preferred transport direction of the two studies on vinylene-linked TFPPy COFs is illustrative of the numerous interrelated factors influencing charge carrier diffusion in COFs. While a single structural parameter such as the linkage may be significant, it is not always the only factor determining the resulting excited state property.

The influence of domain size and morphology on exciton diffusion in 2D COFs was investigated by Flanders and co-workers.<sup>35</sup> Employing TA, the study revealed that exciton diffusion is directly correlated to the COF crystallite size, both increasing for larger COF colloids. Diffusion coefficients *D* increased from 0.02 to 0.09 cm<sup>2</sup> s<sup>-1</sup> with increasing COF colloid domain size (22 nm to 36 nm), while a diffusion length  $L_D$  of not more than 5 nm was determined. This behaviour was attributed to the larger effective volume available for exciton diffusion, as well as the reduction of surface trap states due to a lower surface-to-volume ratio. These findings suggest that maximizing crystalline domain sizes is crucial for achieving efficient energy transport in optoelectronic applications. Ultimately, the use of thin films with crystalline domains extending up to hundreds of nanometres represents a logical next step, combining enhanced transport properties with practical suitability for device fabrication.



Figure 1.4. Model of the photoinduced electronic processes in COFs. (a) Absorption of photons leads to the formation of singlet excitons. (b) These singlets diffuse through the conjugated network (1) and can eventually collide with another one (2), i.e. singlet-singlet annihilation. This process results in free charges (c) which eventually locate onto isolated, trap-like states leading to long lifetimes over tens of microseconds. Adapted with permission.<sup>33</sup> Copyright 2019 American Chemical Society.

The excited state diffusion in 2D COF thin films was described for the first time by Jakowetz and co-workers.<sup>33</sup> Despite encompassing framework structures with different connecting nodes and topologies, a general model for the description of photoinduced processes was suggested, illustrated in Figure 1.4, in which singlet excitons are generated that subsequently diffuse both in and out-of-plane before undergoing singlet-singlet annihilation (SSA). SSA generated long-lived free charges with lifetimes of up to hundreds of microseconds.

Transient absorption, the method of choice for studying excited state diffusion in COFs, is extraordinarily powerful, resolving dynamic processes on the femtosecond to nanosecond timescale over a broad wavelength range. However, information on the diffusion coefficient and length can only be obtained indirectly, as the transport of photogenerated states is usually inferred from excitation intensity-dependent excited state annihilation by its impact on the observed lifetimes. In contrast, a microscopic photoluminescence (PL)-based technique, remote-detected time-resolved PL (RDTR-PL), offers direct access to the diffusion processes of excitons in the studied materials.<sup>43</sup> The microscopic PL technique directly measures emitted light that is spectrally (and spatially) separated from the excitation light, offering the sensitivity of detecting single photons. In addition, RDTR-PL provides high spatial resolution with a small confocal probing volume and local access to a specific sample position on the µm scale. This powerful technique has recently been applied to study the excited state diffusion in 2D COF thin films. In thin films of the WBDT COF (benzodithiophene-dialdehyde BDT and N,N,N',N'tetra(4-aminophenyl)benzene-1,4-diamine W), remarkably high diffusion coefficients of up to  $4 \text{ cm}^2 \text{ s}^{-1}$  and diffusion lengths of 200 - 800 nm were extracted. These large diffusion lengths suggest exciton transport across grain boundaries, an invaluable asset for the implementation of these materials into device architectures. Furthermore, temperature-dependent RDTR PL measurements coupled with extensive theoretical calculations found the exciton diffusion to arise from contributions of both band-like and hopping transport, contributing significantly to the fundamental understanding of the mechanism of charge transport in this materials class. The full study can be found in Chapter 3 of this thesis.

#### 1.2.2 Charge carrier mobility and (photo)conductivity

Parts of this chapter are based on the following book chapter:

## Time-resolved spectroscopy applied to heterogeneous photocatalytic materials (2019 – 2022)

Laura Spies, Jenny Schneider\*, Mariano Curti\*

in *Photochemistry Volume 51*, ed. S. Crespi and S. Protti, Royal Society of Chemistry, 2023, pp. 159-193

The mobility  $\mu$  characterizes how quickly charge carriers move under the influence of an external electric field. In contrast to diffusion, which is random and undirected, mobility reflects a directed, field-driven response. The product of mobility and charge carrier concentration determines the material's conductivity  $\sigma$ , a key property for electronic applications. Understanding the relationship between a material's electronic structure and its charge transport behaviour is essential, particularly in the context of 2D COFs, where optimizing these properties can unlock their potential as next-generation materials for electronics and energy storage. Terahertz (THz) spectroscopy has been established as a versatile technique to study electro-optical processes in a variety of materials, probing the (photo)conductivity  $\sigma(\omega)$  of a material and providing valuable insights into the processes involved in charge carrier dynamics.<sup>44</sup>

THz spectroscopy is highly sensitive to the motion of free charge carriers due to their ability to absorb and respond to THz radiation. It should be noted that while, in principle, it is possible to probe signatures from bound excitonic states in the THz range through time-resolved THz spectroscopy (TRTS) for inorganic semiconductors<sup>45</sup>, these signatures directly depend on the exciton binding energy  $E_b$  (e.g., the lowest energy intra-excitonic transition is at ~3/4  $E_b$ ). For organic materials, such as COFs, however, exciton binding energies usually reach up to ~0.5 eV (i.e., ~120 THz), thus shifting these transitions well outside of the conventional THz range, in the MIR/NIR range and making them hardly measurable with time-resolved THz spectroscopy. Hence, THz spectroscopy provides a complementary perspective on charge carrier dynamics, distinct from techniques like TA or RDTR PL by directly probing the collective and coherent motion of free carriers to understand their transport properties. An increasing number of 2D COFs has been studied in recent years using optical-pump terahertz-probe spectroscopy (OPTP). For instance, Jin *et al.* employed THz spectroscopy to study the charge carrier mobility of a new type of nanographene-based COF using dibenzo[*hi*,*st*]ovalene (DBOV) as building block.<sup>37</sup> The DBOV-COF showed remarkable photocatalytic activity in hydroxylation, which the authors attributed to efficient charge carrier transport following light absorption. Analysis of OPTP and TRTS data yielded an average carrier lifetime of 8 ps (using bi-exponential fits) and charge scattering times of  $36 \pm 6$  fs with an estimated mobility of  $0.6 \pm 0.1$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> using the Drude–Smith model.

When estimating charge carrier mobility in semiconductors, the Drude-Smith model accounts for the backscattering events due to grain boundaries or structural configuration, which lead to partial localization of the charge carriers. Delocalized free charge carriers are well described using the Drude model. The formulas for photoconductivity  $\sigma(\omega)$  and mobility  $\mu$  of the respective models are as follows

Drude model 
$$\sigma(\omega) = \frac{\omega_p^2 \epsilon_0 \tau}{1 - i\omega\tau} \qquad \mu = \frac{q}{m^*} \bar{\tau}$$
Drude-Smith model 
$$\sigma_{DS}(\omega) = \frac{\omega_p^2 \epsilon_0 \tau}{1 - i\omega\tau} \times \left(1 + \frac{c}{1 - i\omega\tau}\right) \qquad \mu_{DS} = \frac{q}{m^*} \bar{\tau}(1 + c)$$

where  $\omega_p^2$ ,  $\epsilon_0$ ,  $\omega$  and  $\tau$  are the plasma frequency, the vacuum permittivity, the angular frequency and the charge scattering time, respectively and q is the elementary charge,  $m^*$  the effective mass of the charge carrier and  $\bar{\tau}$  the average scattering time. The parameter c accounts for the backscattering probability with c = 0 for Drude-like transport and c = -1 for localized charges with preferential backscattering.

The important role of extended  $\pi$  -conjugation in the charge carrier transport in COFs is illustrated by the work of Xing and co-workers, where large  $\pi$ -conjugated building blocks were introduced into the COF lattice, forming flexible (DHP-COF) and rigid (*c*-HBC-COF) lattices.<sup>46</sup> The rigid *c*-HBC-COF with enhanced  $\pi$ -conjugation and compact interlayer  $\pi$ - $\pi$  stacking exhibited much higher photoconductivity (8.3 *vs.* 2.2  $\mu$ S) and larger scattering times (87 fs *vs.* 28 fs), extracted from Drude–Smith fits) compared to the DHP-COF, as depicted in Figure 1.5. The charge carrier mobility of *c*-HBC-COF with 44 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> ranks amongst the highest in 2D COFs determined using a similar measurements technique.



Figure 1.5. (a) Photoconductivity of DHP-COF and *c*-HBC-COF as a function of the pump-probe delay. The samples were excited at 3.1 eV at a pump fluence of 1.3 mJ cm<sup>-2</sup>. TRTS results of DHP-COF (b) and *c*-HBC-COF (c) at 1 ps after photoexcitation. The data are fitted using the Drude-Smith model. Adapted with permission.<sup>46</sup> Copyright 2022 American Chemical Society.

The combination of COFs (with high surface area, porosity, chemical stability and superior light-harvesting abilities) with inorganic co-catalysts yields photocatalytically active hybrids with superior features. A plethora of possible approaches exists for the integration of metallic co-catalysts, of which the implementation of metal-decorated porphyrin or phtalocyanine building units into the COF structure is easily accessible. Besides their crucial role in the selectivity of photocatalytic processes, understanding the influence of the metal centre on the charge carrier transport mechanism is of great importance. Wang *et al.* reported new Zn and Cu phtalocyanine- based pyrazine-linked 2D COFs, ZnPc-pz and CuPc-pz COF, and studied the influence of the metal centre on the conductivity, charge carrier density, scattering time and effective mass of the majority carriers using Hall effect measurements, THz spectroscopy and DFT calculations.<sup>38</sup> The THz measurements revealed average charge scattering times of 30.4 fs (Drude–Smith model) for both samples and mobilities of ~2.0 and ~0.7 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for ZnPc-pz and CuPc-pz, respectively. They found that the different metal-phtalocyanine COF moieties have a negligible effect on the above-mentioned characteristic values and do not affect charge carrier motion in the samples.

Fu and co-workers studied highly crystalline COF thin films using THz spectroscopy, unveiling an intuitive but critical parameter to ensure long-range delocalized charge transport: the crystallinity of the material.<sup>36</sup> Most of the THz measurements on COFs are realized by sandwiching a powdered sample between two fused silica substrates, imposing a morphology of individual crystalline particles compressed by mechanical force. On the contrary, growing transparent crystalline thin films of the COF material allows for interconnected grains, presumably promoting charge transport. Fu *et al.* thus conducted THz spectroscopy of crystalline thin film samples of the 2D COF formed by the condensation of 1,3,5-tris(4aminophenyl)benzene and 1,3,5-triformylbenzene ("TPB–TFB COF"), revealing high photoconductivity with a scattering time of 72 fs and a record charge carrier mobility of  $165 \pm 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Contrary to other COF samples, TPB–TFP COF showed a Drude-type spectral response which is typically observed for delocalized free charge carriers in crystalline inorganic materials. TPB–TFP COF powder showed no photoconductivity within the noise level of the measurements, highlighting the critical role of crystallinity.

# **1.3 Covalent Organic Frameworks as CO<sub>2</sub> Photocatalysts: properties,** preparation strategies, and challenges

This chapter is based on parts of the following review article

From conventional inorganic semiconductors to covalent organic frameworks: advances and opportunities in heterogeneous photocatalytic CO<sub>2</sub> reduction

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**REVIEW ARTICLE** Thomas Bein, Jenny Schneider, Antonio Otavio T. Patrocinio *et al.* From conventional inorganic semiconductors to covalent organic frameworks: advances and opportunities in heterogeneous photocatalytic CO<sub>2</sub> reduction



The enhancement of renewable sources in the global energy matrix is a key step towards a sustainable growth of human society, as so far, the world's primary energy demand is still supplied predominantly by fossil fuels. This scenario brings growing concerns on the intensification of the greenhouse effect due to the increase of atmospheric  $CO_2$  concentration and drives the search for innovative green energy solutions. Such solutions include the large-scale utilization of solar and wind energies as well as the capture and conversion of  $CO_2$ . These targets are part of the UN sustainable goals 7, 11, and 12, and hence, are at the core of intensive research in chemistry, physics, and engineering.

From the material science point of view, intensive research efforts have been devoted to the development of catalytic materials to conduct  $CO_2$  reduction with high selectivity, long-term stability, and at low overpotentials. Both electro- and photo-catalysts have been proposed based on metallic particles, inorganic semiconductors, 2D- materials, and metal complexes.<sup>14, 47-50</sup> Among the investigated electro- and photocatalysts for  $CO_2$  reduction, heterogeneous materials typically exhibit long-term stability but low selectivity, while homogeneous molecular catalysts such as metalloporphyrins and metal complexes exhibit high selectivity but relatively low turnover numbers (TON). Immobilization of a molecular or metallic catalyst on solid supports has been found to hinder the detrimental side reactions of homogeneous catalysts such as dimerization and other radical reactions.<sup>51-52</sup> Metal oxides,<sup>53-55</sup> carbon nanostructures,<sup>56-57</sup> and polymeric<sup>58-59</sup> materials such as  $C_3N_4$  were shown to serve as suitable substrates for the immobilization of molecular photo(electro)catalysts.

To date, several approaches for converting CO<sub>2</sub> into fuels have been proposed. Among those based on renewable energy sources, the photochemical route that mimics the natural photosynthesis has been extensively pursued as it employs the most naturally accessible source of energy (sunlight) and electrons (water) to carry out the desired CO<sub>2</sub> conversion. Both molecular species and crystalline semiconductors have been proposed as photocatalysts for CO<sub>2</sub> reduction, each of them with advantages and disadvantages in terms of production feasibility, stability (turnover number), reactivity (turnover frequency), and selectivity towards the multiple reduction products.<sup>47-48</sup>

More recently, the rise of covalent organic frameworks (COFs) has opened a novel route towards improving the current performance of hybrid catalysts.<sup>60</sup> COFs are molecular frameworks, built by rigid organic building blocks that are connected *via* strong yet slightly reversible covalent bonds. By a rational selection of the building block's symmetry, three-dimensional or two-dimensional frameworks featuring long-range order and porosity are

formed. In addition to their modular structure, COFs are tailor-made materials with a view on their chemical and physical properties. Particularly, COFs can be designed to absorb large portions of solar light and to offer well-defined binding sites for CO<sub>2</sub> molecular catalysts. As a result, COFs provide a variety of options to control and to optimize the catalytic activity through the purpose-directed adjustment of the structural, morphological, and optoelectronic properties.

This remarkably straight-forward "design-follows-function" approach has recently triggered tremendous research on COFs as alternative platforms for photocatalysis<sup>51, 61-63</sup>.

The highly ordered organic polymers feature the following advantages: (a)  $\pi$ -stacking interactions between 2D COF sheets facilitate the charge carrier transport along and between COF planes; (b) chromophore building blocks and  $\pi$  delocalization in an extended conjugated structure promote efficient light harvesting; (c) high crystallinity and a high degree of structural order can prevent the recombination of charge carriers; (d) open porous structures and high surface areas enable rapid mass transport and diffusion of molecules as well as access to a high density of catalytically active sites; (e) the aforementioned flexibility in designing COF structures allows for the incorporation of building blocks, comprising heteroatoms (N, S, O etc.), defined binding sites for Lewis acids (typically metal ions) or specific side groups; and (f) the molecular nature of COFs allows one to conduct fundamental studies on charge carrier kinetics and catalysis, guiding the development of clear atomistic structure-property relationships.

Based on these unique features, COFs have already been tested for the electrocatalytic and photocatalytic CO<sub>2</sub> reduction reaction.<sup>64</sup> The first reported COF-based electrocatalyst for CO<sub>2</sub> reduction was an imine-linked COF comprising a Co(II) porphyrine as catalytic unit, <sup>65</sup> while a Covalent Triazine Framework (CTF) synthesized *via* the condensation polymerization between cyanuric chloride and perylene diimide exhibited photocatalytic activity for the artificial photosynthesis of formic acid from CO<sub>2</sub> in a photocatalyst-enzyme coupled system. <sup>66</sup>

While many excellent review articles are devoted to the application of covalent organic frameworks as photocatalysts, often with a focus on the relationship between structure and catalytic activity of these materials,<sup>14, 51, 61-62, 67-69</sup> only few reports are solely and thoroughly discussing the application of COF-based systems in the photocatalytic CO<sub>2</sub> reduction.<sup>63-64, 68, 70</sup> Hence, this chapter provides an in-depth analysis of the structural parameters affecting the photocatalytic performance of pristine COFs as a CO<sub>2</sub> photocatalyst, followed by a discussion on different methodologies to form COF-hybrid systems comprising metal-based catalysts for enhanced performance.

#### 1.3.1 Pristine covalent organic frameworks

Several pristine COFs have been reported in the literature as photocatalysts for the CO<sub>2</sub>RR. Herein, the crystalline and porous framework itself is able to catalyze the reaction, being in some cases supported by photosensitizers (e.g.  $Ru(bpy)_3Cl_2$ ) and sacrificial electron donors such as triethanolamine (TEOA), triethylamine (TEA) or ascorbic acid (AA). The application of these purely organic systems is pointing towards a more sustainable and green direction of CO<sub>2</sub> utilization compared to modified metalated COF-based catalysts, as there are no secondary environmental effects and no short-term inactivation or loss of the catalytic metal center.<sup>50, 62, 71</sup>

#### **1.3.1.1** Building units

The rational selection of the building units allows for the precise control over the electronic band structure of COFs and thus their light harvesting efficiency and the thermodynamic driving force for CO<sub>2</sub> reduction. By the incorporation of electron-donor and acceptor heterojunctions, enhanced charge carrier generation, separation and transport can be achieved.<sup>72-76</sup> The combination of light-harvesting chromophores as building blocks such as porphyrins, pyrene or imidazole together with extended structural conjugation enables excellent light absorption of COFs with intrinsic band gaps ranging from about 1.3 eV to 2.9 eV.<sup>77</sup> Often, the band gap of the conjugated structure is roughly similar to the smallest HOMO-LUMO gap of the constituting molecules, confirming the concept of reticular chemistry. However, increasing conjugation within the frameworks may lead to a reduction of the COF band gap in comparison to that of the building units.<sup>78-79</sup>

In order to catalyze the CO<sub>2</sub> reduction, the conduction band potential of a COF-based photocatalyst has to be more negative than the reduction potential of CO<sub>2</sub> to the desired product. Introducing heteroatoms (N, S, O) into the COF building units has a significant influence on their electronic donor and acceptor strength and thus on the electronic band structure of the COF. Hence, regulating the HOMO and LUMO energetic levels of the building units has a direct impact on the thermodynamic driving force for the catalytic reaction.<sup>80</sup> In addition, through the combination of electron-rich (high donor strength, e.g. anthracene, carbazole) and electron-deficient (high acceptor strength, e.g. benzothiadiazole, tetrazine) building units, donor-acceptor heterojunctions within the COF structure can be created. Jakowetz *et al.* applied elaborated transient absorption techniques to reveal that Donor-Acceptor (D-A) moieties in COFs enable a significant delocalization of excitons across the lattice, thus creating long lived charge carriers with lifetimes of up to tens or hundreds of microseconds.<sup>33</sup>

Several groups have employed the aforementioned strategies to improve the optoelectronic properties of COF-based photocatalysts. Lei and collaborators constructed a carbazole-triazine based donor-acceptor COF, with the carbazole moiety possessing excellent hole-transporting capabilities and the triazine moiety offering high electron drift mobility. The D-A heterojunction within the COF allowed for an efficient HOMO-LUMO separation facilitating the separation of photogenerated electron-hole pairs and promoting intramolecular charge transfer, Figure 1.6.<sup>74</sup> The so-called CT-COF converted CO<sub>2</sub> to CO at a rate of 102.7  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> and a selectivity of 98% without any additional sacrificial agent, using solely water. As the nitrogen atoms in the triazine ring contribute to both HOMO and LUMO, they are assigned to be the catalytically active centers. Additionally, the heteroatoms stabilize the negative charges effectively, thus prolonging the lifetime of photogenerated electrons. In 2018, Fu *et al.* reported two azine-based COF photocatalysts able to reduce CO<sub>2</sub> in aqueous medium without any photosensitizer or organic sacrificial donor. Both COFs exhibited improved photocatalytic activity in comparison with the well-known g-C<sub>3</sub>N<sub>4</sub> under similar experimental conditions, producing up to 13.7  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> of CH<sub>3</sub>OH.<sup>81</sup>



Figure 1.6. Proposed photoinduced electron transfer from the carbazole to the triazine moiety and the reaction pathway in the photoreduction of  $CO_2$  (PET = Photoinduced Electron Transfer). Reproduced with permission. <sup>74</sup> Copyright 2020, John Wiley and Sons.

An interesting study by Peng *et al.* aimed to rationalize the photocatalytic performance of pristine COFs towards CO<sub>2</sub> reduction as a function of different functional groups in the same host framework. The authors prepared ketoenamine-based COFs TpBD-X, in which  $X = -H_2$ , - (CH<sub>3</sub>)<sub>2</sub>, -(OCH<sub>3</sub>)<sub>2</sub> and -(NO<sub>2</sub>)<sub>2</sub>. The different COFs exhibit similar structural parameters and porosities. However, the electron-donating groups such as - (OCH<sub>3</sub>)<sub>2</sub> and - (CH<sub>3</sub>)<sub>2</sub> affect the light absorption and enhance the photogenerated charge carrier separation efficiency. Together with an increase of the conduction band energy (- 1.04 V vs NHE for TpBD-(OCH<sub>3</sub>)<sub>2</sub> against - 0.81 V for TpBD-H<sub>2</sub>), the authors concluded that the implementation of electron-donating

groups favors CO<sub>2</sub> reduction.<sup>82</sup> The effect of other functional groups on the performance of COF-based photocatalysts has been also reported elsewhere.<sup>83-85</sup>

#### 1.3.1.2 Linkage motifs

A compelling approach towards tuning and controlling the electronic interactions and optoelectronic properties within the COF is to vary the linkage motif which connects the monomers. These linkage motifs differ significantly in chemical stability, conjugation, and flexibility. The first linkage motif employed in a COF was the B-O bond, involving boronate esters and boroxine rings.<sup>3</sup> This linkage motif is moderately stable, yet prone to hydrolysis in acidic and basic conditions, exhibiting limited electronic coupling within the layer as it does not result in conjugated building blocks.<sup>86</sup> Considering charge transport in COFs with limited intralayer conjugation, charge carriers are expected to travel mainly along the stacking direction imposing limits on the charge carrier distribution required for efficient photocatalysis. Yet, the interlayer carrier mobility is generally limited, likely due to a lack of driving force for charge separation between the layers. The imine bond formation *via* the condensation of aldehyde and amine has been established to form highly crystalline COFs with higher chemical stability as well as a conjugation throughout the framework across the linkages.<sup>21, 32</sup>

The conjugation has a direct impact on absorption and optoelectronic properties, offering additional transport paths for charge carriers in the lateral direction. Although imine bonds are still sensitive towards hydrolysis, further stability can be built into COFs by employing a ketoenol tautomerism<sup>87</sup> or post-modifications of the imine bonds. <sup>88-90</sup>. A long-standing goal of the COF research community was reached in 2016 by the first report of a fully sp<sup>2</sup> carbonconjugated COF, employing the Knoevenagel or aldol condensation as C-C coupling reaction. <sup>29</sup> These sp<sup>2</sup>-C COFs with extraordinary chemical stability and extended  $\pi$ -conjugated framework usually yield a narrower band gap material with an improved light-harvesting capability. For example, Xiang *et al.* and Fu *et al.* synthesized sp<sup>2</sup>-C COF for CO<sub>2</sub>RR with high conjugation and crystallinity, which facilitated the long-range delocalization of electrons and improved the electron delivery to the catalytically active sites. Both COFs showed conversion rates of over 1000 µmol g<sup>-1</sup> h<sup>-1</sup> and selectivity towards CO of over 80%.<sup>91-92</sup>

#### **1.3.1.3** Interlayer interactions

The rational choice of building blocks does not only dictate the intrinsic optoelectronic properties but also the structuring ability, as the geometry of these monomers defines different lattices and pore structures. Figure 2a shows that in a 2D arrangement the units are stacked through  $\pi$ - $\pi$  interactions, with a spatial separation between the layers of usually about 3 to 5 Å.

The layered structure is an ideal pre-requisite for photo- and electrocatalysts as the columnar  $\pi$ -arrays enhance the light absorption and on the other hand form one-dimensional open channels with predesigned pathways to facilitate both charge carrier and mass transport. <sup>66, 93-94</sup> Er *et al.* conducted DFT calculations to analyse the electronic properties of a triphenylene donor – benzothiadiazole acceptor COF.<sup>95</sup> The authors studied the dependence of the band structure and carrier effective masses on the number of layers. The study revealed that the experimentally observed high conductivity in layered D-A COFs is a result of enhanced intralayer charge transfer promoted by strong interlayer interactions. The effective mass of charge carriers decreased along the vertical direction as the  $\pi$ - stacking is enhanced.

The very first study of COFs as electrocatalysts for the CO<sub>2</sub>RR showed that porphyrin columns integrated into the framework facilitate electron transport from the electrode to the catalytic site.<sup>65</sup> The Co(II) decorated COF-367-Co exhibited a 4.9-fold increased turnover number for the CO<sub>2</sub>-to-CO reduction than its monomeric counterpart Co(II) porphyrin, indicating that the  $\pi$ - $\pi$  stacking of the COF plays an integral role in the charge carrier separation and transport. However, separated 2D COF nanosheets have also shown significant CO<sub>2</sub> conversion into CO (see next section for details), indicating that intralayer bonding within COFs also contributes to efficient photocatalysis.<sup>96</sup>

Extending the networks into three-dimensional arrangements results in 3D COFs (Figure 1.7b). Only very few 3D COF-based photocatalysts have been reported in the literature, as the interpenetrated structure of 3D COFs often impedes the direct use of the backbones as catalytic centers, while the small pore size, usually in the micropore range, limits the scope of catalysts that can be integrated into the pore walls. <sup>61, 97-98</sup>



Figure 1.7. Schematic representation of 2D and 3D COF networks. (a) 2D COFs consist of 2D sheets in the x-y-plane, stacked through  $\pi$ - $\pi$  interactions in the z-direction. (b) In 3D COFs, the covalent bonds extend in all three spatial directions, often with *n*-fold intercalation.

#### **1.3.1.4** Crystallinity and porosity

High crystallinity and surface area are imperative for COF-based photocatalysts since such properties enhance the adsorption and diffusion of CO<sub>2</sub> and the as formed inherent channels make promising hosts for guest molecules. The highly porous nature of COFs also enables high throughput mass transfer and access to a high density of active sites. Several studies have demonstrated that a lack of periodically ordered COF structures leads to a significantly lower CO<sub>2</sub> conversion rate as it directly translates to a lower degree of accessibility of active sites and longer transportation distances of photogenerated charge carriers.<sup>74, 99-100</sup> The importance of the COF morphology was highlighted by Liu *et al.* who described ultrathin two-dimensional imine-based COFs with Co<sup>2+</sup> centers. The 2D COF nanosheets were able to promote CO evolution from aqueous CO<sub>2</sub> solution at a rate as high as 10162  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> and 78% selectivity, while the same photocatalyst as bulk material yielded only 124  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> of CO under the same experimental conditions.<sup>96</sup> The superior performance of the 2D-COF photocatalyst was attributed for the better CO<sub>2</sub> adsorption capacity, almost twice higher than that for the bulk material, as well as to the improved electron transfer properties since the active Co<sup>2+</sup> sites are not buried in contrast to the bulk photocatalyst.

High porosity and large surface areas are favorable for capturing CO<sub>2</sub> and for stabilizing active sites for the photocatalytic CO<sub>2</sub> reduction.<sup>73, 101</sup> Due to dipole-quadrupole interactions, nitrogen heteroatoms in the COF structure have a high affinity towards CO<sub>2</sub> molecules, thus enhancing the gas uptake as well as promoting the selectivity.<sup>102</sup> This aspect is a forefront advantage of COFs in comparison to inorganic semiconductors. Hence, N-rich building blocks (triazine,
pyridine, azine) are often employed in COF-based catalysts as well as imine bonds as a linkage motif.<sup>81, 99, 103-105</sup>

The Table 1.1 provides an overview of the relevant pristine COF-based photocatalysts for CO<sub>2</sub> reduction. It should be noted that most COFs exhibit surface areas higher than 500 m<sup>2</sup> g<sup>-1</sup>, values not easily reached for traditional metal oxide semiconductors. Most COFs that have been tested for CO<sub>2</sub>RR, are able to perform a two-electron reduction to CO<sub>2</sub>, yielding CO or HCOOH. Yet some groups report CO<sub>2</sub> reduction by four, six or eight electrons yielding formaldehyde, methanol or methane, respectively.

Table 1.1. Relevant examples of pristine COFs applied for CO<sub>2</sub> photoreduction.









<sup>a</sup>TEOA: triethanolamine; <sup>b</sup>co-catalyst; <sup>c</sup>photosensitizer; <sup>d</sup>gas-solid system

The application of pristine COF photocatalysts benefits from the high visible light-harvesting efficiency and high CO<sub>2</sub> adsorption capacity. However, COF as a single photocatalyst suffers from sluggish charge carrier separation and transfer to the adsorbed CO<sub>2</sub>, thus, the purposedirected design of COF-based hybrids embedding redox active molecules or nanoparticles is an attractive strategy to promote the photocatalytic efficiency. COFs with their high crystallinity and porosity are ideal templates for the incorporation of catalytically-active centers. Unlike other materials, these centers can be introduced into the framework with atomistic precision, allowing for a rigorous structural control of the heterogeneous catalysts.<sup>64, 110</sup> This unique feature not only enables the synthesis of novel, more powerful hybrid systems, but also opens up new pathways for a deeper understanding of the underlying photocatalytic mechanism. Hence, the combination of COFs with metal-based co-catalysts such as nanoparticles, complexes or metal oxides is being increasingly adopted to improve the performance of the COF-based photocatalysts. The synergistic effects of COFs combined with metal co-catalysts are discussed in the following section.

#### 1.3.2 COF-based hybrids

The previous section illustrated that pristine COFs with building units containing heteroatoms such as N, S, O can indeed serve as photocatalytic materials themselves. However, the fabrication of multicomponent COF-based hybrid systems is gaining scientific significance due to the synergistic effects between the different classes of materials.<sup>111</sup> The combination of COFs exhibiting high surface area, hierarchical porosity, high chemical stability and enhanced light-harvesting abilities with inorganic co-catalysts yields photocatalytic active hybrids with superior features relevant for applications in photo(electro)catalysis.<sup>64, 110</sup> As the detailed description of the synthetic procedures for COF-based organic-inorganic hybrid systems for the photocatalytic CO<sub>2</sub>RR was reviewed by Lu *et al.*, in the following sections we will focus on the features and performance of the corresponding hybrids.<sup>64</sup>

### 1.3.2.1 COF/Single metal sites hybrids

Metallic co-catalysts can be integrated into the COF structure using various approaches. A rather subtle path is the use of porphyrin-units as anchors for metal ions. Several studies have demonstrated that COFs containing metalated porphyrins have a much stronger photocurrent response than COFs with metal-free porphyrin rings, indicating a more efficient separation of photogenerated electron-hole pairs. <sup>72, 112-114</sup> Porphyrins are also promising alternatives to other complexing building units such as bipyridine or phenanthroline, owing to their strong chelating coordination ability towards metal ions. Implemented in COF photocatalysts, porphyrins can

stabilize the active metal centers more efficiently, avoiding metal leaching during CO<sub>2</sub> reduction and subsequent loss of activity.<sup>115</sup> Lu and co-workers reported a Zn-decorated porphyrin COF for the photocatalytic reduction of CO<sub>2</sub> to CO and simultaneous H<sub>2</sub>O oxidation to O<sub>2</sub>. A conversion rate of 12.33  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> was reached with a product selectivity of 100%.<sup>112</sup> Further examples are listed in Table 1.2.

Not only single metal ions but also molecular catalysts can be integrated into the COF structure *via* a coordination approach using functional groups such as bipyridine, anthraquinone, sulfone and others.<sup>85, 116</sup> Key examples of molecular catalysts involve Re(I) and Mn(II) tricarbonyl units, as well as Ni(II), Co(II), Fe(II) and Ru(II) complexes.<sup>91, 102, 105, 117-118</sup> Often, these molecular catalysts undergo detrimental side reactions in solution such as dimerization, triplet-triplet annihilation or other radical deactivation pathways, undermining their catalytic activity over the long term.<sup>119-120</sup> To overcome such problems, "heterogenization" or hybridization of the molecular catalysts onto suitable solid-state matrices has been proposed, significantly improving their stability and in some cases enhancing their activity as well.<sup>121-122</sup> Studies suggest that the introduction of metal complexes enhances the intramolecular charge transfer between the COF skeleton and the metal center and inhibits charge carrier recombination.<sup>91, 105, 116, 123</sup> Hence, the incorporation into COFs not only enhances the photocatalytic performance of the molecular catalysts but also prolongs their activity, combining two necessary aspects for the design of efficient photocatalysts for CO<sub>2</sub> reduction.

Yang *et al.* employed transient absorption spectroscopy and XPS to show the influence of Re(I) on the intramolecular charge transfer (ICT) in a COF photocatalyst.<sup>123</sup> Upon visible light excitation, an ICT state is formed with electrons being transferred from the COF moiety to the Re(I) center. The as-generated ICT state has a much longer lifetime in relation to the MLCT state of the pristine metal complex (171 ps *vs* 200 fs, respectively), allowing for more efficient quenching by the sacrificial donor TEOA to form a TEOA<sup>+</sup>-(COF-Re)<sup>-</sup> charge separation state. In the presence of CO<sub>2</sub>, the reduced (COF-Re)<sup>-</sup> species dissociates a Cl<sup>-</sup> ligand to yield CO<sub>2</sub> adducts as typically reported for Re(I) tricarbonyl molecular catalysts (Figure 1.8). The studied COF comprises bipyridine as complexing building block and yields CO under visible light irradiation with a rate of 750 µmol g<sup>-1</sup> h<sup>-1</sup> with 98% selectivity. Notably, the hybrid performance is 22 times higher than that for the homogeneous *fac*-[Re(CO)<sub>3</sub>(bpy)(Cl)] molecular catalyst under the same conditions. Another COF bearing Re(I) moieties was reported by Fu and collaborators.<sup>92</sup> The sp<sup>2</sup>-C linked Re-modified COF showed better charge separation and transfer than the pristine COF, producing CO at a rate of 1040 µmol g<sup>-1</sup> h<sup>-1</sup> with 81% selectivity

in acetonitrile/TEOA (30:1). Additional incorporation of Pt nanoparticles enabled the production of syngas, *i.e.*, the co-formation of  $H_2$  and CO.



Figure 1.8. Proposed photocatalytic mechanism for the CO<sub>2</sub> reduction to CO using the Re(I)-decorated COF. Adapted with permission.<sup>123</sup> Copyright 2018, American Chemical Society.

Beyond the incorporation of metal carbonyl complexes, COFs also allow for anchoring other molecular catalysts.<sup>91, 102, 106, 124</sup> Yang *et. al.*, for example, reported a 3,3',5,5'-tetraformyl-4,4'-biphenyldiol-COF (TFBD-COF) modified with a Co<sup>2+</sup> complex having salicylideneaniline (SA) as auxiliary ligand, Figure 1.9a.<sup>125</sup> TFBD-COF-Co-SA showed a CO<sub>2</sub>-to-CO reduction activity of 7400  $\mu$ mol g<sup>-1</sup> in 5 h and a 90% selectivity under visible light illumination in the presence of TEOA as sacrificial agent and [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> as photosensitizer. This COF-hybrid performed better than the pristine COF and the TFBD-COF-Co without the auxiliary ligand and showed similar activities as the homogeneous catalyst [Co(SA)<sub>2</sub>]. The TFBD-COF-Co-SA, however, was considerably more stable than the homogeneous analogue, which evidences the benefits of the heterogenization. The proposed mechanism for the system is shown in Figure 1.9b.



Figure 1.9. (a) Modified TFBD-Co-SA-COF and (b) proposed mechanism of the photocatalytic CO<sub>2</sub> reduction in the presence of TEOA as a hole scavenger. Adapted with permission.<sup>125</sup> Copyright 2021, American Chemical Society.

## 1.3.2.2 COF/metal nanoparticles (NP) hybrids

The use of metal nanoparticles as co-catalysts in photocatalytic systems is an effective approach to suppress recombination of charge carriers. Similar to homogeneous molecular catalysts, metal nanoparticles also suffer from unwanted physicochemical processes under photocatalytic conditions, most prominently aggregation, limiting their storage, processing and further use. <sup>126-128</sup> The spatially controlled incorporation of NP into COF templates promises beneficial synergistic effects, as the restricted space inside the pores of the highly ordered COFs prevents aggregation and promotes a homogeneous distribution of precious metals is drastically reduced when combined with COF templates, offering large surface areas and a high accessibility of the catalytic active centers. However, the nanoparticle loading should be monitored carefully, as an excessive amount of nanoparticles can block the pores of the COFs and shield the active sites during the photocatalytic reduction of CO<sub>2</sub>. In addition, the metallic islands can act as recombination centers for photogenerated charge carriers. <sup>129-130</sup>

In COF/metal nanoparticle hybrids, the generally established mechanism involves the band gap excitation of the COF, followed by electron transfer to the metallic co-catalyst where the  $CO_2$  reduction takes place, as exemplified in Figure 1.10.<sup>109</sup>



Figure 1.10. Schematic energy level diagram of a COF (TpPa-1) decorated with Ru nanoparticles for the conversion of CO<sub>2</sub> to formic acid. Adapted with permission.<sup>109</sup> Copyright 2021, Elsevier.

Similar to metal complexes, the incorporation of metal nanoparticles into COF pores can enhance the electron transfer and inhibit the recombination of photogenerated charge carriers. Key examples involve the incorporation of  $Ru^0$  or  $Pd^0$  nanoparticles, leading to the conversion of CO<sub>2</sub> to formic acid or CO, respectively, with traces of CH<sub>4</sub>. <sup>99, 109, 130-131</sup> An in-depth discussion of the product selectivity in COF-based photocatalysts is given at a later point in this review. Further examples involve the application of bimetallic clusters such as  $Pd_xIn_y@N3-$ COF composites reported by Huang *et al*. The bimetallic system is more efficient than those employing pristine Pd or In nanoparticles, which is attributed to the improved electron mobility in the clusters. Moreover, as CO<sub>2</sub> reduction and H<sub>2</sub>O oxidation occur simultaneously, the authors report the production of methanol and ethanol with a selectivity of 74 and 26%, respectively. <sup>132</sup>

#### 1.3.2.3 COF/metal oxide hybrids

An intriguing strategy to create new photocatalysts is the combination of traditional inorganic semiconductors and COFs to form powerful hybrid systems with improved photocatalytic activity and stability.<sup>133-134</sup> An organic-inorganic Z-scheme heterojunction for artificial photosynthesis was reported for the first time by Zhang *et al.*, who combined semiconductors able to oxidize water (TiO<sub>2</sub>, Bi<sub>2</sub>WO<sub>6</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) with CO<sub>2</sub>-reductive COFs (named as COF-316 and COF-318, respectively).<sup>84</sup> The highest CO production rate of 69.67 µmol g<sup>-1</sup> h<sup>-1</sup> was achieved by the hybrid system COF-318-TiO<sub>2</sub> in a gas-solid system using H<sub>2</sub>O as electron donor under simulated sunlight illumination ( $\lambda$ = 380-800 nm) in the absence of any additional sensitizer or co-catalyst. The CO production rate in this system was six times higher than that

of the individual components. The covalent coupling between the organic framework and the metal oxide semiconductor is crucial, enabling photogenerated electrons to be transferred efficiently to the organic moiety following the bandgap excitation of the metal oxide (Figure 1.11). Hence, photoexcited electrons and holes accumulate in the COF and the metal oxide, respectively, and are available for simultaneous CO<sub>2</sub> reduction and H<sub>2</sub>O oxidation.



Figure 1.11. Schematic illustration of the charge carrier transfer in COF-318-TiO2 under light illumination following the Z-scheme model. Adapted with permission.<sup>84</sup> Copyright 2020, John Wiley and Sons.

The importance of a covalent linkage between the inorganic semiconductor and the COF was highlighted by the work of Xu *et al.*<sup>135</sup> TiO<sub>2</sub> nanoparticles were functionalized with -NH<sub>2</sub> groups for subsequent condensation with -OH sites of the selected COF, resulting in a covalently bonded heterojunction, Figure 1.12. This heterojunction showed a 2.18 times higher photocatalytic activity than the non-covalently bound analogue, due to the improved charge carrier separation and migration. When  $Co^{2+}$  ions were added, the hybrid system TiO<sub>2</sub>@CTF-Py produced CO at a rate of 43.34 µmol g<sup>-1</sup> h<sup>-1</sup>, in aqueous solution and without the addition of photosensitizers or sacrificial electron donors, exceeding the rates of the pristine CTF-Py by 5 and that of TiO<sub>2</sub> by 7 times. The proposed CO<sub>2</sub> photoreduction mechanism involves a Z-scheme, where electrons tend to remain on the CTF-Py surface for CO<sub>2</sub> reduction and holes on the TiO<sub>2</sub> surface for water oxidation. Similar hybrid systems using TiO<sub>2</sub> as inorganic platform have been reported in the literature, showing similar CO generation rates under photocatalytic conditions analogous to the COF-hybrid systems described above.<sup>47, 136-139</sup>. In the Table 1.2, a summary of the photocatalytic activity of COF-based hybrids for CO<sub>2</sub> reduction is presented, including the aforementioned systems.



Figure 1.12. Synthesis route of the CTF-Py COF and the heterogeneous catalyst TiO<sub>2</sub>@CTF-Py. Reproduced with permission.<sup>135</sup> Copyright 2021, Elsevier.

Table 1.2. Relevant examples of COFs- based hybrids applied for the CO<sub>2</sub> photoreduction.

COF	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Conversion rate (µmol g <sup>-1</sup> h <sup>-1</sup> )	Main product (selectivity)	Sacrificial agent / solvent	Light source	Ref.
TFBD-COF-Co-SA	560.65	1480	CO (90%)	TEOA / CH3CN °	>420 nm	125
<i>δ</i> η σ <sup>κ</sup>						
	323	1040	CO (86%)	TEOA / CH3CN°	300 W (Xe) >420 nm	92
Re-Bpy-sp <sup>2</sup> c-COF						









<sup>b</sup>co-catalyst; <sup>c</sup>photosensitizer; <sup>d</sup>solid-gas system

#### 1.3.2.4 Control of product selectivity with COF-based hybrids

A high product selectivity is aimed for an efficient CO<sub>2</sub> photoreduction, favoring the generation of carbonaceous species over H<sub>2</sub> and the simultaneous control over the CO<sub>2</sub>-derived product. While the COF structure in heterogeneous COF/metal catalyst systems is key for light harvesting and charge carrier transport, the product selectivity is mainly controlled by the nature of the co-catalyst. Typically, when the metal centers act as  $\pi$ -donors to their respective ligands (*e.g.* Ni<sup>2+</sup> and Co<sup>2+</sup> complexes), CO is preferentially formed, while metal centers which act as  $\pi$  – acceptors lead to production of formic acid.<sup>115-116</sup> The conversion of CO<sub>2</sub> into alcohols is yet more challenging. Huang and collaborators developed a COF filled with bimetallic PdIn nanoparticles exhibiting dual active sites for the C-C bond coupling, hence, possessing great potential for the photosynthesis of the alcohols.<sup>132</sup> The synergistic effects between COF and nanoparticles facilitated the coupling of key intermediates and subsequent H-electron transfer.

The selective photoreduction of  $CO_2$  in competition with  $H_2$  is greatly dependent on the selective adsorption and activation of  $CO_2$  on the framework or, in the case of modified COFs, on the metal active sites and the special reaction microenvironment.<sup>85, 114</sup> Chen *et al.* conducted DFT calculations, revealing that the adsorption energy of  $CO_2$  on Ni single sites in the presence of polyimide PI-COF-TT was significantly lower than that of  $H_2O$ , Figure 1.13.<sup>102</sup> The authors have shown that the hydrogen bonding interactions between the H atoms of the COF structure and the  $CO_2$  molecules reduced the adsorption energy and, hence, promoted  $CO_2$  adsorption and further conversion.



Figure 1.13. (a) DFT-calculated adsorption energy of  $CO_2$  and  $H_2O$  on  $[Ni(bpy)_2]^0$  with and without PI-COF-TT (inset: activation of  $CO_2$  by  $[Ni(bpy)_2]$ ). (b) Proposed mechanism for the  $CO_2$  photoreduction over PI-COF-TT. Reproduced with permission.<sup>102</sup> Copyright 2020, Royal Society of Chemistry.

The sacrificial donor, often indispensable for photocatalytic reactions, has rarely been discussed, yet it exerts significant influence on the product selectivity. Among others, typical sacrificial donors for the photocatalytic CO<sub>2</sub> reduction are triethylamine, triethanolamine, and ascorbic acid. To date, the influence of sacrificial donors is not fully elucidated, as many parameters seem to play a role, such as the stability of the molecule under reaction conditions, the pH, the solvent mixture, and the concentration of the sacrificial donor. An interesting discussion about this topic is offered by Pellegrin and Odobel.<sup>140</sup> The polarity, dielectric constant, and metal bonding ability of different solvents and solvent mixtures can also have an effect on stabilizing specific intermediate products in the photocatalytic process, greatly influencing the product selectivity.<sup>116, 141</sup>

### **1.3.3** Perspectives and Challenges

The continuing efforts towards the understanding of the correlation between the photocatalyst's constitution and the fundamental steps involved in the  $CO_2$  photoreduction, namely, light absorption, internal and interfacial charge carrier dynamics,  $CO_2$  adsorption, and reaction with the photogenerated charge carriers have enabled the development of materials with enhanced conversion efficiencies and selectivity.

COFs offer well-ordered crystalline channels for structure-directed modifications with atomistic precision, large surface areas, and high synthetic tunability of structural and optoelectronic properties. These features enable the positioning of the light absorption units close to selected catalytic centers and can thus promote the CO<sub>2</sub> conversion. Moreover, the combination of electron rich and electron deficient linkers creates an internal driving force for efficient charge carrier separation. However, COFs still lack long-term stability under photocatalytic reaction conditions, and the synthesis of their linkers can increase the production costs. Further optimization in material design is therefore required to obtain up-scalable photocatalysts able to efficiently contribute to the mitigation of CO<sub>2</sub> emissions. In this context, the development of high-throughput synthesis and screening methods supported by robotic process automation is a promising approach for future COF-based materials development. In conclusion, the novel 2D and 3D COF materials constructed from diverse linkers and building units offer a high potential to become efficient photocatalysts for selective CO<sub>2</sub> reduction.

## 1.4 Covalent Organic Frameworks as CO<sub>2</sub> Electrocatalysts

In parallel with the development of novel photocatalysts for the conversion of CO<sub>2</sub> into valueadded chemicals (CO, HCOOH, CH<sub>3</sub>OH, CH<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>OH, C<sub>2</sub>H<sub>4</sub>, etc.), efficient and selective electrocatalysts are needed to significantly reduce CO<sub>2</sub> emission, thereby mitigating the humanmade climate change.<sup>142-145</sup> Unlike photocatalysis, which harnesses naturally abundant energy and electron sources such as sun and water, electrocatalysis relies on electrical energy to drive the conversion of CO<sub>2</sub>, ideally sourced from renewable energy systems.

The electrocatalytic  $CO_2$  reduction reaction ( $CO_2RR$ ) takes place at the interface between electrolyte and electrode, on which the active catalyst in employed. Various reduction products can be obtained, owing to the different numbers of transferred electrons and mechanistic pathways, making product selectivity an important challenge besides catalytic activity and stability.<sup>146-147</sup> The general cathodic reaction in  $CO_2RR$  can be described as

 $xCO_2 + nH^+ + ne^- \rightarrow \text{carbonaceous product} + yH_2O$ 

At low overpotentials, the competitive hydrogen evolution reaction (HER) occurs along with the CO<sub>2</sub>RR, presenting an additional challenge to achieving efficient CO<sub>2</sub> conversion.

$$2H^+ + 2e^- \rightarrow H_2$$
  $E^0 = 0$  V vs. RHE

Various materials classes have shown promising performance as CO<sub>2</sub> electrocatalyst, namely (carbon-supported) metal-oxides<sup>148-149</sup>, -nitrides<sup>150-151</sup> and -sulphides<sup>152</sup>, metal nanoparticles<sup>153-154</sup>, phthalocyanines<sup>155</sup> or graphene-based materials<sup>156</sup>. Despite significant progress in the field, challenges such as low efficiency and selectivity, as well as poor stability of the catalyst, mass transport limitations and insufficient CO<sub>2</sub> capture remain, often linked to limited structural and chemical tunability and low catalyst surface area.<sup>157-159</sup> Owing to their high structural tunability, allowing for the incorporation of various structures and functional groups, their ultra-high porosity and surface area offering access to active sites and their crystalline, periodic structure, enabling the introduction of metal-based catalysts with atomic-level precision, COFs have gained extensive attention as electrocatalysts for CO<sub>2</sub>RR, promising enhanced catalytic activity and stability.<sup>160-162</sup> However, conductivity, an essential property for the application as electrocatalyst, is not always easy to impart in these materials.<sup>147</sup> Therefore, COFs are often hybridized with other conductive materials like carbon nanotubes or graphene, enhancing the overall electrical conductivity.<sup>163-164</sup>

### 1.4.1 Performance parameters in electrocatalytic CO<sub>2</sub> reduction

To evaluate a catalyst's performance in electrocatalysis, parameters such as overpotential  $(\eta)$ , Faradaic Efficiency (FE), current density (j) and turnover number (TON) and turnover frequency (TOF) are used. Each parameter is briefly discussed in the following.

Overpotential (η): The difference between the actual applied potential E<sub>applied</sub> and the thermodynamic potential E<sub>thermodynamic</sub> for the studied reaction at a given current density. Lower overpotential for a specific reaction indicates lower activation resistance and thereby a higher activity of the catalyst.

$$\eta = E_{applied} - E_{thermodynamic}$$

• Faradaic Efficiency (FE): The percentage of electrons converted by the catalyst to the desired product. FE is a measure for the selectivity of a catalyst.<sup>165</sup>

$$FE(\%) = \frac{Q_{prod}}{Q_{total}} * 100$$

where  $Q_{prod}$  is the charge consumed for the generation of a particular product and  $Q_{total}$  is the total charge passed during electrocatalysis.

The FE can also be expressed as

$$FE(\%) = \frac{z * n * F}{Q_{total}} * 100$$

where *n* is the number of moles of product formed during the CO<sub>2</sub>RR, *z* is the number of  $e^{-}$  transferred per molecule of the product and *F* is the Faraday constant. For gaseous products, *n* is given by

$$n = \frac{P * V}{R * T}$$

where P and V are the pressure and volume of the gas, respectively, R the universal gas constant and T the temperature in Kelvin.

• Current density (*j*): The ratio of current *i* and the geometrical surface area *A* of the electrode. Higher current density at a given overpotential can indicate higher activity of the catalyst.

$$j = \frac{i}{A}$$

• Turnover number (TON): The TON is the total number of moles of product *n*<sub>product</sub> per mole of active sites *n*<sub>cat</sub> (which need to be identified) formed

$$TON = \frac{n_{product}}{n_{cat}}$$

Turnover frequency (TOF): The number of moles of product formed (or the number of moles consumed) per active site per unit time. Hence, it can be expressed as the TON divided by the total time *t<sub>total</sub>* passed. A higher TOF means a greater catalytic activity of the active catalytic sites in the catalyst.<sup>165</sup>

$$TOF = \frac{\# \text{ moles of formed product per unit time}}{\max. \# \text{ moles of active sites}} = \frac{TON}{t_{total}}$$

#### 1.4.2 Pristine COFs as metal-free catalysts for CO<sub>2</sub>RR

While numerous reports on metal-free COF-based catalysts for CO<sub>2</sub> photocatalysis exist (see Chapter 1.3.1), efficient CO<sub>2</sub> electroreduction is yet to be demonstrated using pristine COFs devoid of any metallic co-catalyst. To date, only COF-300-AR, an amine-linked 3D COF, was successfully applied as CO<sub>2</sub> electrocatalyst.<sup>166</sup> Deposited onto a flat silver electrode, the COF provoked an increase of faradaic efficiency (FE) from 13% to 53% and 43% to 80% under the potential of -0.70 V and -0.85 V vs. RHE alongside a simultaneous suppression of the HER from 80% to 22% and 60% to 9% when compared to the performance of the bare Ag electrode (Figure 1.14). However, when deposited onto another surface, e.g. a glassy carbon electrode, no CO<sub>2</sub> conversion was observed, indicating that the concerted interaction of COF-300-AR and the Ag electrode is essential for the reduction process.



Figure 1.14. (a) Illustration of the molecularly defined interface between COF-300-AR and the Ag electrode. Faradaic efficiencies for CO (b) and  $H_2$  (c) generation on the concerted electrode of COF-300-AR and Ag at various potentials. Bare Ag foil and Nafion solution were used as control. Error bars represent the FE from two independent measurements. Adapted with permission.<sup>166</sup> Copyright 2018 Elsevier.

The structurally similar Covalent Triazine Frameworks (CTFs), however, have recently made progress in the field.<sup>167-170</sup> Wang *et al.* reported on the synthesis of a perfluorinated CTF, FN-CTF-400, using tetrafluoroterephtalonitrile as precursor.<sup>167</sup> Notably, FN-CTF-400 is a highly

selective catalyst for the production of CH<sub>4</sub> as evidenced by a high FE<sub>CH4</sub> of 78.7% and a small FE<sub>H2</sub> of just below 15% at potentials between -0.4 and -0.6 V. An increase in potential to -0.7 to -0.9 V results in the FE<sub>CH4</sub> value reaching up to 99.3%. Further thermal treatment of FN-CTF-400 yielded as series of FN-CTF-*X*, where *X* describes the synthesis temperature. Interestingly, FN-CTF-700 and FN-CTF-900 tend to favour the conversion of CO<sub>2</sub> to CO rather than CH<sub>4</sub> and show a poor selectivity of CO over H<sub>2</sub>. The difference in product selectivity is explained by the difference in fluorine doping. FN-CTF-400 contains the highest amount of fluorine, while treatment with higher temperatures results in a continuous loss of fluorine. DFT calculations revealed that the fluorine doping regulates the activity of the catalytically active nitrogen sites, making them more favourable for methane production in FN-CTF-400.

### **1.4.3 Metal-containing COF electrocatalysts**

Metal co-catalysts can be readily introduced into the porous COF structure by a rational choice of the building blocks.<sup>171-173</sup> Porphyrin or phthalocyanine linkers can be used as anchors for metal ions, while linkers bearing heteroatoms (N, S, O) can act as pre-defined binding sites for molecular metallic catalysts. Several COF-based materials containing transition metals (e.g. Co, Mn, Ni, Cu) have been demonstrated as electrocatalysts for the CO<sub>2</sub>RR.

The first metal-bearing CO<sub>2</sub> electrocatalyst was introduced in a pioneering work by Lin *et al.* in 2015.<sup>65</sup> COF-366-Co was prepared by the imine condensation of 5,10,15,20-tetrakis(4-aminophenyl)porphinato]cobalt [Co(TAP)] with 1,4-benzenedicarboxaldehyde (BDA). Deposited onto a porous and conductive carbon fabric, COF-366-Co demonstrated electrocatalytic reduction of CO<sub>2</sub> to CO in neutral aqueous solution with a FE<sub>CO</sub> = 90% at – 0.67 V vs RHE. Within 24 h, 36 mL mg<sup>-1</sup> CO was produced. Replacing BDA with biphenyl-4,4'-dicarboxaldehyde (BPDA), forming COF-367-Co, resulted in an increase in pore size and channel width and a 2.2 times greater enhancement of the catalytic current at the identical potential. With a FE<sub>CO</sub> of 91%, more than 100 mL mg<sup>-1</sup> of CO were produced over the course of 24 h. The improved performance was rationalized by a higher CO<sub>2</sub> adsorption capacity and a higher exposure of electroactive sites to the reactants. Diluting the active sites with inactive copper porphyrin units resulted in bimetallic COF-367-Co (1%), which achieved a turnover number (TON) of 296 000 per electroactive cobalt site.

As mentioned earlier, poor conductivity is one of the main obstacles to overcome in COF electrocatalysis.<sup>147</sup> Implementation of donor-acceptor (D-A) building blocks is a possible way of overcoming this obstacle, creating a preferential electron transport pathway and thereby

enhancing the electron transfer efficiency.<sup>174-176</sup> Wu and co-workers synthesized Co-decorated porphyrin-based COFs containing the electron donors thieno[3,2-b]thiophene-2,5-dicarbaldehyde (TT) and tetrathiafulvalene (TTF), yielding TT-Por(Co)-COF and TTF-Por(Co)-COF, respectively.<sup>177-178</sup> Compared to COF-366-Co, the D-A COFs exhibit a 2 and 20-fold enhancement of conductivity and a 3- and 4-times greater carrier mobility, respectively. Improved electrocatalytic performance was corroborated by high  $FE_{CO} = 91.4$  % at -0.6 V vs. RHE and partial CO current density of 7.28 mA cm<sup>-2</sup> at -0.7 V vs. RHE in aqueous solution for the TT-COF and FE<sub>CO</sub> = 95 % at -0.7 V vs. RHE and a partial CO current density of 6.88 mA cm<sup>-1</sup> at – 0.9 V vs. RHE for the TTF-COF.

Grafting COFs onto conductive surfaces also demonstrated potential to significantly enhance conductivity.<sup>96, 179</sup> Dong and co-workers immobilized COF nanosheets onto carbon nanotubes by the solvothermal reaction of CHO-porphyrin, p-phenylenediamine and NH<sub>2</sub>-modified multi-walled carbon nanotubes (MWCNTs), as illustrated in Figure 1.15.<sup>179</sup> Subsequent treatment with metal salts in THF yielded MWCNT-Por-COF-*M*, where M = Co, Fe, Ni, Cu. The COF-MWCNT composite showed improved electrocatalytic activity and FE compared to the pure Por-COF-*M*. Notably, the Co-decorated composite showed the highest FE<sub>CO</sub> of up to 99.3% at -0.6 V, along with a current density of 18.77 mA cm<sup>-2</sup> and a turnover frequency (TOF) of 70.6 s<sup>-1</sup> at -1.0 V. The superior activity of MWCNT-Por-COF-Co is attributed to the more efficient electron transfer. Interestingly, MWCNT-Por-COF-Cu exhibits the highest FE for CH<sub>4</sub> production (71.2%), which is explained by the *in-situ* generation of Cu-based nanoclusters during the electrocatalytic CO<sub>2</sub>RR process.



Figure 1.15. Schematic representation of the synthetic process of the MWCNT-Por-COF-*M* composite materials, where M = Co, Ni, Fe, Cu). Adapted with permission.<sup>179</sup> Copyright 2022 Elsevier.

In the studies highlighted above, COFs functionalized with Co consistently demonstrate superior performance in CO<sub>2</sub> electrocatalysis. However, considering the scarcity of cobalt, catalysts based on earth-abundant metals such as Mn, Fe and Ni are being increasingly explored. Dubed-Bandomo and co-workers reported the first Mn-based COF,  $COF_{bpyMn}$ .<sup>180</sup> The bipyridine linker of  $COF_{bpy}$  acts as a pre-defined binding site for the [*fac*-Mn(CO)<sub>3</sub>Br] molecular catalyst. By immobilizing the molecular catalyst into the porous framework, the undesired formation of Mn<sup>0</sup>-Mn<sup>0</sup> dimers is suppressed, an intermediate unable to effectively reduce CO<sub>2</sub>. Extensive ATR-IR-SEC (attenuated-total-reflection infrared spectro-electrochemical) studies coupled with in-depth DFT calculations revealed that the COF structure mechanically constrains the Mn active sites, blocking the dimerization and resulting in reduced overpotential and enhanced electrocatalytic performance. The COF<sub>bpyMn</sub> exhibits high current densities of over 12 mA cm<sup>-2</sup> at an overpotential of 550 mV as well as good selectivity of CO over H<sub>2</sub> of 72%.

### 1.4.4 Challenges in CO<sub>2</sub> electrocatalysis using COFs

As illustrated above, COF-based electrocatalysts can show enhanced performance compared to molecular catalysts in both activity and selectivity. The porous structure of COFs facilitates the accessibility of active sites during catalysis and enhances  $CO_2$  adsorption, while the ease of modification of the COF structure by a rational choice of building blocks and linkage chemistry allows for the introduction of numerous functional groups and heteroatoms, thereby regulating

selectivity, stability and affinity to the reactants. The incorporation of metal sites with atomiclevel precision and the control over the microenvironment of the catalytic centres offers unprecedented opportunities to further improve COF catalyst design.

Despite the promising attributes of COF-based catalysts for electrocatalytic  $CO_2$  reduction, several challenges remain, impeding their practical application. The main challenges are the competition with the hydrogen evolution reaction (HER), the inherently low electrical conductivity of COFs, and their limited chemical and mechanical stability in harsh electrochemical environments, leading to compromised long-term performance. Furthermore, the scalability of the often tedious and costly COF synthesis represents another significant present obstacle to large-scale applications of these systems. Addressing these limitations as well as conducting further studies on the underlying mechanistic pathways will be important for advancing COF-based systems in  $CO_2$  electrocatalysis.

## **1.5** Scope of this Thesis

To design, develop and ultimately apply novel materials for energy conversion, a fundamental understanding of the processes governing their optical and electronic properties is essential. This thesis discusses key dynamic processes in covalent organic frameworks, ranging from understanding the diffusion of excited states to applying COF-based catalysts in photo- and electrochemical CO<sub>2</sub> conversion.

In the first project (Chapter 3), the excited-state dynamics in COF thin films were investigated, using spatiotemporal spectroscopy combined with theoretical calculations. The diffusion of photogenerated excitons was monitored and analysed with remote-detected time-resolved photoluminescence, revealing exceptionally high diffusion coefficients and exciton transport across COF grain boundaries. The study suggest that the observed diffusion coefficient arises from contributions of both incoherent *hopping* and coherent *band-like* transport, with the energy transport processes not only influenced by the building units but also significantly by the (dis)order in the molecular framework.

The second project (Chapter 4) involved the design of a novel COF-based hybrid photocatalyst for the conversion of CO<sub>2</sub>. Incorporation of the structure-directing dibenzochrysene (DBC) node allowed for the atomistic-level resolution of immobilized rhenium<sup>I</sup> centers in the highly crystalline and porous structure. The Re<sup>I</sup>-decorated DBC COF exhibited remarkable photocatalytic performance and enhanced stability, rivalling the operational lifetimes of leading COF-based CO<sub>2</sub> photocatalysts.

The final project (Chapter 5) focused on the electrochemical reduction of  $CO_2$  using a COFbased catalyst. Phenanthroline moieties in the COF enabled the immobilization of a homogeneous Mn<sup>I</sup> catalyst, preventing the formation of Mn<sup>0</sup>-Mn<sup>0</sup> dimers, which are detrimental to catalytic performance. The first demonstration of a hybrid COF-based catalyst as an electrode material in a catholyte-free membrane-electrode-assembly (MEA) cell showed enhanced catalytic activity and stability of the Mn-COF compared to its homogeneous counterpart, providing a valuable proof-of-concept for applying this class of materials in industry-relevant cell architectures.

Together, these projects contribute to a comprehensive understanding of selected dynamic processes in COFs and demonstrate their potential as advanced materials for energy conversion applications.

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# CHAPTER 2

Characterization Methods

### **2** Characterization Methods

#### 2.1 X-Ray Diffraction

X-ray diffraction (XRD) is one of the most common yet powerful techniques to study the structure of crystalline materials, providing useful information on lattice constants and geometry, crystallite size and orientation. The wavelength of X-ray radiation is in the same order of magnitude as the interatomic distances in the crystal lattice, allowing for monochromatic electromagnetic radiation to be elastically scattered and undergoing constructive and destructive interference. This phenomenon is described by Bragg's law (equation (2.1), with *n* defined as positive integer,  $\lambda$  as wavelength, *d* as interplanar distance and  $\theta$  as scattering angle between the incident X-rays and the lattice planes.<sup>1</sup>

$$n\lambda = 2d\sin\theta \tag{2.1}$$

When the Bragg condition is fulfilled, the constructive interference of the reflected X-rays is observed as reflections in a one-dimensional diffraction pattern (schematically shown in Figure 2.1).



Figure 2.1. Schematic illustration of constructive interference of X-rays in a crystalline material, where  $\theta$  defines the Bragg angle,  $\lambda$  the wavelength of the X-ray beam and  $d_{hkl}$  the distance between the crystalline planes *hkl*.

The size of the crystallite domains has a significant effect on the diffraction data. Smaller domains lead to a broadening of the reflections compared to larger domains. Based on the peak

broadening, given by the full width at half maximum (FWHM), the size of the crystallite domains can be estimated. The Scherrer equation<sup>2</sup> (2.2) gives the correlation of peak broadening and domain size *D*, where *k* is the form-dependent factor and  $\beta$  is the FWHM of the reflexes.

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{2.2}$$

The incident X-ray is commonly generated by heating a filament in a cathode ray tube, releasing electrons which are then accelerated towards an anode material to produce X-rays, and the X-rays are filtered to achieve monochromatic radiation. Common anode materials are Cu, Fe, Mo or Cr.

#### 2.1.1 Grazing Incidence Wide Angle X-Ray Scattering

Grazing Incidence Wide Angle X-Ray Scattering (GIWAXS) is a highly sensitive XRD technique to investigate the nanostructure of crystalline surfaces. Herein, the incident X-ray beam is kept at small incidence angles to the film surface, typically below  $\alpha_i < 1^\circ$  and close to the critical angle where total external reflection of the beam occurs. The geometry of this technique leads to an enhancement of the intensity of the scattering signal, making it highly suitable for the measurement of ultrathin films.

A two-dimensional detector is used to collect the scattered X-ray beams at angles  $\alpha_f$  and  $2\theta_f$ . These angles are then expressed as scattering vectors  $q_y$  and  $q_z$  in the 2D scattering image. The basic working principle is illustrated in Figure 2.2.



Figure 2.2. Schematic representation of the experimental GIWAXS setup with exemplary 2D diffraction data.  $k_i$  and  $k_f$  define the wavevector of the incident and diffracted X-ray beam, respectively.<sup>3</sup>

The 2D imaging technique allows for precise information on the domain orientation of the crystalline thin film sample. For uniform and parallel (perpendicular) oriented layers, the scattering image reveals discrete dots along the 0° (90°) azimuthal angle  $\chi$ . If orientation is not completely uniform, e.g. in oriented domains, the dots smear out until Debye-Scherrer-like rings are formed for completely random orientation of the crystallites.

#### 2.1.2 Rietveld Refinement

XRD patterns of powder samples are characterized by reflections at defined positions. The shape, intensity and position of these reflections encode information relating to the crystal structure of a material. Rietveld refinement employs a non-liner least squares method to fit a simulated line profile of a material, including structural and instrumental parameters, to its experimental powder XRD data. This method allows for a remarkably precise refinement of the crystal structure, providing details on crystallographic constants, among others the cell dimensions, crystallite sizes, atomic coordinates and bond lengths, lattice strain and vacancies in the structure.

#### 2.2 Gas Sorption

#### 2.2.1 Nitrogen Sorption

Gas sorption measurements are an analytical technique used to determine characteristic features of porous materials such as surface area, pore volume and pore size. The process of physisorption is fundamental to this method, describing the reversible binding of inert gas molecules, the *adsorptive*, to the sample surface, the *adsorbent*, *via* physical interactions such as van-der-Waals forces. Due to the reversible interactions of adsorptive and adsorbent, the adsorbed gas molecules, the *adsorbate*, are in a dynamic equilibrium with the adsorptive. Plotting the relative pressure of adsorptive  $p/p^0$  against the amount of adsorbed gas *n* at constant temperature and standard pressure leads to different types of sorption isotherms, classified by the IUPAC<sup>4</sup> and shown in Figure 2.3:



Figure 2.3. IUPAC classification of physisorption isotherms.<sup>4</sup>

Type I, or *Langmuir*-isotherm is typical for microporous materials. The steep onset at low  $p/p^0$  is due to the micropore filling which converges to a maximum, defined by the accessible micropore volume. Type I can be distinguished in Type I(a) for materials with narrow micropores (<~ 1 nm) and Type I(b) for materials with wider micropores and narrow mesopores (<~ 2.5 nm).

Type II isotherm shows the behavior of non-porous or macroporous materials. The first uptake is characteristic for monolayer formation followed by unrestricted multilayer adsorption at higher relative pressures. The transition from mono- to multilayer adsorption is indicated by point B.

Type III isotherm without a characteristic point B indicates a weak adsorptive-adsorbent interaction.

Type IV isotherm represents the typical sorption behavior of mesoporous materials. After monolayer coverage and multilayer adsorption, capillary condensation occurs leading to a saturation of the amount adsorbed by pore filling. Type IV isotherms can be distinguished in Type IV(a) for mesopores larger than 4 nm, where capillary condensation causes a hysteresis, and the fully reversible Type IV(b).

Type V isotherm for mesoporous materials resembles Type III with weak adsorptive-adsorbent interactions and a pore filling accompanied by hysteresis.

Type VI isotherm is reversible and characteristic for nonporous materials with a highly uniform surface. Each step corresponds to an adsorbed monolayer on the adsorbent.

The porosity of a material is responsible for its adsorption properties. Hence it is important to distinguish and classify pores of different sizes. According to IUPAC recommendations, pores with a diameter larger than 50 nm are classified as macropores, diameters between 50 and 2 nm are defined as mesopores, and diameters < 2 nm correspond to micropores.<sup>5</sup>

The Brunauer-Emmett-Teller (BET) method<sup>6</sup> is a standard tool for retrieving the surface area of porous materials from sorption isotherms. The BET model extends the *Langmuir* theory<sup>7</sup> which only considers the formation of a monolayer, by multilayer adsorption applying the following two assumptions:

- (a) The adsorption enthalpy of the first layer differs from the adsorption enthalpy of the following layers, whereby the following layers are considered equal in adsorption enthalpy.
- (b) No interactions within layers occur.

The BET equation is commonly applied in linear form (2.3)

$$\frac{p}{n(p^0 - p)} = \frac{1}{n_m C} + \frac{(C - 1)}{n_m C} \left(\frac{p}{p^0}\right)$$
(2.3)

where *n* is the amount of adsorbate at  $p/p^0$ ,  $n_m$  the monolayer capacity, *p* the equilibrium pressure,  $p^0$  the saturation pressure and *C* the BET constant.

A reliable value for the monolayer capacity  $n_m$  can be obtained from the linear part of the equation, which is typically restricted to values of  $0.05 \le p/p^0 \le 0.30$ . The total surface area  $a_s$  can be determined using equation (2.4)

$$a_s(BET) = n_m * N_A * \frac{\sigma_m}{m}$$
(2.4)

where  $N_A$  is the Avogadro constant,  $\sigma_m$  the molecular cross-section area and *m* the mass of the adsorbent. Typical adsorbents used for gas sorption analysis are N<sub>2</sub>, Ar or Kr.

#### 2.2.2 CO<sub>2</sub> Sorption

Unlike N<sub>2</sub> sorption, a typical method for analyzing structural properties of porous materials, CO<sub>2</sub> sorption measurements are usually conducted to determine the affinity of a material to the adsorptive as well as its storage capacity. CO<sub>2</sub> sorption is important in the field of CO<sub>2</sub> capture and storage and catalytic CO<sub>2</sub> reduction, as a high gas affinity is often crucial for good performance.<sup>8</sup> Prior to CO<sub>2</sub> sorption, materials are degassed thoroughly at elevated temperatures to ensure accessible pores. During the experiment, gas pressure is increased stepwise until reaching 1 bar (or more), while the adsorbed quantity of CO<sub>2</sub> is monitored as a function of the absolute pressure. Hysteresis often appears, indicating that the material desorbs less gas than in the adsorption process at the same pressure.

In addition to the adsorption isotherms, the isosteric heat of adsorption of the adsorbateadsorbent pair is often determined, providing valuable information on whether the adsorption process is exothermic or endothermic in nature. The application of the Clausius-Clapeyron equation<sup>9-10</sup> (2.5) yields values for the isosteric heat of adsorption. Measurements at two different temperatures, from which a single common adsorption quantity (amount of adsorbed  $CO_2$ ) is selected, are already sufficient for basic calculations, providing a single value for the heat of adsorption.<sup>11</sup>

$$\ln\frac{P_1}{P_2} = -\frac{\Delta H_{ads}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
(2.5)

where  $\Delta H_{ads}$  is the heat of adsorption, *R* the gas constant, *T* the adsorption temperature and *P* the pressure at which a defined quantity of gas is adsorbed.  $T_1$ ,  $P_1$  and  $T_2$ ,  $P_2$  correspond to the values for the higher and lower temperature, respectively.

#### 2.3 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) is a common technique to evaluate the thermal stability and thermally induced transformations of a material. The mass of a substance is monitored as a function of temperature or time while the sample is subjected to a temperature program in a controlled atmosphere. Temperature-dependent mass changes are observed as changes in the shape of the TGA profile and can be attributed to solvent evaporation, dehydration, combustion or decomposition of the specimen. Typically, samples are precisely weighed into a non-reactive crucible and heated under the desired atmosphere with a linear heating rate up to 900 °C, while mass changes over time are simultaneously monitored with a precision balance.

#### 2.4 Electron Microscopy

In classical microscopy, the spatial resolution is limited to about 200 nm, given by the Abbé limit<sup>12</sup> (equation (2.6). By using electrons with De Broglie wavelengths much smaller than those of visible photons (usually in the range of few picometers), electron microscopy (EM) circumvents the Abbé limit, enabling the investigation of micro- and nanostructured materials.

$$d = \frac{\lambda}{2NA} \tag{2.6}$$

In equation 2.6, NA refers to the numerical aperture and  $\lambda$  to the wavelength of light.

In high vacuum, an electron beam is generated using a field emission gun or a tungsten filament cathode. After passing through an array of electromagnetic lenses, the highly focused beam strikes the sample. The interaction of the incident electron beam with the atoms of the sample are fundamental to electron microscopy (Figure 2.4).



Figure 2.4. Interactions of electrons with matter and the corresponding electron microscopy techniques for their detection.

#### 2.4.1 Scanning Electron Microscopy

In Scanning Electron Microscopy (SEM), a convergent electron beam at low acceleration voltages, typically 1 - 30 kV, scans the sample surface in a grid pattern. Secondary electrons (SE) generated through inelastic scattering of the primary electrons (from the electron beam)

provide information on the surface structure as they originate within a few nanometers from the sample surface. The low energy SE can be detected using an Everhart-Thornley detector.<sup>13</sup> In contrast, backscattered electrons (BSE), primary electrons elastically scattered from the sample, disclose the chemical composition of a sample as the detected intensity increases with the atomic number of the sample's constituent atoms. BSE are high in energy and recorded with a semiconductor device. In SEM measurements, the brightness of each pixel on the computer screen corresponds to the detected intensity of the signal and therefore, by scanning the surface, an image of the sample morphology is acquired. Figure 2.5 shows a typical SEM setup in comparison to a Transmission Electron Microscope (TEM).

#### 2.4.2 Transmission Electron Microscopy

In Transmission Electron Microscopy (TEM), a high voltage electron beam (typically between 60 kV and 400 kV) is transmitted through a thin sample. TEM is a powerful characterization technique due to its high resolution in the sub-Ångstrom region and its ability to provide both image and diffraction information from a single sample. The information obtained from the sample is determined by the scattering processes experienced by the electrons when transmitting the sample. Elastic scattering gives rise to diffraction patterns while inelastic interactions of the primary electrons by the sample's electrons lead to a spatial variation in the intensity of the transmitted electrons, generating an image of the specimen. The detection mode in TEM (Diffraction vs. Imaging Mode) can easily be switched by changing the strength of the intermediate lens. Figure 2.5 illustrates a typical TEM setup in comparison to that of an SEM.



Figure 2.5. Schematic illustration of a TEM and an SEM setup, highlighting the main components of the two techniques.<sup>14</sup>

#### 2.4.3 Scanning Transmission Electron Microscopy

Combining the above techniques results in Scanning Transmission Electron Microscopy (STEM), where a focused incident beam scans across a specimen in a grid-like fashion, similar to SEM, while retaining the high resolution of TEM. An annulus-shaped detector records the transmitted and scattered electrons at high angles (high-angle annular dark-field detector, HAADF).<sup>15</sup> In HAADF STEM operation mode, the image contrast is mainly caused by mass contrast in the sample (*Z*-contrast).

## 2.5 Infrared Spectroscopy

Infrared (IR) spectroscopy is based on the excitation of molecular vibrations and rotations by electromagnetic radiation in the infrared, typically in the range of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. As the rotational degrees of freedom are mainly relevant in the gas phase, molecular rotations are not discussed in this chapter. Molecules with a permanent dipole moment or a changing dipole moment during the vibration process exhibit IR active molecular vibrations. Vibrations symmetric to the center of symmetry in a molecule possessing such center, are IR-inactive. The excited vibrations can be categorized in stretching and bending vibrations, and specified by their symmetry in symmetric, anti-symmetric and degenerate vibrations. The vibrational

frequency  $\tilde{\nu}$  depends on the atomic mass and bond strength(s) of the molecule (equation (2.7). Greater bond strengths and lower atomic masses result in higher vibrational frequencies, hence more energy is required to excite these vibrations.

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$
(2.7)

Here, k is the force constant for the bond,  $\mu$  is the reduced mass and c is the speed of light.

Many functional groups of organic molecules show characteristic vibrations corresponding to certain sections in the IR spectrum, making this method also suitable for identifying and distinguishing defined functional groups.

IR spectroscopy is based on the decrease in intensity of the transmitted IR radiation by molecules absorbing radiation to excite vibrations. Generally, Fourier-transform IR (FT-IR) spectroscopy is used, allowing for fast and accurate measurements.<sup>16</sup> In FT-IR, light is guided through a Michaelson interferometer onto the sample. The obtained "interferogram" is then processed using Fourier transformation, resulting in the sample's spectrum (light intensity as a function of wavenumber).

#### 2.6 Ultraviolet-Visible Spectroscopy

Ultraviolet-Visible (UV-Vis) spectroscopy is a common technique to characterize the light absorption and reflection of solid or liquid samples, based on the change of electronic configuration upon absorption of electromagnetic radiation. The sample is irradiated with light in a wavelength region between around 200 nm and 1200 nm, exciting electrons from the valence band to higher lying electronic states. Hereby, the absorbed photon energy corresponds to the energy difference between the ground and the excited state. Absorption is generally described by the Lambert-Beer law  $^{17}$  (2.8)

$$A(\lambda) = -\log_{10}\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = \varepsilon cl$$
(2.8)

Here,  $A(\lambda)$  defines the absorbance as a function of the wavelength  $\lambda$ ,  $I_0(\lambda)$  the intensity of the incident light,  $I(\lambda)$  the intensity of the transmitted light,  $\varepsilon$  the extinction coefficient, c the concentration of the absorbing species and l the thickness of the sample through which the light travels. Absorbance is measured using a white light source and scanning  $\lambda$  with a

monochromator while detecting  $I(\lambda)$ , or alternatively, using an array detector. The term  $\frac{I(\lambda)}{I_0(\lambda)}$  is also referred to as Transmission %*T*.

To approximate the band gap of a semiconducting material, a Tauc plot<sup>18</sup> is used, expressing the absorption coefficient  $\alpha$  as a function of photon energy  $h\nu$  (2.11). The absorption coefficient  $\alpha$  (or absolute absorption A) is obtained by converting the percentage absorbance %A (2.9)

$$A = -\log_{10}(1 - \% A) \tag{2.9}$$

which in turn is given by the following equation (2.10)

$$\% A + \% T + \% R = 1 \tag{2.10}$$

with %T and %R defining the share of incident light that is transmitted or reflected, respectively by the sample. As the Tauc method was initially developed for amorphous semiconductors, the resulting value for the bandgap is but an estimate.

$$(\alpha h\nu)^{1/\lambda} = B(h\nu - E_g) \begin{cases} \lambda = 0.5 & direct allowed \\ \lambda = 1.5 & direct forbidden \\ \lambda = 2.0 & indirect allowed \\ \lambda = 3.0 & indirect forbidden \end{cases}$$
(2.11)

where  $\alpha$  is the absorption coefficient,  $h\nu$  the photon energy, B is defined as a constant and  $\lambda$  as a value accounting for the specific type of transition. Extrapolation of the linear region to the abscissa ( $h\nu$ ) yields the energy of the optical band gap.

To study UV-Vis absorption of solid (powder) materials, the Kubelka-Munk equation<sup>19</sup> is applied, which describes the backscatter from a sample composed of an infinite number of infinitesimal layers, with a key impact of the ratio of absorption and backscatter on the diffuse reflectance R. The diffuse reflectance R of the compound is measured with barium sulfate serving as white standard reference. Using the Kubelka-Munk equation (2.12), the experimental data can be converted into a spectrum approximating the absorption behavior:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} < 1$$
(2.12)

where K and S are the absorption and back-scattered coefficient, respectively.

#### 2.7 Photoluminescence Spectroscopy

Photoluminescence (PL) describes the spontaneous emission of radiation by relaxation from an excited electronic state  $S_1$  to the ground state  $S_0$  after absorption of radiation with a particular

wavelength. The process of photon emission follows two central principles, namely Kasha's rule<sup>20</sup> and the Franck-Condon principle.<sup>21-22</sup> According to these principles, photon emission only occurs from the lowest excited state of a given multiplicity and an electronic transition is more likely to happen if the vibrational wave functions of the involved electronic energy levels overlap. Ultimately this results in the emitted photon being less energetic than the absorbed photon, causing the so-called Stokes shift.

The Jablonski<sup>23</sup> diagram (Figure 2.6) illustrates the possible transitions between ground state and excited state.



Figure 2.6. Jablonski diagram showing possible transitions between ground and excited state.<sup>24</sup>

When a photon of a particular energy is absorbed by a material, a singlet excited state  $S_n$  (n > 0) is created. Subsequently, vibrational or rotational relaxation to the lowest level of  $S_1$  occurs. The system can now either return to the ground state radiatively *via* fluorescence emission within a few nanoseconds or non-radiatively *via* one of the following processes: internal conversion (IC), collisional quenching (CQ) or intersystem crossing to a triplet excited state  $T_1$  (ISC), which lies at lower energies relative to  $S_1$ . From the triplet state, relaxation to the ground state can either occur *via* emission of a photon by phosphorescence or *via* deactivation through internal conversion. As a transition from  $T_1$  to  $S_0$  is formally spin-forbidden, triplet states are generally longer-lived than singlet states.

### 2.8 Time-Correlated Single Photon Counting

In contrast to steady-state PL spectroscopy, where the intensity of the emitted photons as a function of the wavelength is given, Time-Correlated Single Photon Counting (TCSPC) gathers

information on the time-resolved kinetics of the photoemission of the sample. This technique allows for the determination of the excited state fluorescence lifetime.

A pulsed laser with frequencies in the range of 100 kHz to 80 MHz excites the sample which in turn emits a single photon. A detector records the time between excitation of the sample and emission of the single photon, the so-called start-stop-time (Figure 2.7 a). This process is repeated multiple times to ensure sufficient information density. The highly repetitive registration of photons leads to histograms displaying the exponential decay of the fluorescence signal (Figure 2.7 b). Mono-, bi- or multi-exponential fitting of the decay yields the lifetimes of the emissive species.



Figure 2.7. Diagram illustrating the basic principle behind TCSPC. (a) The start-stop time between the pulse emitted by the laser and the detection of the photon is recorded. (b) Histogram of the number of detected photons as a function of time.<sup>25</sup>

#### 2.9 Cyclic Voltammetry

Cyclic voltammetry (CV) is an electrochemical method where the working electrode potential is linearly ramped, and the resulting current is measured. After a set potential is reached, the scanning direction is reversed until the starting potential is reached. The process can be repeated multiple times. Scanning an increase in (positive) potential is called anodic sweep, while a decrease is referred to as cathodic sweep. CV can deliver useful information on the electrochemical properties of the analyte (species of interest) that is either (i) dissolved in solution, or (ii) adsorbed onto the working electrode's surface.

CV measurements can help define the energy levels of molecules, e.g. the energy of the highest occupied molecular orbital (HOMO) can be extracted from the onset of the first redox peak of an anodic sweep. Together with data from UV-Vis spectroscopy and the bandgap determination using Tauc plot, the lowest unoccupied molecular orbital (LUMO) can then be calculated.

Commonly, a three-electrode setup used for CV measurements is comprised of a working electrode (WE), where the electrochemical process of interest occurs, a counter electrode (CE) and a reference electrode (RE) with a defined potential. The electrical connection between the electrodes is ensured by a liquid electrolyte.

## 2.10 Other characterization methods

The following methods are not discussed in this chapter, as they were carried out by collaborators. Detailed information on these methods can be found in the Supporting Information of the respective chapter.

- Remote-detected time-resolved photoluminescence (Chapter 3)
- Optical-pump terahertz-probe spectroscopy (Chapter 3)
- Density functional theory calculations (Chapter 3)
- Photocatalytic CO<sub>2</sub> reduction measurements (Chapter 4)
- Electrocatalytic CO<sub>2</sub> reduction measurements (Chapter 5)
- Gas chromatography (Chapters 4, 5)

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# CHAPTER 3

# Spatiotemporal Spectroscopy of Fast Excited-State Diffusion in 2D Covalent Organic Framework Thin Films

# 3 Spatiotemporal Spectroscopy of Fast Excited-State Diffusion in2D Covalent Organic Framework Thin Films

This chapter is based on the following publication by

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<sup>#</sup>L. Spies and A. Biewald contributed equally to the manuscript. L. Spies synthesized the COF thin films and performed structural, electronic and optical characterization. A. Biewald conducted and analyzed the RDTR-PL measurements. Together, L. Spies and A. Biewald interpreted the data, developed the diffusion model and drafted the manuscript.



# 3.1 Abstract

Covalent organic frameworks (COFs), crystalline and porous conjugated structures, are of great interest for sustainable energy applications. Organic building blocks in COFs with suitable electronic properties can feature strong optical ab-sorption, whereas the extended crystalline network can establish a band structure enabling long-range coherent transport. This peculiar combination of both molecular and solid-state materials properties makes COFs an interesting platform to study and ultimately utilize photoexcited charge carrier diffusion. Herein, we investigated the charge carrier diffusion in a two-dimensional COF thin film generated through condensation of the building blocks benzodithiophene-dialdehyde **BDT** and *N*,*N*,*N*',*N*'-tetra(4aminophenyl)benzene-1,4-diamine W. We visualized the spatiotemporal evolution of photogenerated excited states in the 2D WBDT COF thin film using remote-detected timeresolved PL measurements (RDTR PL). Combined with optical pump terahertz probe (OPTP) studies, we identified two diffusive species dominating the process at different time scales. Initially, short-lived free charge carriers diffuse almost temperature-independently before relaxing into bound states at a rate of 0.7 ps<sup>-1</sup>. Supported by theoretical simulations, these longlived bound states were identified as excitons. We directly accessed the lateral exciton diffusion within the oriented and crystalline film, revealing remarkably high diffusion coefficients of up to 4 cm<sup>2</sup> s<sup>-1</sup> (200 K) and diffusion lengths of several hundreds of nanometers and across grain boundaries. Temperature-dependent exciton transport analysis showed contributions from both incoherent hopping and coherent band-like transport. In the charge transport model developed based on these findings, we discuss the complex impact of order and disorder on carrier diffusion within the WBDT COF thin film.

# 3.2 Introduction

The diffusion of excitons is one of the most fundamental processes in semiconducting materials, characterizing their ability to transport energy.<sup>1-3</sup> Large diffusion coefficients D and long diffusion lengths  $L_D$  of excited states are crucial for applications in optoelectronic and photocatalytic devices.<sup>4-6</sup> In the quest for novel, more efficient photoactive materials, a longstanding goal has been to link the energy transport ability of a material to its molecular structure, thereby understanding the relationship between electronic properties and structural features.<sup>7,8</sup> Two-dimensional covalent organic frameworks (2D COFs) are an emerging class of highly ordered, crystalline porous materials built from organic molecules.<sup>9</sup> Due to their structural versatility, they allow for precise control over their optical and electronic features.<sup>10</sup> Through covalent linking of organic building blocks, an extended  $\pi$ -conjugation can be forged, leading to a delocalized electronic system throughout the crystalline and periodic framework, often imparting semiconducting properties to the 2D COF.<sup>11,12</sup> As a result, COFs have been successfully implemented into optoelectronic devices such as light-emitting diodes<sup>13,14</sup>, sensors<sup>15</sup> or photovoltaic devices<sup>16-18</sup> and used as photocatalysts<sup>19-21</sup>, e.g. for hydrogen evolution and CO<sub>2</sub> reduction. Due to the atomically precise structural control, COFs are highly interesting materials for studying structure-property relationships in photogenerated energy transport.<sup>22-27</sup> So far, excitonic processes in 2D COFs have been studied mostly in colloidal suspensions using transient absorption spectroscopy (TA)<sup>23,25,27</sup> or via optical pump terahertz probe spectroscopy (OPTP) on powder pellets and thin films.<sup>28–30</sup> Employing OPTP, effective charge carrier mobilities ranging from  $10^{-1} - 10^{0}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for bulk powders<sup>28,30,31</sup> to exceptionally high values of  $10^2 - 10^3$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for thin films<sup>29,32</sup> were determined, while TA studies reported diffusion coefficients in the range of  $10^{-5}$ - $10^{-2}$  cm<sup>2</sup> s<sup>-1</sup> and diffusion lengths of tens of nm for colloidal suspensions of 2D COFs.<sup>25,27</sup>

Commonly used techniques to study charge transport in semiconductors include photo<sup>33–36</sup>- and cathodoluminescence<sup>37</sup>, terahertz spectroscopy<sup>38,39</sup>, microwave conductivity<sup>40,41</sup> or Hall effect measurements<sup>42,43</sup>, generally coupled with band structure calculations. However, these methods typically only shed light on particular, often spatially limited aspects of the transport processes and do not provide a full picture of the macroscopic transport properties of emerging semiconducting materials, as these can be strongly affected by structural defects and disorder, interfaces between components, and particularly grain boundaries. Revealing the impact of structural inhomogeneities on energy transport phenomena is key to understanding and developing novel electronic and optoelectronic materials. In recent years, new optical methods

imaging the spatiotemporal evolution of photogenerated energy carriers have been developed, providing a more complete picture.<sup>44</sup> The three main spatiotemporal characterization techniques are time-resolved photoluminescence (TRPL),<sup>45</sup> transient scattering (TS)<sup>46</sup> and transient absorption (TA),<sup>47,48</sup> all of which are based on an incipient laser pulse triggering the formation of photogenerated energy carriers and the subsequent imaging of their spatial propagation as a function of time.

In this study, we employ a nondestructive remote-detected time-resolved photoluminescence (RDTR PL) technique to study the temperature-dependent charge carrier diffusion in 2D COF thin films. RDTR PL is a confocal microscopic technique enabling access to local processes occurring on the micrometer length scale. By directly measuring emitted light (PL), single photon detectors can be used, offering high sensitivity of the collected signal. RDTR PL has already been successfully employed to study large-crystal thin films of methylammonium lead iodide (MAPI), a semiconducting material commonly implemented as active layer in perovskite-based solar cells.<sup>45</sup> In the latter case, the extracted diffusion coefficient decreases with increasing temperature, providing crucial information on the dominant charge transport regime in this material. In semiconductors, a description of charge transport is commonly based on two paradigms: coherent *band-like* vs. incoherent *hopping* transport.<sup>49</sup> As seen in MAPI thin films, prevalent band-like transport results in a decrease of diffusion coefficient with an increase of temperature, whereas hopping transport shows the opposite trend as activation barriers are overcome at higher temperature. Given that COFs are fully organic, crystalline periodic polymers, both types of transport can be relevant for accurately describing the prevailing diffusion regime. The coexistence of band-like and hopping transport of charge carriers is observed in some organic semiconductors and organic crystals.<sup>50–52</sup> Furthermore, structural and electronic disorder in the system can have a significant and nonintuitive impact on the diffusion of charges or excitons in a semiconductor and must therefore be considered when interpreting experimental data and drafting a charge transport model.<sup>53,54</sup> A comprehensive study of the carrier diffusion and transport mechanisms in COF thin films is still lacking and the powerful RDTR PL technique has not yet been applied to this materials class. The imine-linked 2D COF thin films studied here comprise the organic building blocks benzodithiophene-dialdehyde **BDT** and *N*,*N*,*N*',*N*'-tetra(4-aminophenyl)benzene-1,4-diamine W. This WBDT COF, first published by our group in 2020, was chosen for this study because of its significant intrinsic conductivity  $(1.64 \times 10^{-3} \text{ S cm}^{-2})$  and its tendency to form highly crystalline thin films.<sup>55</sup> We use confocal microscopy to detect remote photoluminescence (RDTR PL), helping us to understand intrinsic properties of the radiative excited state energy transport in this material. We extracted an exceptionally high diffusion coefficient of 4 cm s<sup>-1</sup> (at 200 K) and diffusion lengths of several hundreds of nm for the lateral transport.

Through thorough analysis of the RDTR PL data in combination with theoretical simulations and optical-pump terahertz probe (OPTP) spectroscopy, we elucidate the diffusion mechanism in **WBDT** thin films involving excitons as the majority energy carriers. For the first time, the use of RDTR PL provides direct access to large-scale diffusion in 2D COFs, allowing for a correlation of the excited state dynamics to the features of the highly crystalline 2D network. Efficient long-range exciton transport can be observed in this **WBDT** COF thin film, with *D* and  $L_D$  values exceeding those of other COFs and organic semiconducting materials by several orders of magnitude.<sup>1,25,27</sup>

# 3.3 Results

In this study, we combine advanced spectroscopic techniques with in-depth theoretical investigations to understand the diffusion dynamics in 2D COF thin films comprised of **BDT** and **W**. Thin films of this fully conjugated COF are highly crystalline and porous, with a Kagomé-like pore structure introduced by the tetra-functionalized **W** node. Both **W** and **BDT** are electron-rich molecules with the former being the more dominant  $\pi$ -donor.



Figure 3.1. (a) Chemical structure of the two molecular building blocks **W** and **BDT** together with the top view onto a 2×2 supercell, illustrating the Kagomé-like pore structure of the **WBDT** COF. (b) GIWAXS pattern of the **WBDT** thin film on glass with the corresponding *hkl* indices for *in-plane* (100, 110, 200, 210, 300, 220) and *out-of-plane* reflexes (001). (c) SEM top view of the thin film surface. (d) TEM image of the thin film, confirming the preferential crystal orientation within the grains. (d) Normalized steady-state PL and UV-vis absorption spectra of the **WBDT** thin film.

The COF was synthesized according to the literature<sup>55</sup> under solvothermal conditions *via* the acid-catalyzed imine condensation of **W** and **BDT** (Figure 3.1a). Thin films were grown on glass or quartz substrates under similar solvothermal conditions as for the bulk material (see Section **S3** for characterization of the bulk material). The 100, 110, 200, 210, 300, 220 and 001 reflections of the COF crystal lattice are clearly visible in the GIWAXS pattern in Figure 3.1b and appear at identical scattering vectors in the PXRD pattern of the bulk material (Figure S3.1). The intensity of the *hkl* reflections is concentrated in the  $q_v$  direction, indicating a predominant

orientation of the *a-b* plane of the 2D COF sheets parallel to the substrate with the pores extending vertically from the substrate. Scanning electron micrographs in Figure 3.1c show a dense and uniformly covered thin film with grains of 100 - 200 nm in size and a thickness of  $\sim$ 120 nm, which is further confirmed by atomic force microscopy (AFM) (Figure S3.7). TEM images (Figure 3.1d) confirm the preferential parallel orientation of the COF within the grains. The absence of a defined crystal structure at the grain boundaries implies a disordered character in this region.

Steady-state UV-vis absorption and photoluminescence (PL) spectra are shown in Figure 3.1e. The bright red COF thin film exhibits a maximum absorption at 2.51 eV (494 nm) and an emission peak at 1.78 eV (697 nm) with a full width at half maximum (fwhm) of 0.35 eV. Fitting of the absorption onset using a Tauc plot gives a direct band gap of 2.1 eV (Figure S3.6a). Confocal scanning and hyperspectral imaging of a  $10 \times 10 \ \mu\text{m}^2$  section show negligible changes in the normalized intensity, central energy, and spectral width of the PL signal, confirming the homogeneity of the spectral response from the thin film (Figure S3.9).



Figure 3.2. Projected band structure of **WBDT**. Projection on the **W**-based atomic orbitals in red and **BDT** atomic orbitals in blue, calculated using the PBE functional and empirical scissors shift<sup>56</sup> of +0.49 eV to estimate the band gap at Hybrid-DFT (HSE06) level (see Section S8 for more details). Darker colors indicate higher weight of states in certain bands on the fragment's atomic orbitals. The distance between  $\Gamma$  and A points has been scaled by 0.2 for illustration purpose.

The calculated band structure of **WBDT** is shown in Figure 3.2. Both the valence and conduction bands exhibit triplet arrangements, typical of structures based on the Kagomé lattice. **WBDT** displays moderate *in-plane* and strong *out-of-plane* band dispersions, which is

highest for the valence bands. A Dirac cone is only 0.1 eV away from the top of the valence band. The projection of the states on the atoms of W and **BDT** indicates that the frontier electronic levels in the valence band are primarily formed by the atomic orbitals of W. The lowest unoccupied bands show a balanced contribution from the atomic orbitals of both fragments.

**Time-Resolved Measurements.** In this work, we employ a spatiotemporal characterization technique termed remote detected time-resolved photoluminescence (RDTR PL). This method allows for fully contactless access to intrinsic diffusive transport characteristics of crystalline thin film samples. Herein, a confocal microscope is used for the time-resolved PL measurements, enabling access to the micrometer length scale. The detection segment of the microscope comprises a spectrometer and time-correlated single photon counting (TCSPC) electronics for the temporal resolution. For the spatial resolution, a tiltable mirror is implemented in the back focal plane of the detection part, allowing for scanning around the fixed confocal spot. The aperture of the microscope is defined by the chip of an avalanche photo diode (APD), which, used as a single photon detector, is overfilled by the light emitted from the confocal spot. The studied material is excited with a pulsed laser (510 nm), triggering the formation and subsequent diffusion of photoexcited states from the confocal excitation spot to a remote position, where they recombine while emitting a photon. A timestamp is assigned to each of the detected photons, creating a transient. A schematic representation of the methodology is depicted in Figure 3.3a.

In the transients obtained *via* RDTR PL, lateral broadening of the confocal PL spot can be observed (Figure 3.3b). This broadening is caused by two-dimensional diffusion of the excited states in the film. While diffusion in the third dimension (*z*-direction) is likely to be present, it cannot be accessed through RDTR PL. Since the Rayleigh length of the excitation laser is longer than the thickness of the film, the thin film is excited across its entire thickness at the laser spot (Section S5). Therefore, the diffusion extracted from this RDTR PL measurement can be treated as a two-dimensional process. To analyze the spatial broadening of the RDTR PL signal and to determine the temperature-dependent diffusion coefficient D(T), two different methods were used: In method I, a Gaussian peak function is fitted to the RDTR PL data for each time step resulting in the time dependent spatial broadening  $\sigma(t)$ . As a result of the analyzed spatial broadening  $\sigma(t)$  of the confocal PL spot, the diffusion coefficient *D* can be extracted *via* the following relation:

$$\sigma(t) = \sqrt{2Dt}$$



Figure 3.3. (a) Scheme of the remote-detected time-resolved photoluminescence measurement technique. The pulsed laser (yellow) excites the sample at the confocal spot. Photoluminescence emitted from the confocal spot as well as at remote distances from the confocal spot can be detected (red). The temporal resolution is realized *via* TCSPC. (b) RDTR-PL data at 5K. PL intensity as a function of time (y-axis) and distance (x-axis) from the excitation spot. (c) Temperature independent diffusion coefficient of the free charge carriers (*fast species*) during the first picoseconds after excitation. (d) Exciton (*slow species*) diffusion coefficient as a function of the temperature. For data set 1 and 2, the diffusion coefficient is determined for the blue side of the PL spectrum and for the whole spectrum, respectively.

Alternatively, in method II the complete time-dependent data set (Figure 3.3b) is fitted using the analytical solution to the 2D diffusion problem to determine *D* (see Section S5 for details on the analysis and fitting). Due to the finite width of the excitation focus, a Gaussian distribution is assumed as initial condition for both methods. Also, a Gaussian peak function is added with time-independent width attributed to an immobile species in both cases (Figures S3.11 and S3.12). All measurements were analyzed using both methods for cross-verification and resulted in the same values for the diffusion coefficients within the experimental error (Section **S5**). RDTR PL data were collected stepwise across a temperature range from 5 to 300 K.

From the RDTR PL measurements of the **WBDT** film, two diffusion processes at different time scales can be distinguished, visible as two different slopes in the spatial broadening. In the first picoseconds, still within the rise of the PL signal, a fast transport process is observed with a diffusion coefficient  $D \sim 10 \text{ cm}^2/\text{s}$  in Figure 3.3c (termed *fast species*). On the longer nanosecond time scale, a slower temperature-dependent diffusion is detected (Figure 3.3d) with significantly lower diffusion coefficients (termed *slow species*). Together with the immobile

contribution used in the analysis of the RDTR PL data, the slow and the fast species, at least three different species need to be considered in a comprehensive model description of the excited state dynamics in the studied **WBDT** film.

**Immobile Species**: In general, immobile species can result from defect or disorder-related trap states. Remarkably, the steady-state PL spectrum of the **WBDT** film shows no significant narrowing of the PL band for lower temperatures (Figure S3.6b). This indicates the presence of such lower lying trap states,<sup>54</sup> which would dominate the red side of the PL spectrum. Indeed, when limiting the detection range to the red side of the PL spectrum, no significant spatial broadening of the PL spot in the RDTR PL measurements is observed. In contrast, spatial broadening indicative of excited state diffusion of a *mobile species* can be clearly seen while detecting the blue side of the RDTR PL spectrum (2.03 - 2.10 eV, data set 1 in Figure 3.3c, d). Detecting the whole spectrum (1.25 – 2.20 eV, data set 2 in Figure 3.3c, d) results in the same diffusion coefficient but with a larger fraction of the immobile contribution (0.3 *vs.* 0.2, respectively).

Free Charge Carriers in WBDT COF: To identify the highly diffusive (fast) species observed above (Figure 3.3c) optical pump terahertz probe (OPTP) measurements on the picosecond time scale were conducted. Figure 3.4 shows a fluence-independent transient THz signal rising within the first 250 fs upon above band gap excitation (3.1 eV) at three different fluences (100, 80, 60 µJ cm<sup>-2</sup>). We note that an analogous response has been reported for different types of COFs,<sup>28,30</sup> and can be safely attributed to the presence of free charge carriers in the COF film. Here, OPTP measurements cannot exclude the simultaneous formation of bound exciton states which would give rise to resonances outside of our THz probing range (0.5-2.5 THz) because of the high exciton binding energies in COFs.<sup>57</sup> From the initial value of the photoconductivity right after excitation, the effective mobility  $\mu$  of the free ambipolar charge carriers is extracted as  $\varphi \mu \sim 0.12 \pm 0.05 \ cm^2 V^{-1} s^{-1}$ , containing the photon-to-free-charge branching ratio  $\varphi$ . The measured photoconductivity signal decays by ~ 90% of its initial value with a rate of  $k_1$  ~ 0.7 ps<sup>-1</sup>, thus indicating a minimal remaining fraction of free charge carriers, which subsequently decay more slowly ( $k_2 \sim 0.05 \text{ ps}^{-1}$ ). We interpret the initial decay as a rapid formation of bound exciton states, whose resonance either lies outside the probing window and / or shows significantly lower mobility. The slower decay of the residual photoconductivity component indicates the presence of alternative decay channels for the surviving free chargecarrier population, such as trapping or bi-molecular recombination.



Figure 3.4. Optical pump terahertz probe measurements. THz photoconductivity transients of **WBDT** COF thin film, measured following a 3.1 eV excitation pulse, for three different excitation fluences  $(100, 80, 60 \,\mu\text{J/cm}^2)$ . For clarity, transients measured at different fluences are vertically shifted and the measurement zero is indicated by the dashed line. Solid lines correspond to a biexponential fit to the experimental data.

The formation of bound electron-hole pairs as the main species dominating **WBDT** COF's photophysics is further supported by the RDTR PL data, which show significantly longer-lived excited states with lifetimes ranging from ~0.9 to 1.2 ns (Figure S3.13).

Consequently, the initial local broadening of the excitation spot within the first picosecond in the RDTR PL measurements is very likely caused by the diffusion of free charge carriers. Both OPTP and RDTR PL data show that on a fast picosecond timescale, a highly mobile species occurs that rapidly relaxes into bound excitons with lower mobility.

**Exciton Diffusion in WBDT COF:** Exciton (*slow species*) diffusion within the COF thin film is detected by RDTR PL measurements over the nanosecond time scale (Figure 3.3d). To understand and describe the diffusive transport of the excitons, theoretical DFT-based calculations were carried out. Since complete excited state calculations of periodic COF structures are computationally extremely demanding, we opted for a hybrid approach that considers the essential ingredients while being computationally feasible. As illustrated in Figure 3.5, the COF unit cell was disassembled into molecular fragments, six **BDT** and three **W** fragments, respectively. The **W** fragments were H-terminated, while the **BDT** fragments included the imine bonds at the peripheral positions. Time dependent DFT (TDDFT)

calculations of the BDT and W fragments were carried out, including the lowest excitons (at least five per molecule), and provided both localized and delocalized transition densities with variable dipole characteristics of the excited states. The calculated transition dipole moments of **BDT** and **W** fragments have a dominating *in-plane* dipole orientation with moderately large oscillator strengths and asymmetric transition densities (see Section S8 for details on the theoretical calculations). Subsequent resubstitution of the calculated excited states back into the COF structure at the respective fragment position allows for the simulation of exciton interactions between all fragments. These interactions based on the transition charges are dominated by mutually neighboring pairs, leading to an energy dispersion in the COF lattice. The *in-plane* distance between excitons is much larger than the *out-of-plane* distance (51 Å vs. 4 Å), therefore the exciton coupling, although present in the x-y plane, is larger in the zdirection. For the diffusion coefficient, this anisotropy is partially compensated by the geometry prefactor, *i.e.* the lattice constant, which is larger *in-plane*, enabling the diffusive transport in different directions. The different contributions from both BDT and W molecules in some of the excited states may well result in a superposition of molecularly localized and partially delocalized states. RDTR PL data confirm the mixing of localized (immobile species) and delocalized states as for every time step, the diffusion signal consists of a static component with a constant width and a diffusive component with an increasing spatial width  $\sigma(t)$  (Figure 3.3b, S3.11 and S3.13).



Figure 3.5. Schematic representation of the hybrid exciton approach: the COF unit cell is divided into molecular fragments of the building blocks **W** and **BDT** (3 and 6 fragments per unit cell, respectively). The transition charges and exciton couplings of these molecular fragments are calculated and the exciton states are placed at the respective positions within the unit cell (red dots indicate centers of mass of **W**, blue diamonds indicate the centers of mass of **BDT**) to carry out exciton interaction and dispersion simulations *in-plane* and *out-of-plane*.

The overall largest calculated exciton coupling adds up to a moderate value of  $\varepsilon \approx 50$  meV. This energy is significantly smaller than most molecular relaxation energies, which suggests that excitons couple more strongly to vibrational modes of the crystal lattice, making them polaronic excitons. We hypothesize that the COF lattice can be deformed in the area surrounding the exciton. The diffusion of the excitons along the 2D COF layers (*in-plane*) is observed in the RDTR PL measurements while the diffusion in *z*-direction across the COF layers will likely be present but cannot be accessed through RDTR PL and is limited by the thickness of the film (~ 120 nm, Figure S3.7).

#### 3.4 Discussion of the Temperature-Dependent Diffusive Transport

The temperature dependence of the exciton diffusion coefficient contains information on the underlying transport processes in semiconducting materials.<sup>45</sup> Exciton transport in highly ordered, crystalline inorganic semiconductors is typically described as coherent band-like transport, where excitons are scattered by phonons and defects.<sup>58,59</sup> For organic polymers, incoherent hopping transport is commonly observed, where excited states hop from one electronically favorable state to another, which is described by a hopping rate.<sup>2,58,59</sup> Band-like transport is accelerated with decreasing temperature due to reduced phonon scattering while for thermally activated *hopping* transport, the opposite trend is observed. Due to their highly ordered crystalline structure made from molecular building blocks and a delocalized electronic system, COFs can often be described as organic semiconductors, where a combination of both transport phenomena is possible.<sup>11,50,51</sup> As discussed above, the free charge carriers, dominating the dynamics in the first few picoseconds, diffuse almost temperature-independently with  $D \sim$  $10 \text{ cm}^2 \text{ s}^{-1}$ . Due to above-band-gap excitation and a laser pulse duration of  $\leq 1 \text{ ps}$ , the free charge carriers contain excess energy and are thus not in thermal equilibrium with the surrounding environment. With the extracted lifetime  $\tau = 1.4$  ps from the OPTP measurements, free carriers appear to be converted into bound states before temperature dependent phonon scattering can effectively limit transport. The diffusion length  $L_D$  of the free carriers can be estimated using values from the two independent measurements: the lifetime extracted from OPTP and the diffusion coefficient from RDTR PL (see Section S7 in SI for details).<sup>60</sup> A value of  $L_D = \sqrt{2D\tau} \approx$ 50 nm corresponds roughly to the grain size of the WBDT film (Figure 3.1c), which suggests that the carriers can propagate within grains without scattering at grain boundaries.

The combination of the observed and analyzed data supports the hypothesis that the mobile free charge carriers relax into a diffusive exciton state within the first picoseconds (Figure 3.3b and 4) While the initial transient relaxation phase (free charge carriers) is not in the focus of the simulations, diffusion is considered here for the subsequent phase (diffusive excitons). For calculated values of the exciton coupling of  $\varepsilon \cong 50$  meV and an estimated reduced reorganization energy of  $\Lambda \cong 0.1$  eV,<sup>61</sup> a combination of *band-like* and *hopping* transport in the **WBDT** COF thin film can be expected.<sup>50</sup> This suggests a rather flat or a nonmonotonous temperature-dependence of the diffusivity. Also, in this crossover regime *band-like* and *hopping* diffusivities are likely to be comparable in magnitude. Therefore, we apply the simpler *hopping* ansatz for calculations at room temperature (290 K),<sup>62</sup> A diffusion coefficient of
$D = 0.2 \text{ cm}^2 \text{ s}^{-1}$  is estimated for the exciton diffusion, which is in good agreement with the experimentally derived range of 0.2 to 0.4 cm<sup>2</sup> s<sup>-1</sup> at room temperature (Figure 3.3d).

Considering the theoretical model, we tentatively assert that the experimentally observed exciton diffusion coefficient results from a combination of both incoherent (phonon-assisted) hopping and coherent band-like contributions. Disorder can lead to a complex interplay of these mechanisms, resulting in a nonintuitive temperature dependence, as observed in organic crystals.<sup>53</sup> Figure 3.3d shows that, when the temperature decreases below 300 K, the diffusion coefficient D increases until it reaches a maximum value of 4 cm<sup>2</sup> s<sup>-1</sup> at approximately 200 K. This suggests that carrier-phonon scattering dominates the temperature dependence of D in this regime, where scattering is enhanced with temperature. This results in a gradual suppression of coherent transport at high temperatures (around room temperature) and an increasing dominance of phonon-assisted incoherent over coherent transport, justifying the use of the hopping model for room temperature calculations. As the temperature lowers, we propose that the transport-relevant phonons start freezing out at 200 K. Consequently, for temperatures below 200 K, an increase in the diffusion coefficient with cooling would be expected for a band regime. However, the opposite is observed, with a gradual decay to  $2 \text{ cm}^2 \text{ s}^{-1}$  at the lowest measured temperatures. We propose that the disorder in the COF crystal lattice (including grain boundaries and disorder in the grains) significantly impacts exciton transport at low temperatures, thereby impeding further acceleration of diffusion. Given that incoherent transport is strongly thermally driven, it is suppressed at low temperatures, and we expect the observed diffusion at low temperatures to be mainly coherent and limited by disorder. The remarkably large values observed here suggest the relevance of the third transport direction in the diffusion process, which helps to suppress possible weak/strong localization effects typically seen in lower-dimensional systems. Such lower-dimensional systems are prone to localization, often leading to significantly reduced mobilities in particular at low temperatures which are not observed here.

A schematic model illustrating the excited state diffusion in the **WBDT** COF thin film summarizing the discussion above is shown in Figure 3.6. Free charge carriers with a diffusion length of ~ 50 nm are created within the first picoseconds after excitation and quickly relax into excitons at a rate of  $k_1 \sim 0.7$  ps<sup>-1</sup> (lifetime of 1.4 ps). The excitons with longer lifetimes of up to 1.2 ns are diffusive over several grains ( $L_D = 200 - 800$  nm, Figure S3.14), implying that the excitons in **WBDT** thin films can traverse grain boundaries. In addition to the mobile diffusive species, a nonmobile contribution arising from localized states is visible in the RDTR PL data. Since RDTR PL measures diffusion over several grains, impurities like defect states, or grain boundaries as well as lattice disorder will all affect the experimentally observed transport behavior. We note that the strongly preferential orientation of the COF layers parallel to the substrate throughout the whole thin film is crucial for efficient lateral diffusion of excitons. In other words, the *z*-axis of each grain is perpendicular to the substrate's plane. To further elucidate this point, we grew WBDT thin films with random crystallite orientation (see Section **S6** in SI for details), where the angle between *z*-axis and substrate plane varies for every grain. RDTR PL measurements in those films show substantially reduced exciton diffusion coefficients that decrease with decreasing temperature (Figure S3.20). This change in the diffusion characteristics is due to the anisotropy of the COF crystallites with no extension of the two-dimensional COF structure with the same preferential orientation between the crystallites, hence promoting mainly *hopping*-type transport.



Figure 3.6. (a) Macroscopic and (b) energetic representations of excited state diffusion in **WBDT** COF thin films.

Finally, we compare the derived diffusion coefficients and diffusion lengths for the **WBDT** COF thin films to those reported for other 2D COFs in the literature. To date, excited state diffusion in 2D COFs has been mostly studied using transient absorption spectroscopy of colloidal solutions.<sup>25,27</sup> We note that to the best of our knowledge, the exciton diffusion in the **WBDT** COF films measured *via* RDTR- PL reaches unprecedented values for *D* and  $L_D$ . These values significantly exceed those reported for other COFs and organic semiconducting materials by several orders of magnitude.<sup>1,25,27</sup> We assume that the extended crystallinity of the framework and the uniform orientation of the crystallites in the thin film play a major role in enabling efficient diffusive excited state transport within this **WBDT** COF.

# 3.5 Conclusion

In this study we visualized the spatiotemporal evolution of photogenerated excited states in 2D **WBDT** COF thin films using remote detected time-resolved PL measurements. We directly accessed the lateral exciton diffusion within oriented and crystalline thin films of this COF. Remarkably high diffusion coefficients of 4 cm<sup>2</sup> s<sup>-1</sup> (at 200 K) and diffusion lengths of several hundreds of nanometers and across grain boundaries were extracted. Furthermore, we analyzed the temperature-dependent exciton transport regime. Phonon-assisted exciton transport prevails above 200 K, while disorder in the system significantly limits the diffusion at temperature below 200 K. Theoretical simulations suggest that the observed diffusion coefficient arises from contributions of both incoherent hopping and coherent band-like transport. This coexistence of the two regimes was also observed before in organic semiconductors and organic crystals.<sup>50–52</sup> We suggest a dominating coherent transport at low temperatures and a prevailing incoherent transport at room temperature. High crystallinity and preferential orientation of COF thin films allow for a precise definition of the nanoscale structure of the material. Hence, it is evident that energy transport processes are influenced not only by the choice of building units but also significantly by the (dis)order in the molecular framework. With the methodology established here, our work provides a mechanistic understanding of charge and energy transport in macroscopic molecular framework systems, as well as guidance toward enabling efficient transport processes in such materials.

# **3.6 Supporting Information**

The Supporting Information (SI) contains experimental methods, synthetic procedures, characterization of bulk and film material, information on the analysis and fitting of the spectroscopic data as well as details on the theoretical calculations.

#### S1. Materials and Synthesis

All solvents were purchased from *Sigma Aldrich*, *Acros* or *TCI Europe* in the common purities *purum*, *puriss* or *reagent grade*. The materials were used as received without additional purification and handled in air unless otherwise noted. N,N,N',N'-tetra(4-aminophenyl)benzene-1,4-diamine **W** was purchased from Carbosynth/BLDpharm. Benzo[1,2-b:4,5-b']dithiophene-2,6-dicarboxaldehyde **BDT** was synthesized according to the literature.<sup>63</sup>

**COF bulk material** was synthesized according to our prior report in an Argon filled glove box.<sup>55</sup> In a culture tube, a solid mixture of W (0.013mmol, 6 mg) and BDT (0.025 mmol, 6.26 mg) was suspended in 1 mL mesitylene and benzyl alcohol (500  $\mu$ L each). Subsequently, 50  $\mu$ L of acetic acid (aqueous, 6 M) was added. The culture tube was tightly sealed and heated at 100 °C for 72 h. The resulting dark red suspension was filtrated hot and the isolated powder thoroughly washed with THF (~10 mL). The obtained red powder was dried under vacuum, followed by extraction in supercritical CO<sub>2</sub> at 110 bar and 40 °C for 1 hour.

**COF thin films** were synthesized according to our prior report in autoclaves equipped with a teflon liner holding the substrate in a horizontal position.<sup>55</sup> Glass and quartz substrates were cleaned in detergent solution (Hellmanex III, 1%  $\nu/\nu$ , water, acetone and isopropanol). The substrate was immersed into a suspension of W (2.5 µmol, 1.2 mg) and BDT (5 µmol, 1.25 mg) in 2 mL mesitylene and benzyl alcohol (v:v 1:1) and 100 µL of acetic acid (aqueous, 6 M). The autoclave was sealed under Argon and heated at 100 °C for 1 day. After cooling to room temperature, the COF film was rinsed with dry THF and dried under reduced pressure. **Unoriented COF thin films** were grown on an SiO<sub>2</sub> inverse opal structure. The inverse opal structure was grown on a glass substrate following a published procedure.<sup>64</sup> In order to grow an unoriented film with comparable thickness on top of the substrate and account for the COF material growing within the inverse opal structure, the amount of precursor for the film synthesis was increased to 6 mg (12.5 µmol) and 6.25 mg (25 µmol) for W and BDT, respectively. The synthetic procedure remained unchanged.

### S2. Methods

**2D grazing-incidence wide angle X-ray scattering** (GIWAXS) data were recorded with an Anton Paar SAXSpoint 2.0 system equipped with a Primux 100 micro Cu K<sub> $\alpha$ </sub> source and a Dectris EIGER R 1M detector. The oriented (unoriented) COF films were positioned at a sample-detector distance of 140 mm (156 mm) and were measured with an incidence angle of  $0.2^{\circ}$  (0.3°).

**Powder X-ray diffraction** (PXRD) measurements were performed using a Bruker D8 Discover with Ni-filtered Cu  $K_{\alpha}$  radiation and a LynxEye position-sensitive detector.

Scanning electron microscopy (SEM) micrographs were obtained with an FEI Helios NanoLab G3 UC microscope equipped with a Schottky field-emission electron source operated at 1 - 30 kV.

**Transmission electron microscopy** (TEM) was performed on a FEI Titan Themis instrument equipped with a field emission gun operated at 300 kV.

**Nitrogen Sorption isotherms** were recorded with Quantachrome Autosorb 1 and Autosorb iQ instruments at 77 K. The sample was outgassed for 24 h at 120 °C under high vacuum prior to the measurements. Pore size distributions were calculated using the QSDFT model with a carbon kernel for cylindrical pores.

**UV-Vis-NIR** spectra were recorded on a Perkin-Elmer Lambda 1050 spectrometer equipped with a 150 mm integrating sphere, photomultiplier tube (PMT) and InGaAs detectors. **Diffuse reflectance spectra** were collected with a Praying Mantis (Harrick) accessory and were referenced to barium sulfate powder serving as 100 %R standard. The specular reflection of the sample surface was removed from the signal using apertures that allow only light scatter at angles >  $20^{\circ}$  to pass.

The **structure model** of the WBDT COF was constructed using the Accelrys Materials Studio software package, applying a P1 symmetry. The structure model was optimized using the Forcite module with the Universal force-field. Structure refinements using the Pawley method were carried out using the Reflex Powder Refinement module of the Materials Studio software.

Atomic force microscopy was measured using a NANOINK AFM setup. A standard tapping mode silicon AFM tip from NANO WORLD was used. The tip diameter was 20 to 40 nm and the force constant of the cantilever was ~42 N/m (length = 125  $\mu$ m, resonance frequency ~330 kHz). All measurements were performed in tapping mode.

Confocal photoluminescence measurements. For photoluminescence (PL) measurements, hyperspectral images and time-resolved PL images, a home-built confocal laser scanning microscope was used. It is based on a microscope body (NIKON) which is combined with a xyz-piezo-scanning stage (PHYSIK INSTRUMENTE) for the room temperature (RT) measurements. Herein, the samples are measured upside down in epi-direction using an oil immersion objective with 1.4 NA (NIKON). All low temperature (LT) measurements were performed on a self-built microscope with a commercial cryostat system from ATTOCUBE including scanner, positioner, vacuum chamber and pumps and the cooling apparatus. The microscope around this system is self-built and uses a long-working-distance objective with 0.75 NA (ZEISS). Both microscopes are connected to the same detection path. A beamsplitter (MELLES GRIOT 03BTL005 for RT-setup, THORLABS BSW29R for the LT-setup) and a spectral 490 or 550 nm long pass filter is used to separate the laser from the PL-light. A sub picosecond laser (ichrome TOPTICA) tunable from 476 nm to 645 nm is used for excitation. Here, the excitation wavelengths of 476 nm and 510 nm laser light are additionally filtered by a 473/10 nm (CHROMA) or 510/10 nm (THORLABS) band pass respectively, which is positioned in the excitation arm. The detection side consists of two parts, which are separated by a rotatable mirror. Additionally, a tiltable mirror in the back focal plane is installed for the diffusion measurements scanning around the confocal spot. One arm in the detection has an avalanche photo diode (APD, type: MPD PDM, detector size 50 x 50 µm), which can be combined with Time Correlated Single Photon Counting (TCSPC) electronics (BECKER UND HICKEL) measuring time-resolved PL transients. The second part consists of a spectrometer (ANDOR SHAMROCK SRi303) combined with an open electrode CCD camera (ANDOR NEWTON DU920) recording spectra. The data are recorded using a customized LABVIEW (NATIONAL INSTRUMENTS) program that combines the manufacturers' software with our desired measurements. Further processing and analysis are carried out using MATLAB (MATHWORKS) to obtain the PL spectra, TCSPC transients and the images.

#### **S3. WBDT bulk powder characterization**

Characterization of the bulk powder of WBDT COF was conducted including PXRD, FTIR, nitrogen sorption, steady-state PL and UV-Vis spectra as well as SEM measurements. PXRD of the WBDT COF shows distinct reflections at  $2\theta = 2.00^{\circ}$ ,  $3.50^{\circ}$ ,  $4.04^{\circ}$ ,  $5.38^{\circ}$ ,  $6.11^{\circ}$ ,  $7.36^{\circ}$ ,  $8.14^{\circ}$ ,  $8.96^{\circ}$ . Using the Materials Studio software package, Pawley refinement of the PXRD was conducted, assuming P1 symmetry and yielding the unit cell parameters, with  $R_{wp} = 4.20\%$  and  $R_p = 3.40\%$  (Figure S3.1).



Figure S3.1. Experimental PXRD of the WBDT COF powder together with the Pawley refinement and the resulting difference plot. Unit cell lengths and angles are indicated.

FTIR measurements confirm the successful formation of the COF network by the disappearance of the -NH (3342 cm<sup>-1</sup>) and -CO (1664 cm<sup>-1</sup>) vibrational modes and the appearance of the vibrational mode of the imine bond (1609 cm<sup>-1</sup>) in the IR spectrum of the WBDT COF (Figure S3.2).



Figure S3.2. FTIR spectra of the two linker molecules W and BDT and of the WBDT COF.

Surface area and pore sizes of the WBDT COF were determined by nitrogen sorption measurements. The sorption isotherm is a mixture of type I and type IVb with two nitrogen uptake steps. The first step at low partial pressures is characteristic for microporous materials, whilst the second step reveals additional capillary condensation, typical for the presence of mesopores. The calculated Brunauer-Emmet-Teller surface area is  $635 \text{ m}^2 \text{ g}^{-1}$  and the two pore sizes of the Kagomé-like structure, are 1.9 nm and 3.4 nm (Figure S3.3).



Figure S3.3. (a) Sorption isotherm of the WBDT COF with a BET surface area of 645 cm<sup>2</sup> g<sup>-1</sup>. (b) Pore size distribution (PSD) with two pore sizes, 1.9 nm and 3.4 nm, consistent with the dual-pore framework of the Kagomé-like structure.

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Steady-state PL and UV-Vis spectroscopy measurements were conducted to optically characterize the WBDT COF powder. The dark red COF powder emits around 1.83 eV (677 nm) and has a maximum absorption at 2.41 eV (514 nm). Fitting of the absorption onset using Tauc plot gives a direct band gap of 1.98 eV (Figure S3.4).



Figure S3.4. (a) Steady-state PL and UV-Vis spectra (Kubelka-Munk, diffuse reflection) of the WBDT COF powder. (b) Fitting of the absorption onset using Tauc plot.

Scanning electron micrographs reveal a uniform, spherical morphology of the WBDT COF particles. Transmission electron microscopy confirms the crystallinity of the COF. Detection of crystal domains with the *z*-axis oriented parallel to the incident electron beam show the pseudo-hexagonal pattern generated by the dual-pore Kagomé-like structure (Figure S3.5).



Figure S3.5. (a) SEM micrograph visualizing the spherical morphology of the WBDT COF powder. (b) TEM image confirming the crystalline nature of the COF.

#### S4. WBDT thin film characterization

Fitting of the absorption onset of the WBDT COF thin film using a Tauc plot gives a direct band gap of 2.16 eV as indicated in Figure S3.6a.

No significant broadening of the PL spectrum is visible upon decrease of the temperature. This is illustrated in Figure S3.6b, depicting the PL spectrum of the thin film at 5 K and at 300 K.



Figure S3.6. (a) Fitting of the absorption onset of the WBDT COF thin film using Tauc plot for a direct transition. (b) PL spectra of the thin film at 5 K and 300 K.

The thickness of the COF film was determined *via* SEM cross-section analysis (~120 nm) as well as by scanning over a thin scratch on the film's surface using AFM (~130 nm) (Figure S3.7).



Figure S3.7. (a) SEM cross-section of the WBDT COF thin film. (b) AFM image of the measured scratch with the difference in height shown as inset. (c) AFM image of a 2.5 x 2.5  $\mu$ m<sup>2</sup> section of the film surface.

**Linear Power Dependency.** For the steady-state PL and RDTR PL measurements, it is crucial that the response to the incident laser power is linear in the range of the used laser power, assuring that the number of excited states *n* is proportional to the measured intensity. Figure S3.8 confirms the linear power dependency of the PL intensity up to ~50  $\mu$ J/cm<sup>2</sup>. In order to guarantee the stability of the WBDT COF throughout the optical measurements, the laser power was chosen accordingly (see green range in Figure S3.8). All RDTR PL measurements were performed under vacuum, steady-state PL was performed under argon atmosphere.



Figure S3.8. The excitation fluence dependency of the PL intensity. The green range shows the excitation fluence used in the experiments

**Confocal Scan and Hyperspectral Images.** To confirm the homogeneity of the spectral response from the thin film, confocal scanning and hyperspectral imaging of a 10 x 10  $\mu$ m<sup>2</sup> section of the WBDT thin film were conducted, showing negligible changes in normalized intensity, central energy and spectral width of the PL signal (Figure S3.9a, b and c, respectively).



Figure S3.9. Confocal scan and hyperspectral images of the WBDT thin film, mapping differences in (a) normalized intensity, (b) central energy and (c) spectral width of the PL signal, respectively.

#### S5. RDTR PL measurements – Analysis and Fitting

#### **Rayleigh length**

The Rayleigh length is the distance along the beam's propagation direction from the beam waist to the point where the beam's cross-sectional area has doubled. The Rayleigh length  $z_R$  is given by <sup>65</sup>

$$z_R = \frac{\pi r_0^2}{\lambda}$$

where  $r_0$  is the resolution of the confocal microscope:

$$r_0 = \frac{1.22 \,\lambda}{NA}$$

With  $\lambda \approx 500$  nm and NA = 0.75, a Rayleigh length of approx. 4 µm is calculated. The Rayleigh length is an order of magnitude larger than the thickness of the WBDT thin film (around 120 nm), meaning that the focused beam extends beyond the entire film thickness. As a result, the laser uniformly excites the material throughout the film thickness, ensuring that the excitation reaches the entire depth of the film simultaneously. The observed diffusion is therefore treated as a two-dimensional process.

#### **Analysis and Fitting**

The data were collected in the form of a TCSPC transient for every remote position of the tiltable mirror. For each temperature step, transients from two different directions through the confocal spot were recorded. Furthermore, two temperature series were measured to guarantee the reproducibility of the observed diffusive transport. Data set 1 was integrated over the blue part of the PL spectrum (590-610 nm, 2.03 - 2.10 eV) and Data Set 2 was integrated over the whole PL signal. In both sets the same trend of the diffusive transport was observed. Since the spectrum contains not only mobile species but also a localized radiative state, the diffusive transport is more visible in the blue data set (Data Set 1). An exemplary data set at 40 K is shown in Figure S3.10:



Figure S3.10. RDTR PL data obtained at 40 K.

As the COF film is thin (~ 100 nm), and the Rayleigh length is around a micrometer, the focus penetrates the whole film in the direction perpendicular to the substrate (z-direction). This measuring setup only allows for the observation of the in-plane 2D diffusive transport in the thin film (although this does not exclude occasional transport along z followed by in-plane (xy) transport).

The observed diffusive species has a limited lifetime, leading us to the following differential equation (S1):

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$$\frac{dn(x, y, t)}{dt} = D\Delta n(x, y, t) - k_1 n(x, y, t)$$
(S1)

In equation S1, n is the number of excited states that is proportional to the measured PL intensity. This is confirmed by linear power dependency (Figure S3.8). D is the diffusion coefficient and  $k_1$  is the lifetime of the diffusive species. Assuming a Gaussian starting distribution of excited states, this differential equation can be analytically solved by

$$n(x, y, t) = \frac{N_0 2\sigma^2}{2\sigma^2 + 4Dt} \exp\left(\frac{-x^2 - y^2}{2\sigma^2 + 4Dt}\right) \cdot \exp\left(-k_1 t\right),$$
(S2)

where the spatial integration over  $N_0 \exp\left(\frac{-x^2-y^2}{2\sigma^2}\right)$  is the total number of excited states at t = 0and  $\sigma$  is the width of the starting Gaussian distribution. To analyse the RDTR PL data, two different methods were used and subsequently compared for cross-verification. For the first method (method I in the main text), we fit two Gaussians, one with a fixed width corresponding to the initial signal width determined by the excitation focus and the optical resolution of the setup and the other with a variable width (Figure S3.11a). The results show that the variance of the width  $\sigma^2$  follows a linear change in time, as expected from the following relation (equation S3), derived from the 2D diffusion equation S2:

$$\sigma^2 \sim 2Dt \tag{S3}$$

This linear relation is shown in Figure S3.11b. The contribution with fixed (time-independent) width is attributed to a localized, immobile excited species, presumably related to defect trap states.



Figure S3.11. (a) Double Gaussian fit (fixed and flexible width) of the raw RDTR PL data for one time step. (b) Linear fit of the variance of the width as a function of time.

The second method (method II in the main text) involves analysing the full data set using the analytical solution (equation S2) and fitting the whole two-dimensional data with a single diffusion coefficient. This analysis is split into two parts according to the two different timescales observed (*fast* and *slow species*, Figure 3.3b). Figure S3.12 visualizes and compares the diffusion coefficients obtained by the two methods for the *slow species*.



Figure S3.12. Comparison of the two methods I and II for the determination of the diffusion coefficient D for data set 2 (full spectral range). Data are collected in two different scanning directions through the confocal spot, perpendicular to each other (direction 1 and 2).

For the free charge carrier diffusion coefficient, the time interval from -0.025 to 0.005 ns is used. Additionally, the calculated data are convoluted with the instrument response function (IRF, FWHM of 28 ps). The time-zero is defined by the maximum and the overlap of the initial rise of the IRF at the center of the confocal spot (remote distance = 0  $\mu$ m). An additional Gauss distribution with a mono-exponential decay is added, representing the localized excited states.

For the free charge carrier diffusion, only method I was used, and the data were averaged over both directions (Figure S3.13a). The time interval between 0.1 and 1 ns was used for the exciton diffusion coefficient. Here, both methods I and II were applied, and the data were averaged over both directions (Figure S3.13b). 3 Spatiotemporal Spectroscopy of Fast Excited-State Diffusion in 2D Covalent Organic Framework Thin Films



Figure S3.13. Measured and fitted data for the diffusion coefficient of the (a) free charge carriers and (b) excitons.

According to the fits, the lifetimes  $\tau$  of the excitons are at the order of 0.9 - 1.2 ns. Using  $\tau$ , the diffusion length  $L_D$  can be approximated:

$$L_D = \sqrt{2D\tau} \tag{S4}$$

The diffusion length of the excitons as a function of temperature is depicted in Figure S3.14.



Figure S3.14. Diffusion length of the excitons as a function of temperature.

# S6. WBDT un-oriented thin film characterization and diffusion dynamics

#### Characterization

The WBDT COF has a strong tendency to grow highly oriented thin films on most substrates, even when incorrect ratios of building blocks are used or different solvents are chosen for the COF synthesis. Therefore, we changed the substrate's morphology drastically from a smooth surface to a meso-structured SiO<sub>2</sub> inverse opal with a thickness of ~ 4  $\mu$ m and pores of 300 nm diameter. On this substrate, WBDT COF grows as interconnected spherical grains of around 150-200 nm size similar to the bulk powder, both in and on top of the structure. Figure S3.15a and b show SEM top views of the inverse opal structure, and c and d show the WBDT COF@SiO<sub>2</sub> grown on top the macro-structured substrate.



Figure S3.15. (a) and (b) Top view of the SiO<sub>2</sub> inverse opal structure at different magnifications. (c) and (d) WBDT COF@SiO<sub>2</sub> inverse opal structure.

Figure S3.16a and c show cross sections of the WBDT COF@SiO<sub>2</sub>, illustrating the COF growth both into the mesopores and on top of the structure. Figure b and d show the same section of the film, looking only at the backscattered electrons. This method has a higher contrast for the inorganic SiO<sub>2</sub>, revealing the SiO<sub>2</sub> structure below the COF grains.

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Figure S3.16. (a) and (c) Cross section of WBDT COF@SiO<sub>2</sub> with different magnifications, showing the growth of the COF both into the structure as well as on top of it. (b) and (d) Backscattered electron image of the same film sections as in (a) and (c), revealing the SiO<sub>2</sub> structure below the COF.

Additionally, AFM was conducted on a 2.5 x 2.5  $\mu$ m<sup>2</sup> section of the un-oriented thin film to better illustrate the difference in morphology compared to the oriented WBDT film (Figure S3.17)



Figure S3.17. AFM image of a 2.5 x 2.5  $\mu m^2$  section of the un-oriented WBDT thin film.

In Figure S3.18, the reflections in the GIWAXS pattern of the un-oriented film appear at identical scattering vectors in the GIWAXS pattern of the oriented film and in the PXRD pattern of the bulk material, confirming the formation of a crystalline COF. The intensity of the *hkl* 

reflections is uniformly distributed in  $q_z$  and  $q_r$  direction, forming a semi-circle. The scattering pattern indicates a random orientation of the COF crystallites.



Figure S3.18. GIWAXS pattern of the un-oriented WBDT COF grown on an SiO<sub>2</sub> inverse opal structure. The colour map was chosen differently to the main text to improve the visibility of the reflections at low  $q_r$  values.

Steady-state PL and UV-Vis measurements were conducted to optically characterize the WBDT COF@SiO<sub>2</sub> film. The dark red film emits at 1.88 eV (660 nm) and has a maximum absorption at 2.48 eV (500 nm). Fitting of the absorption onset using Tauc plot gives a direct band gap of 2.08 eV (Figure S3.19)



Figure S3.19. (a) Steady-state PL and UV-Vis spectra of the unoriented WBDT COF thin film. (b) Tauc plot of the absorption onset, scaled for a direct transition.

#### **Diffusion Dynamics**

The analysed RDTR PL data for the un-oriented WBDT COF thin film are shown in Figure S3.20. With  $D_{unoriented} \approx 11 \text{ cm}^2 \text{ s}^{-1}$ , the diffusion coefficient for the free charge carriers at the shorter timescale is comparable to that of the oriented thin film ( $D_{oriented} = 10 \text{ cm}^2 \text{ s}^{-1}$ ). This is in line with our interpretation of the carriers diffusing within one grain and the grain size not significantly changing between oriented and un-oriented film. The exciton diffusion coefficient decreases with decreasing temperature, indicating a *hopping* type transport. It is also overall lower, suggesting that the high degree of orientation of the crystallites in the oriented film plays a major role in the diffusive transport.



Figure S3.20. Diffusion coefficient as a function of temperature of the (a) free charge carriers and (b) excitons in the un-oriented WBDT COF thin film.

#### **S7. Optical Pump Terahertz Probe Spectroscopy (OPTP)**

The setup used for optical pump terahertz probe (OPTP) transients is described in full detail elsewhere.<sup>66</sup> Briefly, an amplified Ti:sapphire laser system (Spitfire ACE, Spectra-Physics) provides 800-nm light pulses (35 fs) with 5-kHz repetition rate. The fundamental output of the amplified Ti:sapphire laser is used to generate single-cycle THz radiation pulses in a W/Co<sub>40</sub>Fe<sub>40</sub>B<sub>20</sub>/Pt multilayer film on quartz (spintronic emitter) through the inverse spin Hall effect.<sup>67</sup> Furthermore, the optical excitation pulses (400 nm) used to photoexcite the samples are generated by second-harmonic generation in a beta-barium-borate (BBO) crystal. During OPTP measurements, the fractional changes in the THz transmission (0.5-2.5 THz) following the 400-nm photoexcitation are monitored by using free-space electro-optic sampling (EOS) in a 1-mm-thick (110)-ZnTe crystal. The WBDT COF thin films were deposited onto 2 mm thick z-cut quartz. During OPTP measurements, the THz emission and detection optics and samples are kept under vacuum at pressures below 0.1 mbar.

#### Extraction of charge-carrier mobility from OPTP measurements

We extracted the effective charge-carrier mobility following the method developed by Wehrenfennig *et al.*.<sup>68</sup> Briefly, for semiconductor thin films materials with thicknesses smaller than the wavelength of the incident THz radiation, the sheet photoconductivity can be estimated from the fractional change in the transmitted THz electric field  $\Delta T/T$ , and expressed as

$$\Delta S = -\epsilon_0 c(n_q + n_v) \left(\frac{\Delta T}{T}\right) \tag{S6}$$

where  $n_q = 2.13$  and  $n_v = 1$  are the refractive indexes of quartz and vacuum, respectively.<sup>69</sup> To extract the effective charge-carrier mobility from the sheet photoconductivity, the number of initially photogenerated carriers is estimated as

$$N = \phi \frac{E\lambda}{hc} \left( 1 - R_p - T_p \right) \tag{S7}$$

Where  $\varphi$  is the photon-to-charge branching ratio (i.e., the fraction of generated charges per photon absorbed), *E* is the pump pulse energy,  $\lambda$  is the excitation wavelength, and  $R_p$  and  $T_p$  are the reflectance and transmittance of the sample at the excitation wavelength (3.1 eV, 400 nm). The charge-carrier mobility  $\mu$  can be calculated as

$$\mu = \frac{\Delta S \, A_{eff}}{Ne} \tag{S8}$$

Where  $A_{eff}$  is the effective overlap area between THz and pump beam and e is the elementary charge. By substituting Equation S6 and Equation S7 into Equation S8, the effective charge-carrier mobility is obtained as:

$$\varphi \mu = -\epsilon_0 c(n_q + n_v) \frac{A_{eff} hc}{eE\lambda(1 - R_{pump} - T_{pump})} \left(\frac{\Delta T}{T}\right)$$
(S9)

Here, it is worth noting that the sheet photoconductivity signal measured by OPTP arises from the contributions of both photogenerated free electrons and holes. Therefore, the extracted charge-carrier mobility is the effective electron-hole sum mobility.

#### Calculation of the diffusion length using charge carrier lifetime from OPTP

In this study, we calculated the diffusion length  $L_D$  of the free charge carriers (*fast species*) using the lifetime extracted from OPTP measurements  $\tau = 1.4$  ps and the diffusion coefficient given by RDTR PL  $D \sim 10$  cm<sup>2</sup> s<sup>-1</sup>, assuming that the fast-moving species are equal to the free charge carriers. Both methods are independent and generate two different values. OPTP measures only the free charge carriers, formed shortly after excitation. From the absorbed probe signal, an effective mobility is calculated and a lifetime of the free charge carriers can be extracted. The effective mobility  $\varphi \mu \sim 0.12 \pm 0.05 \text{ cm}^2 V^{-1} \text{s}^{-1}$  contains the photon-to-charge branching ratio  $\varphi$ , since the exact number of contributing free charge carriers is unknown. In RDTR PL measurements however, the PL is generated by a combination of free charge carriers and possible unbound excitons. Here, the diffusive transport is only driven by the chemical potential of the generated excited states, while in OPTP measurements, the excited charge carriers react to the applied THz probing field.

In principle the absolute mobility  $\mu$  and diffusion coefficient *D* can be connected *via* the Einstein-Smoluchowski<sup>70,71</sup> relation:

$$D = \frac{\mu k_B T}{e} \tag{S10}$$

with the Boltzmann constant  $k_B$ , the temperature T and the elemental charge e. However, this formula is only valid in the case of a charged particle with a charge e, moving through a neutral medium. In our case, the excited charges are bound to each other (exciton) or move as ambipolar charge carriers (combined movement of electrons and holes) in a dielectric and periodic crystal lattice. This lattice shields the charges. Therefore, the Einstein-Smoluchowski relation cannot be readily applied here. A more accurate model would be needed to contextualize both numbers.

Additionally, it is not clear if the disorder in the system has an influence on the fast-moving species.

Hence, the calculated diffusion length of the free charge carriers (*fast species*) in this study, combining values from both OPTP and RDTR PL measurements, should be considered as a qualitative estimation.

#### **S8.** Theoretical Calculations

The structure of WBDT is optimized at density functional theory (DFT) level. We use the projector-augmented wave (PAW) method<sup>72,73</sup> in conjugation with Perdew-Burke-Ernzerhof (PBE) exchange and correlation functional<sup>74</sup> as implemented in the Vienna ab-initio simulation package (VASP).<sup>75-77</sup> The atomic positions are relaxed using the conjugate gradient method with an energy convergence value of  $10^{-6}$  eV. The dispersion interactions are described with the nonlocal vdW-DF functionals by Dion *et al.*<sup>78</sup> The band structure of WBDT shown in Figure 2a has been corrected by a scissors shift<sup>79</sup> of +0.49 eV for all conduction bands to estimate the band gap at Hybrid-DFT (HSE06) level (L. Fuchs et al. unpublished).

The Brillouin zone (BZ) for the relaxation simulations is sampled with a 1x1x6  $\Gamma$ -centered mesh. The electronic band structure (Figure 3.2a) is calculated along a path connecting high-symmetry points in the primitive hexagonal cell ( $\Gamma$ -M-K- $\Gamma$ -A) with 20 equally spaced points between two special points. Additionally, atomic projections of the Kohn-Sham states onto W and BDT fragments were calculated.

For the calculation of the transition densities of the excited states, WBDT is divided into two precursor fragments (BDT and W), which are NH- and H-terminal saturated. After a gas phase relaxation of the fragments with VASP, the transition densities describing the excited states are calculated with the software gaussian16<sup>80</sup> and Multiwfn,<sup>81</sup> using M062X as the exchange-correlation functional and a cc-pVTZ basis set. Excitonic transition densities are used to calculate the Coulomb interaction between the exciton states that are placed at the fragment position in the COF as described earlier<sup>82</sup> with an effective screening described by a low relative dielectric permittivity of  $\epsilon = 2$ . The large electron and hole transfer integrals extracted from the calculated band structure are further taken into account for second-order transfer processes to estimate the resulting effective exciton transfer integrals of  $\epsilon \cong 50$  meV.

A Marcus-type hopping ansatz with exciton coupling of  $\varepsilon \approx 50$  meV and an estimated reduced reorganization energy of  $\Lambda \approx 0.1$  eV was used to estimate the diffusion coefficient at 300 K.

# 3.7 References

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# CHAPTER 4

# Designing Atomically Precise and Robust COF Hybrids for Efficient Photocatalytic CO<sub>2</sub> Reduction

# 4 Designing Atomically Precise and Robust COF Hybrids for Efficient Photocatalytic CO<sub>2</sub> Reduction

This chapter is based on the following manuscript by

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<sup>#</sup>L. Spies and M. E. G. Carmo contributed equally to the manuscript. L. Spies synthesized and post-modified the COF and performed structural, optical and electronic characterization, including the development of a structural model. M. E. G. Carmo optimized and conducted all photocatalytic measurements. Together, L. Spies and M. E. G. Carmo interpreted the data and drafted the manuscript.



# 4.1 Abstract

Hybrid photocatalysts based on molecular species and solid substrates are elegant solutions for improving the performance and stability of molecular catalytic systems aiming at solar-driven  $CO_2$  conversion. In this work, a new dibenzochrysene-based Covalent Organic Framework (COF) was developed to accept  $Re^{I}$  centers, keeping its high crystallinity and allowing for atomistic control of the position of the catalytic centers. The rigid structure of the COF leads to long-term stability under illumination, whereas the efficient light-harvesting capability and the strong electronic interactions between the COF and the  $Re^{I}$  centers lead to CO evolution rates of up to 1.16 mmol g<sup>-1</sup> h<sup>-1</sup>. The favorable photocatalytic performance of this novel  $Re^{I}$ -COF offers new insights regarding the development of efficient photocatalytic hybrid systems
# 4.2 Introduction

Photocatalytic  $CO_2$  reduction has attracted growing interest, as it enables direct conversion of  $CO_2$  and solar energy into value-added chemicals.<sup>1-3</sup> A major breakthrough in this field was the development of the molecular rhenium(I) bipyridine (*fac*-[Re(CO)<sub>3</sub>(bpy)Cl]) catalyst by *Lehn* and co-workers, which opened a new avenue for designing  $CO_2$  photocatalysts with high precision and molecular control over reactivity.<sup>4</sup> To leverage the tunability of molecular catalysts while addressing their inherent limitations regarding stability, hybrid photocatalytic systems have emerged in which molecular catalysts are immobilized on solid supports such as metal oxides, nanoparticles, carbon nanostructures, and polymeric materials like g-C<sub>3</sub>N<sub>4</sub>.<sup>5-9</sup> While significant progress has been made with hybrid systems in achieving high selectivity and stability, the structural environment of the catalytic centers often remains poorly-defined, with active sites randomly distributed across the substrate. This lack of atomistic control limits the potential of molecular design for optimizing the catalyst performance and hinders a comprehensive understanding of the photocatalytic  $CO_2$  reduction mechanism.

Two-dimensional (2D) covalent organic frameworks (COFs) have been recognized as a promising platform for designing heterogeneous photocatalysts due to their virtually unlimited structural, chemical, and optoelectronic tunability.<sup>10-11</sup> COFs are crystalline porous frameworks built from organic building blocks that are connected *via* strong covalent bonds.<sup>12</sup> The rational design of the building blocks and the linkage motifs results in tailor-made materials with predefined features.<sup>13</sup> Specifically, this modular approach allows for the integration of welldefined metal binding sites, such as bipyridine or porphyrin, which can effectively confine and stabilize CO<sub>2</sub> molecular catalysts, thereby facilitating rigorous structural control over hybrid photocatalysts.<sup>14-17</sup> Furthermore, the choice of COF linkage motifs was shown to modify the microenvironment around catalytic centers and to influence the  $\pi$ - $\pi$  conjugation and stability of the COFs and thus their performance in photocatalytic CO<sub>2</sub> reduction.<sup>18-20</sup> Despite these advantages, synthesizing highly crystalline and stable 2D COFs is challenging due to constraints related to reaction conditions and characteristics of the building blocks.<sup>21</sup> Achieving high crystallinity in COFs is essential not only for defining the spatial arrangement of catalytic sites but also for advancing the understanding and molecular design of hybrid photocatalysts. Here, we introduce a novel 2D COF for photocatalytic CO<sub>2</sub> reduction, utilizing dibenzo[g,p]chrysenetetraamine (DBC) as a structure-directing building block for the synthesis of a highly crystalline and stable COF. DBC, a planar and rigid monomer with an extended  $\pi$ conjugated structure, promotes tight, ordered stacking of COF layers with a high degree of

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conjugation. Imine-linked DBC-based COFs have been demonstrated to feature high crystallinity, as well as excellent thermal and chemical stability, along with long-lived excited states.<sup>22-24</sup> Despite these promising properties, DBC-COFs have not yet been explored for photocatalytic applications. Here, we combine DBC with 2,2'-bipyridine-5,5'-dicarbaldehyde (bpy), forming the bpyDBC COF. The bpy unit provides docking sites for the immobilization of [Re<sup>I</sup>(CO)<sub>5</sub>Cl], a model molecular CO<sub>2</sub> photocatalyst (Scheme 4.1), thereby forming the hybrid photocatalyst Re<sup>I</sup>bpyDBC COF. For the first time, the detailed X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis allowed us to resolve the atomistic-level distribution and organization of the molecular catalyst within the COF structure. The exceptional stability of the novel RebpyDBC under visible light illumination, maintaining performance for more than 72 h, can directly be correlated to the structural precision provided by the DBC-node.



Scheme 4.1. Synthesis of bpyDBC COF and immobilization of Re<sup>I</sup>(CO)<sub>5</sub>Cl, yielding Re<sup>I</sup>bpyDBC COF.

# 4.3 Results and Discussion

The synthesized bpyDBC COF was structurally analyzed using powder X-Ray diffraction (PXRD). The experimental PXRD pattern, showing sharp reflections at 2.2°, 3.9°, 4.5°, 6.8°, 8.5°, 9.0° and 11.3°  $2\theta$ , confirms the crystallinity of the pristine COF (Figure 4.1a). The diffraction peak at 25° corresponds to the (001) plane, which is attributed to the  $\pi$ -  $\pi$  stacking of the as-formed structure. For the Rietveld refinement<sup>25</sup> of the pristine COF, we considered a combination of four fixed structural variants of the unit cell content to account for the different possible orientations of the bpy unit (Figure S4.2). The N atoms of the bpy unit can either point into the small triangular pore (i and ii) of the Kagomé structure, or into the large hexagonal pore (iii and iv). Depending on the rotation of the imine bonds, using the DBC node as point of reference, either a clockwise (i and iii) or anti-clockwise (ii and iv) rotation is possible. By combining the four structural variants with equal weights of 0.25, we achieved a successful refinement of the COF in P6 symmetry and assuming AA stacking. The PXRD pattern of bpyDBC was fully indexed with a hexagonal lattice with refined lattice constants of a = b = 44.7(1) Å, c = 3.56(1) Å. The refined model yields a weighted R-value (wR) of 3.49 %. The highly porous nature of the COF was confirmed by the Nitrogen sorption measurements (Figure S4.3) at 77 K demonstrating a Brunauer-Emmett-Teller (BET) surface area of 1252 m<sup>2</sup> g<sup>-1</sup> and pore sizes of 1.9 nm and 3.5 nm of the dual-pore Kagomé structure. The absence of the aldehyde and amine vibrations of the building blocks in the FTIR spectrum, along with the appearance of the imine stretching vibration at 1690 cm<sup>-1</sup>, confirm the formation of the covalent bond (Figure S4.4). Additional evidence is provided by solid state <sup>13</sup>C CP-MAS-NMR (Figure S4.5).

The Re<sup>I</sup>-complex was introduced into the framework following a well-established procedure preserving the chemical nature of the complex.<sup>16, 20</sup> Upon the introduction of Re<sup>I</sup>, the crystallinity of the COF network is preserved and additional diffraction peaks appear at 5.9°, 8.0°, 9.9°, 12.0° and 13.9°, due to an increase of the corresponding structure factors (Figure 4.1b). For the Rietveld refinement, the model containing the respective Re<sup>I</sup>-loaded structural variants *i<sub>Re</sub> - iv<sub>Re</sub>* (Figure S4.2) yields wR = 2.66 %, with a refined occupation factor of the bpy sites with Re<sup>I</sup>(CO)<sub>3</sub>Cl of 47%. This is close to the value of 44% (16.2 wt% Re) obtained by ICP OES. Similar refined lattice constants are obtained with a = b = 44.8(1) Å, c = 3.65(1) Å. Nitrogen sorption experiments revealed a BET surface area of 717 m<sup>2</sup> g<sup>-1</sup> and pore sizes of 1.9 nm and 3.3 nm (Figure S4.3). The successful immobilization of [Re<sup>I</sup>(CO)<sub>3</sub>Cl] by the bpyDBC COF was further evidenced by the three CO vibrational bands observed between 1800 and 2100

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cm<sup>-1</sup> in the FTIR, corresponding to the A<sub>1</sub> and the two E modes expected for the *facial* geometry of the Re(CO)<sub>3</sub>Cl moiety,<sup>26-27</sup> and resembling those of the molecular catalyst [Re<sup>I</sup>(bpy)(CO)<sub>3</sub>Cl] (Figure 4.1c). Thermogravimetric analysis (TGA) of bpyDBC and Re<sup>I</sup>bpyDBC shows good thermal stability, with decomposition temperatures of up to 420°C and 300°C, respectively (Figure S4.6). SEM images were taken to examine the morphology of the pristine and modified COFs (Figure S4.7). The bpyDBC COF shows rod-like structures growing from spherical particles that cluster into larger domains, while the Re<sup>I</sup>-functionalized COF has similar spherical particles covered with platelet-like structures.



Figure 4.1. (a), (b) Experimental and Rietveld refined PXRD patterns of bpyDBC and Re<sup>I</sup>bpyDBC. (c) FTIR spectra of bpyDBC, Re<sup>I</sup>bpyDBC and the molecular analog Re<sup>I</sup>(bpy)(CO)<sub>3</sub>Cl. (d) Superposition of the four structural variants of the unit cell, illustrating how the threefold propeller contrast dominated by Re<sup>I</sup> is created. (e) STEM-HAADF image showing the highly ordered Re<sup>I</sup> sub-structure within the COF lattice. (f) Magnified section of (e) with the COF lattice.

To investigate the distribution of the Re<sup>I</sup>-complex within the COF structure at the near atomic level, TEM analysis was performed. TEM images of bpyDBC COF and Re<sup>I</sup>bpyDBC COF (Figure S4.8a, S4.9a, respectively) are similar, showing a fully crystallized, homogenous material with crystallite sizes between 50 and 100 nm. Several research groups have shown that the bpy units in COF networks can serve as binding sites for metal complexes, however, the spatial resolution of distribution of metal centers within the COF framework has yet to be

demonstrated.<sup>16-17, 20, 28</sup> Employing scanning TEM in high-angle annular dark field mode (STEM-HAADF), we were able so resolve, for the first time, the position of the metal centers in the crystalline COF network. Here, the image contrast is approximately proportional to the atomic number squared, making heavy atoms such as Re<sup>I</sup> appear as bright spots. STEM-HAADF images of the Re<sup>I</sup>bpyDBC COF reveal a highly ordered Re<sup>I</sup> sub-structure (Figure 4.1e, S4.9b-d), adopting the crystallographic positions defined by the bpy linker. The superposition of the four structural variants ( $i_{Re}$ ) – ( $iv_{Re}$ ) (Figure 4.1d) used for the Rietveld refinement illustrates how a statistical distribution of the Re<sup>I</sup> centers in the COF lattice creates the threefold propeller-type pattern visible in the STEM-HAADF image (Figure 4.1f). The high crystallinity and well-defined structural properties of the byDBC COF enabled, for the first time, the direct observation of the arrangement of the metal centers within the COF framework at a near-atomic scale. This unprecedented level of resolution underscores the pivotal role of structural order in facilitating the precise localization of metal centers, which is essential for understanding their catalytic behavior and optimizing photocatalytic performance.

It is well established that the incorporation of metal centers affects the electronic transition properties of organic frameworks.<sup>29-30</sup> Hence, changes in the electronic structure of the COF upon immobilization of the Re<sup>I</sup> complex were investigated via UV-vis and photoluminescence (PL) measurements along with cyclic voltammetry (CV). The absorption onset of Re<sup>I</sup>bpyDBC COF is red-shifted by approx. 150 nm compared to bpyDBC. Fitting this onset with a Tauc plot (Figure S4.10) yields direct band gaps of 2.19 eV for bpyDBC and 1.85 eV for Re<sup>I</sup>bpyDBC. Similar red shifts upon incorporation of the Re<sup>I</sup>-complex have been reported by in the literature.<sup>16-17, 20</sup> By calculating the band structure of metal-doped bpy-based COFs, Kamiya et al. found that the 3d Orbitals of the metal are located below the conduction band of the COF thus causing the optical shift.<sup>30</sup> The PL emission of the pristine COF is characterized by a broad band with  $\lambda_{em}$ = 693 nm, which is significantly quenched in Re<sup>I</sup>bpyDBC, indicating the efficient electronic interaction between the COF and the Re<sup>I</sup> center (Figure 4.2a). For estimating the valence band positions of the pristine and modified COFs, CV was performed in accordance with previously reported studies.<sup>31-33</sup> By fitting the onset of the first reversible oxidation peak (Figure S4.11), valence band energies of bpyDBC and Re<sup>I</sup>bpyDBC were determined to be 0.47 V and 0.61 V vs. SHE, respectively. Combining CV and UV-vis results, the conduction band energies of the two materials were estimated (Figure 4.2b), establishing that both COFs are thermodynamically capable of reducing CO<sub>2</sub> to CO. In addition to thermodynamic suitability for catalytic conversion, the incorporation of Re<sup>I</sup> centers into the COF significantly enhanced



Figure 4.2. (a) UV-vis absorption (continuous line, smoothed) and PL emission (dotted line,  $\lambda_{exc} = 476$  nm) of bpyDBC and Re<sup>1</sup>bpyDBC. The normalized PL intensity of the two COFs is shown in the inset. (b) Energy levels of the two COFs determined by CV and Tauc plot analysis, and reduction potentials of the sacrificial donor BIH and the CO<sub>2</sub>-to-CO reduction.

CO<sub>2</sub> uptake, thereby facilitating the interactions between the hybrid catalyst and the reactant (Figure S4.12).

In the photocatalytic CO<sub>2</sub> reduction assays, 1,3-dimethyl-2-phenyl-2,3-dihydro-1Hbenzimidazole (BIH) was used as sacrificial electron donor. BIH has a stronger reduction potential ( $E_{ox} = 0.57$  V vs. SHE)<sup>34</sup> compared to other commonly used sacrificial electron donors such as TEA (triethylamine,  $E_{ox} = 0.693$ V vs. SHE)<sup>35</sup>, TEOA (triethanolamine,  $E_{ox} = 1.06$  V vs. SHE)<sup>36</sup> or BNAH (1-benzyl-1,4-dihydronicotinamide,  $E_{ox} = 0.81$  V vs. SHE)<sup>37</sup> and, upon oxidation, BIH undergoes rapid deprotonation to form the radical BI', which is an even stronger reducing agent ( $E_p = -1.7$  V vs. SHE)<sup>38</sup> (Figure 4.2b). This allows BIH to donate two electrons and one proton during the photocatalytic process, as shown in Scheme S4.3, and thereby boosting the CO<sub>2</sub> conversion. Additionally, the fully oxidized form BI<sup>+</sup> does not negatively impact the photocatalytic CO<sub>2</sub> reduction.<sup>39</sup>

The performance of Re<sup>I</sup>bpyDBC in the photocatalytic CO<sub>2</sub> reduction was investigated using a 300 W Xe lamp as the illumination source equipped with 370 or 400 nm long-pass filters. In both cases the irradiance was set at 100 mW cm<sup>-2</sup>. Acetonitrile suspensions containing the COF catalyst and a 24-fold molar excess of BIH were exposed to light illumination under saturated CO<sub>2</sub> atmosphere. The gaseous products were monitored by gas chromatography. Notably, in the photocatalytic experiments, CO was identified as the only reduction product. Control experiments conducted under argon atmosphere, in the dark, and in the absence of catalyst did not yield any CO. Experiments using isotopically labeled <sup>13</sup>CO<sub>2</sub> yielded <sup>13</sup>CO for both illumination conditions (Figure S4.13-4.14), evincing that the CO originated from the reduction of CO<sub>2</sub>. Figure 4.3a displays the CO evolution using Re<sup>I</sup>bpyDBC COF as photocatalyst under UV-vis (> 370 nm) illumination. A remarkably high rate of 1.16 mmol  $g^{-1} h^{-1}$  was achieved, which ranks amongst the highest CO rates reported in the literature for similar systems without the use of an additional photosensitizer.<sup>16-17, 20</sup> A comparison of the reported rates can be found in Table S4.1, however, comparing rates from different groups is non-intuitive and should be approached with caution, as differences in the photocatalytic setup (e.g. wavelength of source, photon flux, reactor geometry, catalyst concentration, stirring, etc.) can significantly influence the catalyst performance.<sup>40-41</sup> In contrast, the pristine bpyDBC COF did not show any CO evolution under these conditions, underlining the importance of the Re<sup>I</sup> center serving as the active site in the COF structure. Recycling studies carried out under UV-vis light reveal that after 8 h illumination, a new purging with CO2 leads to the production of more CO (Figure S4.15), leading to a maximum turnover number (TON<sub>CO</sub>) of 35. PXRD and FTIR measurements conducted after the reaction confirm the structural integrity of the Re<sup>I</sup>bpyDBC COF following 24 hours of UV-vis illumination (Figure 4.3c-d, orange line).

Under visible light (> 400 nm) illumination, an evolution rate of 0.18 mmol g<sup>-1</sup> h<sup>-1</sup> was achieved after an induction period of approx. 20h (Figure 4.3b). The different behavior under different illumination conditions indicates distinct mechanisms of CO<sub>2</sub> conversion. UV-vis light can directly induce MLCT excitation of the molecular catalyst followed by reductive quenching through BIH and the release of the Cl<sup>-</sup>-ligand. This yields the well-known penta-coordinated 18-electron-species driving the CO<sub>2</sub> to CO conversion.<sup>42</sup> In contrast, under visible light excitation, light harvesting primarily involves internal  $\pi$ - $\pi$ \* transitions within the highly conjugated bpyDBC COF structure. Subsequent electron transfer from the COF to the catalytic



Figure 4.3. CO production of the Re<sup>I</sup>bpyDBC COF under illumination with (a)  $\lambda > 370$  nm and (b)  $\lambda > 400$  nm. Solid lines represent the linear fitting of the data to extract CO production rates. PXRD pattern (c) and FTIR spectra (d) of the Re<sup>I</sup>bpyDBC COF before and after 24 h of photocatalysis under both illumination conditions.

Re<sup>I</sup> centers is required to generate the catalytic active 18-electron species. The efficiency of this electron transfer is most likely limited by the intrinsic charge carrier dynamics of the COF. Consistent with previously reported in-situ spectroscopic studies for Re-COFs, the ~20-hour induction period observed here under visible-light excitation is consequently attributed to the stepwise accumulation of the catalytically active species, which initiates CO<sub>2</sub> conversion once a critical concentration is achieved.<sup>16</sup> We do not attribute the onset of CO production after the induction period to any structural changes or degradation of the COF material. Post-reaction PXRD and FTIR measurements (Figure 4.3c-d, red line) collected after 24h of illumination (i.e. after the onset of CO production) show no evidence of changes in the chemical structure of the COF or the coordination environment of the Re centers. Additionally, the <sup>13</sup>CO labelling experiments validate that the CO product originates from CO<sub>2</sub> reduction rather than

decomposition of the material. The outstanding stability of the Re<sup>I</sup>bpyDBC COF is further evidenced by its continuous CO production for 72 hours under visible light. In contrast, a homogeneous catalyst, released through degradation of the hybrid COF-catalyst, would be unlikely to sustain such prolonged activity. Unlike previously reported COFs, where the loss of crystallinity led to ceased photoactivity,<sup>20</sup> the Re<sup>I</sup>bpyDBC COF demonstrates stability far beyond the state of the art when compared with similar Re-COF systems under standard photocatalytic conditions (Table S4.2). This outstanding stability can be directly correlated to the extremely high crystallinity, the precise definition of the local coordination environment as well as excellent electronic delocalization achieved through the use of the structure-directing DBC-node.

# 4.4 Conclusion

Concluding, in this study we demonstrate that the favorable low curvature and large conjugated structure of the dibenzochrysene-based building unit are key factors for enhancing both the crystallinity and stability of the novel hybrid photocatalyst Re<sup>I</sup>bpyDBC COF for CO<sub>2</sub> reduction. The bpyDBC COF provides predefined binding sites for the immobilization of Re<sup>I</sup>(CO)<sub>5</sub>Cl, yielding structural motifs of the model catalyst *fac*-Re(CO)<sub>3</sub>(bpy)Cl throughout the framework. For the first time, we successfully resolved the highly ordered sub-structure adopted by the Re<sup>I</sup> centers within the COF using STEM-HAADF analysis, providing valuable insights regarding the molecular design of hybrid catalysts. In the photocatalytic CO<sub>2</sub>-to-CO conversion, the Re<sup>I</sup>bpyDBC COF exhibited a remarkable CO production rate of 1.16 mmol g<sup>-1</sup> h<sup>-1</sup> under UV-vis illumination with BIH serving as a sacrificial electron donor. Under visible light, the Re<sup>I</sup> COF maintained catalytic activity for over 72 hours at a reduced rate of 0.18 mmol g<sup>-1</sup> h<sup>-1</sup>, competing with the longest operational lifetime of other COF-based CO<sub>2</sub> photocatalyst. Our work highlights that COFs can function as effective platforms for the hybridization of molecular catalysts, offering atomistic control over structure and exceptional stability.

# 4.5 Supporting Information

The Supporting Information (SI) contains experimental methods and synthetic procedures, structural, optical and electronical characterizations of bpyDBC and Re<sup>I</sup>bpyDBC COF, as well as data on the photostability, isotope-labelled experiments and recycling studies.

## **S1.** Materials and Methods

All solvents were purchased from *Sigma Aldrich*, *Acros* or *TCI Europe* in the common purities *purum*, *puriss* or *reagent grade*. The materials were used as received without additional purification and handled in air unless otherwise noted.

**Powder X-ray diffraction** (PXRD) measurements were performed using a Bruker D8 Discover instrument with Ni-filtered Cu  $K_{\alpha}$  radiation and a LynxEye position-sensitive detector.

Fourier-transform infrared spectroscopy (FTIR) measurements were performed with a Bruker Vertex 70 FTIR instrument by focusing the light of a globar as a MIR light source through a KBr beam splitter with integrated gold mirrors and an ATR sample stage with a Ge crystal. The spectra were recorded with an  $N_2$  cooled MCT detector at a resolution of 2 cm<sup>-1</sup> and averaged over 128 scans.

**Scanning electron microscopy** (SEM) micrographs were obtained with an FEI Helios NanoLab G3 UC microscope equipped with a Schottky field-emission electron source operated at 3 kV.

**Transmission electron microscopy** (TEM) and scanning TEM in high-angle annular dark-field mode (STEM-HAADF) was performed on a probe-corrected FEI Titan Themis instrument equipped with a field emission gun operated at 300 kV.

**Nitrogen sorption** isotherms were recorded with a Quantachrome Autosorb 1 instrument at 77 K. **Carbon dioxide** sorption measurements were conducted on a Quantachrome Autosorb iQ at 273 K and 298 K. The samples were outgassed for 24 h at 120°C under high vacuum prior to the measurements. Pore size distributions based on the nitrogen sorption data were calculated using a QSDFT model with a carbon kernel for cylindrical pores.

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV 400 and AV 400 TR spectrometers. Proton chemical shifts are expressed in parts per million ( $\delta$  scale) and are

calibrated using residual non-deuterated solvent peaks as internal reference (e.g., DMSO- $d_6$ : 2.50 ppm).

**UV-Vis-NIR** spectra were recorded on a Perkin-Elmer Lambda 1050 spectrometer equipped with a 150 mm integrating sphere, photomultiplier tube (PMT) and InGaAs detector. Diffuse reflectance spectra were collected with a Praying Mantis (Harrick) accessory and were referenced to barium sulfate powder as 100%R standard. The specular reflection of the sample surface was removed from the signal using apertures that allow only light scatter at angles >  $20^{\circ}$  to pass. Diffuse reflectance data was smoothed using the LOWESS filter, integrated in the Origin 2022b data analysis software.

Steady-state photoluminescence (PL) and time-correlated single-photon counting (TCSPC). A home-built confocal laser scanning microscope (CLSM) setup was used for characterizing the photoluminescence of the COF samples. The samples were measured in the epi-direction using an air objective (0.85 NA, Fluor 40, NIKON). A beamsplitter (MELLES GRIOT 03BTL005) and a 490 nm long-pass filter were utilized to separate the laser from the photoluminescence (PL) light. Excitation was provided by a sub-picosecond laser (iChrome TOPTICA) operating at 476 nm with a repetation rate of 40 MHz. The detection system was divided into two components. The first part featured an avalanche photodiode (APD, type: MPD PDM, with a detector size of  $50 \times 50 \,\mu\text{m}$ ), which was used in combination with time-correlated single-photon counting (TCSPC) electronics (BECKER UND HICKEL) to measure timeresolved PL transients. The second part comprised a spectrometer (ANDOR SHAMROCK SRi303) connected to a CCD camera (ANDOR NEWTON DU920) for capturing spectra. The data were recorded using a customized LABVIEW (National Instruments) program that integrated the manufacturers' software with our specific measurement requirements. Further data processing and analysis, including extracting PL spectra and TCSPC transients, were performed using MATLAB (MATHWORKS).

**Thermogravimetric analysis** (TGA) measurements were performed using a Netzsch Jupiter ST 449 C instrument equipped with a Netzsch TASC 414/4 controller. The samples were heated from room temperature to 900°C under a synthetic air flow (25 mL min<sup>-1</sup>) at a heating rate of 10 K min<sup>-1</sup>.

**Cyclic Voltammetry** was performed on a Metrohm Autolab Potentiostat using a threeelectrode setup with Pt wire as counter electrode, Ag wire as pseudo-reference electrode and slurry-coated FTO glass as working electrode in 0.1M TBAPF<sub>6</sub> in acetonitrile. The electrolyte was prepared and stored under Ar. The Ag pseudo-reference electrode was referenced against the ferrocene redox couple. Measured potentials *vs.* the ferrocene redox couple  $Fc/Fc^+$  were converted to the absolute electrode potential ( $E_{vac}$ ) and to potentials *vs.* Standard Hydrogen Electrode (SHE) according to the following equations (i) and (ii), respectively. Note that the absolute potential scale equals to the negative physical scale.<sup>43</sup> Potentials *vs.* Standard Calomel Electrode (SCE) were converted to potentials *vs.* SHE according to equation (iii).<sup>44</sup> Reduction potentials for the sacrificial donors retrieved from the literature were converted to SHE accordingly.

(i)  $E_{vac} = E_{Fc/Fc^+} + 4.8 \text{ eV}$ 

(ii) 
$$E_{vac} = E_{SHE} + 4.44 \text{ eV}$$

(iii)  $E_{SHE} = E_{SCE} + 0.241 \text{V}$ 

Slurries for electrode coating were prepared by dispersing 21 mg of COF material, 4.5 mg Ketjen black and 4.5 mg PVDF (70:15:15) in 300  $\mu$ L NMP. The mixture was repeatedly vortexed and ultrasonicated until the desired viscosity was achieved. 15  $\mu$ L of the slurry was then drop-cast onto FTO glass and dried immediately using a heat gun.

**Photocatalytic experiments** were carried out in a quartz cuvette with a total volume of 5.08 mL. The reactor was loaded with 3.50 mL of acetonitrile, 1.0 mg of photocatalyst and 5.0 mg of BIH. The mixture was then purged with  $CO_2$  until saturation was reached and exposed to a 300 W Xe lamp equipped with a water filter and a 370 or 400 nm long-pass filter. At given time intervals, 100 µL of the headspace atmosphere was sampled to quantify the amount of produced CO using a gastight syringe and analyzed using **Gas Chromatography** (GC) (Shimadzu GC2014), equipped with a flame ionization detector (FID) and a methanizer. A PerkinElmer Clarus 580 – GC-TCD was employed to check potential H<sub>2</sub> production.

**Stability experiments** were conducted under the same conditions as the photocatalytic experiments. After 24 h, the COF powder was removed from the reaction suspension *via* filtration, washed with small amounts of THF and subsequently dried under vacuum.

**Gas Chromatography-Mass Spectrometry** (GC-MS). To reveal the carbon source in the photoreaction product, namely carbon monoxide (CO), <sup>13</sup>C isotope labelled CO<sub>2</sub> gas (Sigma Aldrich, 99 atom % <sup>13</sup>C, < 3 atom % <sup>18</sup>O) was used in the photocatalytic reaction following the same procedure described above. In this case, a gas sample (500  $\mu$ L) from the headspace of the cuvette was analysed by GC-MS Shimadzu QP2020-NX with electron ionisation (EI) equipped with a U-Bond column (30 m, ID 0.32 mm) for <sup>13</sup>CO<sub>2</sub> separation and a Molsieve 5A column (30 m, ID 0.32mm) for <sup>13</sup>CO separation without N<sub>2</sub> interference. The standard gas mixture of

CO<sub>2</sub>, CO, CH<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub> as balance (All-in-gas GmbH) was used to set the instrument method and to identify the analytes' retention times (RT). The characteristic ions at  $RT_{CO} = 6.7$  min with m/z 29 (<sup>13</sup>C<sup>16</sup>O), 28 (<sup>12</sup>C<sup>16</sup>O), 16 (<sup>16</sup>O), and 13 (<sup>13</sup>C) were detected in single ion monitoring mode (SIM). Shimadzu Postrun Data Analysis software was used to process the data.

# **S2. Synthetic Procedures**

Synthesis of COF linker molecules. The COF linker 2,2'-bipyridine-5,5'-dicarbaldehyde (bpy) was purchased from BLDpharm. Dibenzo[g,p]chrysenetetraamine, (DBCTA) was synthesized according to the literature.<sup>22</sup> The <sup>1</sup>H NMR spectrum of the compound is shown in Figure S4.1.



Figure S4.1. <sup>1</sup>H NMR spectrum of DBCTA: <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 8.15 (d, J = 8.8 Hz, 4H, C(1)H), 7.55 (d, J = 2.3 Hz, 4H, C(2)H), 6.9 (dd, J = 8.8, 2.3 Hz, 4H, C(3)H), 5.39 (s, 8H, NH<sub>2</sub>).

#### 4 Designing Atomically Precise and Robust COF Hybrids for Efficient Photocatalytic CO2 Reduction



Scheme S4.1. Scheme of the synthesis route for bpyDBC COF.

Synthesis of bpyDBC COF. In a 6 mL Schott-Duran culture tube, a solid mixture of 2,2'bipyridine-5,5'-dicarbaldehyde, 0.03 bpy(CHO)<sub>2</sub> (6.38 mmol) mg, and dibenzo[g,p]chrysenetetraamine, DBCTA (5.84 mg, 0.015 mmol) was suspended in 500 µL 1,4-dioxane and mesitylene (250  $\mu$ L each). Subsequently, 50  $\mu$ L of acetic acid (aqueous, 6 M) was added. The culture tube was tightly sealed and heated at 120°C for 4 days. The resulting suspension was filtered and the isolated brown powder was Soxhlet-extracted with THF for 8 h, followed by extraction in supercritical CO<sub>2</sub> at 110 bar and 40°C for 1 hour. Elemental analysis for (C<sub>50</sub>H<sub>28</sub>N<sub>8</sub>)<sub>n</sub>, calculated: C, 81.07; H, 3.81; N, 15.13. Found: C, 69.94; H, 4.27; N, 12.62. Calculations for the elemental analysis were based on an infinite structure, ignoring the presence of undefined end-groups.

Synthesis of Re<sup>1</sup>bpyDBC COF. BpyDBC COF (30 mg) and [Re(CO)<sub>5</sub>Cl] (14.65 mg, 0.04 mmol) were dispersed in 15 mL toluene and heated to reflux for 40 min. The resulting dark brown powder was filtered hot and washed thoroughly with methanol. The resulting powder was dried under vacuum. ICP-OES analysis was conducted to determine the Re content to 15.87  $\pm$  0.43 wt%, which equals an occupation of bpy sites of 43.5  $\pm$  2.7 %. Despite meticulous execution of experiments, the range of Re content varies slightly for each batch. The batch used for Rietveld analysis and STEM-HAADF contained 16.2 wt% Re with a bpy occupation of 43.9 %, the batch for the photocatalytic measurements contained 16.91 wt% Re, which equals to 0.93 mmol Re g<sup>-1</sup> and an occupation of the bpy sites of 47 %. The percentage of bpy sites occupied by Re<sup>I</sup>(CO)<sub>3</sub>Cl is calculated based on the following considerations:

To estimate the molecular weight of the COF, a fragment reflecting the 2:1 ratio of the bpy to the DBC linker is considered (Scheme S4.1). The molecular weight of this  $C_{50}H_{28}N_8^{4+}$  fragment is M = 740.83 g mol<sup>-1</sup>.



Scheme S4.2. COF fragment reflecting of 2:1 ratio of bpy to DBC.

The weight percent of rhenium given by the ICP-OES can be expressed as the following equation:

$$y = \frac{x * M(\text{Re})}{M(C_{50}\text{H}_{28}\text{N}_8^{4+}) + x * M(\text{Re}(\text{CO})_3\text{Cl})}$$

where x is a number between 0 and 2, corresponding to the number of immobilized Recomplexes per fragment (max. value = 2, since only two bpy sites are available per fragment). A 100% coverage of the two available bpy sites of the fragment translates to two additional  $Re^{I}(CO)_{3}CI$  compounds, each with a weight of M = 305.69 g mol<sup>-1</sup>, thus 2 in the equation. Insertion of the corresponding molecular weights (M(Re) = 182.21 g mol<sup>-1</sup>) yields a value of 0.269, or 26.9 wt% for a 100% coverage of the bpy sites with Re-complex.

In reality, the value obtained by ICP-OES is used to calculate the coverage of bpy sites. For example, ICP-OES measures 16.2 wt% Re in the sample of interest. Replacing 0.162 in the above equation and solving it for yields a value of 0.878. Applying the rule of three, if 2 corresponds to 100%, then 0.878 corresponds to coverage of 43.9% of the bpy sites.

Synthesis of sacrificial donor. The benzimidazolidine derivate, BIH (1,3-dimethyl-2-phenylbenzo[d]imidazolidine) was synthesized as previously reported.<sup>45</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub> 400 MHz)  $\delta$  (ppm): 7.61–7.53 (m, 2H), 7.45–7.37 (m, 3H), 6.71 (dd, J = 5.4, 3.2 Hz, 2H), 6.43 (dd, J = 5.4, 3.2 Hz, 2H), 4.88 (s, 1H), 2.56 (s, 6H).

## **S3. Rietveld Refinement**

Molecular models were constructed by connecting the bpy and DBC building blocks, resulting in the hexagonal Kagomé connectivity shown in Scheme 4.1. As indicated by STEM-HAADF imaging, the Re atoms can be both oriented towards the small pore or the large pore of the COF. The bpy unit can face either into the small trigonal or into the large hexagonal pore of the Kagomé structure and the imine bonds can be rotated either clockwise or anti-clockwise with respect to the DBC node. We combined the four resulting variations (*i*) – (*iv*) for bpyDBC and (*i*<sub>*Re*</sub>) - (*iv*<sub>*Re*</sub>) for Re<sup>I</sup>bpyDBC, reflecting extreme cases (Figure S4.12), thereby expecting to exhaustively cover the space of possible distributions.

Powder X-ray diffraction patterns of bpyDBC and Re<sup>I</sup>bpyDBC were fully indexed with hexagonal lattices and refined lattice constants of a = b = 44.7(1) Å, c = 3.74(1)Å (bpyDBC) and a = b = 44.8(1) Å, c = 3.65(1)Å (Re<sup>I</sup>bpyDBC). For the Rietveld refinement<sup>25</sup> of bpyDBC the four variants (Figure S4.2) were used with a fixed weight of 0.25, fixed atomic positions and constrained to have equal lattice parameters, crystallite sizes and Re<sup>I</sup> fractions.

	bpyDBC	Re <sup>I</sup> bpyDBC
Space group	Р6	P6
a, b	44.7(1)	44.8(1)
c	3.561(4)	3.65(1)
Re <sup>I</sup>		0.468(4)
wR	3.49 %	2.66 %



\*DBC core as point of reference

Figure S4.2. Structural variants of the two COFs.

## S4. Structural and Electronic Characterization of the bpyDBC and Re<sup>I</sup>bpyDBC COF



#### **Nitrogen Sorption experiments**

Figure S4.3. (a) Nitrogen sorption isotherms of bpyDBC and Re<sup>I</sup>bpyDBC COF and (b) pore size distributions of both COFs.

#### **FTIR Spectroscopy**



Figure S4.4. FTIR spectra of the two linkers bpy(CHO)<sub>2</sub> and DBCTA together with the spectrum of the bpyDBC COF.

#### MAS NMR



Figure S4.5. Solid-state <sup>13</sup>C CP-MAS-NMR spectrum of bpyDBC COF. The absence of a peak corresponding to the aldehyde functions at approximately 190 ppm as well as the presence of a peak at approximately 155 ppm corresponding to the imine bond confirms the formation of the imine-linked framework. The peaks were assigned to the most probable carbon atoms. The signals marked with an asterisk correspond to spinning sidebands.

# Thermogravimetric Analysis



Figure S4.6. TGA of bpyDBC and Re<sup>I</sup>bpyDBC, measured under a synthetic air flow (25 mL min<sup>-1</sup>) at a heating rate of 10 K min<sup>-1</sup>.

# **Electron Microscopy**

SEM micrographs were collected to study the morphology of the two COFs. The pristine COF displays rod-like structures growing on spherical particles that merge into larger domains while the Re<sup>I</sup>-decorated COF shows similar spherical particles covered by platelet-like structures.



Figure S4.7. SEM micrographs of (a) bpyDBC and (b) Re<sup>I</sup>bpyDBC COF.

TEM images confirm the crystallinity of the COFs, with domain sizes of 50-100 nm for both bpyDBC and Re<sup>I</sup>bpyDBC (Figures S4.8a and S4.9a). STEM-HAADF images of the pristine COF are not expected to provide further insights since the light atoms of the COF are only weakly scattering into large angles and the COF is further prone to beam damage (Figure S4.8b). In contrast, the highly ordered, periodic Re<sup>I</sup> substructure of the Re<sup>I</sup>bpyDBC COF is clearly observed by STEM-HAADF throughout the sample. Figure S9b-d shows example STEM-HAADF images of the Re<sup>I</sup>bpyDBC COF.



Figure S4.8. (a) TEM and (b) STEM-HAADF images of the bpyDBC COF.

4 Designing Atomically Precise and Robust COF Hybrids for Efficient Photocatalytic CO2 Reduction



Figure S4.9. (a) TEM image and (b) - (d) STEM-HAADF images of the Re<sup>I</sup>bpyDBC COF taken at different positions and magnifications.





Figure S4.10. Tauc plot of the two COFs assuming a direct transition. The band gap energy is reduced upon introduction of the Re-complex into the COF structure.



## Cyclic Voltammetry

Figure S4.11. CV curves for both COFs measured against the ferrocene redox couple. The onset of the first oxidation peak reflects the conduction band energy of the material.

# **CO2 Sorption Experiment**



Figure S4.12. CO<sub>2</sub> adsoption and desorption of both bpyDBC and Re<sup>I</sup>bpyDBC COF at 273 K and 294 K.

## **S5.** Photocatalytic experiments

## Reaction scheme of sacrificial donor



Scheme S4.3. Oxidation process of the sacrificial donor BIH in the photochemical CO<sub>2</sub> reduction. PS stands for photosystem, in this work the Re<sup>I</sup>bpyDBC COF.

## Comparison with the literature

Table S4.1. COF-based hybrid Re<sup>I</sup> complexes applied in the photoreduction of CO<sub>2</sub> to CO.

COF	CO productio n rate [µmol g <sup>-</sup> <sup>1</sup> h <sup>-1</sup> ]	Sacrificial agent/ solvent	Conc. [mg mL <sup>-</sup> <sup>1</sup> ]	Amoun t of Re <sup>I</sup> active sites [μmol]*	TONco	Light source	Ref.
Re <sup>I</sup> bpyDBC	1160	BIH/CH3CN	0.3	0.93	35 (24h, after two addition al purges with CO <sub>2</sub> )	300 W (Xe) >370 nm	[This work]
Re-Bpy- sp <sup>2</sup> -c-COF	1040 1400 <sup>a</sup>	TEOA/ CH3CN	0.2	0.97	18.7 (17.5 h)	300 W (Xe) >420 nm	46
Re-COF	750	TEOA/ CH3CN	0.3	0.27	48	225 W (Xe) >420 nm	16
Re-TpBpy- COF	282	TEOA/ CH <sub>3</sub> CN-H <sub>2</sub> O	1.3	21.3	-	200 W (Xe) >390 nm	17
Re <sup>I</sup> bpyDBC	180	BIH/CH <sub>3</sub> CN	0.3	0.93	7.0 (72 h)	300 W (Xe) >420 nm	[This work]

<sup>a</sup> In the presence of a photosensitizer

\* The Re<sup>I</sup> content was calculated based on the wt% given by ICP OES. For example, in this work, 1 mg of COF used in the photocatalytic experiments contains 16.91 wt% Re, or 169.1 µmol. Divided by the molar mass of Re (182.21 g mol<sup>-1</sup>), a Re content of 0.93 µmol is determined.

# 4 Designing Atomically Precise and Robust COF Hybrids for Efficient Photocatalytic CO2 Reduction

Table S4.2. Comparison of the duration of the photocatalytic experiments for several COF-based CO<sub>2</sub> photocatalysts.

COF	Duration of photocatalytic experiment [h]	Ref.	
Re <sup>I</sup> bpyDBC (> 400 nm)	72	[This work]	
PdIn@N <sub>3</sub> -COF	24	47	
Re-COF	22.5	16	
COFdpy-Co	18	19	
Re-Bpy-sp <sup>2</sup> c-COF	17.5	46	
Re-TpBpy-COF	12	17	



<sup>13</sup>CO<sub>2</sub> isotope labelling experiments

 $\lambda > 370 \text{ nm}$ 

Figure S4.13. GC-MS analysis of photocatalytic experiments under an illumination of  $\lambda > 370$  nm using isotopically labelled <sup>13</sup>CO<sub>2</sub>. (a) Gas chromatography (GC) data showing the retention time of the detected CO and (b) mass spectrometry (MS) confirming the isotopic signature of <sup>13</sup>CO (M = 29 g mol<sup>-1</sup>), indicating its origin from <sup>13</sup>CO<sub>2</sub>.

 $\lambda > 400 \text{ nm}$ 



Figure S4.14. GC-MS analysis of photocatalytic experiments under an illumination of  $\lambda > 400$  nm using isotopically labelled <sup>13</sup>CO<sub>2</sub>. (a) Gas chromatography (GC) data showing the retention time of the detected CO and (b) mass spectrometry (MS) confirming the isotopic signature of <sup>13</sup>CO (M = 29 g mol<sup>-1</sup>), indicating its origin from <sup>13</sup>CO<sub>2</sub>.

# **Recycling studies**



Figure S4.15. Recycling studies under illumination with  $\lambda > 370$  nm. Straight lines indicate the linear fitting to extract the CO production rates of 0.94 mmol g<sup>-1</sup> h<sup>-1</sup> and 1.18 mmol g<sup>-1</sup> h<sup>-1</sup> for the first and second cycle, respectively. The observed plateau in CO production at the end of the second cycle can be attributed to the depletion of BIH, the sacrificial donor.

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# CHAPTER 5

Mn(I)-functionalized Covalent Organic Framework as Efficient Electrocatalyst for CO<sub>2</sub> Reduction in a Catholyte-Free Zero-Gap Electrolyzer
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# 5.1 Abstract

Covalent Organic Frameworks (COFs) have emerged as versatile platforms for the rational design of heterogeneous CO<sub>2</sub> electrocatalysts, offering molecular-level precision due to their well-ordered, porous structure. While COF-based hybrid electrocatalysts have demonstrated potential in lab-scale electrochemical cells with liquid electrolytes, their application in industry-relevant architectures remains largely unexplored. Here, we present the first successful integration of a phenanthroline-based 2D COF modified with Mn(I) single catalytic sites into a catholyte-free membrane-electrode-assembly (MEA) cell for CO<sub>2</sub> electroreduction. The crystalline COF catalyst achieves an outstanding turnover frequency of 618 h<sup>-1</sup> (quantified per total concentration of catalytic sites) and a CO evolution of 62  $\mu$ mol cm<sup>-2</sup> (at a full-cell potential of 3.0 V) within 30 min. Moreover, the COF structure actively suppresses Mn<sup>o</sup>-Mn<sup>o</sup> dimer formation and supports stable operation at high potentials with a *jco* of 3.6 mA cm<sup>-2</sup>. The synergy between the crystalline nature of the COF and the MEA cell architecture, facilitating direct interactions between the modified electrode and the CO<sub>2</sub> gas, enhances both the catalytic activity and stability. This work paves the way for broader adoption of COF-based hybrid materials in advanced electrocatalytic CO<sub>2</sub> reduction technologies.

# 5.2 Introduction

Electrocatalytic CO<sub>2</sub> reduction powered by renewable energy offers an eco-friendly and sustainable approach to carbon recycling, enabling the capture and transformation of CO<sub>2</sub> into valuable chemicals <sup>1,2</sup> Homogeneous electrocatalysts based on *fac*-[Mn(L)(CO)<sub>3</sub>Br] (where L represents a polypyridyl moiety) have garnered significant attention for the reduction of CO<sub>2</sub> to CO, owing to their synthetic tunability, high selectivity and faradaic efficiencies, as well as the natural abundance of manganese in the Earth's crust.<sup>3-4</sup> Molecular Mn(I) tricarbonyl complexes, however, tend to deliberately form Mn<sup>0</sup>-Mn<sup>0</sup> dimeric species, which is unable to catalyze the CO<sub>2</sub> reduction reaction.<sup>5-6</sup> Various strategies have been developed to stabilize the Mn(I) species and prevent dimerization, including the incorporation of bulky or electrondonating ligands to provide steric hindrance, as well as the heterogenization of the homogeneous catalyst onto solid supports such as carbon nanotubes or TiO2.7-12 While significant progress has been made with such hybrid systems in achieving excellent selectivity and high current densities, this approach suffers from several limitations. Poor control over the spatial catalyst distribution due to a lack of well-defined binding sites on the solid support as well as a limited structural tunability restrict the ability to precisely tailor the local environment around the catalytic centers. <sup>13-16</sup>

Covalent organic frameworks (COFs) have been recognized as promising platforms for immobilizing molecular electro- and photocatalysts due to their synthetic versatility, structural robustness and well-defined crystalline and porous structure.<sup>17-18</sup> The rational design of the organic building blocks and the covalent linkage chemistry allow for tailor-made materials with pre-defined features.<sup>19-20</sup> The incorporation of metal-coordinating building blocks (among other bipyridine, porphyrin, or salen) has proven to be a viable way to immobilize metal centers into the porous framework, thereby creating hybrid systems with atomistic control over the structural design.<sup>21-23</sup>

While numerous studies have explored bipyridine (bpy)-based COFs heterogenizing metal centers (e.g., Re(I), Mn(I), Mo(II), Ni(II)),<sup>23-28</sup> only a few have incorporated the more conjugated phenanthroline as a metal-coordinating building block.<sup>29-33</sup> Due to its fused aromatic ring system, phenanthroline offers greater rigidity compared to bipyridine, which enhances the stability of coordinated metal centers. Additionally, its higher degree of electron delocalization can facilitate charge transfer and improve catalytic efficiency.<sup>34-35</sup> López-Magano and co-workers demonstrated the potential of phenanthroline-containing imine-linked

COFs (Phen-COFs) by immobilizing Ni(II) and Ir(III) to create a heterogeneous dual photocatalyst for C–C cross-coupling reactions between aryl bromides and radical precursors.<sup>29-30</sup> The phenanthroline moiety played a crucial role in stabilizing the metal centers, preventing leaching of metal fragments into the reaction medium, thereby enhancing both activity and recyclability. Recently, Lloret-Fillol and co-workers conducted a systematic mechanistic study on a Mn-based COF incorporating a phenanthroline building block. Despite its potential, poor crystallinity and low porosity of the phenanthroline-based COF limited the catalytic performance, including its ability to suppress undesired dimerization of Mn complexes.<sup>32</sup> These findings underscore the need for further research to advance the design and synthesis of phenanthroline-based COFs containing Mn-complexes, aiming to improve their crystallinity, porosity, and catalytic properties to fully harness the potential of phenanthroline in electrocatalytic CO<sub>2</sub> reduction.

To date, the performance of COF-based electrodes for CO<sub>2</sub> reduction has been evaluated applying traditional liquid phase electrochemical cells such as H-cells.<sup>36-37</sup> However, in such studies, the current density has often been limited by the CO<sub>2</sub> solubility in the liquid electrolytes and its poor diffusion. The catholyte-free membrane-electrode-assembly (MEA) represents an elegant alternative offering several advantages for the development of electrochemical CO<sub>2</sub> reduction processes. By enabling direct contact between the catalyst and CO<sub>2</sub> gas while avoiding interaction with aqueous electrolytes, this architecture mitigates mass transport limitations, enhances CO<sub>2</sub> availability at the catalytic sites, reduces parasitic hydrogen evolution reactions and decreases the ionic resistance due to the zero-gap design.<sup>38-39</sup> The combination of this advanced electrochemical cell design with COF-based electrocatalysts, which exhibit highly porous structures and high specific surface areas (~800 to 2000 m<sup>2</sup> g<sup>-1</sup>), opens new opportunities for the precise control of catalytic properties and offers a powerful strategy for developing next generation electrocatalysts with improved performance and stability for sustainable CO<sub>2</sub> reduction applications.<sup>40-41</sup>

In this work, we present the design and synthesis of a crystalline imine-linked 2D COF constructed from 4,4'-(1,10-phenanthroline-3,8-diyl)dibenzaldehyde (Phen) and 4,4',4'',4'''- (pyrene-1,3,6,8-tetrayl)tetraaniline (Py). Post-functionalization of the resulting **PhenPy** framework with [Mn(CO)<sub>5</sub>Br] yields the heterogeneous electrocatalyst **Mn PhenPy** COF, where the nitrogen atoms of Phen serve as predefined coordination sites for the metal centers (Figure 5.1a). Gas diffusion electrodes (GDEs) based on conductive carbon paper were fabricated using **Mn PhenPy** COF and integrated into a catholyte-free membrane-electrode-

assembly (MEA) cell for the electrochemical reduction of CO<sub>2</sub> to CO. This study represents the first example of a COF-based material utilized as an active CO<sub>2</sub> reduction electrocatalyst in an industry-relevant MEA cell architecture, thus providing a proof-of-principle for the successful integration of COF-based materials into scalable and efficient CO<sub>2</sub> reduction technologies. Furthermore, we demonstrate that the **Mn PhenPy** COF mitigates the formation of the detrimental dimeric Mn<sup>0</sup>–Mn<sup>0</sup> species, in contrast to previously reported studies on similar COFs.<sup>32</sup> The high crystallinity and porosity of **Mn PhenPy** are identified as the key factors in suppressing dimerization and enhancing electrocatalytic performance. As a result, **Mn PhenPy** outperforms both the molecular Mn catalyst and previously reported bipyridine (bpy) - and phenanthroline-based Mn COF hybrids in terms of turnover number and frequency.

## 5.3 Results and Discussion

Design and Structural Characterization. Under solvothermal conditions, the building blocks Phen and Py were connected employing a Schiff-base acid-catalyzed imine condensation reaction, resulting in the formation of the crystalline PhenPy COF (Figure 5.1a). The crystallinity of the synthesized COF was confirmed by powder X-ray diffraction (PXRD) analysis, shown in Figure 1b, with the material exhibiting sharp reflections at 2.4°, 4.9°, 7.5° and 10.0° 2 $\theta$ . The reflection at 24° corresponds to the (001) plane, which is attributed to the  $\pi$ - $\pi$  stacking of the two-dimensional COF sheets with a distance of 3.7 Å. A simulated structure model of the PhenPy COF was Pawley-refined based on the triclinic space group P1. In line with the structure of the previously reported, structurally similar  $COF_{bpy}$  (bpy = bipyridine), an AB stacking model was chosen where one layer is rotated by 180° about the b axis to point the stacked phenanthroline groups toward different pores (inset in Figure 5.1c).<sup>23</sup> The refined pattern provides a good fit of the experimentally obtained data, with the refined unit cell parameters a = 57.0 Å, b = 46.8 Å, c = 3.7 Å and  $\alpha = 90.5^{\circ}$ ,  $\beta = 91.5^{\circ}$  and  $\gamma = 90.0^{\circ}$ . SEM micrographs of the PhenPy COF powder in Figure 1d reveal a uniform, fibrillar morphology of interconnected ribbon-like structures. The morphological features suggest a highly porous structure beneficial for gas diffusion and adsorption. The morphology is also reflected in TEM images, with fully crystallized ribbon-like structures visible in Figure S5.4.

Nitrogen sorption experiments at 77 K yielded a Brunauer-Emmett-Teller (BET) surface area of 929 m<sup>2</sup> g<sup>-1</sup>, significantly higher than those reported for other **Phen**-based COFs,<sup>29-30, 32</sup> further confirming the high crystallinity and porosity of the **PhenPy** COF (Figure 5.1e). Pore sizes were analysed using the quenched solid density-functional theory (QSDFT) model for 1D cylindrical pores, revealing a pore size of 3.3 nm, matching the simulated value of about 3.4 nm (inset Figure 5.1e). The successful formation of the COF network was further corroborated by Fourier-transform infrared (FTIR) spectroscopy. The absence of the aldehyde vibration of the **Phen** building block at 1690 cm<sup>-1</sup> and the amine vibrations of the **Py** building block at 1614, 3352 and 3454 cm<sup>-1</sup> in the FTIR spectrum of the COF in Figure S5.5 agree with the formation of the imine bond, visible as a shoulder at 1624 cm<sup>-1</sup>. Hence, PXRD, FTIR, and nitrogen sorption analysis conclusively validate the formation of the COF network with well-defined structural and textural properties, aligning closely with the simulated model.

5 Mn(I)-functionalized Covalent Organic Framework as Efficient Electrocatalyst for CO2 Reduction in a Catholyte-Free Zero-Gap Electrolyzer



Figure 5.1. (a) Synthesis of **PhenPy** COF and immobilization of [Mn(CO)<sub>5</sub>Br], yielding **Mn PhenPy** COF (schematic). (b) Experimental and indexed Pawley-refined PXRD pattern of **PhenPy** COF. Pawley refinement was conducted using the simulated structure model of **PhenPy**, based on the triclinic space group *P1*. (c) Unit cell of **PhenPy** COF. Alternating phenanthroline moieties in adjacent layers face towards different pores (inset). The cell parameters of the refined structure are provided in the Section S7. (d) SEM micrograph of the **PhenPy** COF powder, indicating a fibrillar morphology. (e) Nitrogen sorption experiments reveal high porosity with a BET surface area of 929 m<sup>2</sup>g<sup>-1</sup>. Inset: pore size distribution and cumulative pore volume of **PhenPy**.

Post-functionalization of the **PhenPy** COF with [Mn(CO)<sub>5</sub>Br] was conducted at 85°C in ethyl acetate for 1 h under Ar atmosphere, following a well-established procedure preserving the chemical nature of the complex (Figure 5.1a).<sup>23, 32</sup> Due to the light-sensitivity of the Mn-complex, functionalization reactions were carried out in the dark. The PXRD of **Mn PhenPy** COF exhibits diffraction peaks analogous to the pristine **PhenPy** COF, showing that the crystalline structure of the material is preserved (Figure 5.2a). The amount of Mn(I) incorporated into the COF structure was obtained by ICP-OES, resulting in 2.2 wt% of Mn, which corresponds to 28% of the COF phenanthroline moieties coordinated to Mn centers (see Supporting Information for details on the calculation).

The three characteristic CO vibration bands observed between 1850 and 2050 cm<sup>-1</sup> in the FTIR spectrum provide further evidence of the successful immobilization of the tricarbonyl Mn(I) complex within the porous COF structure (Figure 5.2b). These bands correspond to the  $A_1$  and two E modes expected for the *facial* geometry of the Mn(CO)<sub>3</sub>Br moiety and closely resemble those of the molecular analog *fac*-[Mn(Phen)(CO)<sub>3</sub>Br], where the COF building block Phen acts as ligand to the Mn center.<sup>42</sup> Scanning electron micrographs (SEM) in Figure 5.2c show a similar uniform and fibrillar morphology as for PhenPy, featuring ribbon-like structures. SEM-EDX (energy dispersive X-ray spectroscopy) spectra collected at various spots on the powder surface confirm the presence of Mn and Br while micrographs taken in back-scattered-electron mode exclude the formation of metal-clusters (Figure S5.6, S5.8). As shown in Figure S5.7, SEM-EDX mapping suggests a homogeneous distribution of the Mn-complex in the Mn PhenPy COF structure. The nitrogen sorption experiments of Mn PhenPy COF reveal a reduced BET surface area of 306 m<sup>2</sup> g<sup>-1</sup> (Figure S5.9) in relation to the pristine COF which is commonly observed upon post-modification of COFs with metal centers.<sup>23, 25, 43</sup> Thermogravimetric analysis (TGA) of both COFs shows thermal stability under the dynamic conditions of up to 400 °C for Mn PhenPy and 450 °C for PhenPy (Figure S5.10).

**Physical Properties.** For efficient electrocatalysis, a high affinity of the catalyst for  $CO_2$  adsorption is required, therefore  $CO_2$  sorption experiments were performed at temperatures of 273 K and 294 K and pressures of up to 1000 mbar (100 kPa). **Mn PhenPy** COF showed a maximum  $CO_2$  uptake of 2.5 mmol g<sup>-1</sup> at 273 K, while its pristine counterpart **PhenPy** adsorbed only 1.6 mmol g<sup>-1</sup> at the same temperature (1.5 mmol g<sup>-1</sup> and 1.0 mmol g<sup>-1</sup> at 294 K, respectively, Figure 5.2d, S5.11). Despite the decrease in surface area, these observations suggest an increase of the affinity of the COF towards  $CO_2$  upon introduction of the Mn centers into the porous structure.



Figure 5.2. (a) PXRD patterns of the **PhenPy** and the **Mn PhenPy** COFs. (b) FTIR spectra of **PhenPy** and **Mn PhenPy** COF, as well as of the molecular analog *fac*-[Mn(**Phen**)(CO)<sub>3</sub>Br]. (c) SEM micrographs of the **Mn PhenPy** COF. (d) CO<sub>2</sub> sorption measurements at 273 K (0 °C) indicating an enhanced affinity of **Mn PhenPy** COF towards CO<sub>2</sub> (filled dots: adsorption, open dots: desorption). (e) Energy levels of the two COFs obtained from Tauc plot fitting of the optical absorption onsets and CV measurements (Figures S5.13, S5.14), and the CO<sub>2</sub>-to-CO reduction potential. (f) Cyclic Voltammetry of **Mn PhenPy** COF and *fac*-[Mn(**Phen**)(CO)<sub>3</sub>Br] measured in a three-electrode setup in acetonitrile (TBAPF<sub>6</sub>, 0.1M) under Ar at a scan speed of 10 mV s<sup>-1</sup>.

Such an enhancement in affinity following incorporation of metal centers has also been reported in previous studies.<sup>43-44</sup>

It is well established that the incorporation of metal centers affects the electronic properties of organic frameworks. Hence, changes in electronic structure of the COF upon immobilization of Mn were investigated *via* UV-vis measurements. Figure S5.12 shows that the absorption onset of **Mn PhenPy** is red-shifted by approx. 120 nm compared to its pristine counterpart. Similar red-shifts upon incorporation of metal centers have been reported in the literature.<sup>29, 43, 45</sup> Supported by band structure calculations, Kamiya *et al.* assigned the optical shift to the presence of metal 3*d* orbitals introduced below the conduction band of the COF.<sup>46</sup> Direct band gaps of 2.48 and 2.23 eV, for **PhenPy** and **Mn PhenPy**, respectively, were determined by Tauc plot analysis (Figure S5.13).<sup>47</sup> In accordance with previously reported studies,<sup>48-50</sup> cyclic voltammetry (CV) measurements under oxidative conditions were performed, enabling the

determination of the valence band (VB) energies of the pristine COF and the Mn-decorated COF at -5.02 eV and -5.51 eV, respectively, relative to the vacuum level (Figure S5.14). Combining CV and UV-vis results, the conduction band (CB) energies of the two materials were estimated. The energy levels of **PhenPy** COF and **Mn PhenPy** COF are shown in Figure 5.2e, indicating that both COFs are thermodynamically capable of reducing CO<sub>2</sub> to CO.

To evaluate the ability of the COF structure to prevent the formation of the undesirable Mn<sup>o</sup>-Mnº dimer species upon electroreduction, CV curves were recorded of Mn PhenPy and its molecular analog fac-[Mn(Phen)(CO)<sub>3</sub>Br] at negative applied potentials. Under Ar atmosphere with anhydrous CH<sub>3</sub>CN as the electrolyte, *fac*-[Mn(Phen)(CO)<sub>3</sub>Br] displayed prominent peaks at -1.73 V and -2.05 V vs. SCE in the forward scan and two peaks at -0.75 and 0.21 V vs. SCE during the reverse CV scan, which were absent in Mn PhenPy COF (Figure 5.2f). The electrochemical behavior of molecular and immobilized Mn-complexes has been extensively studied applying a wide range of spectroscopic and electrochemical techniques.<sup>5, 8-9</sup> Accordingly, the obtained CV peaks can be assigned to the formation and respective reoxidation of the Mn<sup>0</sup>–Mn<sup>0</sup> dimer and the mononuclear  $[Mn(L)(CO)_3]^-$ , formed by the twoelectron reduction of the dimer.<sup>3</sup> A more detailed analysis of the redox features of the molecular analog fac-[Mn(Phen)(CO)<sub>3</sub>Br] is presented in Figure S5.15. The absence of these redox reactions in the CV process of the Mn PhenPy COF indicate that immobilizing the Mn complex within the COF structure, through its phenanthroline moieties, effectively inhibits the formation of the undesired Mn dimer. Lloret-Fillol et al. reported on the ability of a bipyridinebased COF to impose structural constraints on the Mn-complex, thereby preventing dimerization.<sup>23</sup> However, they were unable to achieve a similar complete suppression of Mn<sup>0</sup>-Mn<sup>0</sup> formation using a phenantroline-based COF, in contrast to our findings. <sup>32</sup> We propose that the high crystallinity and porosity of the herein synthesized PhenPy COF plays a crucial role in effectively constraining the Mn centers within the COF framework, thereby successfully inhibiting dimerization.

**Electrocatalytic CO<sub>2</sub> Reduction.** Due to its promising electrochemical properties for CO<sub>2</sub> reduction, the **Mn PhenPy** COF was tested as electrocatalyst for the reduction of CO<sub>2</sub> to CO. Gas diffusion electrodes (GDE) were fabricated by spray-coating an ink containing the COF as active material on a carbon paper. The GDE was implemented as cathode in a catholyte-free MEA cell. In this cell architecture, the GDE enables the supply of gaseous CO<sub>2</sub> closer to the catalyst surface and the cathode and anode are located more closely to each other (zero-gap cell) by separation with an anion-exchange membrane (*Sustainion*, 50 µm thick).<sup>51</sup> Thereby, a

MEA cell architecture can overcome the decrease the ionic resistance appreciably, resulting in higher energy efficiency. Additionally, as the CO<sub>2</sub> is directly fed in the cathodic chamber, this cell design addresses the problem related to the mass transport limitation due to the low solubility of CO<sub>2</sub> in aqueous electrolyte.<sup>52</sup> Ni foam was used as anode and 1M KOH as anolyte, with a *Sustainion* anion exchange membrane connecting the anode and cathode (Figure 5.3a).<sup>53-55</sup> To assess the CO<sub>2</sub> reduction ability, selectivity and stability of the **Mn PhenPy** COF, measurements were conducted under potentiostatic conditions applying a full cell potential range of 2.6 to 3.2 V for 30 min for each potential step, while monitoring the current density and CO production. The gaseous products exiting the cell were carried by the continuous CO<sub>2</sub> flow into a gas sampling bag, from which aliquots were collected using a gas-tight syringe and injected into a gas chromatograph for CO quantification.



Figure 5.3. (a) Schematic representation of the catholyte-free MEA cell architecture employing a GDE containing **Mn PhenPy** COF as active electrocatalyst. (b) Turnover number for CO of **Mn PhenPy** COF and *fac*-[Mn(bpy)(CO)<sub>3</sub>Br] at different applied full-cell potentials (details in Table S1) and (c) the respective partial current densities for CO formation  $j_{CO}$ 

(chronoamperometry), measured using a catholyte-free MEA cell with 1 M KOH as anolyte and a *Sustainion* anion-exchange-membrane.

Utilizing the pristine PhenPy COF as an electrocatalyst in this cell assembly resulted in no detectable CO formation. In contrast, the Mn PhenPy COF demonstrated high CO<sub>2</sub>-to-CO conversion, achieving high CO evolution of 62  $\mu$ mol cm<sup>-2</sup> within 30 min under an applied cell voltage of 3.0 V, resulting in a maximum turnover number (TON<sub>CO</sub>) of 309, and a turnover frequency (TOF<sub>CO</sub>) of 618 h<sup>-1</sup> (see Table S5.1 for details on the TON<sub>CO</sub> and TOF<sub>CO</sub> calculations). This confirms that the Mn centers act as catalytically active sites within the COF. To evaluate the catalytic performance of the novel Mn PhenPy COF, comparative measurements were conducted under identical conditions using the well-established fac-[Mn(bpy)(CO)<sub>3</sub>Br] complex as benchmark.<sup>3</sup> Equivalent to the Mn PhenPy COF, the molecular catalyst was spray-coated onto carbon paper and integrated as GDE into the MEA cell. First reported in 2011 by Chardon-Noblat and Deronzier et al. as an active and selective catalyst for CO<sub>2</sub> reduction to CO, *fac*-[Mn(bpy)(CO)<sub>3</sub>Br] has since then been extensively studied as both electro- and photocatalyst.<sup>3, 56</sup> The catalytic performance of both Mn PhenPy COF and the model molecular catalyst fac-[Mn(bpy)(CO)<sub>3</sub>Br] is presented in Figure 5.3b and c. At an applied potential of 3.0 V, the benchmark molecular catalyst achieved a maximum TON<sub>CO</sub> of only 8 and TOF<sub>CO</sub> of 16 h<sup>-1</sup>. In other words, we achieve a 30-fold enhancement in TON<sub>CO</sub> and TOF<sub>CO</sub> when the Mn complex is immobilized within the porous COF structure (Figure 5.3b). Furthermore, the Mn PhenPy COF outperforms previously reported Mn-based hybridelectrocatalysts for CO<sub>2</sub> reduction (Table S5.2).<sup>8-9, 23, 32, 57-59</sup> Notably, in our analysis, we compared data based on the total amount of catalytic sites embedded in the COF, which can underestimate the TON and TOF. In some studies, TON and TOF values are quantified using only the estimated electroactive sites, which, in COF systems, typically represent less than 25% of the total loaded catalytic sites, resulting in significantly higher TON and TOF values.<sup>23, 32, 60</sup> However, determining the fraction of electroactive sites in a MEA cell is particularly challenging, requiring significant modifications to the cell setup. This aspect remains an important area for future studies. We attribute the remarkable catalytic activity to the high crystallinity of the Mn PhenPy COF, which provides catalytically active Mn single sites within an accessible porous framework. Additionally, the MEA cell architecture significantly enhances the performance of porous systems like COFs by facilitating efficient mass transport, improving CO<sub>2</sub> availability at the catalytic sites, and enabling better integration of the catalyst into the electrochemical environment, thereby optimizing overall catalytic efficiency.

To evaluate the stability of **Mn PhenPy**, the partial current densities for CO production (*jco*) at different full-cell potentials were collected and compared to those of *fac*-[Mn(bpy)(CO)<sub>3</sub>Br] (Figure 5.3c). The COF-based hybrid catalyst exhibited increasing current densities, rising from  $j_{CO} = 2.1$  mA cm<sup>-2</sup> at 2.6 V to a maximum value of 3.6 mA cm<sup>-2</sup> at 3.0 V, before declining at higher potentials. In contrast, the model molecular catalyst showed a steady decrease in partial CO current density with increasing potential, dropping from 1.8 mA cm<sup>-2</sup> at 2.6 V to 1.0 mA cm<sup>-2</sup> at 3.2 V. These results indicate that the COF structure not only enhances the catalytic performance of the Mn complex but also provides improved stability, allowing the catalyst to operate at higher potentials. The improved stability of the **Mn PhenPy** COF can be attributed to the immobilization of Mn within the porous COF structure, which prevents the formation of the detrimental Mn<sup>0</sup>–Mn<sup>0</sup> dimer. We assume that the CO<sub>2</sub> electrocatalytic cycle for **Mn PhenPy** aligns with previously reported mechanistic studies on similar Mn-based COF hybrids, in which the formation of the penta-coordinated Mn(-I) species drives the CO<sub>2</sub>-to-CO reduction.<sup>23, 32</sup>

5 Mn(I)-functionalized Covalent Organic Framework as Efficient Electrocatalyst for CO2 Reduction in a Catholyte-Free Zero-Gap Electrolyzer

## 5.4 Conclusion

In conclusion, we presented the successful design and synthesis of a highly crystalline electrocatalyst for CO<sub>2</sub> reduction to CO, Mn PhenPy, and its application in a catholyte-free membrane-electrode-assembly (MEA) cell. The highly ordered and porous PhenPy COF serves as solid support structure for the immobilization of Mn centers, providing pre-defined metal binding sites via its phenanthroline moieties. The resulting Mn PhenPy exhibits enhanced CO<sub>2</sub> affinity and promising electrochemical properties, making it an excellent candidate for use in a gas diffusion electrode (GDE) in a catholyte-free MEA electrolyzer for CO<sub>2</sub> reduction. The COF-based hybrid catalyst significanty outperforms the molecular benchmark catalyst fac-[Mn(bpy)(CO)<sub>3</sub>Br] in catalytic activity, achieving a 30-fold improvement in turnover number (309) and turnover frequency (618 h<sup>-1</sup>) under identical conditions at a full-cell potential of 3.0 V. Moreover, when comparing TOF values, Mn PhenPy surpasses previously reported Mn-based hybrid electrodes applied in electrochemical H-cells. In terms of stability, Mn PhenPy shows an increase in partial CO current density at higher potentials, reaching a maximum value of  $j_{CO} = 3.6 \text{ mA cm}^{-2}$  at 3.0 V, whereas the current densities of fac-[Mn(bpy)(CO)<sub>3</sub>Br] steadily decline at such high potentials. These improvements can be attributed to the unique properties of the COF structure, including the stabilization of catalytically active intermediates and the prevention of deactivation pathways, such as Mnº-Mnº dimer formation. Notably, this study marks the first time that a COF-based material has been successfully employed as an electrocatalyst in a catholyte-free MEA cell architecture, thus paving the way for broader adoption of COF-based hybrid materials in electrocatalytic CO<sub>2</sub> reduction technologies.

# 5.5 Supporting Information

The Supporting Information (SI) contains experimental methods and synthetic procedures, as well as details on the electrochemical and -catalytic measurements and calculations of the catalytic performance metrics. Further structural, optical and electronic characterization of the two COFs is provided including the unit cell parameters of the PhenPy COF.

## S1. Materials and methods

All solvents were purchased from *Sigma Aldrich*, *Acros* or *TCI Europe* in the common purities *purum*, *puriss* or *reagent grade*. The materials were used as received without additional purification and handled in air unless otherwise noted.

**Powder X-ray diffraction** (PXRD) measurements were performed using a Bruker D8 Discover instrument with Ni-filtered Cu  $K_{\alpha}$  radiation and a LynxEye position-sensitive detector.

**Theoretical structure simulations.** The COF structure was constructed using the Accelrys Materials Studio software package. A *P1* symmetry was applied and the structure model optimized using the Forcite module with the Universal Force-Field. Structure refinement using the Pawley method was carried out as implemented in the Reflex module of the Materials Studio software. Thompson-Cox-Hastings peak profiles were used, and peak asymmetry was corrected using the Berar-Baldinozzi method.

Fourier-transform infrared spectroscopy (FTIR) measurements were performed with a Bruker Vertex 70 FTIR instrument by focusing the light of a globar as a MIR light source through a KBr beam splitter with integrated gold mirrors and an ATR sample stage with a Ge crystal. The spectra were recorded by a  $N_2$  cooled MCT detector with a resolution of 2 cm<sup>-1</sup> and averaged over 128 scans.

**Scanning electron microscopy** (SEM) images were obtained with an FEI Helios NanoLab G3 UC microscope equipped with a Schottky field-emission electron source operated at 3 kV. Before measuring, the samples were coated with a 10 nm thick carbon layer. **Energy-dispersive X-ray spectroscopy** (EDX) mapping was performed at an acceleration voltage of 12 kV. The primary electron beam current was optimized as a compromise between achievable resolution and a good signal-to-noise ratio at the EDX detector. The mapping acquisition time was 15–20 minutes, with drift correction applied during the process. The acceleration voltage

for **back-scattered electron** (BSE) images was 4 kV. The beam current was adjusted as a compromise between the required image resolution and the signal-to-noise ratio at the CBS detector. The CBS detector is a doped Si detector where back-scattered electrons generate electron-hole pairs.

**Transmission electron microscopy** (TEM) was performed with a probe-corrected FEI Titan Themis instrument equipped with a field emission gun operated at 300 kV.

**Thermogravimetric analysis** (TGA) measurements were performed using a Netzsch Jupiter ST 449 C instrument equipped with a Netzsch TASC 414/4 controller. The samples were heated from room temperature to 900°C under a synthetic air flow (25 mL min<sup>-1</sup>) at a heating rate of 10 K min<sup>-1</sup>.

**Nitrogen sorption isotherms** were recorded with a Quantachrome Autosorb 1 or Autosorb iQ instrument at 77 K. **Carbon dioxide sorption** measurements were conducted on a Quantachrome Autosorb iQ at 273 K and 298 K. The sample was outgassed for 24 h at 120 °C under high vacuum prior to the measurements. Pore size distributions from nitrogen sorption data were calculated using the QSDFT model with a carbon kernel for cylindrical pores.

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV 400 and AV 400 TR spectrometers. Proton chemical shifts are expressed in parts per million ( $\delta$  scale) and are calibrated using residual non-deuterated solvent peaks as internal reference (e.g. DMSO-d<sub>6</sub>: 2.50 ppm).

**UV-vis-NIR** spectra were recorded on a Perkin-Elmer Lambda 1050 spectrometer equipped with a 150 mm integrating sphere, photomultiplier tube (PMT) and InGaAs detectors. **Diffuse reflectance spectra** were collected with a Praying Mantis (Harrick) accessory and were referenced to barium sulfate powder as 100 %R standard. The specular reflection of the sample surface was removed from the signal using apertures that allow only light scatter at angles >  $20^{\circ}$  to pass.

**Cyclic voltammetry** (CV) was performed on a Metrohm Autolab potentiostat using a threeelectrode setup with Pt wire as counter electrode, Ag wire as pseudo-reference electrode and slurry-coated FTO glass as working electrode in 0.1 M TBAPF<sub>6</sub> in acetonitrile. The electrolyte was prepared and stored under Ar. The Ag pseudo-electrode was referenced against the ferrocene redox couple. Measured potentials vs. the ferrocene redox couple  $Fc/Fc^+$  were converted to the absolute electrode potential ( $E_{vac}$ ) and to potentials vs. Standard Hydrogen Electrode (SHE) according to the following equations (i) and (ii), respectively. Note that the absolute potential scale is equal to the negative physical scale.<sup>61</sup> Potentials vs. Standard Calomel Electrode (SCE) were converted to potentials vs. SHE according to equation (iii).<sup>62</sup> Reduction potentials for the sacrificial donors retrieved from the literature were converted to SHE accordingly.

- (i)  $E_{vac} = E_{Fc/Fc^+} + 4.8 \text{ eV}$
- (ii)  $E_{vac} = E_{SHE} + 4.44 \text{ eV}$
- (iii)  $E_{SHE} = E_{SCE} + 0.241 V$

Slurries were prepared by dispersing 14.1 mg of COF material, 11.3 mg Super C65 carbon black and 2.8 mg PVDF (50:40:10) in 400  $\mu$ L NMP. The mixture was ultrasonicated for 30 min and stirred at room temperature for a minimum of 2 days to guarantee homogeneous dispersion of all components. 20  $\mu$ L of the slurry was then drop-cast onto FTO glass, covering an area of ~ 1 cm<sup>2</sup> and dried overnight at 60 °C.

**Preparation of gas diffusion electrodes.** Gas diffusion electrodes (GDEs) were prepared by spray coating on a carbon paper substrate (GDL-Sigracet, 39B) using an airbrush (Vonder). The ink was composed of 1.0 mg of catalyst, 1.0 mg of carbon black (amorphous carbon, CAS 1333-86-4), 5.0  $\mu$ L of ionomer (Sustainion XA-95% in Ethanol, Dioxide Materials Inc.) and 1.0 mL of dimethylformamide (Aldrich 99.8 %). The mixture was submitted to an ultrasonic probe sonicator (Sonics & Materials INC, VCX130) with a power rating of 130 W for 15 min. The homogenized solution was then deposited onto a 1.0 cm<sup>2</sup> area of carbon paper using the airbrush, with approximately 50% of the slurry mass lost during deposition, as determined by the difference between the initial and final mass of the carbon paper electrode. The electrode was subsequently dried in an oven at 80 °C for 24 h. Finally, the prepared electrode was applied as cathode for the electrochemical reduction of CO<sub>2</sub>.

Electrochemical CO<sub>2</sub> reduction in MEA cell. All electrochemical measurements were carried out on a potentiostat/galvanostat (Autolab PGSTAT204, Metrohm). CO<sub>2</sub> reduction performance was evaluated in a commercial catholyte-free Membrane Electrode Assembly (MEA) cell (Dioxide Materials®). GDEs containing Mn PhenPy or *fac*-[Mn(bpy)(CO)<sub>3</sub>Br] were used as cathodes, Ni foam as anode and 1 M KOH was used as anolyte, circulating at 5 mL min<sup>-1</sup>. The half-cells were connected with an anion exchange membrane (Sustainion®) and CO<sub>2</sub> gas was directly fed to the cathode at 30 mL min<sup>-1</sup>, excluding the use of an aqueous

electrolyte. Measurements were carried out under potentiostatic conditions applying a full-cell potential range from 2.6 to 3.2 V for 30 min for each potential step. The current density was monitored to assess the electrode's performance. Gaseous products leaving the cell were transported by the continuous  $CO_2$  flow cell to a gas sampling bag, where aliquots of 500  $\mu$ L were collected with a gas-tight syringe and injected into a gas chromatograph equipped with thermal conductivity detection (GC-TCD, PerkinElmer Clarus 580) for the quantification of CO. The GC-TCD is equipped with two columns (Porapak N 2 mm and molecular sieve) and a detector for thermal conductivity. The measurements were performed at 120 °C on the injector and 150 °C on the detector, with a thermal ramp of 35–120 °C. Ar was used as carrier gas at 30 mL min<sup>-1</sup>.

**TON**<sub>CO</sub> calculations. For the  $TON_{CO}$  calculations, the moles of CO produced at each potential were divided by the moles of catalytic centers (Mn) present in the catalyst deposited on the carbon paper electrode. For **Mn PhenPy** COF, ICP-OES was used to determine the amount of Mn. The parameters used in these calculations, along with the  $TON_{CO}$  values at each potential, are summarized in Table S5.1.

Catalyst	wt% of Mn (from ICP-OES)	Deposited mass of catalyst [mg]	Number of moles of catalytic centers <sup>a)</sup> [µmol]	Potential [V]	nco[µmol]	TONco
<i>fac-</i> Mn(CO) <sub>3</sub> (bpy)Br	-	0.5	1.34	2.6	19.1	14.2
				2.8	9.56	7.1
				3.0	11.1	8.3
				3.2	11.4	8.5
Mn PhenPy COF	2.22	0.5	0.202	2.6	31.7	157.0
				2.8	38.7	191.6
				3.0	62.4	309.0
				3.2	14.3	70.8

Table S5.1. Parameters considered for TON<sub>CO</sub> calculation.

<sup>a)</sup> For details on calculating the moles of Mn in the Mn PhenPy COF catalyst using ICP-OES data, refer to the *Synthesis of Mn PhenPy COF* section below.

**TOF**<sub>CO</sub> calculations. The turnover frequency for CO production (TOF<sub>CO</sub>) was calculated by dividing the TON<sub>CO</sub> by the time (i.e. 30 min) the potential was held at each potential step.

#### **S2.** Synthetic procedures

Synthesis of 4,4'-(1,10-phenanthroline-3,8-diyl)dibenzaldehyde (Phen)



Scheme S5.1. Reaction scheme of the synthesis of the COF building block 4,4'-(1,10-phenanthroline-3,8-diyl)dibenzaldehyde (Phen).

#### Synthesis of 1.



2,2-Dimethylpropane-1,3-diol (4 eq., 4155.6 mg, 40 mmol), p-toluenesulfonic acid (0.09 eq., 171.2 mg, 0.9 mmol) and (4-formylphenyl)-boronic acid (1 eq., 1497.9 mg, 10 mmol) were mixed in a Schlenk flask under argon atmosphere. The solids were dissolved in 100 mL toluene and heated to reflux for 1.5 h. The reaction solution was poured into a saturated aqueous solution of sodium hydrogen carbonate (300 mL), and  $CH_2Cl_2$  (3 x 150 mL) was added. The organic layer was separated and dried over sodium sulphate. *In vacuo* removal of all solvents yielded colourless platelet-like crystals of 1 (3022.3 mg, 9.9 mmol, 99%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.80 (d, *J* = 6.4 Hz, 2H, H-3 ), 7.48 (d, *J* = 6.3 Hz, 2H, H-4), 5.40 (s, H-5), 3.76 (d, *J* = 11.94 Hz, 2H, H-9), 3.76 (s, 4H, H-2,10), 3.64 (d, *J* = 10.6 Hz, 2H, H-6), 1.29 (s, 3H, H-11), 1.00 (s, 6H, H-7,8), 0.80 (s, 3H, H-1)

#### Synthesis of 2.



3,8-Dibromophenanthroline (1 eq., 338 mg, 1 mmol), 1 (3 eq., 912.6 mg, 3 mmol), aqueous sodium carbonate solution (2.6 eq., 1 M, 2.6 mL, 2.6 mmol) and tetrakis-(triphenylphosphine)palladium(0) (15 mol%, 173.33 mg) were mixed in a Schlenk flask and dissolved in a degassed THF/toluene mixture (7.4 mL, 1:1) under argon atmosphere. The reaction mixture was heated to reflux for 72 h. After cooling to room temperature, an aqueous solution of sodium hydroxide (1 M, 10 mL) and brine (sat. aq. NaCl, 20 mL) was added to the reaction mixture. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 50 mL). The combined organic phases were dried over sodium sulphate and the solvents removed *in vacuo*. A yellow powder was obtained (450.5 mg, 80%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 9.81 (d, J = 2.1 Hz, 2H, H-6), 8.75 (d, J = 2.1 Hz, H-8), 8.13 (s, 2H, H-7), 7.83 (d, J = 8.6 Hz, 4H, H-5), 7.75 (d, J = 9.1 Hz, 4H, H-4), 5.50 (s, 2H, H-3), 3.83 (d, J = 11.3 Hz, 4H, H-2/9), 3.71 (d, J = 10.5 Hz, 4H, H-2/9), 1.33 (s, 6H, H-1/10), 0.84 (s, 6H, H-1/10)

Synthesis of Phen.



2 (1 eq., 265.5 mg, 0.476 mmol) was dissolved in degassed THF (50 mL). Hydrochloric acid (5%, 6.44 mL) was added and the solution heated to reflux for 18 h. The reaction mixture was cooled to room temperature and all solvents removed *in vacuo*. The residual solid was thoroughly washed with water (40 mL) and small amounts of THF. 4,4'-(1,10-phenanthroline-3,8-diyl)dibenzaldehyde (Phen) was obtained as a light yellow powder (160.4 mg, 0.423 mmol, 87%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 10.20 (s, 2H, H-1), 9.51 (d, *J* = 2.2 Hz, 2H, H-4), 8.51 (d, *J* = 2.4 Hz, 2H, H-6), 8.10 (d, *J* = 8.5 Hz, 4H, H-2), 7.99 (d, *J* = 8.4 Hz, 4H, H-3), 7.97 (s, 2H, H-5)



#### NMR spectra

Figure S5.1. <sup>1</sup>H NMR spectrum of **1**.



Figure S5.2. <sup>1</sup>H NMR spectrum of **2**.



Figure S5.3. <sup>1</sup>H NMR spectrum of Phen.

**Synthesis of PhenPy COF**. In a 6 mL Schott-Duran culture tube, a solid mixture of 4,4'-(1,10phenanthroline-3,8-diyl)dibenzaldehyde Phen (3.88 mg, 0.01 mmol) and 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetraaniline Py (2.83 mg, 0.005 mmol, 98%, BLD Pharm, CAS: 1610471-69-6) was suspended in 500  $\mu$ L 1,4-dioxane and mesitylene (1:3). Subsequently, 50 mL of acetic acid (aqueous, 6 M) was added. The culture tube was tightly sealed and heated to 120 °C for 4 days. The resulting suspension was filtrated and the isolated brown powder was Soxhlet extracted with EtOAc for 6 h, followed by treatment in supercritical CO<sub>2</sub> at 110 bar and 40 °C for 2 h. Elemental analysis for (C<sub>68</sub>H<sub>42</sub>N<sub>8</sub>)<sub>n</sub>, calculated: C, 84.4 ; H, 4.4 ; N, 11.5. Found: C, 74.9 ; H, 4.3 ; N, 7.1. Calculations for the elemental analysis were based on an infinite structure, ignoring the presence of undefined end-groups or possible residues in the pore system.

Synthesis of Mn PhenPy COF. PhenPy COF (30 mg) and  $[Mn(CO)_5Br]$  (30 mg) were dispersed in 10 mL EtOAc and heated to reflux for 1 h under Ar atmosphere. The resulting powder was filtrated, thoroughly washed with EtOAc and dried under reduced pressure. ICP-OES analysis was conducted to determine the Mn content to be 2.2 wt%, corresponding to 28 % of the Phen sites occupied. The percentage of Phen sites immobilizing  $[Mn(CO)_3Br]$  is calculated as follows.

To estimate the molecular weight of the COF, a fragment reflecting the 2:1 ratio of the Phen to the Py linker is considered (Scheme S5.2). The molecular weight of this  $C_{92}H_{54}N_8^{12}$  fragment is M = 1271.50 g mol<sup>-1</sup>.



Scheme S5.2. PhenPy COF fragment reflecting the 2:1 ratio of Phen to Py.

The weight percent y of Mn given by the ICP-OES can be expressed as the following equation:

$$y = \frac{x * M(Mn)}{M(C_{92}H_{54}N_8^{12\bullet}) + x * M(Mn(CO)_3Br)}$$

where x is a number between 0 and 2, corresponding to the number of immobilized Mncomplexes per fragment (max. value = 2, since only two Phen sites are available per fragment). A 100% coverage of the two available Phen sites of the fragment translates to two additional Mn(CO)<sub>3</sub>Br compounds, each with a weight of M = 218.87 g mol<sup>-1</sup>, thus x = 2 in the equation. Insertion of the corresponding molecular weights (M(Mn) = 54.94 g mol<sup>-1</sup>) yields a value of y = 0.064, or 6.4 wt% for a 100% coverage of the Phen sites with Mn-complex.

In reality, a value given by ICP-OES is used to calculate the coverage of Phen sites. For example, ICP-OES measures 2.2 wt% Mn in the sample of interest. Replacing y = 0.022 in the above equation and solving it for x yields a value of x = 0.558. Applying the rule of three, if x = 2 corresponds to 100%, then x = 0.558 corresponds to a coverage of 28% of the Phen sites.

**Synthesis of** *fac-*[**Mn(Phen)(CO)**<sub>3</sub>**Br**]. Phen (1.1 eq., 30 mg, 0.077 mmol) and Mn(CO)<sub>5</sub>Br (1 eq., 24.7 mg, 0.07 mmol) were dissolved in 10 mL EtOAc and heated to reflux for 3 h under Ar atmosphere. The resulting powder was thoroughly washed with EtOAc and dried under

reduced pressure. Yield: 71%. FTIR:  $v_{C=0}$  s(2025, 1952 and 1917 cm<sup>-1</sup>). <sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>)  $\delta$  (ppm) = 10.11 (s, 2H), 9.56 (d, J = 1.9 Hz, 2H), 8.68 (d, J = 2.0 Hz, 2H), 8.10 (d, J = 8.3 Hz, 4H), 8.09 (s, 2H), 7.94 (d, J = 8.2 Hz, 4H).

Synthesis of *fac*-[Mn(bpy)(CO)<sub>3</sub>Br]. Bpy (110 mg, 0.71 mmol) and Mn(CO)<sub>5</sub>Br (200 mg, 0.72 mmol) were dissolved in 30 mL EtOAc and heated to reflux for 1 h under Ar atmosphere. The resulting powder was thoroughly washed with Et<sub>2</sub>O and dried under reduced pressure. Yield: 85%. FTIR:  $v_{N-H}$  m(3068 cm<sup>-1</sup>),  $v_{C=O}$  s(2017, 1910 and 1883 cm<sup>-1</sup>). <sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>)  $\delta$  (ppm) = 9.31 (d, *J* = 5.5 Hz, 2H), 8.58 (d, *J* = 8.1 Hz, 2H), 8.23 (t, *J* = 7.7 Hz, 2H), 7.75 (t, *J* = 6.4 Hz, 2H).

# S3. Structural characterization of PhenPy COF

Transmission electron microscopy

Figure S5.4. TEM micrograph of the PhenPy COF





Figure S5.5. FTIR spectra of the building blocks Phen and Py together with the spectrum of the synthesized PhenPy COF. Carbonyl, amine and imine vibrations are indicated by the dotted lines.

## S4. Structural characterization of Mn PhenPy COF

#### **SEM-EDX and BSE**

SEM-EDX spectra were collected at various locations and magnifications on the Mn PhenPy COF powder surface, confirming the presence of Mn and Br in the porous structure (Figure S5.6). SEM-EDX mapping reveals a homogeneous distribution of Mn and Br in the Mn PhenPy COF (Figure S5.7).



Figure S5.6. SEM-EDX spectra of Mn PhenPy COF powder, collected at the indicated area on the powder's surface.



Figure S5.7. SEM EDX mapping of Mn PhenPy COF powder, collected at the indicated area on the powder's surface.

SEM micrographs acquired in back-scattered electron (BSE) mode are shown below (Figure S8). In this mode, the backscattering coefficient is proportional to the atomic number, with elements of higher atomic number appearing brighter than those with lower atomic numbers. Consequently, the formation of metal clusters in Mn PhenPy can be excluded, as such clusters would be visible as bright spots in the images.



Figure S5.8. SEM micrographs of Mn PhenPy taken in the back-scattered electron mode and at various spots and magnifications.

# N<sub>2</sub> sorption experiments



Figure S5.9.  $N_2$  sorption experiments of the Mn PhenPy COF reveal a BET surface area of  $306 \text{ m}^2 \text{ g}^{-1}$ .

## Thermogravimetric analysis



Figure S5.10. Thermogravimetric analysis of the two COFs measured under a synthetic air flow (25 mL min<sup>-1</sup>) at a heating rate of 10 K min<sup>-1</sup>.



## CO<sub>2</sub> sorption experiments

Figure S5.11. CO<sub>2</sub> Adsorption isotherms of PhenPy and Mn PhenPy COF at 273 K and 294 K.

## **S5. Optical characterization of PhenPy and MnPhenPy COF**



UV-vis absorption and photoluminescence

Figure S5.12. UV-Vis absorption and photoluminescence spectra of both PhenPy and Mn PhenPy COFs.



Figure S5.13. Tauc plots of the two COFs assuming a direct transition. The band gap energy is reduced upon introduction of the Mn-complex into the COF structure.

# S6. Electrochemical characterization of PhenPy and Mn PhenPy COF



Cyclic voltammetry for energy level determination

Figure S5.14. CV curves for both PhenPy and Mn PhenPy COFs measured against the ferrocene redox couple at a scan rate of 10 mV/s. The onset of the first oxidation peak reflects the conduction band energy of the material.



#### CV of molecular analog *fac-*[Mn(Phen)(CO)<sub>3</sub>Br]

Figure S5.15. Assignment of the redox features in the CV of the molecular analog *fac*- $[Mn(Phen)(CO)_3Br]$  according to the literature.<sup>3, 8-9</sup> The CV was measured in a three-electrode setup in acetonitrile (TBAPF<sub>6</sub>, 0.1 M), using a Pt wire as the reference electrode, under Ar at a scan speed of 10 mV s<sup>-1</sup>. The reduction peaks at -2.25 V and -2.85 V are not discussed in the literature. We therefore tentatively assign them to irreversible reductions of the Phen building block.

# Comparison of Mn-based CO<sub>2</sub> reduction electrocatalysts

catalyst		electrolyte	cell type	псо	<i>ј</i> со	TOFco	Ref.
				[µmol cm <sup>-2</sup> ]	[mA cm <sup>-2</sup> ]	[ <b>h</b> <sup>-1</sup> ] <sup>a)</sup>	
Mn PhenPy	2.6 V	catholyte-free	MEA cell	32	2.1	314	This
COF	2.8 V	anolyte: 1M KOH		39	2.8	383	work
	3.0 V			62	3.6	618	
	3.2 V			14	0.4	142	
<i>fac-</i> [Mn(bpy)	2.6 V	catholyte-free	MEA cell	19	1.8	28	This
(CO) <sub>3</sub> Br]	2.8 V	anolyte: 1M KOH		10	1	14	work
	3.0 V			11	1.2	16	
	3.2 V			11	1	17	
COF <sub>bpyMn</sub>  NT <sup>b</sup>	)	NaHCO <sub>3</sub> (0.5 M) pH 7.4	H-cell	114	15	190	23
COF <sub>PTMn</sub>  NT <sup>c)</sup>		NaHCO <sub>3</sub> (0.5 M) pH 7.4	H-cell	10	8 <sup>d)</sup>	10	32
Mn-MOF		CH <sub>3</sub> CN + 0.25% acetic acid	H-cell	0.03	-	3.5	57
CNT Mn(pyr)		KHCO <sub>3</sub> (0.5 M) pH 7.4	three- electrode setup	46	2	175	8
[Mn- CH <sub>3</sub> CN] MWCNT		K <sub>2</sub> B <sub>4</sub> O <sub>7</sub> (0.1 M), K <sub>2</sub> SO <sub>4</sub> (0.2 M) pH 6.6	three- electrode setup, flow reactor	74	5.2	70	58
Mn(bpy) MWCNT		PB (0.06 M) pH 7.4	three- electrode setup	3	1	25	63
[Mn(bpy)(CO) <sub>3</sub> Br] GC		CH <sub>3</sub> CN + 8% MeOH	three- electrode setup	0.45	-	362	59

Table S5.2. Comparison of performance of a selection of Mn-based CO<sub>2</sub> reduction electrocatalysts.

<sup>a)</sup> TOF ( $n_{CO}/(n_{Mn,total} \cdot time)$ ).<sup>b), c)</sup> Total amount of Mn deposited: 225 nmol cm<sup>-2</sup> and 900 nmol cm<sup>-2</sup>, respectively. <sup>d)</sup> Value calculated from information provided in the reference. PB, NT and GC stand for phosphate buffer, nanotubes and glassy carbon, respectively.

# **S7.** Appendix

Unit cell parameters (P1) and atomic coordinates for PhenPy

$$a = 57.0 \text{ Å}, b = 46.8 \text{ Å}, c = 3.7 \text{ Å}$$

 $\alpha = 90.5^{\circ}, \beta = 91.5^{\circ} \text{ and } \gamma = 90.0^{\circ}$ 

Atom	a/x	b/y	c/z	 C28	0.55975	0.43408	0.06619
C1	0.49828	0.48910	0.26129	C29	0.45498	0.42574	0.23222
C2	0.49831	0.51926	0.29248	C30	0.43398	0.43413	0.14477
C3	0.47706	0.53352	0.33225	C31	0.41419	0.41652	0.14425
C4	0.47645	0.56382	0.34217	C32	0.41495	0.38993	0.22766
C5	0.49764	0.57884	0.33401	C33	0.43606	0.38100	0.31228
C6	0.51921	0.56520	0.30846	C34	0.45579	0.39882	0.31506
C7	0.51948	0.53506	0.28212	C35	0.45410	0.58080	0.34381
C8	0.47698	0.47349	0.27165	C36	0.43442	0.57227	0.23809
C9	0.47658	0.44389	0.22887	C37	0.41401	0.58873	0.23130
C10	0.49754	0.43044	0.18353	C38	0.41321	0.61528	0.32129
C11	0.51923	0.44458	0.18990	C39	0.43280	0.62417	0.42430
C12	0.51959	0.47459	0.22489	C40	0.45292	0.60708	0.43769
C13	0.54044	0.49065	0.22780	N41	0.60178	0.63642	0.30320
C14	0.54019	0.52019	0.24494	C42	0.60511	0.65982	0.21405
C15	0.45694	0.48778	0.33124	C43	0.62796	0.67469	0.22348
C16	0.45712	0.51695	0.36423	C44	0.63018	0.70127	0.14038
C17	0.54066	0.58368	0.30627	C45	0.65172	0.71550	0.14341
C18	0.54004	0.60989	0.21467	C46	0.67156	0.70353	0.23085
C19	0.55963	0.62788	0.21593	C47	0.66922	0.67693	0.31543
C20	0.58063	0.61967	0.30508	C48	0.64763	0.66265	0.31168
C21	0.58113	0.59401	0.39987	C49	0.69450	0.71878	0.23272
C22	0.56124	0.57653	0.40446	C50	0.69534	0.74876	0.23885
C23	0.54065	0.42624	0.17156	C51	0.71686	0.76305	0.23393
C24	0.54172	0.39975	0.26026	C52	0.73781	0.74699	0.22844
C25	0.56172	0.38263	0.25235	N53	0.73663	0.71791	0.22442
C26	0.58138	0.39168	0.16031	C54	0.71581	0.70371	0.22541
C27	0.58024	0.41755	0.06533	C55	0.75957	0.76121	0.22594

C56	0.76016	0.79136	0.22311	C88	0.73761	0.26218	0.21178
C57	0.73923	0.80703	0.22656	N89	0.71497	0.25280	0.20044
C58	0.71770	0.79295	0.23366	C90	0.69648	0.27115	0.19471
N59	0.78011	0.74633	0.22701	C91	0.76533	0.30187	0.22698
C60	0.80133	0.75958	0.22521	C92	0.78401	0.28271	0.21775
C61	0.80282	0.78956	0.21978	C93	0.77973	0.25328	0.20670
C62	0.78183	0.80529	0.21720	C94	0.75649	0.24280	0.20786
C63	0.82596	0.80436	0.21805	N95	0.75268	0.21407	0.20106
C64	0.82900	0.83117	0.30296	C96	0.77060	0.19500	0.19030
C65	0.85059	0.84526	0.29994	C97	0.79399	0.20445	0.18164
C66	0.86971	0.83279	0.21329	C98	0.79830	0.23399	0.19100
C67	0.86682	0.80603	0.12907	C99	0.81372	0.18388	0.16000
C68	0.84517	0.79197	0.13097	C100	0.83614	0.18999	0.23478
C69	0.89254	0.84759	0.20699	C101	0.85484	0.17123	0.20974
N70	0.89610	0.87132	0.29640	C102	0.85157	0.14574	0.11104
C71	0.91701	0.88851	0.30107	C103	0.82922	0.13931	0.03828
C72	0.91668	0.91412	0.39916	C104	0.81051	0.15823	0.06167
C73	0.93642	0.93189	0.40864	C105	0.87129	0.12584	0.08315
C74	0.95659	0.92515	0.31171	N106	0.89195	0.13169	0.15204
C75	0.95695	0.89915	0.21461	C107	0.91290	0.11478	0.14341
C76	0.93755	0.88084	0.21113	C108	0.91418	0.08866	0.04875
N77	0.60198	0.37404	0.17015	C109	0.93497	0.07267	0.05410
C78	0.62254	0.37965	0.10727	C110	0.95433	0.08150	0.16242
C79	0.64219	0.35947	0.13458	C111	0.95314	0.10831	0.24960
C80	0.66432	0.36621	0.06880	C112	0.93276	0.12478	0.23804
C81	0.68307	0.34725	0.09090	N113	0.39388	0.37304	0.22244
C82	0.68019	0.32121	0.18141	C114	0.39060	0.34852	0.29874
C83	0.65803	0.31474	0.24986	C115	0.36767	0.33394	0.28183
C84	0.63921	0.33362	0.22598	C116	0.34835	0.34673	0.19305
C85	0.70016	0.30086	0.20103	C117	0.32661	0.33283	0.18276
C86	0.72333	0.31093	0.21909	C118	0.32377	0.30587	0.26136
C87	0.74217	0.29181	0.22100	C119	0.34326	0.29306	0.34853

C120	0.36496	0.30691	0.35811	C152	0.35700	0.67734	0.30284
C121	0.30061	0.29120	0.25535	C153	0.33818	0.69656	0.30266
C122	0.27958	0.30667	0.27020	C154	0.31682	0.68961	0.21307
N123	0.25858	0.29291	0.27283	C155	0.31485	0.66307	0.12323
C124	0.25695	0.26387	0.26234	C156	0.33360	0.64392	0.12405
C125	0.27761	0.24747	0.24648	C157	0.29656	0.70965	0.21399
C126	0.29929	0.26133	0.24041	C158	0.29987	0.73940	0.20982
C127	0.23506	0.25004	0.27016	N159	0.28114	0.75741	0.20854
C128	0.23410	0.21990	0.26781	C160	0.25860	0.74760	0.20938
C129	0.25472	0.20388	0.25192	C161	0.25442	0.71789	0.21191
C130	0.27634	0.21759	0.23941	C162	0.27349	0.69914	0.21699
N131	0.21476	0.26527	0.28068	C163	0.23947	0.76665	0.20658
C132	0.19345	0.25237	0.28982	C164	0.21633	0.75575	0.20034
C133	0.19162	0.22239	0.29177	C165	0.21244	0.72622	0.20083
C134	0.21239	0.20632	0.28191	C166	0.23139	0.70738	0.20856
C135	0.16838	0.20790	0.30244	N167	0.24291	0.79544	0.21078
C136	0.14973	0.22059	0.39528	C168	0.22470	0.81422	0.20907
C137	0.12803	0.20673	0.40522	C169	0.20135	0.80438	0.20047
C138	0.12458	0.17982	0.32413	C170	0.19744	0.77477	0.19441
C139	0.14308	0.16713	0.23138	C171	0.18122	0.82469	0.19975
C140	0.16465	0.18103	0.21980	C172	0.16010	0.81745	0.28276
C141	0.10185	0.16499	0.33832	C173	0.14119	0.83643	0.28229
N142	0.09863	0.13905	0.25821	C174	0.14300	0.86317	0.20004
C143	0.07925	0.12219	0.25714	C175	0.16397	0.87049	0.11669
C144	0.05817	0.12967	0.33948	C176	0.18286	0.85145	0.11604
C145	0.03900	0.11092	0.33172	C177	0.12328	0.88360	0.19976
C146	0.04016	0.08428	0.24202	N178	0.10463	0.87861	0.29236
C147	0.06096	0.07655	0.15680	C179	0.08417	0.89641	0.30537
C148	0.08047	0.09446	0.16346	C180	0.06513	0.88609	0.39999
N149	0.39317	0.63393	0.31088	C181	0.04466	0.90234	0.41679
C150	0.37431	0.63018	0.21066	C182	0.04252	0.92959	0.33679
C151	0.35481	0.65085	0.21360	C183	0.06182	0.93936	0.23841
C184	0.08245	0.92346	0.22624	H216	0.39813	0.42332	0.07666
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C185	0.97788	0.94398	0.31805	H217	0.43749	0.36066	0.37861
C186	-0.00031	0.93061	0.34421	H218	0.47166	0.39177	0.38475
C187	0.97722	0.97394	0.28859	H219	0.43506	0.55332	0.15409
C188	0.95608	0.98855	0.25424	H220	0.39948	0.58091	0.14904
C189	0.95554	0.01792	0.23184	H221	0.43217	0.64429	0.49704
C190	0.97627	0.03404	0.22455	H222	0.46739	0.61425	0.52415
C191	0.97613	0.06381	0.18579	H223	0.59142	0.66889	0.12908
C192	0.99761	0.07834	0.18124	H224	0.61532	0.71077	0.06941
C193	0.02111	0.94558	0.34297	H225	0.65300	0.73543	0.07159
C194	0.02007	0.97598	0.33175	H226	0.68391	0.66746	0.38839
C195	0.99839	0.98989	0.29419	H227	0.64617	0.64231	0.37889
C196	0.99794	0.01995	0.26168	H228	0.67934	0.76104	0.24875
C197	0.01891	0.06549	0.23035	H229	0.71596	0.68065	0.21724
C198	0.01911	0.03595	0.27186	H230	0.73956	0.83016	0.22512
C199	0.03963	0.02213	0.33228	H231	0.70169	0.80539	0.23751
C200	0.03987	0.99315	0.36782	H232	0.81703	0.74663	0.23066
H201	0.49737	0.60186	0.34496	H233	0.78223	0.82834	0.20862
H202	0.49703	0.40805	0.14573	H234	0.81490	0.84098	0.37649
H203	0.55745	0.48103	0.21708	H235	0.85251	0.86578	0.36744
H204	0.55665	0.53101	0.22768	H236	0.88122	0.79624	0.05876
H205	0.44077	0.47671	0.35388	H237	0.84332	0.77183	0.05916
H206	0.44128	0.52637	0.41477	H238	0.90593	0.83834	0.12401
H207	0.52454	0.61616	0.13718	H239	0.90117	0.91978	0.47277
H208	0.55825	0.64758	0.14243	H240	0.93604	0.95068	0.49409
H209	0.59694	0.58804	0.47420	H241	0.97207	0.89332	0.13670
H210	0.56182	0.55764	0.48704	H242	0.93865	0.86132	0.13353
H211	0.52745	0.39282	0.34321	H243	0.62588	0.39931	0.03711
H212	0.56248	0.36279	0.32609	H244	0.66697	0.38587	-0.00379
H213	0.59458	0.42464	-0.01526	H245	0.69963	0.35262	0.03141
H214	0.55873	0.45273	-0.01845	H246	0.65533	0.29539	0.32544
H215	0.43283	0.45430	0.07702	H247	0.62236	0.32828	0.28114

H248	0.72679	0.33361	0.22954	H280	0.02310	0.11710	0.39882
H249	0.67897	0.26244	0.17938	H281	0.06207	0.05664	0.08413
H250	0.76895	0.32457	0.23453	H282	0.09637	0.08843	0.09610
H251	0.80181	0.29088	0.21813	H283	0.37231	0.61186	0.12207
H252	0.76649	0.17246	0.18866	H284	0.37318	0.68292	0.37448
H253	0.81598	0.24215	0.18112	H285	0.34012	0.71643	0.37726
H254	0.83917	0.20892	0.31690	H286	0.29902	0.65739	0.04736
H255	0.87185	0.17642	0.26990	H287	0.33166	0.62380	0.05185
H256	0.82637	0.11993	-0.04007	H288	0.31731	0.74838	0.20450
H257	0.79375	0.15314	-0.00253	H289	0.27029	0.67641	0.22457
H258	0.86803	0.10642	0.00666	H290	0.19475	0.71773	0.19674
H259	0.89957	0.08080	-0.03274	H291	0.22807	0.68461	0.21041
H260	0.93594	0.05347	-0.02720	H292	0.22853	0.83681	0.21730
H261	0.96759	0.11596	0.33474	H293	0.17974	0.76641	0.18356
H262	0.93188	0.14484	0.31122	H294	0.15838	0.79747	0.35342
H263	0.40435	0.33839	0.37809	H295	0.12526	0.83050	0.34919
H264	0.35019	0.36742	0.13078	H296	0.16561	0.89084	0.04988
H265	0.31218	0.34293	0.11022	H297	0.19850	0.85739	0.04551
H266	0.34154	0.27273	0.41525	H298	0.12486	0.90262	0.11966
H267	0.37953	0.29680	0.42916	H299	0.06650	0.86553	0.46491
H268	0.27984	0.32968	0.28437	H300	0.03109	0.89393	0.50092
H269	0.31509	0.24884	0.22446	H301	0.06069	0.95869	0.16092
H270	0.25408	0.18075	0.24842	H302	0.09648	0.93217	0.14883
H271	0.29210	0.20490	0.22642	H303	-0.00026	0.90766	0.35559
H272	0.17794	0.26563	0.29330	H304	0.93945	0.97772	0.24394
H273	0.21183	0.18326	0.28766	H305	0.93842	0.02748	0.22171
H274	0.15209	0.24078	0.46558	H306	0.99770	0.10060	0.14253
H275	0.11410	0.21671	0.47997	H307	0.05588	0.03342	0.35347
H276	0.14070	0.14660	0.16489	H308	0.05595	0.98432	0.42364
H277	0.17813	0.17101	0.14086	C309	0.49884	0.48939	0.78394
H278	0.08827	0.17497	0.41625	C310	0.49837	0.51954	0.81529
H279	0.05630	0.14961	0.41165	C311	0.47686	0.53329	0.85409

C312	0.47568	0.56358	0.86211	C344	0.43347	0.57058	0.75606
C313	0.49663	0.57913	0.85345	C345	0.41277	0.58649	0.74624
C314	0.51846	0.56601	0.82944	C346	0.41142	0.61317	0.83379
C315	0.51930	0.53583	0.80596	C347	0.43082	0.62292	0.93587
C316	0.47780	0.47328	0.79364	C348	0.45128	0.60647	0.95134
C317	0.47792	0.44368	0.75099	N349	0.59936	0.63987	0.81365
C318	0.49902	0.43083	0.70288	C350	0.60225	0.66340	0.72467
C319	0.52049	0.44548	0.70916	C351	0.62502	0.67847	0.73251
C320	0.52039	0.47539	0.74792	C352	0.62728	0.70498	0.64803
C321	0.54104	0.49181	0.75550	C353	0.64887	0.71923	0.65089
C322	0.54035	0.52133	0.77300	C354	0.66865	0.70730	0.73926
C323	0.45750	0.48710	0.85254	C355	0.66622	0.68075	0.82442
C324	0.45722	0.51624	0.88662	C356	0.64469	0.66649	0.82077
C325	0.53953	0.58510	0.82350	C357	0.69175	0.72221	0.74161
C326	0.53840	0.61075	0.72592	C358	0.69321	0.75221	0.74815
C327	0.55759	0.62938	0.72411	N359	0.71443	0.76553	0.75054
C328	0.57864	0.62238	0.81653	C360	0.73498	0.75068	0.74916
C329	0.57973	0.59711	0.91515	C361	0.73441	0.72052	0.74544
C330	0.56024	0.57905	0.92296	C362	0.71274	0.70653	0.73868
C331	0.54224	0.42784	0.68589	C363	0.75675	0.76495	0.75230
C332	0.54387	0.40092	0.76881	N364	0.75788	0.79401	0.74934
C333	0.56429	0.38462	0.75860	C365	0.77774	0.74893	0.75715
C334	0.58379	0.39485	0.66937	C366	0.79926	0.76325	0.76294
C335	0.58206	0.42104	0.57849	C367	0.80007	0.79320	0.75791
C336	0.56118	0.43684	0.58216	C368	0.77870	0.80824	0.75089
C337	0.45676	0.42489	0.75830	C369	0.82302	0.80842	0.75640
C338	0.43552	0.43226	0.67057	C370	0.82595	0.83528	0.84091
C339	0.41617	0.41398	0.67354	C371	0.84757	0.84943	0.83772
C340	0.41765	0.38770	0.76046	C372	0.86669	0.83697	0.75074
C341	0.43895	0.37986	0.84635	C373	0.86387	0.81015	0.66760
C342	0.45826	0.39834	0.84536	C374	0.84229	0.79608	0.66985
C343	0.45298	0.57995	0.86104	C375	0.88956	0.85159	0.74261

N376	0.89362	0.87511	0.83304	C408	0.81344	0.16268	0.60142
C377	0.91496	0.89153	0.83631	C409	0.87396	0.13010	0.62348
C378	0.91520	0.91761	0.92947	N410	0.89477	0.13559	0.69087
C379	0.93532	0.93476	0.93513	C411	0.91531	0.11793	0.68114
C380	0.95540	0.92676	0.84056	C412	0.91604	0.09221	0.58159
C381	0.95528	0.90013	0.75071	C413	0.93645	0.07553	0.58375
C382	0.93546	0.88254	0.75041	C414	0.95594	0.08316	0.69394
N383	0.60481	0.37799	0.67826	C415	0.95529	0.10948	0.78746
C384	0.62522	0.38400	0.61388	C416	0.93532	0.12672	0.77876
C385	0.64506	0.36408	0.64116	N417	0.39707	0.36998	0.75687
C386	0.66717	0.37072	0.57424	C418	0.39427	0.34559	0.83592
C387	0.68600	0.35183	0.59782	C419	0.37152	0.33056	0.82048
C388	0.68315	0.32595	0.69013	C420	0.35226	0.34290	0.72883
C389	0.66098	0.31964	0.75930	C421	0.33067	0.32880	0.71812
C390	0.64215	0.33837	0.73402	C422	0.32774	0.30216	0.80083
C391	0.70294	0.30529	0.71001	C423	0.34715	0.28974	0.89138
C392	0.72640	0.31465	0.72365	C424	0.36882	0.30378	0.90068
N393	0.74433	0.29554	0.73200	C425	0.30438	0.28790	0.79695
C394	0.74050	0.26681	0.73151	C426	0.28371	0.30417	0.80341
C395	0.71725	0.25638	0.72473	C427	0.26178	0.29077	0.80045
C396	0.69863	0.27574	0.71156	C428	0.26065	0.26065	0.79561
N397	0.78198	0.25684	0.72749	N429	0.28091	0.24523	0.78980
C398	0.75938	0.24744	0.73353	C430	0.30236	0.25797	0.78916
C399	0.75485	0.21778	0.73550	C431	0.23865	0.24696	0.79784
C400	0.77366	0.19866	0.73112	N432	0.23704	0.21796	0.80201
C401	0.79676	0.20879	0.71861	C433	0.21795	0.26354	0.79863
C402	0.80044	0.23852	0.72001	C434	0.19617	0.24977	0.80032
C403	0.81666	0.18851	0.69788	C435	0.19489	0.21984	0.80701
C404	0.83906	0.19477	0.77228	C436	0.21602	0.20428	0.80748
C405	0.85777	0.17589	0.74847	C437	0.17174	0.20512	0.81537
C406	0.85443	0.15023	0.65127	C438	0.15284	0.21808	0.90361
C407	0.83207	0.14369	0.57964	C439	0.13111	0.20436	0.91158

C440	0.12783	0.17725	0.83343	C472	0.15774	0.81368	0.81772
C441	0.14653	0.16426	0.74423	C473	0.13883	0.83277	0.81743
C442	0.16823	0.17806	0.73487	C474	0.14071	0.85952	0.73494
C443	0.10498	0.16272	0.84788	C475	0.16171	0.86683	0.65254
N444	0.10144	0.13664	0.77065	C476	0.18054	0.84780	0.65227
C445	0.08169	0.12041	0.77097	C477	0.12114	0.88014	0.73278
C446	0.06075	0.12879	0.85229	N478	0.10240	0.87574	0.82548
C447	0.04124	0.11055	0.84796	C479	0.08232	0.89424	0.83692
C448	0.04186	0.08355	0.76228	C480	0.06309	0.88480	0.93288
C449	0.06249	0.07494	0.67760	C481	0.04299	0.90176	0.94821
C450	0.08231	0.09236	0.68069	C482	0.04138	0.92878	0.86460
N451	0.39102	0.63120	0.82158	C483	0.06084	0.93767	0.76490
C452	0.37217	0.62684	0.72210	C484	0.08116	0.92116	0.75523
C453	0.35255	0.64737	0.72315	C485	0.97708	0.94493	0.84285
C454	0.35471	0.67387	0.81200	C486	-0.00138	0.93106	0.87133
C455	0.33589	0.69298	0.81219	C487	0.97701	0.97479	0.80977
C456	0.31451	0.68609	0.72256	C488	0.95620	0.98975	0.77035
C457	0.31254	0.65960	0.63226	C489	0.95611	0.01913	0.74865
C458	0.33134	0.64044	0.63300	C490	0.97707	0.03491	0.74666
C459	0.29444	0.70645	0.72359	C491	0.97740	0.06480	0.71191
C460	0.29836	0.73606	0.72456	C492	0.99909	0.07880	0.70717
C461	0.27948	0.75508	0.73041	C493	0.02030	0.94541	0.86865
C462	0.25636	0.74418	0.72947	C494	0.01986	0.97580	0.85497
N463	0.25292	0.71539	0.72716	C495	0.99844	0.99024	0.81653
C464	0.27111	0.69662	0.72546	C496	0.99850	0.02031	0.78422
C465	0.23723	0.76318	0.73204	C497	0.02024	0.06535	0.75377
N466	0.21471	0.75333	0.72467	C498	0.01993	0.03581	0.79522
C467	0.24139	0.79290	0.74132	C499	0.04019	0.02150	0.85608
C468	0.22230	0.81159	0.74650	C500	0.03998	0.99247	0.89001
C469	0.19922	0.80103	0.73661	H501	0.49597	0.60217	0.86201
C470	0.19595	0.77127	0.72573	H502	0.49877	0.40852	0.66301
C471	0.17888	0.82099	0.73540	H503	0.55819	0.48243	0.74857

H504	0.55675	0.53239	0.75966	H536	0.90266	0.84222	0.65751
H505	0.44146	0.47567	0.87308	H537	0.89980	0.92422	100.140
H506	0.44127	0.52529	0.93806	H538	0.93528	0.95415	101.500
H507	0.52281	0.61609	0.64670	H539	0.97033	0.89324	0.67533
H508	0.55590	0.64861	0.64602	H540	0.93627	0.86248	0.67833
H509	0.59566	0.59197	0.99054	H541	0.62817	0.40359	0.54195
H510	0.56121	0.56062	100.973	H542	0.66974	0.39026	0.50020
H511	0.52978	0.39307	0.85032	H543	0.70256	0.35713	0.53826
H512	0.56553	0.36451	0.82904	H544	0.65825	0.30054	0.83716
H513	0.59632	0.42901	0.50040	H545	0.62533	0.33299	0.78950
H514	0.55979	0.45595	0.50215	H546	0.73056	0.33717	0.72773
H515	0.43393	0.45206	0.59868	H547	0.68089	0.26764	0.69772
H516	0.39992	0.41994	0.60509	H548	0.77024	0.17593	0.73533
H517	0.44085	0.35983	0.91569	H549	0.81791	0.24726	0.70950
H518	0.47437	0.39204	0.91445	H550	0.84203	0.21392	0.85250
H519	0.43442	0.55135	0.67533	H551	0.87481	0.18106	0.80821
H520	0.39842	0.57815	0.66418	H552	0.82916	0.12416	0.50277
H521	0.42977	0.64320	100.641	H553	0.79669	0.15750	0.53739
H522	0.46557	0.61431	103.720	H554	0.87036	0.11059	0.54883
H523	0.58835	0.67222	0.64057	H555	0.90139	0.08529	0.49717
H524	0.61241	0.71441	0.57677	H556	0.93708	0.05686	0.49712
H525	0.65023	0.73914	0.57879	H557	0.96993	0.11621	0.87391
H526	0.68082	0.67128	0.89834	H558	0.93489	0.14646	0.85565
H527	0.64327	0.64622	0.88895	H559	0.40817	0.33607	0.91692
H528	0.67751	0.76511	0.75412	H560	0.35401	0.36342	0.66426
H529	0.71230	0.68345	0.72910	H561	0.31640	0.33857	0.64188
H530	0.81532	0.75098	0.77257	H562	0.34538	0.26966	0.96095
H531	0.77849	0.83127	0.74311	H563	0.38335	0.29407	0.97445
H532	0.81175	0.84504	0.91359	H564	0.28462	0.32722	0.81385
H533	0.84952	0.87000	0.90450	H565	0.31781	0.24466	0.78123
H534	0.87826	0.80034	0.59719	H566	0.18031	0.26247	0.79562
H535	0.84054	0.77590	0.59836	H567	0.21593	0.18126	0.81566

H568	0.15500	0.23844	0.97224	H600	0.05597	0.98327	0.94448
H569	0.11702	0.21461	0.98310	C601	0.75537	0.70490	0.74861
H570	0.14419	0.14359	0.67939	C602	0.77692	0.71903	0.75557
H571	0.18202	0.16784	0.66016	H603	0.79295	0.70660	0.75826
H572	0.09146	0.17321	0.92377	H604	0.75509	0.68177	0.74705
H573	0.05922	0.14899	0.92187	C605	0.26442	0.80342	0.74468
H574	0.02554	0.11738	0.91550	C606	0.28335	0.78461	0.73770
H575	0.06329	0.05468	0.60886	H607	0.30103	0.79314	0.73949
H576	0.09806	0.08564	0.61376	H608	0.26775	0.82618	0.75123
H577	0.37038	0.60828	0.63518	C609	0.71299	0.22692	0.72825
H578	0.37086	0.67950	0.88394	C610	0.73169	0.20773	0.73666
H579	0.33787	0.71276	0.88775	H611	0.72808	0.18503	0.73987
H580	0.29669	0.65397	0.55653	H612	0.69521	0.21874	0.72348
H581	0.32945	0.62031	0.56091	C613	0.21931	0.29340	0.79964
H582	0.31604	0.74441	0.71911	C614	0.24111	0.30696	0.80304
H583	0.26727	0.67403	0.72843	H615	0.24184	0.33008	0.80709
H584	0.22549	0.83432	0.75980	H616	0.20351	0.30626	0.80011
H585	0.17850	0.76224	0.71504				
H586	0.15603	0.79359	0.88725				
H587	0.12284	0.82690	0.88373				
H588	0.16342	0.88717	0.58561				
H589	0.19620	0.85380	0.58211				
H590	0.12302	0.89901	0.65182				
H591	0.06403	0.86439	0.99988				
H592	0.02928	0.89404	103.353				
H593	0.06002	0.95673	0.68425				
H594	0.09534	0.92927	0.67693				
H595	-0.00175	0.90817	0.88619				
H596	0.93949	0.97916	0.75529				
H597	0.93914	0.02891	0.73430				
H598	0.99944	0.10113	0.67025				
H599	0.05658	0.03244	0.87956				

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# CHAPTER 6

Conclusion and Outlook

# 6 Conclusion and Outlook

In summary, the scope of this thesis was the exploration and study of dynamic processes in Covalent Organic Frameworks, as well as investigating how structural features of the porous material influence such processes and how these structure-property relations can be harnessed for catalytical applications.

In the first section, advanced spatiotemporal microscopy and spectroscopy in combination with theoretical simulations were applied to elucidate the diffusion process of photogenerated charge carriers in thin films of the 2D COF WBDT, a material well-known for its strong tendency to form highly crystalline, porous and uniform films. Remote-detected time-resolved photoluminescence (RDTR PL) and optical-pump terahertz probe (OPTP) spectroscopy enabled the identification of two species dominating the diffusive process in this material. A fast species associated with free charge carriers, diffuses almost temperature-independently with a diffusion coefficient of  $D \approx 10 \text{ cm}^2 \text{ s}^{-1}$  and an estimated diffusion length of  $L_D = 50 \text{ nm}$ , roughly corresponding to the grain size of the COF film. The free charge carriers form within fs after photoexcitation and quickly relax into bound excitons at a rate of k = 0.7 ps<sup>-1</sup>. RDTR PL allowed for directly accessing the lateral diffusion of these excitons, demonstrating remarkably high diffusion coefficients of up to  $D = 4 \text{ cm}^2 \text{ s}^{-1} (200 \text{ K})$  and diffusion lengths of several 100s of nm across grain boundaries and structural defects. Analysis of the temperaturedependent diffusion process provided valuable insights into the energy transport processes in the WBDT COF thin films. Theoretical simulations suggest that the observed diffusion coefficient arises from contributions of both incoherent hopping and coherent band-like transport in which phonon-assisted exciton transport prevails above 200 K, while disorder in the system significantly limits the diffusion at temperature below 200 K. This coexistence reflects the peculiar combination of both molecular and solid-state materials properties in COFs and underlines the significant and nonintuitive impact of structural and electronic disorder on the diffusion of charges or excitons in this materials class. Summing up, this project provided a mechanistic understanding of energy transport in macroscopic molecular framework systems, as well as guidance toward enabling efficient transport processes in such materials.

The second section focused on the development and application of a novel COF-based photocatalyst for the reduction of  $CO_2$  to CO. Capitalizing on the modular design of COFs, the structure-guiding building block dibenzochrysene (DBC) was combined with the nitrogen-rich bipyridine (bpy) linker, forming the bpyDBC COF. Due to its slightly twisted and rigid

structure with extended  $\pi$ -conjugation, DBC promotes high crystallinity through tight and ordered stacking of the COF layers, as well as excellent thermal and chemical stability along with long-lived excited states. Bipyridine, on the other hand, acts as pre-defined binding site for the immobilization of molecular metal catalysts with atomistic precision. The Re<sup>l</sup>bpyDBC COF, synthesized by immobilizing Re(CO)<sub>5</sub>Cl into the porous network, retained its structural integrity and allowed for the atomic-level resolution of the position and distribution of the metal centers in the crystalline COF. Employing scanning TEM in high-angle annular dark field mode (STEM-HAADF), the three-fold propeller-shape sub-structure adopted by Re and guided by the positions of the bpy unit was resolved, providing valuable insights regarding the molecular design of hybrid catalysts. Applied as catalyst in the photocatalytic CO<sub>2</sub>-to-CO conversion, the Re<sup>I</sup>bpyDBC COF demonstrated a remarkable CO production rate of 1.16 mmol g<sup>-1</sup> h<sup>-1</sup> under UV-vis illumination with BIH serving as a sacrificial electron donor. Under visible light, the Re<sup>I</sup>-COF maintained catalytic activity for over 72 hours at a reduced rate of 0.18 mmol  $g^{-1} h^{-1}$ , competing with the longest operational lifetime of other COF-based CO<sub>2</sub> photocatalysts. In a nutshell, the remarkable performance of the new hybrid photocatalyst Re<sup>I</sup>bpyDBC in terms of both reactivity and stability, combined with the detailed structural and electronic characterization, provides compelling experimental evidence of the conceptual advance in the design of efficient hybrid systems for solar-driven CO<sub>2</sub> conversion.

The final section of this work demonstrated the successful synthesis of Mn PhenPy COF, a novel electrocatalyst for the CO<sub>2</sub>-to-CO conversion, and its application in a catholyte-free membrane electrode assembly (MEA) cell. This cell design allows for direct contact between the catalyst and the CO<sub>2</sub> gas feed, while avoiding interactions of the COF with the aqueous electrolyte. Building on the design principle of the second project, phenanthroline moieties were introduced into the COF network as pre-defined binding sites for metal centers, enabling the immobilization of Mn(CO)<sub>5</sub>Br. This strategy not only increased the material's affinity for CO<sub>2</sub>, but also effectively suppressed the formation of dimeric Mn<sup>0</sup>-Mn<sup>0</sup> species, which can act as detrimental reaction intermediates. When employed as active material on a gas diffusion electrode (GDE) in a MEA cell, the hybrid Mn-COF exhibited significantly enhanced catalytic performance compared to the molecular benchmark catalyst *fac*-[Mn(bpy)(CO)<sub>3</sub>Br]. Specifically, it achieved a 30-fold improvement in turnover number (309) and turnover frequency (618 h<sup>-1</sup>) at a full-cell potential of 3.0 V and under identical conditions. Additionally, Mn PhenPy COF demonstrated increased partial CO generation current density at higher potentials, reaching a maximum value of *j<sub>CO</sub>* = 3.6 mA cm<sup>-2</sup> at 3.0 V, whereas the current

densities of *fac*-[Mn(bpy)(CO)<sub>3</sub>Br] steadily decline, indicating superior stability of the COFbased electrocatalyst. In brief, this work introduces Mn PhenPy COF as a promising heterogeneous CO<sub>2</sub>-to-CO electrocatalyst and represents the first instance of a COF-based material being integrated into a catholyte-free MEA cell architecture, thereby paving the way for broader adoption of COF-based hybrid materials in industry-relevant electrocatalytic CO<sub>2</sub> reduction technologies.

In conclusion, this thesis provides valuable insights into the dynamic processes governing the optoelectronic properties of COFs. By exploring exciton diffusion and advancing COF-based catalysts for photo- and electrochemical CO<sub>2</sub> conversion, it bridges fundamental understanding with practical application. These findings underscore the immense potential of COFs as versatile materials for energy conversion, and contribute to their future development in addressing global energy challenges.

# CHAPTER 7

**Publications and Presentations** 

# 7 Publications and Presentations

# 7.1 Publications

• Mn-decorated Covalent Organic Framework as efficient electrocatalyst for CO<sub>2</sub> reduction to CO

Laura Spies, Marcos Eduardo G. Carmo, Goncalves J. Marrenjo, Stephan Reuther, Patrick Ganswindt, Antonio Otavio T. Patrocinio, Thomas Bein, Osmando F. Lopes, Jenny Schneider

Submitted to Advanced Functional Materials, January 31st, 2025

- 2D Covalent Organic Framework as a Platform for Atomically Precise Design of a Rhenium(I)-Hybrid CO<sub>2</sub> Photocatalyst <u>Laura Spies</u><sup>#</sup>, Marcos Eduardo G. Carmo<sup>#</sup>, Markus Döblinger, Zehua Xu, Tianhao Xue, Achim Hartschuh, Thomas Bein, Antonio Otavio T. Patrocinio, Jenny Schneider *Submitted to Small, January 17<sup>th</sup>, 2025*
- Spatiotemporal Spectroscopy of Fast Excited-State Diffusion in 2D Covalent Organic Framework Thin Films
   <u>Laura Spies</u><sup>#</sup>, Alexander Biewald<sup>#</sup>, Laura Fuchs, Konrad Merkel, Marcello Righetto, Zehua Xu, Roman Guntermann, Rik Hooijer, Laura M. Herz, Frank Ortmann, Jenny Schneider, Thomas Bein, Achim Hartschuh
   *J. Am. Chem. Soc.*, 2025, 147, 2, 1758 – 1766
- From conventional inorganic semiconductors to covalent organic frameworks: advances and opportunities in heterogeneous photocatalytic CO<sub>2</sub> reduction
   <u>Laura Spies</u><sup>#</sup>, Marcos Eduardo G. Carmo<sup>#</sup>, Gabriela N. Silva<sup>#</sup>, Osmando F. Lopes,
   Thomas Bein, Jenny Schneider, and Antonio Otavio T. Patrocinio
   *J. Mater. Chem. A*, 2023, *11*, 13815

• Time-resolved spectroscopy applied to heterogeneous photocatalytic materials (2019 – 2022)

Laura Spies, Jenny Schneider, Mariano Curti Photochemistry Volume 51, ed. S. Crespi and S. Protti, Royal Society of Chemistry, 2023, 159–193

- Stable Multi-Emitter All-Lead Halide Perovskite Nanocrystal Film via Cross-linking of Nanocrystal-Templating Polymer Shells
   Patrick Ganswindt, Isabella Tepfenhart, Andreas Singldinger, Anna Ablfalterer, <u>Laura</u> <u>Spies</u>, Ekaterina Kostyurina, Mareike Stadler, Bert Nickel, Alexander S. Urban *Submitted to Advanced Optical Materials, January 16<sup>th</sup>*, 2025
- Electrically Conductive Carbazole and Thienoisoindigo-Based COFs Showing Fast and Stable Electrochromism
   Katharina Muggli, <u>Laura Spies</u>, Derya Bessinger, Florian Auras, Thomas Bein ACS Nanosci. Au 2023, 3, 153–160
- Protonation of γ-Butyrolactone and γ-Butyrolactam
   Stefanie Beck, Michael Feller, <u>Laura Spies</u>, Kai J. Dietrich, Christoph Jessen, Karin Stierstorfer, Andreas J. Kornath
   *Chemistry Open*, **2021**, *10*, 8–15
- Identifying and controlling phase purity in 2D hybrid perovskite thin films Yinghong Hu, <u>Laura Spies</u>, Diego Alonos-Álvarez, Priyanka Mocherla, Harry Jones, Jonas Hanisch, Thomas Bein, Piers R. F. Barnes, Pablo Docampo *J. Mater. Chem. A.*, **2018**, *6*, 22215–22225

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# 7.2 Conference Contributions

- e-conversion / CeNS Conference (Venice, Italy) 2024 Spatiotemporal Spectroscopy of Fast Excited-State Diffusion in 2D Covalent Organic Framework Thin Films (poster)
- Porous Materials in Energy Science (Herrsching, Germany) **2024** Ultrafast Spectroscopy of Efficient Excited State Diffusion in 2D COF Thin Films (poster)
- 35. DZT 35. Deutsche Zeolith Tagung (Jena, Germany) 2024 Ultrafast Spectroscopic Investigation of Excited State Dynamics in 2D COF Thin Films (talk)
- EuroMOF 2023 5<sup>th</sup> European Conference on Metal Organic Frameworks and Porous Polymers (Granada, Spain) 2023 – Ultrafast Spectroscopic Investigation of Excited State Dynamics in 2D COF Thin Films (poster)
- ISPPCC 2023 25<sup>th</sup> International Symposium on the Photochemistry and Photophysics of Coordination Compounds (Ulm, Germany) 2023 – Covalent Organic Frameworks as Novel Support Materials for Heterogeneous Photo(electro)catalysis (poster)
- 34. DZT 34. Deutsche Zeolith Tagung (Wien, Austria) 2023 Ultrafast Spectroscopic Investigation of Excited State Dynamics in 2D COF Thin Films (poster)
- MOF 2022 8<sup>th</sup> International Conference on Metal-Organic Frameworks and Open Framework Compounds (Dresden, Germany) 2022 – Phenanthroline-based Covalent Organic Framework for (Photo)electrochemical CO<sub>2</sub> Reduction (poster)

# 7.3 Workshops

- 32<sup>nd</sup> Jyväskylä Summer School (University of Jyväskylä, Finland) **2023** Ultrafast Spectroscopy: Phenomena, Measurements and Data Analysis Methods
- COORNETs Summer School (online) **2021** *Conductive Metal-Organic Frameworks* – *From Synthesis to Function*