

# Ultrafast Excited-state Dynamics in metaled 2, 2'-Bipyridine Covalent Organic Frameworks Photocatalysts

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Technical University of Denmark



# Ultrafast Excited-state Dynamics in metaled 2, 2'-Bipyridine Covalent Organic Frameworks Photocatalysts

Qinying Pan Ph.D. Thesis

Department of Chemistry Technical University of Denmark May 2021

# Ultrafast Excited-state Dynamics in metaled 2, 2'-Bipyridine Covalent Organic Frameworks Photocatalysts

Ph.D. Thesis

May 31th, 2021

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## Abstract

Semiconductor photocatalysis technology has attracted much attention in recent years, it can convert solar energy into chemical energy and store it in solar fuel, which is regarded as an effective way to resolve energy and environmental crises nowadays. Covalent organic frameworks (COFs) are a kind of very potential photocatalytic material. Despite the welldocumented recent advances in material development and photocatalytic application of those COFs structures, the fundamental catalytic process, especially, excited-state dynamics that dominate the catalytic performance has not been fully understood. In particular, the photogenerated excitons or charge carriers can undergo transfer and recombination within a broad temporal regime, containing multiple charge separation mechanisms. Therefore, it is necessary to create a systematic profile to review such photophysical processes and consequently rationalize the high catalytic activity of COFs photocatalysts. In this thesis, the excited state kinetics of two covalent organic backbone materials modified by metalcomplexes molecular catalysts, (i.e. Re-TpBpy and Ni-TpBpy), were explored experimentally by advanced spectroscopic measurements and theoretical by time-dependent density functional theory (TD-DFT) calculations. The results are utilized to explain the photocatalytic performance. The main contents are as follows:

1) TpBpy, a two-dimensional (2D) COFs with 2,2'-bipyridine, was successfully prepared by a one-step reversible Schiff base reaction and one-step irreversible enol keto tautomerism, then Re-TpBpy and Ni-TpBpy were obtained by modifying TpBpy with Re and Ni-based metal-complex catalysts using impregnation method. Various characterization techniques showed that the two materials possess high crystallinity, large specific surface area, good chemical stability, and perfect visible light response. Both Re-TpBpy and Ni-TpBpy exhibit excellent CO<sub>2</sub> reduction activity in photocatalytic measurement. However, the catalytic performance is excitation wavelength-dependent: CO<sub>2</sub> reduction can only be observed when excited with high-energy photons well above the band edge (i.e. 440 nm). We put our assumption to explain such phenomenon based on the electronic structure and charge carrier dynamics after excitation. In addition, the CO yield in Ni-TpBpy is higher than that of Re-TpBpy. We interpret such differences by comparing the morphology and intrinsic photophysics of the two structures. We concluded that: 1) the CO<sub>2</sub> adsorption capacity of NiTpBpy is higher than that of Re-TpBpy; 2) the electronic structure of Ni-TpBpy is more conducive to the separation and transfer of photogenerated charges.

2) We revealed the excited-state structure in TpBpy, Re-TpBpy, and Ni-TpBpy by TD-DFT calculation. We found that the light absorption of the three samples can be classified by low energy and high energy optical transitions. The low-energy optical transition of TpBpy, Re-TpBpy, and Ni-TpBpy are barely in Bpy moiety. The high energy optical transition of TpBpy and Re-TpBpy is evenly distributed at the whole COFs moiety, while the high energy optical transition of Ni-TpBpy is partially distributed throughout the COFs and partially in the Ni<sup>2+</sup>.

3) Through steady-state and time-resolved spectroscopy methods, such as ultraviolet-visible (Uv-Vis) absorption spectroscopy, time-resolved photoluminescence (TRPL) spectroscopy, femtosecond transient absorption (fs-TA) spectroscopy, and femtosecond time-resolved midinfrared absorption (fs-TRIR) spectroscopy, the excited state dynamics of these three samples were explored. We demonstrate that the coupling of metal-complex catalysts can indeed facilitate the charge transfer in COFs, where an efficient electron transfer process from COFs to Re/Ni can be observed. Moreover, we found such an electron transfer process together with excited-state lifetime is highly dependent on excitation phonon energy. The photogenerated electrons and holes tend to separate in metal-center and COFs moiety after charge transfer under band-edge excitation. When excited with high energy photon (400 nm, 3.1 eV) much larger than the band-gap, the generated hot carriers will undergo different relaxation pathways depends on the initial orbital they locate. The photo-generated electrons can reside both in COFs moiety and metal center simultaneously in this case, which promotes the twoelectron-mediated CO<sub>2</sub> reduction. In addition, such phenomenon is produced in Ni-TpBpy compared with Re-TpBpy due to its more diverse excited structure that allows the relaxation of excited electrons and holes highly depends on the initially excited orbitals.

## Abstract – Danish

Halvlederfotokatalyseteknologi har tiltrukket sig stor opmærksomhed de seneste år, den kan konvertere solenergi til kemisk energi og gemme den i solbrændstof, hvilket betragtes som en effektiv måde at løse energi og miljøkriser i dag. Kovalente organiske rammer (COF'er) er en slags meget potentielt fotokatalytisk materiale. På trods af de veldokumenterede nylige fremskridt inden for materialeudvikling og fotokatalytisk anvendelse af disse COFsstrukturer er den grundlæggende katalytiske proces, der er specielt ophidset, dynamik, der dominerer den katalytiske vdelse, ikke blevet forstået fuldt ud. Især kan de foto-genererede excitoner eller ladningsbærere gennemgå overførsel og rekombination inden for et bredt tidsmæssigt regime, der indeholder flere ladningsseparationsmekanismer. Derfor er det nødvendigt at oprette en systematisk profil for at gennemgå sådanne fotofysiske processer og dermed rationalisere den høje katalytiske aktivitet af COFs fotokatalysatorer. I denne afhandling blev den exciterede tilstandskinetik af to kovalente organiske rygradsmaterialer modificeret af metalmolekylære katalysatorer (dvs. Re-TpBpy og Ni-TpBpy), undersøgt eksperimentelt ved avancerede spektroskopiske målinger og teoretisk ved tidsafhængig densitetsfunktionsteori DFT) beregninger. Resultaterne bruges til at udforske den fotokatalytiske ydeevne. Hovedindholdet er som følger:

1, TpBpy, en 2D-kovalent organisk ramme (COF'er) med 2,2'-bipyridin, blev med succes fremstillet ved en et-trins reversibel Schiff-basereaktion og et-trins irreversibel enol-ketotautomerisme, derefter blev Re-TpBpy og Ni-TpBpy opnået ved at modificere TpBpy med Re- og Ni-baserede metal-komplekse katalysatorer ved hjælp af imprægneringsmetode. Forskellige karakteriseringsteknikker viste, at de to materialer besidder høj krystallinitet, stort specifikt overfladeareal, god kemisk stabilitet og perfekt synligt lysrespons. Både Re-TpBpy og Ni-TpBpy udviser fremragende CO<sub>2</sub>-reduktionsaktivitet i fotokatalytisk måling. Den katalytiske ydeevne er imidlertid excitationsbølgelængdeafhængig: CO<sub>2</sub>-reduktion kan kun observeres, når den exciteres med højenergifoton langt over båndkanten (440 nm). Vi lægger vores antagelse til at forklare et sådant fænomen baseret på den elektroniske struktur og ladningsbærerdynamik efter excitation. Derudover er CO-udbyttet i Ni-TpBpy højere end Re-TpBpy. Vi fortolker sådanne forskelle ved at sammenligne morfologien og den iboende fotofysik af de to strukturer. Vi konkluderede, at: 1) CO<sub>2</sub>-adsorptionskapaciteten for Ni-TpBpy er højere end for Re-TpBpy; 2) energibåndstrukturen i Ni-komplekset matches bedre med TpBpy end Re-TpBpy, hvilket er mere befordrende for adskillelse og overførsel af fotogenererede ladninger.

2, Vi afslørede den ophidsede tilstandsstruktur i TpBpy, Re-TpBpy og Ni-TpBpy ved tidsafhængig-DFT-beregning. Vi fandt ud af, at lysabsorptionen af de tre prøver kan overvåges af optiske overgange med lav energi og høj energi. Den optiske lavenergiovergang af TpBpy, Re-TpBpy og Ni-TpBpy er næppe i Bpy-del. Den høje energi optiske overgang af TpBpy og Re-TpBpy fordeles jævnt ved hele COF-delen, mens den høje energi optiske overgang af Ni-TpBpy er delvist fordelt gennem COF'erne og delvist i Ni<sup>2+</sup>.

3, Gennem steady-state og tidsopløste spektroskopimetoder, såsom ultraviolet-synlig (Uv-Vis) absorptionsspektroskopi, tidsopløst fotoluminescens (TRPL) spektroskopi og femtosekund transient absorption (fs-TA) spektroskopi og Femtosekund tidsopløst midtinfrarød absorption (fs-TRIR) spektroskopi blev den ophidsede tilstandsdynamik af disse tre prøver undersøgt. Vi viser, at koblingen af metal-komplekskatalysatorer faktisk kan lette overførslen af ladning i COF'er, hvor effektiv elektronoverførselsproces fra COF'er til Re / Ni kan observeres. Desuden fandt vi, at en sådan elektronoverførselsproces sammen med ophidset tilstands levetid er meget afhængig af excitationsfononenergi. De foto-genererede elektroner og huller har tendens til at adskilles i metal-center- og COF-dele efter overførsel af ladning under båndkant-excitation. Når de ophidses med højenergifoton (400 nm, 3,1 eV), der er meget større end båndgabet, vil de genererede varme bærere gennemgå forskellige afslapningsveje afhænger af den oprindelige orbitale, de finder. De foto-genererede elektroner kan ligge både i COF-enheden og metalcenteret simutaonouly i dette tilfælde, hvilket fremmer den to-elektron-medierede CO2-reduktion. Derudover er et sådant fænomen udtalt i Ni-TpBpy sammenlignet med Re-TpBpy på grund af dets mere varierede ophidsede struturer, der tillader afslapning af ophidsede elektroner, hvor huller i høj grad afhænger af de første exciterede orbitaler.

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Graduation is not the end, nor does it mean goodbye, but the beginning of a new phase of life. I will bound forward with a grateful heart in my future work and life.

May 2021, Kgs. Lyngby Qinying Pan

# List of publications

This thesis is based on the following papers, which are referred to in the text by Roman numerals.

# I. Photocatalytic Reduction of CO<sub>2</sub> by Metaled 2, 2'-bipyridine Covalent Organic Framework

<u>**Qinying Pan</u>**, Yuehan Cao, Quan Zhou, Zonglong Li, Hao Cui, David Ackland Tanner, Ying Zhou, Hong Xu, and Kaibo Zheng. Manuscript to be submitted</u>

## II. Ultrafast charge transfer dynamics in 2D Covalent Organic Frameworks/Recomplex hybrid photocatalyst: Hot electrons vs. cold electrons

Qinying Pan, Mohamed Abdellah, Yuehan Cao, Yang Liu, Weihua Lin, Jie Meng, Quan Zhou, Zonglong Li, Hao Cui, David Ackland Tanner, Ying Zhou, Tonu Pullerits, Sophie E. Canton, Hong Xu, and Kaibo Zheng.

Nature communications: in revision.

## III. Ultrafast Excited-state Dynamics in a Ni-2, 2'-Bipyridine Covalent Organic Framework Photocatalyst

<u>**Qinying Pan</u>**, Mohamed Abdellah, Yuehan Cao, Yang Liu, Weihua Lin, Jie Meng, Quan Zhou, Zonglong Li, Hao Cui, David Ackland Tanner, Ying Zhou, Sophie E. Canton, Hong Xu, and Kaibo Zheng.</u>

Journal of the American Chemical Society: in review.

# My contribution to the papers

**I.** I designed the study and conducted the experiments together, did the analysis, and wrote these parts of the manuscript.

**II.** I designed the experiments, synthesized the samples. I analyzed the data and wrote the manuscript with help from Kaibo.

**III.** I designed the experiments, synthesized the samples. Then, I analyzed the data and wrote the manuscript with help from Kaibo.

## Other publications are not included in the thesis.

I contributed to these papers, which are outside the scope of this thesis.

#### V. Orientation Effect of Zinc Vanadate Cathode on Zinc Ion Storage Performance

Huili Cao, Chao Peng, Zhiyong Zheng, Zhenyun Lan, <u>Qinying Pan</u>, Ulla Gro Nielsen, Poul Norby, Xinxin Xiao, Susanne Mossin

Electrochimica Acta. Accepted.

### VI. Photostability and Photodegradation Processes in Colloidal CsPbI<sub>3</sub> Perovskite Quantum Dots

Yang Liu, Ying Zhou, Mohamed Abdellah, Weihua Lin, Jie Meng, Qian Zhao, Shan Yu, Zhanghui Xie, **Qinying Pan**, Fengying Zhang, Tonu Pullerits, Kaibo Zheng

Manuscript

# Abbreviations

**COFs:** Covalent organic frameworks **Tp:** Triformylphloroglucinol **Bpy:** Bipyridine **2D:** Two-dimensional **TD-DFT:** Time-dependent density functional theory **OER:** One-electron reduced **ICT:** Intramolecular charge transfer fs-TA: Femtosecond transient visible Spectroscopy **fs-TRIR**: Femtosecond transient infrared absorption spectroscopy **PXRD:** Powder X-ray diffraction **XPS:** X-ray photoelectron spectroscopy FT-IR: Fourier Transform Infrared PL: Photoluminescence **VBM:** Valence Band Maximum **CBM**: Conduction band minimum HOMO: Highest energy Occupied Molecular Orbital LUMO: Lowest energy Unoccupied Molecular Orbital TRPL: Time-resolved photoluminescence TCSPC: Time correlated single photon counting FWHM: Full width at half maximums **GSB**: Ground state bleach **ESA**: Excited-state absorption SVD: Singular value decomposition CTS: charge-transfer state **XPS**: X-ray photoelectron spectroscopy **SEM**: Scanning electron microscopy **AFM**: Atomic force microsc **TGA**: Thermogravimetric analyses NMR: Nuclear magnetic resonance TEM: Transmission electron microscope

BET: Brunauer-Emmett-Teller (BET) theory



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# Chapter 1

## Introduction

The gradual increase in fossil fuel and energy consumption has caused global warming, attracting more and more concerns. Moreover, industrial organic chemicals and pollutants affect the ecological environment system in various ways. People seek effective ways to solve this problem with various methods to overcome pollution and other environmental problems. Although there is no immediate solution to environmental and energy-related issues, photocatalysis is a promising solution. Photocatalysis can convert clean solar energy into electrical and chemical energy to be used in various aspects, for instance, hydrogen or oxygen evolution, CO<sub>2</sub> conversion, batteries devices manufacturing, pollutants/dyes degradation, and other bionic experimental research. Therefore, as a "green", pollution-free, and sustainable reaction method, photocatalysis exhibits great application value.

Photocatalysis makes it possible to use light to drive catalytic reactions. The extra energy introduced by the photons can promote kinetic hindered reactions.<sup>1</sup> Its photosensitive center can be highly chemically active and regioselective in the reaction if the photocatalyst is adequately selected. In addition, photocatalysis is also highly efficient and "green" in nature, which complies with the sustainable development within the green transition framework.

In general, photocatalytic technology involves the multidisciplinary combination of various research fields such as electrochemistry, photochemistry, catalysis, and biochemistry. I also derive many research directions, such as wastewater treatment, water decomposition, air purification, and photocatalytic sterilization. However, up to now, the fundamental understanding of the photocatalysis process is still very limited, while most of the current studies focused on the synthesis and screening of the catalysts. There is little knowledge on the structure correlation on the catalytic performance, the dynamics of catalytic reactions, and the role of photophysics, etc. This has greatly hindered the actual application of efficient photocatalysts.

#### **1.1 Semiconductor Photocatalysts**

#### 1.1.1 Mechanism of semiconductor photocatalysis

Semiconductor photocatalysis is promising for solar energy absorption and conversion<sup>2,3</sup> as their strong continuous light absorption capacity (compared with molecular absorption system),<sup>4,5</sup> low cost (compared with noble metal plasma photocatalyst),<sup>6,7</sup> and simple preparation technology. The optical band gap and the position of the conduction band (CB)/ valence band (VB) edges of photocatalyst, which determines the optical absorption capacity and thermodynamics of the catalytic reaction, are the first crucial characteristics of the photocatalyst. During the photocatalytic process, excitation of the catalysts first leads to the transition of electrons from VB to CB, leaving holes in VB. As shown in Figure 1-1, the mechanism of semiconductor photocatalysis generally includes the following processes<sup>8</sup>: (1)Light absorption, the light radiation with energy equal or greater than the bandgap triggers the generation of electron and hole pairs in the semiconductor; (2) Separation and transfer of photo-generated charges, here photo-generated electrons and holes migrate to the spatially separated semiconductor surface through a series of pathways; (3) some of the excited electrons will be back to the ground state and recombine with the holes, releasing energy in other forms such as heat and photoluminescence; the separated electrons will migrate to the semiconductor surface and be captured by electron acceptors (such as reductive cocatalyst) to reduce H<sub>2</sub>O or CO<sub>2</sub> to high valued H<sub>2</sub> and hydrocarbons; the remaining holes are used for oxidation process, (e.g. H<sub>2</sub>O to O<sub>2</sub> oxidation or organic pollutants degradation).

The interface charge transfer process of photocatalysis mainly includes the charge transfer among semiconductors and cocatalyst, active sites, and reaction species. Those multi-stepped kinetic processes of photocatalysis interact and compete with each other and ultimately determine photocatalytic efficiency. Therefore, it is necessary to study the photophysical and photochemical processes to understand the mechanism of semiconductor photocatalysis.

The state-of-the-art application of semiconductor photocatalysts focused mainly on photocatalytic water splitting, photocatalytic reduction of  $CO_2$ , and photocatalytic degradation of pollutants, etc. In the following, the detailed catalytic process in photocatalytic  $CO_2$  reduction, which is the main focus of our thesis, will be introduced.



Fig. 1-1 The general process of semiconductor-based photocatalysis.

#### 1.1.1.1 Mechanism of photocatalytic CO2 reduction

Table 1 The main products of  $CO_2$  reduction and corresponding reduction potentials regarding NHE at pH=7 in aqueous solution, 25 °C.

Reactions	$E^0$ redox/V (vs. NHE)
$CO_2+e^-\rightarrow CO_2^{-}$	-1.85
$CO_2+2H^++2e^-\rightarrow HCOOH$	-0.61
$CO_2+2H^++2e^-\rightarrow CO+H_2O$	-0.53
$CO_2+4H^++4e^-\rightarrow HCHO+H_2O$	-0.48
$CO_2+4H^++4e^-\rightarrow C+2H_2O$	-0.20
$CO_2+6H^++6e^-\rightarrow CH_3OH+H_2O$	-0.38
$CO_2+8H^++8e^-\rightarrow CH_4+2H_2O$	-0.24
$2CO_2+12H^++12e^-\rightarrow C_2H_4+4H_2O$	-0.34
$2CO_2+12H^++12e^-\rightarrow C_2H_5OH+3H_2O$	-0.33
$2CO_2+14H^++14e^-\rightarrow C_2H_6+4H_2O$	-0.27
$2H^++2e^-\rightarrow H_2$	-0.42

With the rapid consumption of fossil fuels, in the past century, the concentration of  $CO_2$  in the atmosphere is overtopped, which limits social development and leads to increasingly serious environmental problems.<sup>9,10</sup> Photocatalytic converting  $CO_2$  into renewable fuels, such as CO, CH<sub>4</sub>, HCOOH, CH<sub>3</sub>OH, and other hydrocarbons are considered one of the most promising strategies to reduce greenhouse concentration and solve the energy shortage.<sup>11–13</sup>

Thermodynamically,  $CO_2$  is an extremely stable molecule, the dissociation energy of the C=O bond (750 kJ·mol<sup>-1</sup>) is significantly higher than the C-H bond (430 kJ·mol<sup>-1</sup>) and C-C bond (336 kJ·mol<sup>-1</sup>) bond, which means that a large amount of energy needs to be injected into the system to trigger the activation and conversion of  $CO_2$ .<sup>14</sup> As shown in Table 1, in the photocatalytic reaction,  $CO_2$  can usually be reduced to CO, CH<sub>4</sub>, HCOOH, or ethanol and other substances, and accompanied by the side reaction of water reduction to hydrogen, which significantly reduces the selectivity of the target product.<sup>13</sup> However, to achieve efficient photocatalytic  $CO_2$  reduction, the challenge in conversion efficiency and selectivity remains to be solved. To obtain higher efficiency of  $CO_2$  photoreduction, the catalyst needs to have not only an appropriate energy band structure with decent light harvest capability but also an optimal surface and electronic structure to guarantee the chem-adsorption and activation of  $CO_2$ .<sup>14</sup>



Fig. 1-2 Schematic illustration of reaction steps in photocatalytic CO<sub>2</sub> reduction.

Similar to many photocatalytic reactions, the reaction of  $CO_2$  photocatalytic reduction can be divided into three steps: charge generation, charge diffusion to surface, and charge transfer for the oxidation and reduction reaction<sup>14</sup> (see Fig. 1-2): However, the detailed mechanism of  $CO_2$  reduction is complicated, and the products may be obtained through different reaction paths for different catalysts.<sup>13,14</sup>

In CO<sub>2</sub> photocatalytic reduction, CO<sub>2</sub> molecules are first bonded to the surface of the catalyst through chemical adsorption, the reaction intermediate is obtained through the activation process, and then the final product is obtained through complex multi-step transformation. Nowadays, there are two main views on the above process, namely, single-electron transfer and proton-coupled multiple-electron transfer (PCMET).<sup>14</sup> In the process of single electron transfer, a curved and unstable CO<sub>2</sub><sup>-</sup> active intermediate was formed when the CO<sub>2</sub> adsorbed on the catalyst surface and activated by a single electron. It can be seen from Table 1 that the reduction electrode potential is -1.85 V, which is far beyond the reduction ability of photogenerated electrons in most photocatalysts, so it is thermodynamically unfavorable. In contrast, PCMET is thermodynamically much easier. The reaction system always maintains the zero net charge when electrons and protons migrate to the reactants synchronously, which is conducive to reducing the activation energy. Therefore, the reduction potential is significantly reduced. However, PCMET requires sufficient electrons and protons to participate in the reaction at the same time.<sup>14</sup> Therefore, increasing the local charge density and accelerate the CO<sub>2</sub> reduction kinetics has been considered as effective strategies to realize the PCMET.

#### 1.1.2 Factors affecting photocatalytic performance

Generally speaking, several main photophysical factors are affecting the photocatalytic conversion efficiency of a semiconductor catalyst system<sup>15</sup>: 1) The light absorption capacity: The higher the absorptive capacity of the catalyst in the visible light region ( $\lambda \ge 420$  nm), the more sunlight will be utilized to generate electrons and holes, thereby enhancing the photocatalytic activity. 2) The efficient carrier charge separation: This is to ensure sufficient electrons and holes involved in the photocatalytic reaction before they recombine. In contrast, inefficient charge separation is associated with a short excited-state lifetime and small charge diffusion length, which prevents the charge carriers to migrate to the surface of the catalyst.

Therefore, effective suppression of electron-hole recombination is the key to improving photocatalytic activity.

The cognition of the above-mentioned physical processes encourages people to achieve highefficiency photocatalytic reactions through the reasonable construction of composite photocatalysts. For example, a heterojunction catalyst is based on two kinds of semiconductor materials. By forming an interface region through the close contact of different semiconductors, an electric field will be formed due to the potential difference between the different electronic structures of the semiconductors. Under the action of this electric field, the photogenerated electrons and holes will migrate rapidly, promoting the effective separation of electron-hole pairs and thus enhancing the photocatalytic efficiency.<sup>16</sup>

#### 1.1.3 The charge separation that determines the photocatalytic efficiency

The charge separation and transfer play a decisive role in the overall efficiency of photocatalytic solar energy conversion.<sup>17–19</sup> In general, electron-hole pairs are photoexcited within fs, while the timescale for the surface reaction with photogenerated electrons and holes is ms. Within such a huge time gap, recombination or defect state trap can all occur to prevent the charge carrier migration and transfer into the reaction system.<sup>20–22</sup> Therefore, the final concentration of charges that can be transferred to the semiconductor surface to participate in the chemical reaction is very limited, which is also the fundamental reason for the low efficiency of the photocatalytic reaction. In recent years, a series of strategies have been developed to improve charge separation and enhance photocatalytic efficiency.<sup>23</sup> These strategies mainly include the construction of heterojunctions,<sup>24</sup> phase junctions,<sup>25</sup> co-catalysts,<sup>26</sup> nanosteps,<sup>27</sup> interfaces or crystal facet engieering,<sup>28,29</sup> and so on.

Loading cocatalyst is the most widespread method to improve the efficiency of photogenerated charge separation, that is, to improve the efficiency of photocatalytic reduction (oxidation) reaction by depositing cocatalyst particles which can guide electron (hole) transfer on the surface of semiconductor photocatalysts.<sup>30–33</sup> Due to the difference in energy level, after the promoter contacts the semiconductor, a driving force for the charge separation is formed at the interface, which leads to the directional transfer of electrons or holes and consequently improves the photocatalytic activity. A good heterojunction needs not only above mentioned band matching but also lattice matching. This is because the interface defect states induced from the lattice mismatch usually act as recombination centers to increase the probability of charge recombination. Lattice matching can reduce the formation of interface defect states to inhibit charge recombination.<sup>34,35</sup> In contrast, homojunction may have more potential for efficient carrier interface transfer due to reduced interfacial lattice mismatch.<sup>25,36,37</sup> These strategies prove that building an asymmetric driving force in the photocatalyst to efficiently separate electrons and holes in space is the fundamental way to improve the efficiency of photocatalysis.

### 1.2 Semiconductor photocatalytic materials

In 1972, Fujishima and Honda<sup>38</sup> made the pioneering discovery of photocatalytic hydrolysis in a titanium dioxide electrode system. Four years later, Carey et al.<sup>39</sup> reported the photocatalytic decomposition of organic pollutants in the presence of titanium dioxide photocatalysts, and Inoue et al.<sup>40</sup> published that the photocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders (e.g., titanium dioxide, zinc oxide, cadmium sulfide, gallium phosphide, and silicon carbide suspensions) in 1979. Since then, more and more researchers have started their research on efficient and stable semiconductor photocatalysts, as reported in the literature.<sup>41–44</sup>

At the early time, most studied photocatalytic materials are wide bandgap semiconductors such as titanium dioxide, bismuth phosphate, zinc oxide, tin dioxide, and bismuth chloride oxide. However, they exhibit the limitation on the light absorption only within the ultraviolet light region. The narrow bandgap semiconductor photocatalysts were then developed, including bismuth vanadate, copper oxide, tungsten oxide, cadmium sulfide, iron oxide, and carbon nitride.<sup>45–48</sup>

#### 1.3 Covalent organic framework (COFs) photocatalytic materials

Visible light materials have received much attention in the field of photocatalysis as visible light (400-700 nm) accounts for about 43 % of the total solar spectrum while UV light (300-400 nm) accounts for only about 5 %.<sup>49–54</sup> Therefore, it is of great research significance to develop photocatalysts for CO<sub>2</sub> reduction that respond to visible light.<sup>55</sup> A variety of

semiconductor-based visible light catalysts have been developed, but most of them are limited by the poor catalytic efficiency and instability during the catalytic reaction.



**Fig. 1-3** Structural representations of (A) COF-1 and (B) COF-5 based on powder diffraction and modeling projected along their c axes (H atoms are omitted). This figure was taken from Reference [60] with permission.

In recent years, researchers gradually focus on organic polymer materials. The most prominent example recently in this category is covalent organic frameworks (COFs). COFs are highly crystalline porous polymers composed of lightweight elements with ultra-high surface area and chemical stability.

COFs are usually formed by the expansion of organic monomers in two or three dimensions through covalent bonding.<sup>56–63</sup> The history of COFs can be traced back to 2005, Yaghi et al<sup>60</sup> formed covalent organic frameworks (COF-1 and COF-5) (Fig. 1-3) through the direct condensation reaction of two organic monomers (phenylboronic acid and hexahydroxytriphenyl), marking the advent of COFs materials. The structural units of this new type of material can be ordered in atomic dimensions by utilizing the reversible reactions in dynamic covalent chemistry, which leads to the formation of a periodic crystalline mesh skeleton structure. Different from the conventional covalent bond formation via kinetic control, this kind of dynamic covalent chemistry is controlled by thermodynamics where the process of "self-diagnosis" and "self-repair" is continuously cycled in a reversible reaction system until the thermodynamic stable structure is formed.



**Fig. 1-4** Developmental milestones of COF-based materials: single COFs to functionalized COFs. This figure was taken from Reference [69] with permission.



**Fig. 1-5** Topology diagrams for designing 2D COFs and 3D COFs (a). This figure was taken from Reference [69] with permission. Schematic illustration of the photoinduced charge transfer (b). This figure was taken from Reference [77] with permission.

In recent years, COFs have attracted extensive attention from researchers, and a variety of COFs with different structures and functions have been reported (Fig. 1-4).<sup>64–73</sup> According to their molecular dimensionality, it can be divided into 2D COFs and 3D COFs (Fig.1-5a).<sup>69</sup> In the 2D-COFs, the organic building blocks are connected by covalent bonds and extend in an ordered manner in the 2D plane, and the individual 2D-COFs layers are further stacked by  $\pi$ - $\pi$  interactions to form a crystalline laminar structure.<sup>57,63,74,75</sup> The close eclipsed stacking leads to large electronic coupling between the  $\pi$ -orbitals in the molecular units,  $\pi$ -matrix, which is difficult to obtain through traditional chemical bonding methods. The  $\pi$  orbitals in

this " $\pi$ -matrix" configuration provide enhanced intramolecular electronic coupling and open up efficient charge transport pathways along the  $\pi$  channel (Fig. 1-5b).<sup>76,77</sup>

#### 1.3.1 Synthesis of COFs

The key to achieving long-range ordered networking in COFs is the thermodynamic equilibrium state of the reaction during the formation of covalent bonds. Here a variety of factors need to be considered in regulating such thermodynamic equilibrium state, including reaction temperature, time, pressure, and solvent environment, etc. In the past decade, scientists have developed several successful methodologies to synthesize COFs materials, involving solvothermal, ionothermal, microwave, mechanochemical, and light-induced processes, etc (Fig. 1-6).<sup>58,59,62,78</sup>



**Fig. 1-6** Schematic representation of the properties and advantages of various synthetic routes toward COFs. This figure was taken from Reference [78] with permission.

Solvothermal is one of the most widely used and applicable synthetic methods. The COFs is obtained by the solvothermal with the advantages of high crystallinity, high specific surface area, and good reproducibility. However, this method requires high temperature and pressure, with an extremely long reaction time (usually 2-8 days), which is unsuitable for large-scale production. Moreover, some of the COFs constructed from boric acid are not stable in wet environments and are prone to hydrolysis, which hinders the practical application of these materials.<sup>79–83</sup> The ionothermal synthesis method uses ionic liquids or low eutectic mixtures

as a medium in a high-temperature environment. The reaction conditions of this method are harsh, and the obtained Covalent Triazine Framework (CTFs) are defective. Meanwhile, the selection of the building units is limited by the ultra-high temperature reaction, and the obtained CTFs are mostly amorphous without long-range ordered structures.<sup>84–86</sup> Table 1 summarizes the advantages and disadvantages of the synthesis methods investigated so far.<sup>78</sup>

Methods	Advantages	Disadvantage
Solvothermal	<ul> <li>Widely used methods due to the simplicity and providing high crystalline products, with almost 100% defects healing</li> <li>A large combination of solvents can be used</li> </ul>	<ul> <li>Products are insoluble and unprocessable powders, which potentially limiting their applications</li> <li>Long reaction time (3–5 days)</li> <li>Can not be used for insoluble building blocks</li> </ul>
Ionothermal	• Significantly shorter reaction time (12 h) when compared with the times required for traditional solvothermal methods (3–7 days)	<ul> <li>Require high temperature</li> <li>Undesirable decomposition and side reactions</li> </ul>
Microwave	<ul> <li>Generate fast and clean products</li> <li>The ability to monitor the phase behavior</li> <li>Simultaneous control of reaction temperature and pressure</li> </ul>	• Not as simple as other methods
Sonochemical	• Rapid and economic • Increased the reaction batch size up to 0.5 L	• Only applicable for small COFs
Mechanochemical	<ul> <li>Room temperature synthesis</li> <li>Requires only manual grinding</li> <li>Simple, rapid, solvent-free, and environmentally friendly synthesis</li> <li>Provide exfoliated structure</li> </ul>	<ul> <li>Only applicable for small building blocks.</li> <li>Does not have a medium for orientation and crystalline arrangements.</li> </ul>
Light-induced	<ul> <li>Use of abundant light as an energy source</li> <li>Simple and solvent-free</li> <li>Improved crystallinity</li> </ul>	• Limited to the synthesis of conjugated COFs structures

 Table 1-1 Comparison of the advantages and disadvantages of the synthesis strategies of COFs. This table was taken from Reference [78] with permission.

#### 1.3.2 Application of COFs in photocatalytic CO<sub>2</sub> reduction

COFs materials can be a powerful candidate for photocatalysts mainly because of the following advantages: (1) The large chemical tunability of COFs can be merit to optimize the basic functions of light capture, charge separation, and transport in the photocatalytic process; (2) COFs possess permanent nanoscale pore structure and ultra-high specific surface area, which allows rapid diffusion of photo-generated charges to the surface for the catalytic reaction. The large specific surface area also promotes the participation of sensitizers, electrolytes, sacrificial agents, and co-catalysts in the reaction; (3) Compared with molecular catalysts, COFs lock the photoactive building blocks in the rigid structure to prevent the collisional deactivation of photon thereby to prolong the lifetime of the excited state, and strong  $\pi$ -conjugation in the structure increase the mobility of charge carriers; (4) The good crystallinity of COFs reduces the possibility of charge trapping at defect sites; (5) COFs possess excellent chemical stability. (6) COFs are composed of light elements with low-density characteristics.<sup>87–91</sup>

However, COFs are metal-free polymers, the most significant disadvantage of COFs materials is the lack of bare metal active centers that can be used for photocatalytic reactions, so there are some problems such as low catalytic activity and poor selectivity. Therefore, molecular metal catalyst-modified COFs as photocatalysts are the current research hotspots for improving their photocatalytic activity.

Rhenium complexes are the most frequently selected co-catalyst as they serve as an excellent class of homogeneous CO<sub>2</sub> reduction photocatalysts.<sup>92–94</sup> Cao et al.<sup>95</sup> synthesized a pyridine-containing CTF and obtained a CO<sub>2</sub>-reducing photocatalyst, Re-CTF-py, by anchoring the Re(CO)<sub>3</sub>Cl complex with pyridine nitrogen atoms in the organic backbone. Re-CTF-py has high stability, strong CO<sub>2</sub> adsorption capacity, and good photoactivity. The reduction rate of CO<sub>2</sub> to CO was 353.05 umol·h<sup>-1</sup>·g<sup>-1</sup> with high selectivity under visible light irradiation with triethanolamine as the cavity sacrificial agent. The leaching of Re(CO)<sub>3</sub>Cl can be effectively avoided in Re-CTF-py due to the coordination effect of pyridine, which provides excellent recyclability.



**Fig. 1-7** (a) Synthesis of COFs and Re-COFs; (b) Side View and (c) Unit Cell of AA Stacking COFs; (d) Proposed Catalytic Mechanism for CO<sub>2</sub> Reduction. This figure was taken from Reference [96] with permission.

Yang et al.<sup>96</sup> reported a new molecular photocatalyst (Re-COFs) formed by using a 2D triazine COFs as a photosensitizer combined with a Re complex (Fig. 1-7). Such a hybrid system successfully achieved CO<sub>2</sub> reduction to CO with high selectivity (98 %). It exhibits much better CO<sub>2</sub> reduction activity and stability than the Re counterpart. They investigated the mechanism of CO<sub>2</sub> reduction by transient absorption (TA) spectroscopy, X-ray transient absorption (XTA) spectroscopy, and in situ diffuse reflectance spectroscopy, which shows that the photoexcited electrons are transferred from COFs to Re, and the charge lifetime increases significantly with the intramolecular charge transfer. Therefore the anchoring of Re-complex on COFs can not only provides catalytic sites but also contribute to inhibiting the recombination of photo-generated charge carriers.

#### 1.3.3 Photo-induced charge separation and transfer in COF materials

As mentioned in the previous sections, the excited state dynamics, especially the capability of photo-induced charge separation and/or transfer significantly dominate the photocatalytic performance. Such processes had thereby also been investigated in COFs-based photocatalysts.

In 2019, Tae Wu Kim et al.<sup>97</sup> constructed a 2D donor-acceptor (D-A) COFs by combining the 3,4,9,10-perylenetetracarboxylic acid diimide (PDI) and porphyrin building blocks and studied its ultrafast excited-state dynamics by femtosecond optical spectroscopy and non-adiabatic molecular dynamics simulation. The result shows that the initial excitation in the COF exhibits dynamics spatial localization. The charge generated by the photoexcitation is first located in the PDI unit of COFs, and then the holes are injected into the porphyrin ring from the PDI chromophore, leading to the appearance of polarons in the framework lattice. The charge transfer with a time constant of 124 fs is assisted by the phonons of the scaffold, particularly through the motion of the phenyl ring connected to the porphyrin core (Fig. 1-8). Such instantaneous charge separation should be a merit for the catalytic reaction.



**Fig. 1-8** Schematic of charge carrier dynamics in photoinduced 2D D-A COFs. This figure was taken from Reference [97] with permission.

In the same year, jakowetz et al.<sup>98</sup> investigated the ultrafast excited-state dynamics of a series of imine-linked fully conjugated 2D COFs using highly sensitive optical spectroscopy and proposed a general model. They suggest that the excited state dynamics are independent of the topology of the COFs with fixed excite state depopulation pathways. However, the initial 28

photogenerated singlet states diffuse through the framework and possibly collide, and these singlet-singlet annihilations will produce spatially isolated charges with lifetimes of tens of microseconds, which is several orders of magnitude longer than that of the charge in the classical polymer system (Fig. 1-9).

In summary, COFs materials can serve as an essential stepping stone towards sustainable and inexpensive photocatalytic systems. In detail, COFs utilize as perfect photosensitizers in the photocatalytic system due to their excellent crystallinity, porosity, stiffness, stability, as well as perfect photophysical feature including decent light-harvesting, efficient charge separation, and transport capabilities. More importantly, the easy access to the cooperation of molecular metal catalysts in the pore structure can effectively promote the separation of photogenerated electron-hole pairs and prolong the lifetime of the excited states, thus improving the photocatalytic activity. However, the excited state dynamics in such a hybrid system is still to be known. Therefore, this paper focuses on studying the photophysics of this metal-complex/COFs hybrid system through a complementary study between theoretical calculation and experimental spectroscopy characterization.



**Fig. 1-9** Model of the photoinduced electronic processes in COFs. (a) The formation of singlet excitons. (b) These singlets diffuse and collide leads to singlet–singlet annihilation. (c) isolated free charges with long lifetimes over tens of microseconds. This figure was taken from Reference [98] with permission.

## Chapter 2

## **Experimental Methods**

To investigate the underlying mechanism of the photocatalytic reaction in metaled COFs materials, which is the main focus of this thesis, we mainly utilize various optical spectroscopic technics to reveal the photophysical processes. This chapter briefly introduces the spectroscopic methods involved in the study, which consists of both steady-state and time-resolved spectroscopies.

#### 2.1 Steady-state spectroscopy

#### 2.1.1 Ultraviolet-visible (UV-Vis) Absorption spectroscopy

Ultraviolet-visible (UV-Vis) absorption spectroscopy technology is a mature technology that can probe the optical transitions of the sample. UV-Vis spectroscopy is used to analyze the electron transition when the electromagnetic (EM) radiation incident on the sample is in the range of 190-900 nm (that is, the ultraviolet-visible range). Taking molecular system as examples, band-edge excitation will usually trigger the optical transition from the VB to the CB, which involves three types of ground state orbitals,  $\sigma$  and  $\pi$  bonded orbitals, and n nonbonded orbitals, as well as two excited state orbitals, namely antibonding orbitals,  $\sigma^*$  and  $\pi^*$ . The valence electron in the molecule will transition to an excited state when the organic compound absorbs ultraviolet or visible light. There are four main types of transition modes,  $\sigma \rightarrow \sigma^*, n \rightarrow \sigma^*, \pi \rightarrow \pi^*, n \rightarrow \pi^*$ . In general, the energy required for various transitions is:  $\sigma \rightarrow \sigma^*$  $> n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$ .  $\sigma \rightarrow \sigma^*$ : With the largest transition energy, the  $\sigma$  electron can only be excited when absorbing the photon with the energy in far-ultraviolet light. The optical absorption of saturated alkanes appears in the far ultraviolet region (the absorption wavelength  $\lambda < 200$  nm, which can only be detected by a vacuum ultraviolet spectrophotometer). The absorption wavelengths to a typical  $n \rightarrow \sigma^*$  transition are around 150 - 250 nm. The saturated hydrocarbon derivatives containing non-bond electrons (heteroatoms such as N, O, S, and halogen atoms) all exhibit this transition. The favored transitions mode in a molecular system is  $\pi \rightarrow \pi^*$  transition. Without conjugation, the absorption band is usually located around 200 nm. In a conjugated system, the absorption band shifts to a longer 30

wavelength, which is between 200-700 nm. The absorption wavelengths of  $n \rightarrow \pi^*$  transition are around 300 nm, which is common in unsaturated organic compounds containing heteroatoms (such as C=O, C=S, O=N-).<sup>99,100</sup>



Fig. 2-1 Typical electronic transitions for organic molecules.

#### 2.1.2 Steady-state photoluminescence (PL) spectroscopy

Photoluminescence spectroscopy is a widely used technique to measure the optical emission of semiconductors and molecules. In general, PL is a de-excitation process that occurs when the molecules are excited by photons. After molecules are excited to excited states, most molecules will dissipate the excess energy as heat by colliding with other molecules; while some molecules release this energy in the form of light with a wavelength different from that of the absorbed radiation, the latter process is called PL.<sup>101–103</sup> A Jablonski diagram is commonly used to describe the relaxation of a molecule to its ground state in the form of luminescence, as in Fig. 2-2.<sup>101</sup>

Each molecule has a series of strictly discrete electronic energy levels, and each electronic energy level contains a series of vibrational and rotational energy levels, as seen in Fig. 2-2. In the figure, the ground state is represented by S0, the first excited singlet state and the second excited singlet state are represented by S1 and S2, respectively, and T1 is the first excited triplet state. At room temperature, most molecules are in the lowest vibrational energy level of the ground state. Molecules in the ground state are excited to the excited state after absorbing energy. The excited state is unstable, and electrons may return to the ground state

through de-activation processes such as radiative transition and non-radiative transition. There are several basic de-activation processes, (1) Vibrational relaxation, (2) Internal conversion, (3) Fluorescence, (4) Intersystem crossing, and (5) Phosphorescence.



Fig. 2-2 Jablonski Diagram.

It is worth noting that the actual pathway of the excitation depopulation depends on the time scale of each channel. The faster the transition, the more likely it is to occur.<sup>101,104,105</sup> Table 2-1 summarize some basic radiative and non-radiative timescales in molecular system (table 2-1).

Transition	Time Scale	Radiative Process?
Absorption	10 <sup>-15</sup> s	yes
Internal Conversion	10 <sup>-14</sup> -10 <sup>-11</sup> s	no
Vibrational Relaxation	10 <sup>-14</sup> -10 <sup>-11</sup> s	no
Fluorescence	10 <sup>-9</sup> -10 <sup>-7</sup> s	yes
Intersystem Crossing	10 <sup>-8</sup> -10 <sup>-3</sup> s	no
Phosphorescence	10 <sup>-4</sup> -10 <sup>-1</sup> s	yes

 Table 2-1 A timescale table for basic radiative and non-radiative timescales.

In our work, all the steady-state PL spectra were acquired via Spex Fluorolog 1681 standard spectrofluorometer under a specific excitation wavelength.

#### 2.2 Time-resolved spectroscopy

The above spectroscopic methods can only characterize the steady-state optical feature of the materials, and cannot reflect the dynamic evolution of the samples at the excited state after excitation. Ultrafast laser pulses make such characterization feasible. A series of time-resolved ultrafast spectroscopy techniques have been developed using precision controlling the time decay between excitation and signal probing. The ultrafast spectroscopy techniques employed in this thesis are described below.

#### 2.2.1 Time-resolved PL (TRPL) spectroscopy

For materials with fluorescence emission, the time-resolved detection of the fluorescence lifetime can directly reflect the decay characteristics of the fluorescence emission state, so the Time-resolved PL (TRPL) spectra also become one of the most important kinetic properties of such materials.<sup>106–110</sup> Several techniques can be used to obtain temporal and

spectral information on PL emission from semiconductors, such as time-correlated singlephoton counting (TCSPC) and streak cameras.<sup>111–113</sup>

#### 2.2.1.1 Time correlated single photon counting (TCSPC)

Time correlated single photon counting (TCSPC) is a common method to monitor the timeresolved photoluminescence (TRPL) spectrum, which was first proposed by Bollinger and Thomas in 1961.<sup>114,115</sup> TCSPC technology can effectively detect weak signals from fluorescence with high sensitivity and high accuracy. It is based on the principle of continuously irradiating the sample with a high repetition rate pulsed light source, which makes the sample emit photons followed by collecting the fluorescence signal of the sample in a direction perpendicular to the incident light to avoid the interference of the incident light, which is especially important for the study of weakly fluorescent sample components. During the measurement, a temporal counter is set to synchronize with the excitation pulse to trigger the count. When the detector receives a photon, the counter stops timing and records the number of photons in the corresponding time channel. After collecting the fluorescence signal into the spectrometer, the fluorescence lifetime of the sample can be obtained by deconvolution analysis of the signal, collecting multiple cycles of photons through periodic excitation, and then constructing a single cycle of decay processes through the collected single-photon events. By repeatedly recording the time difference between the collected single photon and the corresponding excitation pulse, the histogram of the photon arrival counts in each time gate is accumulated to represent the time decay.<sup>116–118</sup> The principle is illustrated in Fig. 2-3.



Fig. 2-3 Schematic diagram of TCSPC measurement mode.

The time resolution of this method generally depends on the pulse width of the excitation light source and the time response of the detector. In this thesis, we used a pulse diode laser triggered externally at 2.5 MHz (TCSPC device of PicoQuant) to excite the sample at 438 nm. After passing through a 470 nm long band-pass filter, the emitted photons are detected by a rapid avalanche photodiode (SPAD), and the response time is less than 50 ps.

#### 2.2.1.2 Streak camera

Streak camera is another TRPL characterization methodology. Its key functional concept is to scan and map the indistinguishable ultrafast time axis information can convert it into spatial axis information that can be visualized on the fluorescent screen. In basic frontier science research fields such as biomedicine, materials science, condensed matter physics, and photochemistry, a streak camera is a key tool for the measurement of ultrafast emission-related phenomena.<sup>119–126</sup>


Fig. 2-4 Schematic diagram of streak camera measurement mode.

In our work, the streak camera is employed to measure the TRPL of our samples. Fig. 2-4 shows the schematic diagram of how such measurement is achieved. A short laser pulse at 800 nm with a 100 fs pulse duration and repetition rate of 80 MHz was frequency-doubled to 400 nm for the excitation. The transient PL signal is collected by two quartz plano-convex lenses and focused on the input slit of the spectrometer, which is converted into a onedimensional optical signal when passing through the slit, and then clearly imaged and photoelectrically converted on the photocathode, obtaining a one-dimensionally distributed electron beam in space, due to the photocathode having a linear response interval in which the number of photoelectrons is proportional to the radiation intensity. These photoelectrons are accelerated and focused by the high-voltage electric field provided by the high-voltage power supply module. Afterward, they will enter the scanning system consisting of a scanning plate, where the plate is provided with a high-voltage ramp-like scanning voltage (scanning speed can reach 2c~3c, c is the speed of light). Therefore the super-fast scanning of the electronic signal is realized. Within the linear range of the voltage, the vertical distance between the position of the photoelectron and the original direction of motion is proportional to the time when the photoelectron enters the scanning plate, thus realizing the conversion from time information to space information. At this stage, the image signal is still too weak to be recorded. The image intensifier is then used to enhance the image signal which

bombards the phosphor screen to get the fluorescent image. The photosensitive surface of the CCD recording system detects and records the fluorescence image, and finally uses the correlation between the spatial information of the light signal and the scanning speed of the streak camera to obtain the time information of the light signal.

#### 2.2.2 Femtosecond transient absorption (fs-TA) spectroscopy

Transient Absorption (TA) spectroscopy technology can probe the excited state dynamics of samples with both radiative and non-radiative pathways.

It is essentially a pump-probe technology (Fig. 2-5). During the operation, the laser pulses are divided into two beams,<sup>127,128</sup> one beam is usually used to excite the sample defined as pump pulse, and the other ultra-short pulse (probe pulse) is used to detect the transient change in absorbance of the sample before and after excitation, and the signal obtained is the transient absorption signal.<sup>129,130</sup> TA measurements can be achieved using a precision optical displacement stage to change the time delay between the pump pulse and the probe pulse. The TA has become one of the important experimental tools to investigate the excited state dynamics due to it can effectively monitor this series of processes.



Fig. 2-5 Schematic diagram of femtosecond transient absorption.

Since transient absorption detects the change in absorbance of the sample before and after excitation, the transient absorption signal  $\triangle$  OD can be defined as:

$$\Delta OD = OD_{pump-on} - OD_{pump-off} \tag{2-1}$$

where  $OD_{pump-on}$  and  $OD_{pump-off}$  denote the absorbance of the sample with and without pump pulse, respectively. We assume that the extinction coefficient and concentration of a molecule in the ground state are  $\varepsilon$  and c, respectively. According to the Lambert-Beer law,  $OD_{pump-off}$ can be expressed as:

$$OD_{pump-off} = \varepsilon lc \tag{2-2}$$

A certain concentration of transient component X will be produced when the sample is excited, which has a specific extinction coefficient  $\varepsilon'$  and concentration C'. In this case, the overall absorbance of the sample is composed of the absorbance of the remaining ground-state molecules and the absorbance of the transient component X. which is:

$$OD_{pump-on} = (c - c') + \varepsilon' lc'$$
(2-3)

The transient absorption signal and be obtained by substituting Eqs. (2-4) and (2-5) into Eq. (2-1).

$$\Delta OD = (\varepsilon' - \varepsilon)' \tag{2-4}$$

From Eq. (2-4), the signal of transient absorption is proportional to the concentration of transient component X. Therefore, observing the evolution of transient absorption signal with time can reflect the kinetic properties of transient component X. in general, the transient absorption signal obtained in the experiment is a two-dimensional data matrix concerning the wavelength  $\lambda$  and time t. The signal can be expressed as:

$$\Delta(\lambda, t) = [\varepsilon'(\lambda) - \varepsilon(\lambda)]lc'(t)$$
(2-5)

For transient processes that undergo only photophysical changes, the transient absorption spectral data mainly contains three kinds of signals (Fig. 2-6).<sup>127</sup> (1) Ground state bleach (GSB). After the sample is excited by the pump pulse, the number of molecules in the ground state will be relatively reduced. As a result, the intensity of the ground state absorption spectrum is weakened, which is lower than the absorption without excitation. According to equation (2-1), the transient absorption signal measured in the experiment is a negative signal, which reflects the change of the number of molecules in the ground state. The GSB signal usually appears in the region of ground-state absorption wavelength. (2) Excited-state absorption (ESA). After the sample is excited by the pump pulse, the molecules in the excited state will absorb the energy of the probe pulse and transition to a higher energy level. For

example, the molecules on the single or triplet excited state can absorb energy and transition to the higher level of the singlet or triplet excited state, respectively. Such a physical process will weaken the intensity of the detection pulse, and lead to the enhancement of the absorption spectrum intensity of the sample, which will show a positive signal in the transient absorption spectrum. Some of the hidden information of the molecules in the excited state within or between different states, such as molecular intra-transitions, vibrational chirality and intersystem crossing, and a series of other processes, can be obtained from the excited state absorption signal. (3) Stimulated emission (SE). SE is mainly due to the interaction of the molecules in the excited state of the sample with the pump pulse and appears as a negative signal in the transient absorption spectrum. For a two-energy molecular system, the Einstein coefficients  $(A_{12})$  for the energy absorbed by the molecule from the ground state to the excited state are the same as the exciting emission coefficients  $(A_{21})$  for the molecule from the excited state to the ground state. In the process of stimulated emission, the molecule in the excited state is induced by the photon in the probe pulse and emits another photon, which has the same energy and momentum as the photon in the probe pulse. The band range of stimulated emission is consistent with the steady-state fluorescence spectrum of the sample. The physical process will enhance the intensity in the direction of the probe pulse, thus disguising the weakening of the absorption spectrum of the sample, which leads to a negative signal shows in the TA spectrum. SE only occurs during transitions permitted by optics. Theoretically, there is an obvious stokes shift between the SE signal and the GSB signal. But in the actual measurement process, these two kinds of negative signals often overlap in the spectrum and give a wider absorption spectrum finally.



Fig. 2-6 Schematic diagram of the composition of singles in the TA spectrum.

The fs-TA setup used in our work is mainly composed of the following three parts. (1) A Ti: Sapphire amplifier (Coherent Legend) with a center wavelength of 800 nm. Its pulse width is about 120 fs, and its repetition rate is 3 kHz. (2) An optical parametric amplifier (Topas C, Light Conversion) for generating pump light at different wavelengths (400 nm and 530 nm were used in our work). (3) A commercially available TA spectrometer. After beam splitting, one part of the primary beam generated by the laser enters the optical parametric amplifier to generate excitation light, and the other part generates a white light continuum as the detection beam through CaF<sub>2</sub>.

# 2.2.3 Femtosecond time-resolved mid-infrared absorption (fs-TRIR) spectroscopy

Conventional steady-state IR spectroscopy measures the vibration and rotation modes of molecules. The TA technology and IR spectroscopy technology are combined to obtain the femtosecond time-resolved infrared absorption spectroscopy technology (TRIR). Since IR spectra can provide fingerprints on molecular functional groups and chemical bonds, fs-TRIR spectra not only reflect molecular excited states dynamics but also provide the structural dynamic information of such molecules. The schematic diagram of the femtosecond time-resolved infrared spectrum device is shown in Fig. 2-7, which is similar to the fs-TA device except the probe light is IR pulse, and the detector is also changed to the IR-detector.



Fig. 2-7 Femtosecond time-resolved mid-infrared absorption (fs-TRIR) spectroscopy.

As for the TRIR experiment in this thesis, the laser source is a Ti: sapphire amplifier (Spitfire Pro, Spectra-Physics). The laser emits fundamental frequency light with a central wavelength of 800 nm, a repetition frequency of 1 kHz, and pulse width (full width at half-height, FWHM) of 45 fs. The 800 nm fundamental frequency light is then split into two paths, one of which enters the commercial optical parametric amplifiers (TOPAS-C, Light Conversion), which generate the visible pump at 418 nm and the mid-IR probe (1850–2200 cm<sup>-1</sup>) pulses. Before reaching the sample, the probe beam was split into equal intensity probe and reference beams using a wedged ZnSe window. Both beams pass through the sample, but only the probe beam interacts with the photoexcited volume of the sample. All beams are focused with a single f = 10 cm off-axis parabolic mirror to a ~70 µm spot size in the sample. The pump intensity was attenuated to 650 µW. The probe and reference beams were dispersed by a commercial monochromator (Triax 190, HORIBA Jobin Yvon) equipped with a 75 groove/mm grating and detected on a dual array, 2 × 64-pixel mercury cadmium telluride detector (InfraRed Associates, Inc.). The instrument response function for the experiments was approximately 100 fs. The sample was mounted in a Harrick flow cell.

# Chapter 3

#### **Results & Discussion**

### 3.1 Photocatalytic Reduction of CO2 by Metaled 2,2'-bipyridine Covalent Organic Framework (Paper I)

Efficient solar-driven photocatalytic CO<sub>2</sub> reduction capture to fuel materials (i.e. CO, CH<sub>4</sub>, HCOOH, and CH<sub>3</sub>OH) has been considered as a promising strategy to tackle the issue of fossil fuel storage and global warming.<sup>9,10 40,131-134</sup> As mentioned in Chapter 1.3.2, COFsbased photocatalytic material as one kind of semiconductor material is considered to be promising photocatalytic materials due to their unique structural characteristics. Despite the above-mentioned advantages, the photocatalytic CO<sub>2</sub> activity of pure COFs has been proved unsatisfactory due to the rapid charge recombination.<sup>135</sup> Therefore, the loading of metal nanomaterials such Rh, Ru, Ir, Co, Ni, or Re catalytic complexes into COFs to enhance the charge carrier separation and provide catalytic reaction sites have been implemented to improve the catalytic performance.<sup>22–27</sup> Among them, the Re-complex/COFs and Ni-complex/COFs hybrid systems are the benchmark systems to exhibit high CO<sub>2</sub> reduction activity selectivity in separate reports.<sup>136,141–143</sup> However, there is no systematic comparison between those two photocatalysts in terms of intrinsic structures, morphology, electronic states as well as catalytic performance.

In this chapter 3.1, we first compared the structure, morphology, and electronic structures between Ni-TpBpy and Re-TpBpy catalysts. The photocatalytic  $CO_2$  reduction experiments using triethanolamine (TEOA) as the sacrificial agents demonstrate the higher catalytic performance of Ni-TpBpy than Re-TpBpy. We attributed such difference to the different  $CO_2$  capture capability and internal charge transfer efficiency. In addition, both catalysts exhibit highly excitation wavelength-dependent catalytic activity, which should require the study of detailed excited state dynamics, which will be presented in Chapters 3.2 and 3.3.



**Fig. 3-1** (a) Schematic presentation of the synthesis of TpBpy, Re-TpBpy, and Ni-TpBpy. (b) PXRD of TpBpy (cyan curve), Re-TpBpy (green-blue curve), Ni-TpBpy (blue curve), simulated AA stacking mode (purple curve), and simulated AB stacking mode (pink curve).

A two-dimensional (2D) COFs (TpBpy) with 2,2'-bipyridine was synthesized by the condensation of 1,3,5-triformylphloroglucinol and 5,5'-diamino-2,2'-bipyridine under solvothermal conditions, both Re-TpBpy and Ni-TpBpy are prepared by a simple solvent immersion method, as shown in Fig. 3-1a. The experimental PXRD patterns of these three samples match well with the simulated AA stacking structure of COFs, which demonstrates the unchanged crystalline structure of TpBpy after Re-complex or Ni-complex incorporation (Fig. 3-1b). The overview spectrum of the X-ray photoelectron spectroscopy (XPS) (Fig. 3-2a) and EDX mapping analysis of Re-TpBpy and Ni-TpBpy (Fig. 3-2e&f) suggesting the actual incorporation of the Re-complex or Ni-complex in the host COFs. In addition, the N 1s spectra bands (Fig. 3b-d) indicate that the Re-complex or Ni-TpBpy is anchored to the TpBpy only through its bipyridinic units.



**Fig. 3-2 (a)** XPS overview of TpBpy, Re-TpBpy, and Ni-TpBpy, (b), (c), and (d) correspond to the XPS N 1s core-level spectra of TpBpy, Re-TpBpy, and Ni-TpBpy, respectively. EDX mapping analysis of Re-TpBpy (E), Ni-TpBpy (F).

Before the photocatalytic measurement, we first evaluated the in-situ gap adsorption capability of both samples, which should be the first dominant factor that influences photocatalytic performance. N<sub>2</sub> adsorption isotherms were measured at 77 K to investigate the porosity of TpBpy, Re-TpBpy, and Ni-TpBpy (Fig. 3-3a). TpBpy, Re-TpBpy, and Ni-TpBpy showed type I reversible N<sub>2</sub>-sorption isotherms with a steep nitrogen gas uptake indicating the predominance of microporous. The surface area of pristine TpBpy is 952.49 m<sup>2</sup> g<sup>-1</sup> according to Brunauer-Emmett-Teller (BET) calculations, while the surface area of both Re-TpBpy and Ni-TpBpy decreases (648.75 m<sup>2</sup> g<sup>-1</sup> and 679.9 m<sup>2</sup> g<sup>-1</sup>). The reduced surface area should be due to the Re(CO)<sub>3</sub>Cl and Ni(II) occupying part of the pore space in COF. It is noteworthy that the BET-specific surface area of Re-TpBpy and Ni-TpBpy are still high, meaning the porous structure is well preserved. This ensured the high accessibility of Re or Ni active sites in the COFs channel. The impregnation of polar rhenium and nickel complexes contributes to increasing the polarity of TpBpy, which in turn facilitates the improvement of CO<sub>2</sub> adsorption capacity. As shown in Fig. 3-3b, the CO<sub>2</sub> adsorption volume of Re-TpBpy and Ni-TpBpy is 37.5 cm<sup>3</sup> g<sup>-1</sup> 39.5 cm<sup>3</sup> g<sup>-1</sup>, respectively. In addition, compared with TpBpy, Re-TpBpy and Ni-TiBpy show a steeper CO<sub>2</sub> uptake at lower relative pressure, which implies a stronger interaction of CO<sub>2</sub> in Re-TpBpy and Ni-TpBpy (see the inset of Fig.

3-3b). The higher adsorption capacity and stronger interactions Re-TpBpy, as well as Ni-TpBpy, can be considered as merits for promising CO<sub>2</sub> photocatalysts.

In addition, given that Ni-TpBpy has a higher specific surface area and better  $CO_2$  capture capacity than Re-TpBpy, they should exhibit better performance in photocatalytic reduction of  $CO_2$ . We then evaluate their photocatalytic efficiency for  $CO_2$  conversion in gas-solid reaction systems. Figure 3-3c displays the amount of CO production from Re-TpBy and Ni-TpBpy catalysts at 440 and 520 nm wavelengths. Neither TpBpy nor Ni-TpBpy produces CO after irradiating with 520 nm light for 8 h. However, the CO production of Re-TpBpy and Ni-TpBpy increased substantially under 400 nm light. Here the yield of CO from Ni-TpBpy  $(192.6 \text{ umol } g^{-1})$  is indeed higher than that from Re-TpBpy (131 umol  $g^{-1}$ ), which is consistent with our conjecture, i.e. the large specific surface area and high CO<sub>2</sub> adsorption rate are more favorable for photocatalytic  $CO_2$  conversion. The excitation-dependent photocatalytic performance, i.e. there is CO production upon 440 nm excitation but not upon 520 nm excitation can be attributed to the different excited state dynamics between two excitation conditions that modulate the charge transfer for the catalytic reduction or oxidation process. Therefore, we assume that the electronic structure of Ni complexes is better matched to TpBpy than the energy bands of Re complexes and are more favorable for the charge separation and transfer. We will confirm the above assumption in the following two chapters.



**Fig. 3-3** (a) N<sub>2</sub> adsorption isotherm of TpBpy, Re-TpBpy, and Ni-TpBpy, (b) CO<sub>2</sub> uptakes on TpBpy, Re-TpBpy, and the Ni-TpBpy at 298 K. The inset image zoom on the low pressure. Time course of CO production during photocatalytic CO<sub>2</sub> reduction on Re-TpBpy, and Ni-TpBpy photocatalysts under 440 nm and 520 nm. P<sub>0</sub> here refers to the 1.0 bar.

## 3.2 Ultrafast charge transfer dynamics in 2D Covalent Organic Frameworks/Re-complex hybrid photocatalyst: Hot electrons vs. cold electrons (Paper II)

In the previous chapter, we mentioned that in the photocatalytic  $CO_2$  reduction experiment, neither Re-TpBpy nor Ni-TpBpy produced CO when excited upon band edge at 520 nm, and the CO yield of Ni-TpBpy was higher than that of Re-TpBpy upon 440 nm excitation. We assume that in addition to the  $CO_2$  adsorption capacity mentioned in the previous chapter, such phenomenon is strongly related to the excited-state dynamics. In this chapter, we systematically investigate the excited state dynamics and charge transfer process in the Re-TpBpy. The time-dependent density functional theory (TD-DFT) calculations first display the available electronic transition after excitation of the hybrids. The femtosecond transient visible (fs-TA) and Time-resolved infrared (fs-TRIR) absorption spectroscopies provide complementary information for the charge transfer dynamics. Photons with energy close to the bandgap of the COFs directly excite the electron from the ground state to the excited states within Bpy moiety in the COFs followed by sub-picosecond electron injection to Re(CO)<sub>3</sub>Cl. However, the injected electrons rapidly undergo geminated recombination with the residual holes in the COFs moiety within 13 ps. When the excitation is well above the band edge, hot electrons would directly inject into the higher energy orbital of Re(CO)<sub>3</sub>Cl within 2 ps and rebound to the Bpy within 24 ps. The hot holes slowly relax to the HOMO level of COFs (340 ps). The prolonged excited electron lifetime in Re(CO)<sub>3</sub>Cl and the higher energy levels, together with the additional long-lived free electrons in COF moiety contributes as merits for a two-electron transfer mediated CO<sub>2</sub> catalytic reaction.

To clarify the ground state features of the Re-TpBpy hybrid and its units. Steady-state absorption and PL spectra were employed (Fig. 3-4a). The absorption spectrum of TpBpy and Re-TpBpy exhibit dual absorption bands, a narrow bipyridine  $n-\pi^*$  transition band as well as broadband for delocalized  $\pi$  electrons<sup>138</sup>. Similarly, there is still a slight blue shift of the spectrum for Re-TpBpy compare to TpBpy, which also should be due to the metal-to-ligand charge transfer (MLCT) [d(Re)- $\pi^*$ (bpy)].



**Fig. 3-4** (a) Normalized UV–vis absorption (black) and steady-state photoluminescence spectra excited at 400 nm (red) and 530 nm (blue) of TpBpy, Re-TpBpy and their starting materials dispersed in Nafion (5% w/w in water and 1-propanol); (b) Tauc plots of the absorption spectra determining the optical band gap of TpBpy, Re-TpBpy, and their starting materials; (c) XPS VB spectra, and (d) band alignment established from XPS and UV-vis measurement of TpBpy, Re-TpBpy, and their starting materials.

Fig. 3-4a also shows the emission spectra of all samples excited at the band edge (530 nm, blue curve) and well above the band edge (400 nm, red curve). Upon the 400 nm excitation, TpBpy and Re-TpBpy exhibit dual emission bands (i.e., 427 nm and 531 nm for TpBy, 431 nm, and 562 nm for Re-TpBpy), which supports that the excited state depopulation should involve two parallel processes with radiative recombination from the higher level and lowest excited state. When excited at 530 nm, the emission spectra of TpBpy and Re-TpBpy are identical with emission bands at 620 nm. This indicates similar emissive states from delocalized  $\pi$  electrons in the two samples.



**Fig. 3-5** (a) and (b) Steady-state PL emission spectra of TpBpy and Re-TpBpy normalized according to the absorbance at the excitation wavelength; (b) PL decays measured in TCSPC of the TpBpy and Re-TpBpy. Excitation wavelength=438 nm; (c) PL decays of the TpBpy and Re-TpBpy measured with streak camera excited at 400 nm.

In the next step, the photoluminescence (PL) dynamics of the samples were studied. Fig. 3-5a and Fig. 3-5b show that the steady-state PL spectra of TpBpy and Re-TpBpy are identical in terms of emission energy and spectral shapes. However, the relative PL quantum yield (extracted from absorption calibrated PL intensities) of Re-TpBpy is significantly lower. This should be attributed to the PL quenching by the integration of the Re-complex. The timecorrelated single-photon counting (TCSPC) identified the Re-TpBpy with a shorter PL lifetime, which verifies the additional non-radiative process (Fig.3-5c). In addition, a faster decay rate of Re-TpBpy was observed by streak camera (Fig. 3-6).



**Fig. 3-6** UV–vis absorption spectra of (a) TpBpy and (b) Re-TpBpy compared with TD-DFT calculated fragment.

To obtain insight into the excited-state structure of the compounds, the time-dependent density functional theory (TD-DFT) calculation at the M06-L<sup>144–147</sup>/def 2 TZVP<sup>148,149</sup> level of theory was employed to calculate the electronic structure and model the electronic transitions. Fig. 3-6 exhibits the calculated electronic excitation spectra of the TpBpy and Re-TpBpy (orange curves), and the experimental absorption spectra (red curves). This calculation is found to be in line with the experimental results.

The excited-state dynamics of the samples were explored by transient absorption (TA) spectroscopy. Upon 530 nm excitation, the TA spectra of TpBpy show a wide negative ground state bleach (GSB, B1) and two positive excited absorption bands (ESA, A1 and A2) (Fig. 3-7a). However, Re-TpBpy shows only one A2 in addition to one B1 (Fig. 3-7b), this has shown the charge transfer of the excited state.



**Fig. 3-7** Transient absorption (TA) spectra under 530 nm excitation at the fluence of  $2 \times 10^{13}$  ph/cm<sup>2</sup> and the respective SVD fitting results of TpBpy (a), and Re-TpBpy (b). TA kinetics at some characteristic wavelength of B1 at 535 nm (c), A1 at 625 nm (d), and A2 at 675 nm (e). All the samples were measured in Nafion (5% w/w in water and 1-propanol) solution.

Then use singular value decomposition (SVD) fitting for more quantitative analysis (Fig. 3-7a&b, lower panel). The TA dynamics of TpBpy can be decomposed into four decayassociated components ( $t_1 = 2$  ps,  $t_2 = 70$  ps,  $t_3 = 4$  ns and one ultra-long component). TA kinetics at the A1 (Fig. 3-7d) and A2 (Fig. 3-7e) reveal the concurrent rising of A1 and decay of A2. This indicates the transformation of the lowest excited state (e.g. polaron formation) within 2 ps corresponding to the transition of ESA from A2 to A1 in TA spectra. Components 2 and 3 exhibits the same spectral feature corresponding to the depopulation dynamics of the same lowest excited state. The slowest component 4 featured as a broad negative band with a lifetime exceeding the TA time window. This can also be visualized in the TA kinetics in Fig. 7c-e. After functionalization by the Re-complex, the TA dynamics of Re-TpBpy can also be decomposed into four components ( $t_1 = 990$  fs,  $t_2 = 13$  ps,  $t_3 = 262$  ps and one ultra-long component) ((Fig. 3-7b). Component t1- t3 of Re-TpBpy resembles the GSB feature as TpBpy while the ESA bands are completely absent in components t2 and t3. This suggests the ultrafast charge transfer from the excited-state S<sub>2</sub> instead of relaxing down to the lowest excited state S<sub>1</sub>.



**Fig. 3-8** Two-dimensional transient absorption (TA) spectra under 400 nm excitation at the fluence of  $2 \times 10^{13}$  ph/cm<sup>2</sup> and the respective SVD fittings of TpBpy (a), Re-TpBpy (b). TA kinetics of two samples at various emission wavelengths representing B1 (c), B2 (d), A1 (e), A2 (f). All spectra are recorded in Nafion (5% w/w in water and 1-propanol).

To monitor the dynamics of hot carriers, high energy excitation has also been employed in both samples. Compared with TA spectra excited at 530 nm, one additional negative band (B2) around 450 nm appears in both TpBpy and Re-TpBpy, which should be attributed to the population of high energy/hot levels in the COFs unit. Four main components of TpBpy can be obtained by SVD fitting,  $t_1 = 2$  ps,  $t_2 = 34$  ps,  $t_3 = 480$  ps, and one ultra-long component. In the PL decay of TpBpy (Fig. 3-5c), a lifetime (481ps) similar to the lifetime of component  $t_3$  can also be extracted, indicating the radiative recombination of the band-edge charge carriers. TA spectra of Re-TpBpy can also be fitted with four main components ( $t_1 = 2$  ps,  $t_2$ = 24 ps,  $t_3 = 340$  ps and one ultra-long component). The additional B2 band and the wider ESA band in components t1, t3 reflect the long-live hot excited level population. On the other hand, the absence of A1 in component  $t_2$  confirms the charge transfer of hot electrons to Re<sup>T</sup> centers within 2 ps. In addition, the lifetime  $t_3$  (340 ps) can be obtained from the TRPL decay in Fig. 3-5c, manifesting radiative recombination with hot carriers, which accounts for the high energy emission band in the steady-state PL spectrum (Fig. 3-4a).



**Fig. 3-9** TRIR spectra of TpBpy, Re-Bpy, and Re-TpBpy excited at 530 nm (a-c) and 400 nm (e-g). (d) TRIR kinetics at 2040 cm<sup>-1</sup> of Re-TpBpy excited at 530 nm. (h) TRIR kinetics at 2040 cm<sup>-1</sup> (red), 1850 cm<sup>-1</sup> (blue), and their differential curve (orange) of Re-TpBpy excited at 400 nm. The kinetics at 2040 cm<sup>-1</sup> of Re-Bpy excited at 400 nm is also presented (green). All spectra are recorded in Nafion (5% w/w in water and 1-propanol).

To further characterize the excited state dynamics at the two excitation wavelengths, we measured the time-resolved IR (TRIR) spectra of the samples. When excited at 530 nm (Fig.3-9a and Fig. 3-9b), only Re-TpBpy exhibits fingerprint features of excited [Re<sup>I</sup>(bpy)(CO)3]\*. The TRIR kinetics in Fig. 3-9d suggests that the rising of transient Re<sup>I\*</sup> radical formation spectra, which combined with the sub-picosecond depopulation of excited states in the TA spectra demonstrated the electron transfer from the LUMO located at Bpy to the Re<sup>I</sup> center within 0.8-0.9 ps. However, according to the TD-DFT calculation, the holes can reside both at Tp and Bpy. Therefore, we can expect different depopulation pathways of those holes after electron injection corresponding to two-lifetime components in TA (t2 and t3) (Fig. 3-7b). The holes on Bpy should undergo rapid initiation and recombination with the electrons in the Re<sup>I</sup> center, while the holes on Tp will cool to the HOMO level in a relatively long time (262ps), which is still strongly localized in Tp. The above analysis shows that the low-energy excitation in Re-TpBpy is very close to the Re-COFs interface, which promotes the injection of electrons from the COFs to the Re<sup>I</sup> center. However, due to the close spacing

between the injected electrons and the residual holes in the COFs, the Gemini recombination is also effective.

When excited at 400 nm, the TRIR spectra of both TpBpy and Re-TpBpy are dominated by the featureless positive absorption (Fig. 3-9 e&g), which is widely accepted as the sign of free carrier generation in semiconductor materials.<sup>150–152</sup> This means that the hotly excited states reflected by the B2 and the broad A1 band in TA should all be populated by free carriers when excited at 400 nm. Combining with the remaining of A2 after 2 ps in TA measurement (Fig. 3-8a), suggest that the initial fastest component t<sub>1</sub> in TA measurement should be related to the partial polaron formation where some of the generated species also remain as free carriers. Moreover, the TRIR spectrum in Re-TpBpy features additional differential dips of the Re<sup>I</sup> radical, indicating the COFs-Re electron transfer occurs. The kinetics shows in Fig. 3-9h proves the process of electron transfer from COFs to Re<sup>I</sup> center and back to COFs, and back transfer or geminate recombination of injected electrons in the Re<sup>I</sup> center is faster than the electron-hole recombination in the Re<sup>I</sup>(bpy) moiety.

In conclusion, as summarized by Fig. 3-10. Upon 530 nm excitation, the excited state dynamics of TpBpy (Fig. 3-10a) undergoes 2 ps formation of exciton polarons, 70 ps exciton polarons annihilation in COFs materials. 4 ns excitonic recombination within the same COFs sheet, and the ultra-long lived electrons and holes recombination at a different sheet of COFs. For Re-TpBpy (Fig. 3-10b), excited-state depopulation follows sub-picosecond electron transfer from the Bpy to the Re<sup>I</sup> center, 13 ps recombination of holes at Bpy with electrons at the Re<sup>I</sup> center. Moreover, holes at Tp cool down to the HOMO level within 262 ps and this is another ultra-long component of the recombination of holes at Tp with electrons at the Re<sup>1</sup> center. When excited at 400 nm, TpBpy will undergo fast polaron formation followed by radiative recombination between the electron at LUMO+1 and the hole at HOMO-3 as well as the recombination between electrons and holes relaxed to the HOMO and LUMO levels (480 ps) (Fig. 3-10c). For Re-TpBpy (Fig. 3-10d), the excited electron at LUMO+2 and LUMO+1 would be injected to Re<sup>I</sup> center within 2 ps and then recombines to HOMO at Bpy within 24 ps, such a 24 ps lifetime for such intermediate excited state can be a merit for hotcarrier harvesting. After hot carrier cooling, the depopulation of the excited states depends on the spatial location of the charge carriers. If the hole is located at Bpy orbitals (HOMO-4 level), the hot carrier emission will occur similarly to the case of TpBpy with a lifetime of 340 ps. If holes locate at Tp orbitals in HOMO, it will recombine with the relaxed electron at LUMO both radiatively and nonradiative but with a longer lifetime.



**Fig. 3-10** Schematic diagram of the pathway and lifetime excited state dynamics of TpBpy and Re-TpBpy under (a&b) 530 nm, and (c&d) 400 nm excitation.



**Fig. 3-11** Photocatalytic evolutions of CO by Re-TpBpy under 520 nm and 440 nm excitation (a) and Schematic diagram to rationalize the catalytic performance under two excitation conditions (b).

The evolution of CO by our Re-COFs catalyst exhibit a much higher yield when 440 nm excitation is used compared with band-edge excitation at 530 nm (Fig. 3-11a), this can be perfect rationalized by the above-conclusion photophysics: 1) injected electrons are located at high energy levels in Re<sup>I</sup> centers with a longer lifetime which favorable for the electron transfer process for the CO<sub>2</sub> reduction, and 2) when excited with high energy besides the injected electrons to Re<sup>I</sup> center, there remain long-lived electrons in COF moiety which is

transferred back from  $\text{Re}^{I}$ . This makes the two-electron reaction of  $\text{CO}_2$  conversion to CO work as illustrated in Fig. 3-11b.

# **3.3 Ultrafast Excited-state Dynamics in a Ni-2,2'-Bipyridine Covalent Organic Framework Photocatalyst (Paper III)**

In the last chapter, we discussed the excited state dynamics of the Re<sup>I</sup>(bpy)(CO)<sub>3</sub>/TpBpy hybrid photocatalyst. The results show that the coupling of the Re<sup>I</sup> complex indeed promotes the separation of photogenerated charges, which is beneficial for photocatalytic CO<sub>2</sub> reduction. However, rhenium is a noble metal with high cost, which seriously affects its largescale application. Recently, nickel (Ni (II)) has been reported as a promising alternative to Re-complex to be integrated into COFs structures with moderate photocatalytic activity for the reduction of CO<sub>2</sub>.<sup>142,153,154</sup> However, such a system currently operates as a "black box" since neither the charge relaxation dynamics nor the transfer pathways within the Nimodified COFs hybrids are known. In this chapter, we will discuss the excited-state dynamics of Ni-TpBpy, which is constructed by Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and TpBpy.

Fig. 3-12 displays the steady-state absorption and PL emission of Ni-TpBpy and TpBpy. The shape of the absorption spectrum of TpBpy and Ni-TpBpy are similar, both exhibit a narrow  $n-\pi^*$  transition band ascribed to bipyridine and broadband ascribed to the delocalized  $\pi$  electrons.<sup>138</sup> However, the bipyridine  $n-\pi^*$  transition of Ni-TpBpy with a bathochromic shift, which stems from a Stark effect on the bipyridine due to the charged central Ni<sup>2+</sup> ion.<sup>155</sup> Under band-edge excitation at 530 nm, both TpBpy and Ni-TpBpy exhibit an emission band. Interestingly, the emission spectra of Ni-TpBpy exhibit one board band at 473 nm when excited at higher energy (i.e. 400 nm), which is different from the dual emission peak observed in TpBpy (Fig. 3-12a).

To obtain detailed insight into photogenerated carrier dynamics, the Time-resolved Photocluminisence (TRPL) measurements of TpBpy and Ni-TpBpy were measured. Fig.3-12b showed the PL kinetics measured by time-correlated single-photon counting (TCSPC) focusing on long time window and streak camera technique focusing on a short time scale. Overwell, the PL lifetime of Ni-TpBpy is longer than that of TpBpy, indicating the existence of an additional non-radiative process to quench the emissive states.



**Fig. 3-12** (a) Normalized UV–vis absorption and steady-state photoluminescence spectra excited at 400 nm (pink) and 530 nm (blue) of TpBpy and Ni-TpBpy. (b) PL decays measured in TCSPC of the TpBpy and Ni-TpBpy, excitation wavelength=438 nm; (c) PL decays of the TpBpy and Ni-TpBpy measured in streak camera.

To obtain the intrinsic electronic excited-state structure of the samples, we used the same calculation method as the previous chapter to calculate. The difference is that this calculation is more detailed because it starts from 200 nm. In addition, Open-shell calculations have been carried out using a spin-unrestricted formalism as Ni<sup>2+</sup> is an open-shell system with a 3d<sup>8</sup> ground state. Thus, the initial calculations were carried out for two sets of orbitals, namely for spin-up (a orbitals) electrons and spin-down (b orbitals) electrons, respectively. Fig. 3-13 displays the calculated electronic excitation spectrum (blue curves) of TpBpy and Ni-TpBpy with the comparison to the experimental absorption spectra (purple curves). Compared with TpBpy, the low energy electronic transition in Ni-TpBpy involves the promotion of electronic density at the linked moieties Bpy and Ni (II) complex. Compared with Re-TpBpy in Chapter 3-2, both HOMO and LUMO in Ni-TpBpy are in metallic nickel.



**Fig. 3-13** UV–vis absorption spectra of (a) TpBpy and (b) Ni-TpBpy compared with the Calculated DFT fragment.

Next, we analyze the excited state dynamics of Ni-TpBpy by fs-TA using the excited-state calculations described above as references. We first excited the samples at 530 nm, which corresponds to energy close to their optical bandgap. In this case, all the excited species are expected to populate the lowest excited state quickly. The excited-state dynamics of TpBpy has been discussed in the last chapter (Fig. 3-14a),

After loading the Ni-complex, the fs-TA spectrum (Fig. 3-14b) exhibits one additional negative band (B2) around 470 nm. The SVD fitting can extract three components with a lifetime of  $\tau_1 = 5$  ps,  $\tau_2 = 68$  ps as well as an ultra-long lifetime (the lower panel of Fig. 3-14b). The absence of ESA in t1 and t2 could be attributed to charge transfer from the initial excited states, which should occur only by electron injection from a orbital sets due to LUMO<sub>b</sub> is located at the Ni<sup>2+</sup> cation. The existence of B2 in the components t1 and t2 are contributed by the population of the LUMO<sub>b</sub> to cause the breach of the calculated S2 transition shown in Fig. 3-14b. The amplitude ratio of B1 over B2 significantly decreases in the t2 component. This should be attributed to the hole relaxation from deeper levels (HOMO<sub>b-2</sub> and HOMO<sub>a-2</sub>) to the HOMOs (HOMO<sub>b</sub> and HOMO<sub>a</sub>) levels. However, the long-lived t<sub>3</sub> only exhibits a single B1 band without B2, which indicates that not all the hot holes have relaxed to the HOMO level over the early timescale (t1). From Fig.3-14b, we can see that HOMO<sub>b</sub> locates at Ni<sup>2+</sup> where all the deep HOMO level of b orbital set at COFs moieties,

while all the energy level of a orbital at COFs moieties, so the relaxation from the HOMO<sub>b-2</sub> to the HOMO<sub>b</sub> should be less efficient than the relaxation from a orbital set. Therefore, the B1 in the t3 should be attributed to the recombination of holes at HOMO<sub>b-2</sub> and electrons at LUMO<sub>b</sub>. In this scenario, the holes in the b orbital sets with higher energies, leading to a potentially complex process of compounding with electrons, accounting for such a long recombination time. On the contrary, the holes at HOMO<sub>a-2</sub> should quickly relax to the lowest excited level (HOMO<sub>a</sub>) within COFs moiety as shown in Fig. 3-14b. The t<sub>2</sub> component (68 ps) is attributed to the recombination of electrons and holes at a orbital sets (i.e. hole at HOMO<sub>a</sub> and electron at Ni<sup>2+</sup>) where the population at HOMO<sub>a</sub> leads to the bleach at B2.



**Fig. 3-14** Transient absorption (TA) spectra under 530 nm (a),(b) and 400 nm (c), (d) excitation at the fluence of  $2 \times 10^{13}$  ph/cm<sup>2</sup> of TpBpy and Ni-TpBpy.

When excited at 400 nm with photon energy (3.1 eV) much larger than the band-gap, the excited state evolution becomes more complicated. In Ni-TpBpy, The fs-TA spectra can also be fitted by four components with lifetimes of  $t_1 = 4$  ps,  $t_2 = 59$  ps,  $t_3 = 517$  ps together with an ultra-long lifetime (Fig. 3-14d). Components t1 and t2 exhibit characteristics similar to those in pure TpBpy but with longer lifetimes (Fig. 3-14c&d). Therefore, t1 should be attributed to the cooling of photo-generated hot electrons and holes at the deep levels to the lower orbitals and/or polaron formation (Fig. 3-14d). The lifetime of the  $t_2$  component (59 ps) is similar to the value obtained for t2 at 530 nm excitation (Fig. 3-14b). In addition, the spectral lineshape shows the same coexistence of B1 and B2. Therefore, it should also be assigned to the same recombination of injected electrons at Ni<sup>2+</sup> and holes at HOMO<sub>a</sub> at a orbital set (Fig. 3-14d). On the other hand, t3 exhibits distinctive features, combining B2,

A1 and a red-shifted B1. As the electrons and holes at a orbital sets have already undergone fast geminate recombination as discussed above. We believe this t3 component should be assigned to the radiative recombination between hole at  $HOMO_{b-1}$  and electrons at  $LUMO_{b+1}$ . The longest component t4 in Ni-TpBpy features the individual B1 band corresponding to the band-edge recombination process. This should correspond to the recombination of electrons at  $LUMO_b$  in Ni<sup>2+</sup> directly excited from S2 transition and the holes at  $HOMO_b$  directly excited from S4 transition.

The above-excited state dynamics of Ni-TpBpy have been summarized in Fig. 3-15. In summary, upon 530 nm excited. Ni-TpBpy will first undergo fast hot hole cooling together with the electron injection from COFs to  $Ni^{2+}$  at the *a* orbital set (5 ps) followed by 68 ps geminate recombination of electron and hole. T3 component refers to the electron-hole recombination at the b orbital set. Under 400 nm excitation, excited state dynamics vary at a and b orbital sets. At the a orbital sets, exciting hot electrons and holes will quickly cool down to the band edge followed by the electron injection from COF moiety to  $Ni^{2+}$ . At b orbital sets, hot electrons and holes excited at COF unity will lead to hot emission due to the less efficient cooling process while electrons directly excited at  $Ni^{2+}$  will live a longer lifetime before recombining with residue holes in the COFs.



**Fig. 3-15** Schematic diagram of the pathway and lifetime excited state dynamics of Ni-TpBpy under a&b) 530 nm, and c&d) 400 nm excitation.

Finally, we did the photocatalytic  $CO_2$  reduction reaction with Ni-TpBpy as a photocatalyst. From fig. 3-16 (a) we can see that the evolution of CO exhibits a much higher yield when 440 nm excitation is used compared with band-edge excitation at 530 nm, which is similar to Re-TpBpy. However, the detailed dynamics account for this phenmenon is different as mentioned above. We believe 1) the two sets of photo-generated electrons at b orbital set (i.e. electrons at Ni<sup>2+</sup> and electrons at LUMO<sub>b+1</sub> in COFs) enable the stable donation of two electrons for  $CO_2$  reduction. 2) long-lived holes at both a and b orbitals can promote the hole injection to the scavengers to prevent the hole accumulation that can lead to the deactivation of the photocatalytic performance.



**Fig. 3-16** Photocatalytic evolutions of CO by Ni-TpBpy under 520 nm and 440 nm excitation (a) and Schematic diagram to rationalize the catalytic performance under the two excitation conditions (b).

#### Conclusions

In this thesis, two metaled COFs photocatalysts Re-TpBpy and Ni-TpBpy were obtained and various characterization techniques showed that the two materials with high crystallinity, specific surface area, good stability, and decent visible light response. Both Re-TpBpy and Ni-TpBpy exhibit excellent photocatalytic reduction activity. However, the reduction is only efficient when the excitation photon energy is well above the band edge. Moreover, the CO yield produced by Ni-TpBpy is higher than that of Re-TpBpy. This is due to 1) the CO<sub>2</sub> adsorption capacity of Ni-TpBpy is higher than that of Re-TpBpy; 2) different excited state dynamics. To better understand the latter factor, we conducted systematic steady-state and time-resolved spectroscopic studies on the excited state dynamic process Re-TpBpy and Ni-TpBpy combining with the analysis from the TD-DFT calculations. We confirmed the intramolecular charge transfer pathways in Re-TpBpy and Ni-TpBpy strongly dependent on the excitation wavelength. For Re-TpBpy, the electrons excited at the LUMO level of Re-TpBpy can to quickly injected from Bpy moiety into the Re<sup>I</sup> center within ps but followed by fast-backward geminate recombination (13 ps). Under excitation with high energy photon, however, the photo-generated hot-electrons are first injected into the higher unoccupied orbitals of the Re<sup>I</sup> center within 1-2 ps and then relax back to the HOMO in COF with longer time (24 ps). In addition, there remain long-lived holes in the COFs. For Ni-TpBpy, under band-edge excitation, the electrons of LUMOa level are quickly injected into Ni<sup>2+</sup> center within 5 ps but recombine with the holes residing in TpBpy for a short time (68 ps). Electrons at orbital b are directly excited to Ni<sup>2+</sup> center and recombined with holes localized in TpBpy for a much longer time. Under high energy excitation, the dynamics of excited charges at the a orbital remain the same with under band-edge excitation whereas the hot electrons at b orbital at TpBpy can only relax down to the second-lowest excited states remaining in COFs moiety. Through the above analysis, we know that the intromolecue charge transfer in Ni-TpBpy is more instantaneous and long-lived, which should explain why the photocatalytic performance of Ni-TpBpy is better than that of Re-TpBpy.

Our in-depth understanding of the complex charge separation and transfer processes in COFs modified with metal-molecule photocatalysts on femtosecond to second-time scales will provide important guidance for the understanding and rational design of efficient

photocatalysts, as well as expand the practical applications of COFs materials and initiate the research on photocatalysis of COFs materials.

#### References

- (1) Wang, X.; Blechert, S.; Antonietti, M. Polymeric Graphitic Carbon Nitride for Heterogeneous Photocatalysis. *ACS Catal.* **2012**, *2*, 1596–1606.
- (2) Green, M. A.; Bremner, S. P. Energy Conversion Approaches and Materials for High-Efficiency Photovoltaics. *Nat. Mater.* **2017**, *16*, 23–34.
- (3) Sivula, K.; van de Krol, R. Semiconducting Materials for Photoelectrochemical Energy Conversion. *Nat. Rev. Mater.* **2016**, *1*, 15010.
- (4) Esswein, A. J.; Nocera, D. G. Hydrogen Production by Molecular Photocatalysis. *Chem. Rev.* **2007**, *107*, 4022–4047.
- (5) Schultz, D. M.; Yoon, T. P. Solar Synthesis: Prospects in Visible Light Photocatalysis. *Science* (80-. ). **2014**, *343*, 1239176.
- (6) Aslam, U.; Rao, V. G.; Chavez, S.; Linic, S. Catalytic Conversion of Solar to Chemical Energy on Plasmonic Metal Nanostructures. *Nat. Catal.* **2018**, *1*, 656–665.
- (7) Linic, S.; Aslam, U.; Boerigter, C.; Morabito, M. Photochemical Transformations on Plasmonic Metal Nanoparticles. *Nat. Mater.* **2015**, *14*, 567–576.
- (8) Linsebigler, A. L.; Lu, G.; Yates, J. T. Photocatalysis on TiO2 Surfaces: Principles, Mechanisms, and Selected Results. *Chem. Rev.* **1995**, *95*, 735–758.
- (9) Song, C. Global Challenges and Strategies for Control, Conversion and Utilization of CO2 for Sustainable Development Involving Energy, Catalysis, Adsorption and Chemical Processing. *Catal. Today* **2006**, *115*, 2–32.
- (10) Omae, I. Aspects of Carbon Dioxide Utilization. Catal. Today 2006, 115, 33-52.
- (11) Li, K.; An, X.; Park, K. H.; Khraisheh, M.; Tang, J. A Critical Review of CO2 Photoconversion: Catalysts and Reactors. *Catal. Today* **2014**, *224*, 3–12.
- (12) White, J. L.; Baruch, M. F.; Pander, J. E.; Hu, Y.; Fortmeyer, I. C.; Park, J. E.; Zhang, T.; Liao,
  K.; Gu, J.; Yan, Y.; Shaw, T. W.; Abelev, E.; Bocarsly, A. B. Light-Driven Heterogeneous Reduction of Carbon Dioxide: Photocatalysts and Photoelectrodes. *Chem. Rev.* 2015, *115*, 12888–12935.
- (13) Sun, Z.; Talreja, N.; Tao, H.; Texter, J.; Muhler, M.; Strunk, J.; Chen, J. Catalysis of Carbon Dioxide Photoreduction on Nanosheets: Fundamentals and Challenges. *Angew. Chemie Int. Ed.* 2018, *57*, 7610–7627.
- (14) Chang, X.; Wang, T.; Gong, J. CO2 Photo-Reduction: Insights into CO2 Activation and Reaction on Surfaces of Photocatalysts. *Energy Environ. Sci.* **2016**, *9*, 2177–2196.
- (15) Zhao, K.; Zhao, S.; Gao, C.; Qi, J.; Yin, H.; Wei, D.; Mideksa, M. F.; Wang, X.; Gao, Y.; Tang, Z.; Yu, R. Metallic Cobalt–Carbon Composite as Recyclable and Robust Magnetic Photocatalyst for Efficient CO2 Reduction. *Small* **2018**, *14*, 1800762.
- (16) Cheng, M.; Liu, Y.; Huang, D.; Lai, C.; Zeng, G.; Huang, J.; Liu, Z.; Zhang, C.; Zhou, C.; Qin, 64

L.; Xiong, W.; Yi, H.; Yang, Y. Prussian Blue Analogue Derived Magnetic Cu-Fe Oxide as a Recyclable Photo-Fenton Catalyst for the Efficient Removal of Sulfamethazine at near Neutral PH Values. *Chem. Eng. J.* **2019**, *362*, 865–876.

(17) Bai, S.; Jiang, J.; Zhang, Q.; Xiong, Y. Steering Charge Kinetics in Photocatalysis: Intersection of Materials Syntheses, Characterization Techniques and Theoretical Simulations. *Chem. Soc. Rev.* 2015, *44*, 2893–2939.

(18) Xu, Y.; Li, A.; Yao, T.; Ma, C.; Zhang, X.; Shah, J. H.; Han, H. Strategies for Efficient Charge Separation and Transfer in Artificial Photosynthesis of Solar Fuels. *ChemSusChem* **2017**, *10*, 4277–4305.

(19) Zhang, P.; Wang, T.; Chang, X.; Gong, J. Effective Charge Carrier Utilization in Photocatalytic Conversions. *Acc. Chem. Res.* **2016**, *49*, 911–921.

(20) Baxter, J. B.; Richter, C.; Schmuttenmaer, C. A. Ultrafast Carrier Dynamics in Nanostructures for Solar Fuels. *Annu. Rev. Phys. Chem.* **2014**, *65*, 423–447.

(21) Ponseca, C. S.; Chábera, P.; Uhlig, J.; Persson, P.; Sundström, V. Ultrafast Electron Dynamics in Solar Energy Conversion. *Chem. Rev.* **2017**, *117*, 10940–11024.

(22) Cowan, A. J.; Durrant, J. R. Long-Lived Charge Separated States in Nanostructured
Semiconductor Photoelectrodes for the Production of Solar Fuels. *Chem. Soc. Rev.* 2013, *42*, 2281–2293.

(23) Chen, R.; Fan, F.; Dittrich, T.; Li, C. Imaging Photogenerated Charge Carriers on Surfaces and Interfaces of Photocatalysts with Surface Photovoltage Microscopy. *Chem. Soc. Rev.* **2018**, *47*, 8238–8262.

(24) Zong, X.; Yan, H.; Wu, G.; Ma, G.; Wen, F.; Wang, L.; Li, C. Enhancement of Photocatalytic H2 Evolution on CdS by Loading MoS2 as Cocatalyst under Visible Light Irradiation. *J. Am. Chem. Soc.* **2008**, *130*, 7176–7177.

(25) Zhang, J.; Xu, Q.; Feng, Z.; Li, M.; Li, C. Importance of the Relationship between Surface Phases and Photocatalytic Activity of TiO2. *Angew. Chemie Int. Ed.* **2008**, *47*, 1766–1769.

(26) Yang, J.; Wang, D.; Han, H.; Li, C. Roles of Cocatalysts in Photocatalysis and Photoelectrocatalysis. *Acc. Chem. Res.* **2013**, *46*, 1900–1909.

(27) Kato, H.; Asakura, K.; Kudo, A. Highly Efficient Water Splitting into H2 and O2 over Lanthanum-Doped NaTaO3 Photocatalysts with High Crystallinity and Surface Nanostructure. *J. Am. Chem. Soc.* **2003**, *125*, 3082–3089.

(28) Tan, S.; Argondizzo, A.; Ren, J.; Liu, L.; Zhao, J.; Petek, H. Plasmonic Coupling at a Metal/Semiconductor Interface. *Nat. Photonics* **2017**, *11*, 806–812.

(29) Li, R.; Zhang, F.; Wang, D.; Yang, J.; Li, M.; Zhu, J.; Zhou, X.; Han, H.; Li, C. Spatial Separation of Photogenerated Electrons and Holes among {010} and {110} Crystal Facets of BiVO4. *Nat. Commun.* **2013**, *4*, 1432.

(30) Yang, J.; Yan, H.; Zong, X.; Wen, F.; Liu, M.; Li, C. Roles of Cocatalysts in Semiconductor-Based Photocatalytic Hydrogen Production. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **2013**, *371*, 20110430.

(31) Wang, Z.; Xue, N.; Chen, J. Semiconductor–Cocatalyst Interfacial Electron Transfer Dominates Photocatalytic Reaction. *J. Phys. Chem. C* **2019**, *123*, 24404–24408.

(32) Zhong, S.; Xi, Y.; Wu, S.; Liu, Q.; Zhao, L.; Bai, S. Hybrid Cocatalysts in Semiconductor-Based Photocatalysis and Photoelectrocatalysis. *J. Mater. Chem. A* **2020**, *8*, 14863–14894.

(33) Ng, Y. H. Cocatalysts on Semiconductor Photocatalyst: A Mini Review. J. Indones. Chem. Soc. 2019, 2.

(34) Shockley, W.; Read, W. T. Statistics of the Recombinations of Holes and Electrons. *Phys. Rev.* **1952**, *87*, 835–842.

(35) Zhou, Z.; Liu, J.; Long, R.; Li, L.; Guo, L.; Prezhdo, O. V. Control of Charge Carriers Trapping and Relaxation in Hematite by Oxygen Vacancy Charge: Ab Initio Non-Adiabatic Molecular Dynamics. *J. Am. Chem. Soc.* **2017**, *139*, 6707–6717.

(36) Wang, X.; Li, C. Roles of Phase Junction in Photocatalysis and Photoelectrocatalysis. *J. Phys. Chem. C* 2018, *122*, 21083–21096.

(37) Wang, X.; Xu, Q.; Li, M.; Shen, S.; Wang, X.; Wang, Y.; Feng, Z.; Shi, J.; Han, H.; Li, C. Photocatalytic Overall Water Splitting Promoted by an α–β Phase Junction on Ga2O3. *Angew. Chemie Int. Ed.* 2012, *51*, 13089–13092.

(38) FUJISHIMA, A.; HONDA, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37–38.

(39) Wrangham, R. W.; Conklin, N. L.; Chapman, C. A.; Hunt, K. D.; Milton, K.; Rogers, E.; Whiten, A.; Barton, R. A.; Widdowson, E. M.; Whiten, A.; Bone, Q. The Significance of Fibrous Foods for Kibale Forest Chimpanzees. *Philos. Trans. R. Soc. London. Ser. B Biol. Sci.* 1991, *334*, 171–178.
(40) INOUE, T.; FUJISHIMA, A.; KONISHI, S.; HONDA, K. Photoelectrocatalytic Reduction of Carbon Dioxide in Aqueous Suspensions of Semiconductor Powders. *Nature* 1979, *277*, 637–638.
(41) Chen, L.; Tang, J.; Song, L.-N.; Chen, P.; He, J.; Au, C.-T.; Yin, S.-F. Heterogeneous Photocatalysis for Selective Oxidation of Alcohols and Hydrocarbons. *Appl. Catal. B Environ.* 2019, *242*, 379–388.

(42) Dash, P.; Manna, A.; Mishra, N. C.; Varma, S. Synthesis and Characterization of Aligned ZnO Nanorods for Visible Light Photocatalysis. *Phys. E Low-dimensional Syst. Nanostructures* 2019, *107*, 38–46.

(43) Zhang, P.; Sun, D.; Cho, A.; Weon, S.; Lee, S.; Lee, J.; Han, J. W.; Kim, D.-P.; Choi, W. Modified Carbon Nitride Nanozyme as Bifunctional Glucose Oxidase-Peroxidase for Metal-Free Bioinspired Cascade Photocatalysis. *Nat. Commun.* **2019**, *10*, 940.

(44) Phuruangrat, A.; Siri, S.; Wadbua, P.; Thongtem, S.; Thongtem, T. Microwave-Assisted 66

Synthesis, Photocatalysis and Antibacterial Activity of Ag Nanoparticles Supported on ZnO Flowers. *J. Phys. Chem. Solids* **2019**, *126*, 170–177.

(45) Tang, J.; Durrant, J. R.; Klug, D. R. Mechanism of Photocatalytic Water Splitting in TiO2. Reaction of Water with Photoholes, Importance of Charge Carrier Dynamics, and Evidence for Four-Hole Chemistry. *J. Am. Chem. Soc.* **2008**, *130*, 13885–13891.

(46) Yu, J.; Jin, J.; Cheng, B.; Jaroniec, M. A Noble Metal-Free Reduced Graphene Oxide–CdS Nanorod Composite for the Enhanced Visible-Light Photocatalytic Reduction of CO2 to Solar Fuel. *J. Mater. Chem. A* **2014**, *2*, 3407–3416.

(47) Humayun, M.; Qu, Y.; Raziq, F.; Yan, R.; Li, Z.; Zhang, X.; Jing, L. Exceptional Visible-Light Activities of TiO2-Coupled N-Doped Porous Perovskite LaFeO3 for 2,4-Dichlorophenol Decomposition and CO2 Conversion. *Environ. Sci. Technol.* **2016**, *50*, 13600–13610.

(48) Li, Z.; Qu, Y.; Hu, K.; Humayun, M.; Chen, S.; Jing, L. Improved Photoelectrocatalytic Activities of BiOCl with High Stability for Water Oxidation and MO Degradation by Coupling RGO and Modifying Phosphate Groups to Prolong Carrier Lifetime. *Appl. Catal. B Environ.* **2017**, *203*, 355–362.

(49) Mubeen, S.; Hernandez-Sosa, G.; Moses, D.; Lee, J.; Moskovits, M. Plasmonic
 Photosensitization of a Wide Band Gap Semiconductor: Converting Plasmons to Charge Carriers.
 *Nano Lett.* 2011, *11*, 5548–5552.

(50) Chu, H.; Liu, X.; Liu, B.; Zhu, G.; Lei, W.; Du, H.; Liu, J.; Li, J.; Li, C.; Sun, C. Hexagonal 2H-MoSe2 Broad Spectrum Active Photocatalyst for Cr(VI) Reduction. *Sci. Rep.* **2016**, *6*, 35304.

(51) Li, X.; Ren, H.; Zou, Z.; Sun, J.; Wang, J.; Liu, Z. Energy Gap Engineering of Polymeric Carbon Nitride Nanosheets for Matching with NaYF4:Yb,Tm: Enhanced Visible-near Infrared Photocatalytic Activity. *Chem. Commun.* **2016**, *52*, 453–456.

(52) Hao, Q.; Wang, C.; Huang, H.; Li, W.; Du, D.; Han, D.; Qiu, T.; Chu, P. K. Aluminum Plasmonic Photocatalysis. *Sci. Rep.* **2015**, *5*, 15288.

(53) Xing, M.; Li, X.; Zhang, J. Synergistic Effect on the Visible Light Activity of Ti3+ Doped TiO2 Nanorods/Boron Doped Graphene Composite. *Sci. Rep.* **2014**, *4*, 5493.

(54) No Title https://www.pinterest.it/pin/4574037099007741/.

(55) Chen, X.; Burda, C. The Electronic Origin of the Visible-Light Absorption Properties of C-, Nand S-Doped TiO2 Nanomaterials. *J. Am. Chem. Soc.* **2008**, *130*, 5018–5019.

(56) Diercks, C. S.; Yaghi, O. M. The Atom, the Molecule, and the Covalent Organic Framework. *Science (80-. ).* **2017**, *355*, eaal1585.

(57) Feng, X.; Ding, X.; Jiang, D. Covalent Organic Frameworks. *Chem. Soc. Rev.* **2012**, *41*, 6010–6022.

(58) Ding, S.-Y.; Wang, W. Covalent Organic Frameworks (COFs): From Design to Applications. *Chem. Soc. Rev.* **2013**, *42*, 548–568.

- (59) Diercks, C. S.; Kalmutzki, M. J.; Yaghi, O. M. Covalent Organic Frameworks—Organic Chemistry Beyond the Molecule. *Molecules*. 2017.
- (60) Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. Porous, Crystalline, Covalent Organic Frameworks. *Science (80-. ).* **2005**, *310*, 1166 LP 1170.
- (61) Bisbey, R. P.; Dichtel, W. R. Covalent Organic Frameworks as a Platform for Multidimensional Polymerization. *ACS Cent. Sci.* **2017**, *3*, 533–543.
- (62) Waller, P. J.; Gándara, F.; Yaghi, O. M. Chemistry of Covalent Organic Frameworks. *Acc. Chem. Res.* 2015, *48*, 3053–3063.
- (63) Huang, N.; Wang, P.; Jiang, D. Covalent Organic Frameworks: A Materials Platform for Structural and Functional Designs. *Nat. Rev. Mater.* **2016**, *1*, 16068.
- (64) Wang, Z.; Zhang, B.; Yu, H.; Sun, L.; Jiao, C.; Liu, W. Microporous Polyimide Networks with Large Surface Areas and Their Hydrogen Storage Properties. *Chem. Commun.* 2010, *46*, 7730–7732.
  (65) Colson, J. W.; Mann, J. A.; DeBlase, C. R.; Dichtel, W. R. Patterned Growth of Oriented 2D
- Covalent Organic Framework Thin Films on Single-Layer Graphene. J. Polym. Sci. Part A Polym. Chem. 2015, 53, 378–384.
- (66) Wang, L.; Xu, H.; Qiu, Y.; Liu, X.; Huang, W.; Yan, N.; Qu, Z. Utilization of Ag Nanoparticles Anchored in Covalent Organic Frameworks for Mercury Removal from Acidic Waste Water. *J. Hazard. Mater.* **2020**, *389*, 121824.
- (67) Sun, B.; Liu, J.; Cao, A.; Song, W.; Wang, D. Interfacial Synthesis of Ordered and Stable Covalent Organic Frameworks on Amino-Functionalized Carbon Nanotubes with Enhanced Electrochemical Performance. *Chem. Commun.* **2017**, *53*, 6303–6306.
- (68) Yao, B.-J.; Li, J.-T.; Huang, N.; Kan, J.-L.; Qiao, L.; Ding, L.-G.; Li, F.; Dong, Y.-B. Pd NP-Loaded and Covalently Cross-Linked COF Membrane Microreactor for Aqueous CBs Dechlorination at Room Temperature. *ACS Appl. Mater. Interfaces* **2018**, *10*, 20448–20457.
- (69) Liu, X.; Pang, H.; Liu, X.; Li, Q.; Zhang, N.; Mao, L.; Qiu, M.; Hu, B.; Yang, H.; Wang, X. Orderly Porous Covalent Organic Frameworks-Based Materials: Superior Adsorbents for Pollutants Removal from Aqueous Solutions. *Innov.* **2021**, *2*, 100076.
- (70) El-Kaderi, H. M.; Hunt, J. R.; Mendoza-Cortés, J. L.; Côté, A. P.; Taylor, R. E.; O'Keeffe,
  M.; Yaghi, O. M. Designed Synthesis of 3D Covalent Organic Frameworks. *Science (80-. ).* 2007, 316, 268 LP 272.
- (71) Kuhn, P.; Antonietti, M.; Thomas, A. Porous, Covalent Triazine-Based Frameworks Prepared by Ionothermal Synthesis. *Angew. Chemie Int. Ed.* **2008**, *47*, 3450–3453.
- (72) Zhao, Y.; Yao, K. X.; Teng, B.; Zhang, T.; Han, Y. A Perfluorinated Covalent Triazine-Based Framework for Highly Selective and Water–Tolerant CO2 Capture. *Energy Environ. Sci.* **2013**, *6*, 3684–3692.
- (73) Yang, H.; Yang, L.; Wang, H.; Xu, Z.; Zhao, Y.; Luo, Y.; Nasir, N.; Song, Y.; Wu, H.; Pan, F.; 68

Jiang, Z. Covalent Organic Framework Membranes through a Mixed-Dimensional Assembly for Molecular Separations. *Nat. Commun.* **2019**, *10*, 2101.

(74) Kandambeth, S.; Dey, K.; Banerjee, R. Covalent Organic Frameworks: Chemistry beyond the Structure. J. Am. Chem. Soc. **2019**, *141*, 1807–1822.

(75) Chen, X.; Geng, K.; Liu, R.; Tan, K. T.; Gong, Y.; Li, Z.; Tao, S.; Jiang, Q.; Jiang, D. Covalent Organic Frameworks: Chemical Approaches to Designer Structures and Built-In Functions. *Angew. Chemie Int. Ed.* **2020**, *59*, 5050–5091.

(76) Patwardhan, S.; Kocherzhenko, A. A.; Grozema, F. C.; Siebbeles, L. D. A. Delocalization and Mobility of Charge Carriers in Covalent Organic Frameworks. *J. Phys. Chem. C* **2011**, *115*, 11768–11772.

(77) Calik, M.; Auras, F.; Salonen, L. M.; Bader, K.; Grill, I.; Handloser, M.; Medina, D. D.; Dogru, M.; Löbermann, F.; Trauner, D.; Hartschuh, A.; Bein, T. Extraction of Photogenerated Electrons and Holes from a Covalent Organic Framework Integrated Heterojunction. *J. Am. Chem. Soc.* **2014**, *136*, 17802–17807.

(78) Abuzeid, H. R.; EL-Mahdy, A. F. M.; Kuo, S.-W. Covalent Organic Frameworks: Design Principles, Synthetic Strategies, and Diverse Applications. *Giant* **2021**, *6*, 100054.

(79) Hunt, J. R.; Doonan, C. J.; LeVangie, J. D.; Côté, A. P.; Yaghi, O. M. Reticular Synthesis of Covalent Organic Borosilicate Frameworks. *J. Am. Chem. Soc.* **2008**, *130*, 11872–11873.

(80) Huang, N.; Zhai, L.; Xu, H.; Jiang, D. Stable Covalent Organic Frameworks for Exceptional Mercury Removal from Aqueous Solutions. *J. Am. Chem. Soc.* **2017**, *139*, 2428–2434.

(81) Zhang, X.; Zhu, G.; Wang, M.; Li, J.; Lu, T.; Pan, L. Covalent-Organic-Frameworks Derived N-Doped Porous Carbon Materials as Anode for Superior Long-Life Cycling Lithium and Sodium Ion Batteries. *Carbon N. Y.* **2017**, *116*, 686–694.

(82) Wang, P.; Xu, Q.; Li, Z.; Jiang, W.; Jiang, Q.; Jiang, D. Exceptional Iodine Capture in 2D Covalent Organic Frameworks. *Adv. Mater.* **2018**, *30*, 1801991.

(83) Xu, H.; Gao, J.; Jiang, D. Stable, Crystalline, Porous, Covalent Organic Frameworks as a Platform for Chiral Organocatalysts. *Nat. Chem.* **2015**, *7*, 905–912.

(84) Liu, M.; Guo, L.; Jin, S.; Tan, B. Covalent Triazine Frameworks: Synthesis and Applications. *J. Mater. Chem. A* **2019**, *7*, 5153–5172.

(85) Ayed, C.; Huang, W.; Zhang, K. A. I. Covalent Triazine Framework with Efficient
Photocatalytic Activity in Aqueous and Solid Media. *Front. Chem. Sci. Eng.* 2020, *14*, 397–404.
(86) Luo, R.; Xu, W.; Chen, M.; Liu, X.; Fang, Y.; Ji, H. Covalent Triazine Frameworks Obtained
from Nitrile Monomers for Sustainable CO2 Catalysis. *ChemSusChem* 2020, *13*, 6509–6522.
(87) Banerjee, T.; Gottschling, K.; Savasci, G.; Ochsenfeld, C.; Lotsch, B. V. H2 Evolution with
Covalent Organic Framework Photocatalysts. *ACS Energy Lett.* 2018, *3*, 400–409.

(88) Yang, Q.; Luo, M.; Liu, K.; Cao, H.; Yan, H. Covalent Organic Frameworks for Photocatalytic

Applications. Appl. Catal. B Environ. 2020, 276, 119174.

(89) Zhang, F.-M.; Sheng, J.-L.; Yang, Z.-D.; Sun, X.-J.; Tang, H.-L.; Lu, M.; Dong, H.; Shen, F.-C.; Liu, J.; Lan, Y.-Q. Rational Design of MOF/COF Hybrid Materials for Photocatalytic H2 Evolution in the Presence of Sacrificial Electron Donors. *Angew. Chemie Int. Ed.* 2018, *57*, 12106–12110.
(90) Krishnaraj, C.; Sekhar Jena, H.; Bourda, L.; Laemont, A.; Pachfule, P.; Roeser, J.; Chandran, C. V.; Borgmans, S.; Rogge, S. M. J.; Leus, K.; Stevens, C. V; Martens, J. A.; Van Speybroeck, V.; Breynaert, E.; Thomas, A.; Van Der Voort, P. Strongly Reducing (Diarylamino)Benzene-Based Covalent Organic Framework for Metal-Free Visible Light Photocatalytic H2O2 Generation. *J. Am. Chem. Soc.* 2020, *142*, 20107–20116.

(91) Wang, H.; Wang, H.; Wang, Z.; Tang, L.; Zeng, G.; Xu, P.; Chen, M.; Xiong, T.; Zhou, C.; Li, X.; Huang, D.; Zhu, Y.; Wang, Z.; Tang, J. Covalent Organic Framework Photocatalysts: Structures and Applications. *Chem. Soc. Rev.* **2020**, *49*, 4135–4165.

(92) Takeda, H.; Koike, K.; Inoue, H.; Ishitani, O. Development of an Efficient Photocatalytic System for CO2 Reduction Using Rhenium(I) Complexes Based on Mechanistic Studies. *J. Am. Chem. Soc.* 2008, *130*, 2023–2031.

(93) Morimoto, T.; Nakajima, T.; Sawa, S.; Nakanishi, R.; Imori, D.; Ishitani, O. CO2 Capture by a Rhenium(I) Complex with the Aid of Triethanolamine. *J. Am. Chem. Soc.* 2013, *135*, 16825–16828.
(94) Kou, Y.; Nabetani, Y.; Masui, D.; Shimada, T.; Takagi, S.; Tachibana, H.; Inoue, H. Direct

Detection of Key Reaction Intermediates in Photochemical CO2 Reduction Sensitized by a Rhenium Bipyridine Complex. J. Am. Chem. Soc. **2014**, 136, 6021–6030.

(95) Xu, R.; Wang, X. S.; Zhao, H.; Lin, H.; Huang, Y. B.; Cao, R. Rhenium-Modified Porous Covalent Triazine Framework for Highly Efficient Photocatalytic Carbon Dioxide Reduction in a Solid-Gas System. *Catal. Sci. Technol.* **2018**, *8*, 2224–2230.

(96) Yang, S.; Hu, W.; Zhang, X.; He, P.; Pattengale, B.; Liu, C.; Cendejas, M.; Hermans, I.; Zhang, X.; Zhang, J.; Huang, J. 2D Covalent Organic Frameworks as Intrinsic Photocatalysts for Visible Light-Driven CO2 Reduction. *J. Am. Chem. Soc.* 2018, *140*, 14614–14618.

(97) Kim, T. W.; Jun, S.; Ha, Y.; Yadav, R. K.; Kumar, A.; Yoo, C.-Y.; Oh, I.; Lim, H.-K.; Shin, J.
W.; Ryoo, R.; Kim, H.; Kim, J.; Baeg, J.-O.; Ihee, H. Ultrafast Charge Transfer Coupled with Lattice Phonons in Two-Dimensional Covalent Organic Frameworks. *Nat. Commun.* 2019, *10*, 1873.

(98) Jakowetz, A. C.; Hinrichsen, T. F.; Ascherl, L.; Sick, T.; Calik, M.; Auras, F.; Medina, D. D.; Friend, R. H.; Rao, A.; Bein, T. Excited-State Dynamics in Fully Conjugated 2D Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2019**, *141*, 11565–11571.

(99) Absorption of Ultraviolet, Visible, and Near-Infrared Radiation. *Molecular Fluorescence*. May 3, 2012, pp 31–51.

(100) Wolstenholme, R. Ultraviolet–Visible and Fluorescence Spectroscopy. *Analytical Techniques in Forensic Science*. January 5, 2021, pp 115–143.

(101) Lichtman, J. W.; Conchello, J.-A. Fluorescence Microscopy. *Nat. Methods* 2005, *2*, 910–919.
(102) Erbe, A.; Nayak, S.; Chen, Y.-H.; Niu, F.; Pander, M.; Tecklenburg, S.; Toparli, C. How to Probe Structure, Kinetics, and Dynamics at Complex Interfaces In Situ and Operando by Optical Spectroscopy; Wandelt, K. B. T.-E. of I. C., Ed.; Elsevier: Oxford, 2018; pp 199–219.

(103) Islam, M. M. Photoluminescence in Analysis of Surface and Interfaces of Semiconductor Nanostructures. *Int. Lett. Chem. Phys. Astron.* **2015**, *57*, 102–113.

(104) Jaffe, H. H.; Miller, A. L. The Fates of Electronic Excitation Energy. J. Chem. Educ. 1966, 43, 469.

(105) Priestley, E. B.; Haug, A. Phosphorescence Spectrum of Pure Crystalline Naphthalene. J. Chem. Phys. **1968**, 49, 622–629.

(106) Chábera, P.; Fredin, L. A.; Kjær, K. S.; Rosemann, N. W.; Lindh, L.; Prakash, O.; Liu, Y.; Wärnmark, K.; Uhlig, J.; Sundström, V.; Yartsev, A.; Persson, P. Band-Selective Dynamics in

Charge-Transfer Excited Iron Carbene Complexes. Faraday Discuss. 2019, 216, 191-210.

(107) Luo, M.; Yang, Q.; Liu, K.; Cao, H.; Yan, H. Boosting Photocatalytic H2 Evolution on G-C3N4 by Modifying Covalent Organic Frameworks (COFs). *Chem. Commun.* **2019**, *55*, 5829–5832.

(108) Li, Y.; Qian, F.; Xiang, J.; Lieber, C. M. Nanowire Electronic and Optoelectronic Devices. *Mater. Today* **2006**, *9*, 18–27.

(109) Frontmatter. Physics of Semiconductor Devices. October 13, 2006, pp i-x.

(110) Espinet-Gonzalez, P.; Barrigón, E.; Otnes, G.; Vescovi, G.; Mann, C.; France, R. M.; Welch, A.

J.; Hunt, M. S.; Walker, D.; Kelzenberg, M. D.; Åberg, I.; Borgström, M. T.; Samuelson, L.; Atwater,

H. A. Radiation Tolerant Nanowire Array Solar Cells. ACS Nano 2019, 13, 12860-12869.

(111) Spears, K. G.; Cramer, L. E.; Hoffland, L. D. Subnanosecond Time-correlated Photon Counting with Tunable Lasers. *Rev. Sci. Instrum.* **1978**, *49*, 255–262.

(112) Bessolov, V. N.; Ivankov, A. F.; Lebedev, M. V. Sulfide Passivation of III–V Semiconductors: The Starting Electronic Structure of a Semiconductor as a Factor in the Interaction between Its Valence Electrons and the Sulfur Ion. *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct. Process.* 

Meas. Phenom. 1995, 13, 1018–1023.

(113) Ohno, T. Sulfur Passivation of GaAs Surfaces. Phys. Rev. B 1991, 44, 6306–6311.

(114) Shah, J. Ultrafast Luminescence Spectroscopy Using Sum Frequency Generation. *IEEE J. Quantum Electron.* **1988**, *24*, 276–288.

(115) Wahl, M.; Rahn, H.-J.; Gregor, I.; Erdmann, R.; Enderlein, J. Dead-Time Optimized Time-Correlated Photon Counting Instrument with Synchronized, Independent Timing Channels. *Rev. Sci. Instrum.* **2007**, *78*, 33106.

(116) Hwang, W.; Kim, D.; Moon, S.; Kim, D. Y. Achieving a High Photon Count Rate in Digital Time-Correlated Single Photon Counting Using a Hybrid Photodetector. *Opt. Express* **2021**, *29*, 9797–9804.
(117) Lenci, F.; Checcucci, G.; Sgarbossa, A.; Martin, M. M.; Plaza, P.; Angelini, N. Fluorescent Biomolecules; Bassani, F., Liedl, G. L., Wyder, P. B. T.-E. of C. M. P., Eds.; Elsevier: Oxford, 2005; pp 222–235.

(118) Wahl, M.; Röhlicke, T.; Kulisch, S.; Rohilla, S.; Krämer, B.; Hocke, A. C. Photon Arrival Time Tagging with Many Channels, Sub-Nanosecond Deadtime, Very High Throughput, and Fiber Optic Remote Synchronization. *Rev. Sci. Instrum.* **2020**, *91*, 13108.

(119) Kulig, M.; Zipfel, J.; Nagler, P.; Blanter, S.; Schüller, C.; Korn, T.; Paradiso, N.; Glazov, M.
M.; Chernikov, A. Exciton Diffusion and Halo Effects in Monolayer Semiconductors. *Phys. Rev. Lett.*2018, *120*, 207401.

(120) Biskup, C.; Zimmer, T.; Benndorf, K. FRET between Cardiac Na+ Channel Subunits Measured with a Confocal Microscope and a Streak Camera. *Nat. Biotechnol.* **2004**, *22*, 220–224.

(121) Kim, D.-H.; D'Aléo, A.; Chen, X.-K.; Sandanayaka, A. D. S.; Yao, D.; Zhao, L.; Komino, T.;

Zaborova, E.; Canard, G.; Tsuchiya, Y.; Choi, E.; Wu, J. W.; Fages, F.; Brédas, J.-L.; Ribierre, J.-C.;

Adachi, C. High-Efficiency Electroluminescence and Amplified Spontaneous Emission from a

Thermally Activated Delayed Fluorescent near-Infrared Emitter. Nat. Photonics 2018, 12, 98–104.

(122) Day, R. N. Measuring Protein Interactions Using Förster Resonance Energy Transfer and Fluorescence Lifetime Imaging Microscopy. *Methods* **2014**, *66*, 200–207.

(123) Massuyeau, F.; Perry, D. L.; Kalashnyk, N.; Faulques, E. Spectroscopic Markers for Uranium(vi) Phosphates. Part II: The Use of Time-Resolved Photoluminescence. *RSC Adv.* 2017, *7*, 919–926.

(124) Allgaier, M.; Ansari, V.; Eigner, C.; Quiring, V.; Ricken, R.; Donohue, J. M.; Czerniuk, T.; Aßmann, M.; Bayer, M.; Brecht, B.; Silberhorn, C. Streak Camera Imaging of Single Photons at Telecom Wavelength. *Appl. Phys. Lett.* **2018**, *112*, 31110.

(125) Furuya, Y.; Yanagida, T.; Fujimoto, Y.; Yokota, Y.; Kamada, K.; Kawaguchi, N.; Ishizu, S.; Uchiyama, K.; Mori, K.; Kitano, K.; Nikl, M.; Yoshikawa, A. Time- and Wavelength-Resolved Luminescence Evaluation of Several Types of Scintillators Using Streak Camera System Equipped with Pulsed X-Ray Source. *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.* **2011**, *634*, 59–63.

(126) Peng, B.; Yu, G.; Liu, X.; Liu, B.; Liang, X.; Bi, L.; Deng, L.; Sum, T. C.; Loh, K. P. Ultrafast Charge Transfer in MoS 2 /WSe 2 p–n Heterojunction. *2D Mater.* **2016**, *3*, 25020.

(127) Berera, R.; van Grondelle, R.; Kennis, J. T. M. Ultrafast Transient Absorption Spectroscopy: Principles and Application to Photosynthetic Systems. *Photosynth. Res.* **2009**, *101*, 105–118.

(128) Cerullo, G.; Manzoni, C.; Lüer, L.; Polli, D. Time-Resolved Methods in Biophysics. 4.

Broadband Pump-Probe Spectroscopy System with Sub-20 Fs Temporal Resolution for the Study of

Energy Transfer Processes in Photosynthesis. Photochem. Photobiol. Sci. 2007, 6, 135-144.

(129) Klimov, V. I.; McBranch, D. W. Femtosecond High-Sensitivity, Chirp-Free Transient

Absorption Spectroscopy Using Kilohertz Lasers. Opt. Lett. 1998, 23, 277-279.

(130) Ruckebusch, C.; Sliwa, M.; Pernot, P.; de Juan, A.; Tauler, R. Comprehensive Data Analysis of Femtosecond Transient Absorption Spectra: A Review. *J. Photochem. Photobiol. C Photochem. Rev.* **2012**, *13*, 1–27.

(131) Roy, S. C.; Varghese, O. K.; Paulose, M.; Grimes, C. A. Toward Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons. *ACS Nano* **2010**, *4*, 1259–1278.

(132) Wu, J.; Huang, Y.; Ye, W.; Li, Y. CO2 Reduction: From the Electrochemical to Photochemical Approach. *Adv. Sci.* **2017**, *4*, 1700194.

(133) Wang, C.; Sun, Z.; Zheng, Y.; Hu, Y. H. Recent Progress in Visible Light Photocatalytic Conversion of Carbon Dioxide. *J. Mater. Chem. A* **2019**, *7*, 865–887.

(134) Tu, W.; Zhou, Y.; Zou, Z. Photocatalytic Conversion of CO2 into Renewable Hydrocarbon Fuels: State-of-the-Art Accomplishment, Challenges, and Prospects. *Adv. Mater.* **2014**, *26*, 4607–4626.

(135) Wang, D.-G.; Qiu, T.; Guo, W.; Liang, Z.; Tabassum, H.; Xia, D.; Zou, R. Covalent Organic Framework-Based Materials for Energy Applications. *Energy Environ. Sci.* **2021**, *14*, 688–728.

(136) Fu, Z.; Wang, X.; Gardner, A. M.; Wang, X.; Chong, S. Y.; Neri, G.; Cowan, A. J.; Liu, L.; Li,

X.; Vogel, A.; Clowes, R.; Bilton, M.; Chen, L.; Sprick, R. S.; Cooper, A. I. A Stable Covalent

Organic Framework for Photocatalytic Carbon Dioxide Reduction. Chem. Sci. 2020, 11, 543-550.

(137) Guo, K.; Zhu, X.; Peng, L.; Fu, Y.; Ma, R.; Lu, X.; Zhang, F.; Zhu, W.; Fan, M. Boosting Photocatalytic CO2 Reduction over a Covalent Organic Framework Decorated with Ruthenium Nanoparticles. *Chem. Eng. J.* **2021**, *405*, 127011.

(138) Aiyappa, H. B.; Thote, J.; Shinde, D. B.; Banerjee, R.; Kurungot, S. Cobalt-Modified Covalent Organic Framework as a Robust Water Oxidation Electrocatalyst. *Chem. Mater.* **2016**, *28*, 4375– 4379.

(139) Bhadra, M.; Sasmal, H. S.; Basu, A.; Midya, S. P.; Kandambeth, S.; Pachfule, P.; Balaraman,
E.; Banerjee, R. Predesigned Metal-Anchored Building Block for In Situ Generation of Pd
Nanoparticles in Porous Covalent Organic Framework: Application in Heterogeneous Tandem
Catalysis. ACS Appl. Mater. Interfaces 2017, 9, 13785–13792.

(140) Wu, D.; Xu, Q.; Qian, J.; Li, X.; Sun, Y. Bimetallic Covalent Organic Frameworks for Constructing Multifunctional Electrocatalyst. *Chem. – A Eur. J.* **2019**, *25*, 3105–3111.

(141) Li, J.; Zhao, D.; Liu, J.; Liu, A.; Ma, D. Covalent Organic Frameworks: A Promising Materials Platform for Photocatalytic CO2 Reductions. *Molecules*. 2020.

(142) Zhong, W.; Sa, R.; Li, L.; He, Y.; Li, L.; Bi, J.; Zhuang, Z.; Yu, Y.; Zou, Z. A Covalent Organic Framework Bearing Single Ni Sites as a Synergistic Photocatalyst for Selective Photoreduction of CO2 to CO. *J. Am. Chem. Soc.* **2019**, *141*, 7615–7621.

(143) Mereshchenko, A. S.; Myasnikova, O. S.; Olshin, P. K.; Matveev, S. M.; Panov, M. S.;

Kochemirovsky, V. A.; Skripkin, M. Y.; Tarnovsky, A. N. Ultrafast Excited-State Dynamics of Ligand-Field and Ligand-to-Metal Charge-Transfer States of CuCl42– in Solution: A Detailed Transient Absorption Study. *J. Phys. Chem. B* **2018**, *122*, 10558–10571.

(144) Agarwal, J.; Fujita, E.; Schaefer, H. F.; Muckerman, J. T. Mechanisms for CO Production from CO2 Using Reduced Rhenium Tricarbonyl Catalysts. *J. Am. Chem. Soc.* **2012**, *134*, 5180–5186.

(145) Tao, Y.; Zou, W.; Luo, G.-G.; Kraka, E. Describing Polytopal Rearrangement Processes of Octacoordinate Structures. I. Renewed Insights into Fluxionality of the Rhenium Polyhydride Complex ReH5(PPh3)2(Pyridine). *Inorg. Chem.* **2021**, *60*, 2492–2502.

(146) Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-Group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Phys.* **2006**, *125*, 194101.

(147) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Function. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(148) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(149) Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.

(150) Gaubas, E.; Simoen, E.; Vanhellemont, J. Review—Carrier Lifetime Spectroscopy for Defect Characterization in Semiconductor Materials and Devices. *ECS J. Solid State Sci. Technol.* **2016**, *5*, P3108–P3137.

(151) Munson, K. T.; Grieco, C.; Kennehan, E. R.; Stewart, R. J.; Asbury, J. B. Time-Resolved Infrared Spectroscopy Directly Probes Free and Trapped Carriers in Organo-Halide Perovskites. *ACS Energy Lett.* **2017**, *2*, 651–658.

(152) Paz, Y. Transient IR Spectroscopy as a Tool for Studying Photocatalytic Materials. *J. Phys. Condens. Matter* **2019**, *31*, 503004.

(153) Do, J. Y.; Kwak, B. S.; Park, S.-M.; Kang, M. Effective Carbon Dioxide Photoreduction over Metals (Fe-, Co-, Ni-, and Cu-) Incorporated TiO2/Basalt Fiber Films. *Int. J. Photoenergy* **2016**, *2016*, 5195138.

(154) Gao, Y.; Qian, K.; Xu, B.; Li, Z.; Zheng, J.; Zhao, S.; Ding, F.; Sun, Y.; Xu, Z. Recent Advances in Visible-Light-Driven Conversion of CO2 by Photocatalysts into Fuels or Value-Added Chemicals. *Carbon Resour. Convers.* **2020**, *3*, 46–59.

(155) Über Die UV-Absorptionsspektren von Komplexionen Mit  $\pi$ -Elektronensystemen Als Liganden. Zeitschrift für Phys. Chemie **1956**, *8*, 373–386.

## **Publications**

#### Paper I

Photocatalytic Reduction of CO<sub>2</sub> by Metaled 2, 2'-bipyridine Covalent Organic Framework

Paper II

Ultrafast charge transfer dynamics in 2D Covalent Organic Frameworks/Re-complex hybrid photocatalyst: Hot electrons vs. cold electrons

Paper III

Ultrafast Excited-state Dynamics in a Ni-2,2'-Bipyridine Covalent Organic Framework Photocatalyst

## Photocatalytic Reduction of CO<sub>2</sub> by Metaled 2, 2'-bipyridine Covalent Organic Framework

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**KEYWORDS:** covalent organic frameworks, photocatalyst, CO<sub>2</sub> reduction, CO<sub>2</sub> capture, wavelength-dependent Supporting Information Placeholder

**ABSTRACT:** Metal-complex incorporated covalent organic frameworks (COFs) emerge as promising photocatalyst for CO<sub>2</sub> reduction. In the paper, the photocatalytic CO<sub>2</sub> reduction in two kinds of metaled 2, 2'-bipyridine COFs (i.e. Re-TpBpy and Ni-TpBpy) has been studied and compared. Both catalysts exhibit good CO<sub>2</sub> reduction performance with long-term stability. While the CO yield from Ni-TpBpy was obtained to be 192.6 umol  $g^{-1}$ , which is higher than that from Re-TpBpy (131 umol  $g^{-1}$ ). We first characterized the structure, morphology, fundamental optical properties, and electronic states of both catalysts. The BET characterization, as well as N<sub>2</sub> and CO<sub>2</sub> uptake experiment, indicates Ni-TpBpy possesses a high surface ratio with better CO<sub>2</sub> capture capability, this could be the main reason accounting for the better photocatalytic performance. In addition, we found both catalysts exhibit highly excitation wavelength-dependent catalytic activity. Photocatalytic CO<sub>2</sub> reduction is efficient under high-energy excitation at 440 nm. On the other hand, no catalytic performance was observed when excited at the band edge of both catalysts (i.e. 520 nm). We believe such dependence should be related to the intrinsic electronic structure as well as photo-induced excited state dynamics of two catalysts which need to be further explored.

#### INTRODUCTION

Efficient solar-driven photocatalytic CO2 reduction capture to fuel materials (i.e. CO, CH4, HCOOH, and CH3OH) has been considered as a promising strategy to tackle the issue of fossil fuel storage and global warming.<sup>1,2 3–7</sup> In recent years, covalent organic frameworks (COFs) have attracted particular attention as an excellent category of photocatalysts.<sup>8–13</sup> COFs can be defined as crystalline porous polymeric material constructed by organic building blocks through covalent bonds in two-dimensional (2D) and three-dimensional (3D) directions.<sup>14–17</sup> According to the literature reports, 2D COFs have special photo-catalytic advances.<sup>16,18–20</sup> In 2D COFs, the COF monolayers are stacked by  $\pi - \pi$  interaction to form an ordered column  $\pi$ -array structure perpendicular to the COFs layers. Therefore, by selecting the organic building blocks to accommodate different  $\pi$ -conjugated modules, electron donors, and acceptor groups, the optical absorption bands of COFs can be tuned from ultra-violet (UV), visible-light (Vis) to near-infrared light (NIR) regions. The inter-layer  $\pi$ - $\pi$  interaction between the stacked layers also promotes the charge carrier mobility for efficient charge transport. Besides these, the intrinsic pore structure of COFs provide an ideal scaffold for CO2 adsorption, diffusion, and activation. Despite the above advantages, the photocatalytic CO<sub>2</sub> activity of pure COFs has been proved unsatisfactory due to the rapid charge recombination.<sup>21</sup> Therefore, the loading of metal nanomaterials such Rh, Ru, Ir, Ni, Co, or Re catalytic complexes into COFs to enhance the charge carrier separation and provide catalytic reaction sites have been implemented to improve the catalytic performance.<sup>22-27</sup> Among them, the Re-complex/COFs and Ni-complex/COFs hybrid systems are the benchmark systems to exhibit

high CO<sub>2</sub> reduction activity selectivity in separate reports.<sup>10,28</sup> Their good catalytic performance has been rationalized as efficient intromolecular charge transfer to broaden the visible light absorbance and prevent photodecomposition.<sup>23,28,29</sup> However, there is no systematic comparison between those two photocatalysts in terms of intrinsic structures, morphology, electronic states as well as catalytic performance. Due to the different molecular topology, oxidation states, etc, clarification on the difference in catalytic behavior between these two systems can help us to optimize the selection of the metal-complex in metaled COFs hybrid catalysts.

In this paper, we first compared the structure, morphology, and electronic structures between Ni-TpBpy and Re-TpBpy catalysts via XRD, SEM, XPS, and EDX characterization. In particular, the surface ratio and CO<sub>2</sub> capture capability of both compounds are evaluated by the BET and gas uptake experiment, respectively. The photocatalytic CO<sub>2</sub> reduction experiments using triethanolamine (TEOA) as the sacrificial agents demonstrate the higher catalytic performance of Ni-TpBpy than Re-TpBpy. We attributed such difference to the different CO<sub>2</sub> capture capability and internal charge transfer efficiency. In addition, both catalysts exhibit highly excitation wavelength-dependent catalytic activity, which should require the study of detailed excited state dynamics in the future.

#### **RESULTS AND DISCUSSION**

In this study, a two-dimensional (2D) COFs (TpBpy) with 2,2'-bipyridine was synthesized by the condensation of 1,3,5-triformylphloroglucinol (Tp) and 5,5'-diamino-2,2'-bipyridine (Bpy) through the Schiff base reaction under solvothermal conditions. Through the Schiff base reaction, Tp and Bpy are connected by the

 $\beta$ -ketoenamine bond to form a hexagonal structure, which extends into 2D layers. These 2D layers form a layered crystal structure by  $\pi$ - $\pi$  stacking along the Z-axis (Fig. 1a & S4)). This COFs was chosen because of its excellent chemical stability and easily accessible active sites to metal ions. The Re-complex incorporated TpBpy (Re-TpBpy) was prepared by refluxing TpBpy and Re(CO)5Cl in toluene solution, and Ni-TpBpy was prepared by solution dipping method to implant the Ni-complex into TpBpy (Ni-TpBpy) in acetonitrile solution. The crystalline structures of the as-obtained TpBpy, Re-TpBpy, and Ni-TpBpy were confirmed by the powder X-ray diffraction (PXRD) measurement as shown in Fig. 1b. The experimental PXRD patterns of these three samples match the simulated AA stacking structure (Fig. S4) of COFs in the hexagonal space group (P6). The pronounced peak at 20 of 3.6° of both samples can be assigned to the (100) plane of the TpBpy, demonstrating the unchanged crystalline structure of TpBpy after Re-complex or Ni-complex incorporation. As mentioned above, the 2D COFs layers are aggregated by non-bonding  $(\pi - \pi)$  in the z-axis direction, and the tolerances accumulated in the long-range can easily cause the peaks to broaden. The broad peak between  $2\theta = 25.1^{\circ}-28.1^{\circ}$  is caused by the diffraction peak formed by the (001) crystal plane



**Figure 1.** (A) Schematic presentation of the synthesis of TpBpy, Re-TpBpy, and Ni-TpBpy. (B) PXRD of TpBpy (cyan curve), Re-TpBpy (green-blue curve), Ni-TpBpy (blue curve), simulated AA stacking mode and (purple curve), and simulated AB stacking mode (pink curve).

perpendicular to the z-axis.<sup>30,31</sup> From the thermogravimetric analysis (TGA) curves, TpBpy did not show any significant decomposition under nitrogen until 400°C. The decomposition of Re-TpBpy started at 350 °C while Ni-TpBpy started at 280°C. Moreover, due to the embedded crystal water, the mass loss of Ni-TpBpy was more severe than that of Re-TpBpy and TpBpy at about 100 °C (Figure S4).

The chemical composition and the surface chemical state of the materials were characterized via X-ray photoelectron spectroscopy (XPS). As shown in Fig. 2a, the overview spectra of Re-TpBpy and Ni-TpBpy display the presence of the Re, Ni, and Cl elements in addition to C, O, N in pristine TpBpy. This suggests the actual incorporation of the Re-complex or Ni-complex in the host COFs. More importantly (Figure 2b), the two N 1S bands observed at 400.03 eV and 398.71 eV can ascribe to the secondary nitrogen and pyridinic nitrogen in TpBpy, respectively.<sup>25,32</sup> Such pyridinic nitrogen bands in both Re-TpBpy and Ni-TpBpy, are shifted to higher binding every (i.e. from 398.71 eV to 399.39 eV and 399.7 eV for Re-TpBpy and Ni-TpBpy, respectively) with the peak position of the secondary nitrogen (Fig. 2c and d) remains unchanged. This indicates that the Re-complex or Ni-TpBpy is chemically anchored to the TpBpy only through its bipyridinic units, which consistent



**Figure 2.** (A) XPS overview spectra of TpBpy, Re-TpBpy, and Ni-TpBpy, (B), (C), and (D) correspond to the XPS N 1s corelevel spectra of TpBpy, Re-TpBpy, and Ni-TpBpy, respectively.

with the literature reports on Re-complex/COFs and Ni-complex/COFs hybrid has revealed that the complexation of Re or Ni to the TpBpy matrix by its bipyridinic units only (Fig.1a).<sup>22,23,25,33</sup>

Afterward, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and partial energy dispersive X-ray (EDX) spectroscopy were utilized to further evaluate the incorporation and distribution of rhenium and nickel in Re-TpBpy and Ni-TpBpy, respectively. According to the microscopic observation, there is no noticeable morphological difference between the neat TpBpy and the TpBpy COFs functionalized by the metal-complex catalyst. (Figure S5 and S6). In particular, those metal-COFs still preserve the two-dimensional (2D) layered structure of neat COF. (Figure S3). In addition, the TEM image in Figure S6 proved the absence of metal aggregates or clusters in either Re-TpBoy or Ni-TpBpy. Finally, it is worth noting that the elemental mapping in TEM characterization confirmed the even distribution of Re, Ni, N, C, and O in Re-TpBpy and Ni-TpBpy, respectively (Figure 2). This



Figure 3. Elemental mapping results of Re-TpBpy (A), Ni-TpBpy (B).

means that the dispersion of rhenium and nickel species in Re-TpBpy and Ni-TpBpy should all be highly homogeneous. In addition, the atomic ratios of N to Re and Ni in Re-TpBpy and Ni-TpBpy are 5:1 and 6:1 according to their EDX Spectrum (Fig. S8&S9), respectively, which are much less than the theoretical



**Figure 4.** (A) N<sub>2</sub> adsorption isotherm of TpBpy, Re-TpBpy, and Ni-TpBpy, (B) CO<sub>2</sub> uptakes on TpBpy and Re-TpBpy, and the Ni-TpBpy at 298 K. The inset image zoom on the low pressure. P<sub>0</sub> here refers to the 1.0 bar.

value of 3:1 where each pore in the COFs contains one metal-complex, further suggest that Re and Ni are not aggregated in Re-TpBpy and Ni-TpBpy.

Before the photocatalytic measurement, we first evaluated the insitu gap adsorption capability of both samples, which should be the first dominant factor that influences photocatalytic nice performance. N2 adsorption isotherms were measured at 77 K to investigate the porosity of TpBpy, Re-TpBpy, and Ni-TpBpy (Figure 4a). TpBpy, Re-TpBpy, and Ni-TpBpy showed type I reversible N<sub>2</sub>sorption isotherms with a steep nitrogen gas uptake at low relative pressure ( $P/P_0 < 0.001$ ) according to the IUPAC (International Union of Pure and Applied Chemistry) classification, indicating the predominance of microporous. In addition, there is a significant hysteresis and a slight increase in the medium and high-pressure regions, indicating the existence of medium and large pores, respectively.<sup>34</sup> The surface area of pristine TpBpy is 952.49 m<sup>2</sup> g<sup>-1</sup> according to Brunauer-Emmett-Teller (BET) calculations, while the surface area of both Re-TpBpy and Ni-TpBpy decreases (648.75 m<sup>2</sup> g<sup>-1</sup> and 679.9 m<sup>2</sup> g<sup>-1</sup>). The reduced surface area should be due to the Re(CO)<sub>3</sub>Cl and Ni(II) occupying part of the pore space in COF. It is noteworthy that the BET-specific surface area of Re-TpBpy and Ni-TpBpy are still high, meaning the porous structure is well preserved. This ensured the high accessibility of Re or Ni active sites in the COFs channel. In short, the N2 adsorption isotherms suggest that TpBpy and its composites with a high specific surface area and abundant ultramicroporous properties, which inspired us to investigate their gas uptake capacity since it is known that the CO<sub>2</sub> absorption capacity of porous polymeric materials is related to their physical adsorption and that CO<sub>2</sub> adsorption on the catalyst surface is a prerequisite for subsequent catalytic processes.<sup>35,36</sup> The porous structures in Re-TpBpy and Ni-TpBpy may facilitate CO<sub>2</sub> capture and play a critical role in facilitating CO<sub>2</sub> conversion. The impregnation of polar rhenium and nickel complexes contributes to increasing the polarity of TpBpy, which in turn facilitates the improvement of CO<sub>2</sub> adsorption capacity. As shown in Figure 4b, the CO<sub>2</sub> adsorption volume of Re-TpBpy and Ni-TpBpy is 37.5 cm<sup>3</sup> g<sup>-1</sup> 39.5 cm<sup>3</sup> g<sup>-1</sup>, respectively. In addition, compared with TpBpy, Re-TpBpy and Ni-TiBpy show a steeper CO2 uptake at lower relative pressure, which implies stronger chemisorption of CO2 in Re-TpBpy and Ni-TpBpy (see the inset of Figure 4b). The higher adsorption capacity and stronger chemisorption in Re-TpBpy as well as Ni-TpBpy render more promising CO2 photocatalysts.

The above characterization indicates a higher specific surface area and better  $CO_2$  capture capacity of Ni-TpBpy than Re-TpBpy, which is favorable for photocatalytic  $CO_2$  reduction. Therefore, we investigated their photocatalytic efficiency for  $CO_2$  conversion in

gas-solid reaction systems. The reaction conditions were similar to those used in the literature,<sup>22</sup>, except for the controlled excitation conditions. Re-TpBpy and Ni-TpBpy compounds were first dispersed in acetonitrile and an aqueous solution containing triethanolamine (TEOA) as a sacrificial reagent. These solutions are then purged with argon to ensure an oxygen-free environment. An LED lamp was used as a light source with a selected excitation wavelength region during the test. Figure 5 display the CO production from Re-TpBy and Ni-TpBpy catalysts with excitation wavelengths from 440 and 520 nm as a function of illumination time. No CO production was observed for both Re-TpBpy and Ni-TpBpy with 520 nm excitation up till 8 h. However, the CO production of Re-TpBpy and Ni-TpBpy increased substantially under 400 nm light. More interestingly, the yield of CO from Ni-TpBpy (24.1  $\mu$ mol g<sup>-1</sup>h<sup>-1</sup>) is higher than that from Re-TpBpy (16.4  $\mu$ mol g<sup>-1</sup>h<sup>-1</sup>), which is consistent with the above assumption for structural characterization of both samples. The excitation wavelength-dependent photocatalytic performance of both samples should be attributed to the excited state dynamics at these two excitation conditions, which is related to the electronic structure and optical transition. As well accepted, the internal charge transfer in hybrid catalysts systems dominantly influences the photocatalytic performance since such



**Figure 5.** Time course of CO production during photocatalytic CO2 reduction on Re-TpBpy, and Ni-TpBpy photocatalysts under 440 nm and 520 nm.

process determines the lifetime and transport pathway of the excited charges to be utilized for the reduction or oxidation process in the medium.<sup>22,28,37,38</sup> In this scenario, we can expect more efficient inter-molecular charge transfer as well as a longer excited-state lifetime when excited at high energy compared with the situation in band edge excitation for our samples. However, detailed ultrafast photophysical studies are needed in the future to confirm such assumptions.

#### CONCLUSIONS

In this work, we investigated the photocatalytic CO<sub>2</sub> reduction of Re-TpBpy and Ni-TpBpy with systematic materials characterization of two systems. The structural characterization and gas adsorption uptake measurement indicates Ni-TpBpy exhibited a higher surface ratio and CO<sub>2</sub> capture capability. This can partially rationalize the better CO<sub>2</sub> reduction activity in Ni-TpBpy compared to Re-TpBpy. In addition, we found the catalytic performance of both samples is highly excitation wavelength dependent. Excitation with higher photon energy well above the band edge (i.e. 440 nm) pro-

vides more efficient photoreduction of  $CO_2$  than band-edge excitation. We expected it to be due to the favorable internal charge transfer and enhanced excited state lifetime under high energy excitation.

#### **Supporting Information**

Materials, methods, detailed characterization of TpBpy, Re-TpBpy, and Ni-TpBpy, and DFT calculations (PDF). This material is available free of charge via the internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interests.

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#### REFERENCES

(1) Omae, I. Aspects of Carbon Dioxide Utilization. *Catal. Today* **2006**, *115*, 33–52.

(2) Song, C. Global Challenges and Strategies for Control, Conversion and Utilization of CO2 for Sustainable Development Involving Energy, Catalysis, Adsorption and Chemical Processing. *Catal. Today* **2006**, *115*, 2–32.

(3) Roy, S. C.; Varghese, O. K.; Paulose, M.; Grimes, C. A. Toward Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons. *ACS Nano* **2010**, *4*, 1259–1278.

(4) Wu, J.; Huang, Y.; Ye, W.; Li, Y. CO2 Reduction: From the Electrochemical to Photochemical Approach. *Adv. Sci.* **2017**, *4*, 1700194.

(5) Wang, C.; Sun, Z.; Zheng, Y.; Hu, Y. H. Recent Progress in Visible Light Photocatalytic Conversion of Carbon Dioxide. *J. Mater. Chem. A* **2019**, *7*, 865–887.

(6) INOUE, T.; FUJISHIMA, A.; KONISHI, S.; HONDA, K. Photoelectrocatalytic Reduction of Carbon Dioxide in Aqueous Suspensions of Semiconductor Powders. *Nature* **1979**, *277*, 637–638.

(7) Tu, W.; Zhou, Y.; Zou, Z. Photocatalytic Conversion of CO2 into Renewable Hydrocarbon Fuels: State-of-the-Art Accomplishment, Challenges, and Prospects. *Adv. Mater.* **2014**, *26*, 4607–4626.

(8) Zhong, H.; Sa, R.; Lv, H.; Yang, S.; Yuan, D.; Wang, X.; Wang, R. Covalent Organic Framework Hosting Metalloporphyrin-Based Carbon Dots for Visible-Light-Driven Selective CO2 Reduction. *Adv. Funct. Mater.* **2020**, *30*, 2002654.

(9) Huang, N.; Wang, P.; Jiang, D. Covalent Organic Frameworks: A Materials Platform for Structural and Functional

Designs. Nat. Rev. Mater. 2016, 1, 16068.

(10) Li, J.; Zhao, D.; Liu, J.; Liu, A.; Ma, D. Covalent Organic Frameworks: A Promising Materials Platform for Photocatalytic CO2 Reductions. *Molecules*. 2020.

(11) Yang, Q.; Luo, M.; Liu, K.; Cao, H.; Yan, H. Covalent Organic Frameworks for Photocatalytic Applications. *Appl. Catal. B Environ.* **2020**, *276*, 119174.

(12) Huang, W.; Li, Y. Semiconducting 2D Covalent Organic Frameworks: A New Opportunity for Efficient Solar Fuel Production. *Chinese J. Chem.* **2019**, *37*, 1291–1292.

(13) Huang, W.; Luo, W.; Li, Y. Two-Dimensional Semiconducting Covalent Organic Frameworks for Photocatalytic Solar Fuel Production. *Mater. Today* **2020**, *40*, 160–172.

(14) Evans, A. M.; Ryder, M. R.; Ji, W.; Strauss, M. J.; Corcos, A. R.; Vitaku, E.; Flanders, N. C.; Bisbey, R. P.; Dichtel, W. R. Trends in the Thermal Stability of Two-Dimensional Covalent Organic Frameworks. *Faraday Discuss.* **2021**, *225*, 226–240.

(15) Abuzeid, H. R.; EL-Mahdy, A. F. M.; Kuo, S.-W. Covalent Organic Frameworks: Design Principles, Synthetic Strategies, and Diverse Applications. *Giant* **2021**, *6*, 100054.

(16) Liu, R.; Tan, K. T.; Gong, Y.; Chen, Y.; Li, Z.; Xie, S.; He, T.; Lu, Z.; Yang, H.; Jiang, D. Covalent Organic Frameworks: An Ideal Platform for Designing Ordered Materials and Advanced Applications. *Chem. Soc. Rev.* **2021**, *50*, 120–242.

(17) Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. Porous, Crystalline, Covalent Organic Frameworks. *Science (80-. ).* **2005**, *310*, 1166 LP – 1170.

(18) You, J.; Zhao, Y.; Wang, L.; Bao, W. Recent Developments in the Photocatalytic Applications of Covalent Organic Frameworks: A Review. J. Clean. Prod. **2021**, 291, 125822.

(19) Keller, N.; Bein, T. Optoelectronic Processes in Covalent Organic Frameworks. *Chem. Soc. Rev.* **2021**, *50*, 1813–1845.

(20) Jiang, D. Covalent Organic Frameworks: A Molecular Platform for Designer Polymeric Architectures and Functional Materials. *Bull. Chem. Soc. Jpn.* **2021**, *94*, 1215–1231.

(21) Wang, D.-G.; Qiu, T.; Guo, W.; Liang, Z.; Tabassum, H.; Xia, D.; Zou, R. Covalent Organic Framework-Based Materials for Energy Applications. *Energy Environ. Sci.* **2021**, *14*, 688–728.

(22) Yang, S.; Hu, W.; Zhang, X.; He, P.; Pattengale, B.; Liu, C.; Cendejas, M.; Hermans, I.; Zhang, X.; Zhang, J.; Huang, J. 2D Covalent Organic Frameworks as Intrinsic Photocatalysts for Visible Light-Driven CO2 Reduction. *J. Am. Chem. Soc.* **2018**, *140*, 14614–14618.

(23) Fu, Z.; Wang, X.; Gardner, A. M.; Wang, X.; Chong, S. Y.; Neri, G.; Cowan, A. J.; Liu, L.; Li, X.; Vogel, A.; Clowes, R.; Bilton, M.; Chen, L.; Sprick, R. S.; Cooper, A. I. A Stable Covalent Organic Framework for Photocatalytic Carbon Dioxide Reduction. *Chem. Sci.* **2020**, *11*, 543–550.

(24) Guo, K.; Zhu, X.; Peng, L.; Fu, Y.; Ma, R.; Lu, X.; Zhang, F.; Zhu, W.; Fan, M. Boosting Photocatalytic CO2 Reduction over a Covalent Organic Framework Decorated with Ruthenium Nanoparticles. *Chem. Eng. J.* **2021**, *405*, 127011.

(25) Aiyappa, H. B.; Thote, J.; Shinde, D. B.; Banerjee, R.; Kurungot, S. Cobalt-Modified Covalent Organic Framework as a Robust Water Oxidation Electrocatalyst. *Chem. Mater.* **2016**, *28*, 4375–4379.

(26) Bhadra, M.; Sasmal, H. S.; Basu, A.; Midya, S. P.; Kandambeth, S.; Pachfule, P.; Balaraman, E.; Banerjee, R. Predesigned Metal-Anchored Building Block for In Situ Generation of Pd Nanoparticles in Porous Covalent Organic Framework: Application in Heterogeneous Tandem Catalysis. ACS Appl. Mater. Interfaces 2017, 9, 13785–13792.

(27) Wu, D.; Xu, Q.; Qian, J.; Li, X.; Sun, Y. Bimetallic Covalent Organic Frameworks for Constructing Multifunctional Electrocatalyst. *Chem. – A Eur. J.* **2019**, *25*, 3105–3111.

(28) Zhong, W.; Sa, R.; Li, L.; He, Y.; Li, L.; Bi, J.; Zhuang, Z.; Yu, Y.; Zou, Z. A Covalent Organic Framework Bearing Single Ni Sites as a Synergistic Photocatalyst for Selective Photoreduction of CO2 to CO. J. Am. Chem. Soc. **2019**, *141*, 7615–7621.

(29) Mereshchenko, A. S.; Myasnikova, O. S.; Olshin, P. K.; Matveev, S. M.; Panov, M. S.; Kochemirovsky, V. A.; Skripkin, M. Y.; Tarnovsky, A. N. Ultrafast Excited-State Dynamics of Ligand-Field and Ligand-to-Metal Charge-Transfer States of CuCl42– in Solution: A Detailed Transient Absorption Study. J. Phys. Chem. B 2018, 122, 10558–10571.

(30) Chandra, S.; Kandambeth, S.; Biswal, B. P.; Lukose, B.; Kunjir, S. M.; Chaudhary, M.; Babarao, R.; Heine, T.; Banerjee, R. Chemically Stable Multilayered Covalent Organic Nanosheets from Covalent Organic Frameworks via Mechanical Delamination. *J. Am. Chem. Soc.* **2013**, *135*, 17853–17861.

(31) Singh, V.; Jang, S.; Vishwakarma, N. K.; Kim, D.-P. Intensified Synthesis and Post-Synthetic Modification of Covalent Organic Frameworks Using a Continuous Flow of Microdroplets Technique. *NPG Asia Mater.* **2018**, *10*, e456–e456.

(32) Chandra, S.; Kundu, T.; Dey, K.; Addicoat, M.; Heine, T.; Banerjee, R. Interplaying Intrinsic and Extrinsic Proton Conductivities in Covalent Organic Frameworks. *Chem. Mater.* **2016**, *28*, 1489–1494.

(33) Li, S.-Y.; Meng, S.; Zou, X.; El-Roz, M.; Telegeev, I.; Thili, O.; Liu, T. X.; Zhu, G. Rhenium-Functionalized Covalent Organic Framework Photocatalyst for Efficient CO2 Reduction under Visible Light. *Microporous Mesoporous Mater.* **2019**, *285*, 195–201.

(34) Rouquerol, J.; Avnir, D.; Fairbridge, C. W.; Everett, D. H.; Haynes, J. M.; Pernicone, N.; Ramsay, J. D. F.; Sing, K. S. W.; Unger, K. K. Recommendations for the Characterization of Porous Solids (Technical Report). *Pure Appl. Chem.* **1994**, *66*, 1739–1758.

(35) Tan, L.; Tan, B. Hypercrosslinked Porous Polymer Materials: Design, Synthesis, and Applications. *Chem. Soc. Rev.* **2017**, *46*, 3322–3356.

(36) Wang, J.; Huang, L.; Yang, R.; Zhang, Z.; Wu, J.; Gao, Y.; Wang, Q.; O'Hare, D.; Zhong, Z. Recent Advances in Solid Sorbents for CO2 Capture and New Development Trends. *Energy Environ. Sci.* **2014**, *7*, 3478–3518.

(37) Yu, J.; Wang, W.; Cheng, B.; Su, B.-L. Enhancement of Photocatalytic Activity of Mesporous TiO2 Powders by Hydrothermal Surface Fluorination Treatment. *J. Phys. Chem. C* **2009**, *113*, 6743–6750.

(38) Yu, J.; Xiong, J.; Cheng, B.; Liu, S. Fabrication and Characterization of Ag–TiO2 Multiphase Nanocomposite Thin Films with Enhanced Photocatalytic Activity. *Appl. Catal. B Environ.* **2005**, *60*, 211–221.

# 1 Supplementary Information

# Photocatalytic Reduction of CO<sub>2</sub> by Metaled 2, 2'bipyridine Covalent Organic Framework

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## **36** Materials and methods

37 5,5'-diamino-2,2'-bipyridine (95%, Yuhao Chemical), Pentacarbonylchlororhenium (98%, Sigma-

Aldrich), 2,2'-bipyridine (≥ 99%, Sigma-Aldrich), Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (≥ 98.0 %, Sigma-Aldrich),
Triformylphloroglucinol (95%, Yuhao Chemical), Mesitylene (98%, Sigma-Aldrich), 1,4Dioxane (anhydrous, 99.8%, Sigma-Aldrich), glacial acetic acid (ACS reagent, Aldrich), Nafion
(10 wt% in H<sub>2</sub>O), 1-Propanol ( for HPLC, ≥ 99.9%, Sigma-Aldrich), Toluene (for HPLC, VWR
Chemicals), Acetonitrile (for HPLC, VWR Chemicals), Tetrahydrofuran (for HPLC, VWR

43 Chemicals), Methanol (for HPLC, VWR Chemicals), Triethanolamine (TEOA) (≥ 99.0 %, Sigma44 Aldrich).

Synthesis of TpBpy. TpBpy was prepared according to literature methods with a little 45 modification.<sup>1</sup> A Pyrex tube (o.d.  $\times$  i.d. = 10  $\times$  8 mm<sup>2</sup> and length 25 cm)) was charged with 46 triformylphloroglucinol (Tp) (21 mg, 0.10 mmol), 5,5'- diamino-2,2'- bipyridine (Bpy) (27.9 mg, 47 0.15 mmol), 0.5 mL 1,4-dioxane, 0.5 mL mesitylene, 0.1mL 6 M aqueous acetic acid. This mixture 48 49 was sonicated for 20 min to get a homogeneous dispersion. The tube was flash-frozen in a liquid 50 nitrogen bath, evacuated to an internal pressure of ca.0.15 mmHg, and flame-sealed. The tube was placed in an oven at 120 °C for 5 days upon warming to room temperature to afford an orange-red 51 precipitate. The precipitate was isolated by filtration over a medium glass frit and washed with 52 53 anhydrous tetrahydrofuran (THF, 20.0 mL). The product was immersed in anhydrous THF (20.0 mL) for 8 h, during which the activation solvent was decanted and freshly replenished four times. 54 The solvent was removed by filtration and the precipitate dried under vacuum at 60 °C overnight 55 56 to afford TpBpy (42 mg, 86%).

Synthesis of Re(bpy)(CO)<sub>3</sub>Cl. This complex was prepared with slight modifications to literature
methods.<sup>2,3</sup> Re(CO)<sub>5</sub>Cl (0.3020 g, 0.83 mmol) was dissolved in 50 mL of hot toluene, then 2,2-

bipyridine (0.130 g, 0.83 mmol) was added, the mixture was stirred and reflux for 1h to get yellow
product. Upon cooling, the product was filtered, washed with methanol for 3 times, dried under
vacuum at 60 °C overnight and used without further purification. <sup>1</sup>H NMR (δ, 400 MHz, DMSOd<sub>6</sub>): 9.02 (d, 1H), 8.77 (d, 1H), 8.34(t, 1H), 7.76(t, 1H).

63 Synthesis of Re-TpBpy. The process of synthesis Re-TpBpy was similar to that of Re-Bpy.
64 Re(CO)<sub>5</sub>Cl (10 mg, 0.025 mmol) were dispersed in 10 mL hot toluene, then TpBpy (25 mg) was
65 added, the mixture was refluxed 40 min while stirring. The scarlet products were filtered, washed
66 with methanol 3 times, dried under vacuum at 60 °C overnight, and used without further
67 purification.

Synthesis of Ni-TpBpy. Ni-TpBpy was prepared according to literature methods with a little modification.<sup>1</sup> Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (30 mg) were dispersed in 20 mL acetonitrile, then TpBpy (50 mg) was added, the mixture was stirred for 8 h at room temperature. The orange products were filtered, washed with acetonitrile 3 times, dried under vacuum at 60 °C overnight, and used without further purification.

Photocatalytic Reduction of CO<sub>2</sub>. The method of photocatalytic reduction of CO<sub>2</sub> was carried out according to literature methods with a little modification. TpBpy, Re-TpBpy, or Ni-TpBpy (1 mg) was dispersed in 3 mL of CH<sub>3</sub>CN, and 0.2 mL of TEOA (triethanolamine) in 11 mL septumsealed glass vials. The mixture was purged with Ar for 5 min and CO<sub>2</sub> for 15 min first, then irradiated by a LED lamp with 520 nm and 440 wavelengths for 8 h and kept stirring during the photocatalytic reaction. The amount of CO generated was quantified using Shimadzu gas chromatography (GC-2010) by analyzing 500  $\mu$ L of the headspace.

## **80** Computational methods

To investigate the relationship of the optical properties with molecular structures and electronic 81 structures, we used a triformylphloroglucinol (Tp) terminated bipyridine (Bpy) molecular 82 83 fragment (Fig. S10) to represent the COFs structure. An implicit solvent model was used to reflect the solvation environment and implemented using SMD solvation model<sup>4</sup> in Gaussian 16 package.<sup>5</sup> 84 Considering the transition metal complex in the fragment,  $M06-L^{6-11}$  was selected as the functional 85 and def 2-TZVP<sup>12,13</sup> was selected as the basis set for DFT calculations. Water and *n*-propanol 86 parameters were used to represent the solvents in the SMD models.<sup>14</sup> Time-dependent density 87 functional theory (TD-DFT) calculations were also performed using these parameters. The UV-88 vis absorption spectra and electron excitations were analyzed using the Multiwfn program.<sup>15</sup> 89

### 90 Characterization

PXRD data were collected by using Rigaku Miniflex600 at room temperature with Cu Ka1 source 91  $(\lambda = 1.5418 \text{ Å})$  over the range of  $2\theta = 3.0-40.0^{\circ}$  with a step size of  $0.02^{\circ}$  and a counting time of 1 92 s per step. X-ray photoelectron spectroscopy (XPS) data were obtained by using XPS-93 ThermoScientific with Al Ka (1486 eV) as the excitation X-ray source. The peak of C 1s at about 94 284.8 eV was used to calibrate the energy scale. The pressure of the analysis chamber was 95 maintained at  $2 \times 10^{-10}$  mbar during measurement. The sample material was prepared by dispersing 96 it in ethanol and then dripping it onto a silicon wafer sprayed with 39.7 nm gold by Quorum Coater, 97 then dried in air. N<sub>2</sub> adsorption and desorption isotherms were carried out at 77k using 98 99 Micromeritics ASAP 2020. Prior to the measurement, samples were outgassed under vacuum at 120 °C for 10h. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method 100 based on the adsorption branch of nitrogen adsorption/desorption isotherms. Thermal gravimetric 101 (TGA) were measured under N<sub>2</sub> atmosphere with a ramping rate of 10 °C min<sup>-1</sup> and heated up to 102

800 °C. Scanning electron microscopy (SEM) images were obtained by using AFEG 250
Analytical ESEM at an accelerating voltage of 20.0 kV. Transmission electron microscopy (TEM)
images and Energy dispersive X-ray (EDX) mapping images were obtained with a Tecnai G2 T20
TEM.

## 107 Supplementary Figures



- **Supplementary Figure 1:** Crystalline Structures of TpBpy, top-view and side-view of 1 unit cell
- and 4 unit cells.



- **Supplementary Figure 2:** Crystalline Structures of Re-Tp-Bpy, top-view and side-view of 1unit
- cell and 4 unit cells.



Supplementary Figure 3: Crystalline Structures of Ni-TpBpy, top-view and side-view of 1unit
cell and 4 unit cells.



119 Supplementary Figure 4: Simulated structure of AA (B) and AB stacking (C) using Materials

120 Studio software package.<sup>16</sup>

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**Supplementary Figure 5:** TGA spectra of TpBpy (red), Re-TpBpy (green) and Ni-TpBpy

124 (blue).



**Supplementary Figure 7:** HR-TEM image of TpBpy (A), Re-TpBpy (B), and Ni-TpBpy (C).





**Supplementary Figure 8:** EDX Spectrum of Re-TpBpy.



Supplementary Figure 9: EDX Spectrum of Ni-TpBpy.

# 138 Supplementary Table

- **Table 1.** Atomistic coordinates of TpBpy.
- 140 Space group: *P-6;*
- 141 a = b = 29.7171 Å, c = 3.6389 Å;
- 142  $\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}.$

Atom	x/a	v/b	z/c
С	0.49116	-0.53801	-0.5
С	0.46237	-0.59268	-0.5
С	0.48805	-0.62084	-0.5
С	0.5425	-0.59427	-0.5
С	0.56808	-0.53958	-0.5
Ν	0.54351	-0.51267	-0.5
Ν	0.56825	-0.62263	-0.5
С	0.61968	-0.60395	-0.5
С	0.64178	-0.63547	-0.5
С	0.60945	-0.69194	-0.5
0	0.72587	-0.5605	-0.5
Н	0.54775	-0.66336	-0.5
С	0.46618	-0.50549	-0.5
Ν	0.49804	-0.45354	-0.5
С	0.4775	-0.42303	-0.5
С	0.42373	-0.44121	-0.5
С	0.39028	-0.49511	-0.5
С	0.41183	-0.52713	-0.5
Ν	0.40769	-0.40456	-0.5
С	0.35901	-0.41314	-0.5
С	0.34736	-0.37339	-0.5
С	0.3885	-0.31912	-0.5
0	0.25741	-0.43582	-0.5
Н	0.4349	-0.36467	-0.5
Н	0.42004	-0.61353	-0.5
Н	0.46641	-0.66325	-0.5
Н	0.61053	-0.51653	-0.5
Н	0.64576	-0.56197	-0.5
Н	0.5046	-0.38099	-0.5
Н	0.3482	-0.51194	-0.5
Н	0.3859	-0.56908	-0.5
Н	0.32677	-0.45314	-0.5

- **Table 2.** Atomistic coordinates of Re-Tp-Bpy.
- 145 Space group: *P3;*
- a = b = 29.712 Å, c = 9.4234 Å;
- $\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}.$

Atom	x/a	<i>y/b</i>	z/c
Re	0.57908	0.57082	0.5352
С	0.60166	0.58892	0.34135
Cl	0.54602	0.54449	0.78023
0	0.68667	0.58674	0.61612
С	0.64675	0.582	0.58653
С	0.60202	0.64273	0.5769
0	0.61562	0.60044	0.22551
0	0.61466	0.68552	0.60177
С	0.48933	0.46083	0.49026
С	0.4618	0.40629	0.48633
С	0.48793	0.37874	0.49493
С	0.54243	0.40611	0.50666
С	0.56796	0.4605	0.51088
Ν	0.54246	0.48739	0.50342
Ν	0.56875	0.37811	0.51435
С	0.62057	0.39706	0.51711
С	0.64222	0.36509	0.52049
С	0.60939	0.30854	0.52068
0	0.7267	0.4395	0.52
Н	0.54844	0.33716	0.51562
С	0.46514	0.49306	0.47984
Ν	0.49831	0.54578	0.48838
С	0.47857	0.57783	0.47794
С	0.42546	0.55988	0.45909
С	0.39141	0.50598	0.44906
С	0.41174	0.47313	0.45927
N	0.40945	0.59684	0.45145
С	0.36015	0.5875	0.44806
С	0.348	0.62692	0.44386
С	0.3888	0.6815	0.44366
0	0.25812	0.56379	0.44451
Н	0.43625	0.63703	0.45091
Н	0.41962	0.38518	0.47753
Н	0.46677	0.33636	0.49251
Н	0.60991	0.48385	0.52191
Н	0.64687	0.439	0.51552

Н	0.5062	0.61931	0.48614
Н	0.34989	0.48991	0.43266
Н	0.38579	0.43139	0.45068
Н	0.32813	0.54743	0.45028

- **Table 3.** Atomistic coordinates of Ni-Tp-Bpy.
- 150 Space group: *P3;*
- a = b = 29.6054 Å, c = 6.7459 Å;
- $\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}.$

Atom	x/a	<i>y/b</i>	z/c
С	0.48835	0.45996	0.51269
С	0.46385	0.40563	0.5146
С	0.49363	0.38167	0.50214
С	0.54815	0.41251	0.48114
С	0.57116	0.46714	0.47916
N	0.54182	0.49007	0.50206
N	0.57597	0.38615	0.46617
С	0.6278	0.40405	0.46445
С	0.64607	0.36881	0.45813
С	0.60982	0.31246	0.45734
0	0.73301	0.43897	0.45732
Н	0.55549	0.34457	0.46268
С	0.46283	0.49073	0.51279
N	0.49765	0.54347	0.51113
С	0.47998	0.57736	0.49147
С	0.42635	0.56011	0.48045
С	0.39056	0.50629	0.49013
С	0.40922	0.47184	0.50474
N	0.41118	0.59773	0.46279
С	0.36164	0.58839	0.4559
С	0.34889	0.62739	0.44725
С	0.38933	0.68238	0.44523
0	0.25894	0.5631	0.44317
Н	0.43856	0.63775	0.45794
Н	0.42157	0.38265	0.52789
Н	0.47545	0.33933	0.50782
Н	0.61294	0.49319	0.46352
Н	0.65551	0.44595	0.4713
Н	0.50935	0.61862	0.48823
Н	0.34873	0.4911	0.48462

Н	0.38218	0.42995	0.50912
Н	0.32949	0.5482	0.45867
Ni	0.56516	0.55921	0.55635
0	0.63354	0.57479	0.58413
0	0.5853	0.62747	0.61781
Cl	0.65469	0.56006	0.77388
Cl	0.57472	0.64226	0.83148
0	0.68182	0.53487	0.69448
0	0.61018	0.52489	0.89207
0	0.68905	0.60748	0.87343
0	0.53568	0.5947	0.92518
0	0.55577	0.67765	0.79144
0	0.62311	0.66643	0.93546

## 153 **Reference**

154 (1) Zhong, W.; Sa, R.; Li, L.; He, Y.; Li, L.; Bi, J.; Zhuang, Z.; Yu, Y.; Zou, Z. A Covalent Organic

155 Framework Bearing Single Ni Sites as a Synergistic Photocatalyst for Selective Photoreduction of CO2 to

- 156 CO. J. Am. Chem. Soc. 2019, 141, 7615–7621.
- 157 (2) Schneider, T. W.; Ertem, M. Z.; Muckerman, J. T.; Angeles-Boza, A. M. Mechanism of Photocatalytic
- 158 Reduction of CO2 by Re(Bpy)(CO)3Cl from Differences in Carbon Isotope Discrimination. ACS Catal.
- **2016**, *6*, 5473–5481.
- 160 (3) Yang, S.; Hu, W.; Zhang, X.; He, P.; Pattengale, B.; Liu, C.; Cendejas, M.; Hermans, I.; Zhang, X.;
- 161 Zhang, J.; Huang, J. 2D Covalent Organic Frameworks as Intrinsic Photocatalysts for Visible Light-Driven
- 162 CO2 Reduction. J. Am. Chem. Soc. 2018, 140, 14614–14618.
- 163 (4) Marenich, A. V; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron
- 164 Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic
- 165 Surface Tensions. J. Phys. Chem. B 2009, 113, 6378–6396.
- 166 (5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. a.; Cheeseman, J. R.; Scalmani,
- 167 G.; Barone, V. G16\_C01. 2016, p Gaussian 16, Revision C.01, Gaussian, Inc., Wallin.
- 168 (6) Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-Group Thermochemistry, Transition
- 169 Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions. J. Chem. Phys. 2006, 125,
- 170 194101.

- 171 (7) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry,
- 172 Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New
- 173 Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Function. *Theor. Chem.*
- 174 *Acc.* **2008**, *120*, 215–241.
- 175 (8) Tao, Y.; Zou, W.; Luo, G.-G.; Kraka, E. Describing Polytopal Rearrangement Processes of
- 176 Octacoordinate Structures. I. Renewed Insights into Fluxionality of the Rhenium Polyhydride Complex
- 177 ReH5(PPh3)2(Pyridine). *Inorg. Chem.* **2021**, *60*, 2492–2502.
- 178 (9) Agarwal, J.; Fujita, E.; Schaefer, H. F.; Muckerman, J. T. Mechanisms for CO Production from CO2
- 179 Using Reduced Rhenium Tricarbonyl Catalysts. J. Am. Chem. Soc. 2012, 134, 5180–5186.
- 180 (10) Dürr, A. B.; Fisher, H. C.; Kalvet, I.; Truong, K.-N.; Schoenebeck, F. Divergent Reactivity of a
- 181 Dinuclear (NHC)Nickel(I) Catalyst versus Nickel(0) Enables Chemoselective Trifluoromethylselenolation.
- 182 Angew. Chem. Int. Ed. Engl. 2017, 56, 13431–13435.
- 183 (11) Cammarota, R. C.; Vollmer, M. V; Xie, J.; Ye, J.; Linehan, J. C.; Burgess, S. A.; Appel, A. M.;
- 184 Gagliardi, L.; Lu, C. C. A Bimetallic Nickel–Gallium Complex Catalyzes CO2 Hydrogenation via the
- 185 Intermediacy of an Anionic D10 Nickel Hydride. J. Am. Chem. Soc. 2017, 139, 14244–14250.
- 186 (12) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple
- Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* 2005, *7*,
  3297–3305.
- (13) Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.* 2006, *8*, 1057–1065.
- 191 (14) Borodin, O.; Behl, W.; Jow, T. R. Oxidative Stability and Initial Decomposition Reactions of
- 192 Carbonate, Sulfone, and Alkyl Phosphate-Based Electrolytes. J. Phys. Chem. C 2013, 117, 8661–8682.
- (15) Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. J. Comput. Chem. 2012, 33,
  580–592.
- 195 (16) Shinde, D. B.; Aiyappa, H. B.; Bhadra, M.; Biswal, B. P.; Wadge, P.; Kandambeth, S.; Garai, B.;
- 196 Kundu, T.; Kurungot, S.; Banerjee, R. A Mechanochemically Synthesized Covalent Organic Framework

as a Proton-Conducting Solid Electrolyte. J. Mater. Chem. A 2016, 4, 2682–2690.

## Ultrafast charge transfer dynamics in 2D Covalent Organic Frameworks/Re-complex hybrid photocatalyst: Hot electrons vs. cold electrons

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Abstract: Rhenium(I)-carbonyl-diimine complexes have emerged as promising photocatalysts for  $CO_2$  reduction since their electronic structure is favorable for the two-electron transfer mediated reduction processes. Covalent organic frameworks (COFs) are recognized as perfect sensitizers for such Re-complexes catalysts as well as scaffold support to improve the  $CO_2$  capture. Such Re-complexes/COF hybrid catalysts have demonstrated high  $CO_2$  reduction activities, but the underlying photophysical mechanism has yet to be rationalized. In this paper, we systematically investigated the excited state dynamics of hybrid catalysts two-dimensional (2D) COF (TpBpy) with 2,2'-bipyridine incorporating Re(CO)<sub>5</sub>Cl (Re-TpBpy). The time-dependent density functional theory (TD-DFT) calculation first identified that the light absorption of Re-TpBpy is mainly contributed by a low energy optical transition barely in Bpy moiety, and the high energy optical transition evenly distributed at the whole COF moiety. Combining the studies from transient visible and infrared spectroscopies, we provided a full picture of the excited state dynamics in Re-TpBpy. The pathways of internal photo-induced charge transfer are highly excitation energy-dependent. Under band-edge excitation, the electrons excited at the LUMO level are quickly injected from Bpy moiety into Re<sup>I</sup> center within ps followed by backward geminate recombination about 13 ps. Under excitation with high energy photon, the photo-generated hot-electrons are first injected into the higher unoccupied level of Re<sup>I</sup> center within 1-2 ps and then relax back to the HOMO in COF with longer time (24 ps). In addition, there remain long-lived free electrons in the COF moiety. This can rationalize the excitation energy-dependent CO<sub>2</sub> reduction performance of the hybrid catalysts.

#### Introduction

The solar-driven photocatalytic conversion is regarded as one of the most promising approaches for CO2 transformation to tackle the rising issue of greenhouse gas emission<sup>1-7</sup>. Among the state-of-theart photocatalysts for CO2 reduction, Rhenium(I)-carbonyl-diimine complexes have attracted considerable attention due to their high photocatalytic quantum yield and selectivity for  $CO_2$  reduction<sup>8-12</sup>. In general, one photon excitation in the molecule can usually trigger one-electron transfer highly endergonic for CO<sub>2</sub> reduction<sup>10</sup>. The one-electron reduced (OER) Re-complexes is still energetically favorable to donate the second electron. This is vital for CO<sub>2</sub> reduction which is usually mediated by a two-electron transfer process<sup>8,9,11–15</sup>. However, the short excited-state lifetime and accessible annihilation of multi-excitons in the molecules remains an obstacle for such a process. In addition, the intrinsic <sup>1</sup>MLCT absorption transition in Re-complexes covers a limited spectral region (350-450 nm)<sup>13,16</sup>. Therefore Re-complexes are usually paired with suitable photosensitizer to provide efficient and long-lived excited electrons

for photocatalytic reaction<sup>17-20</sup>. One emerging stradigy is to immobilize such Re-complexes into porous scaffolds such as covalent organic frameworks (COFs) to construct heterogeneous molecular photocatalysts<sup>21-24</sup>. COFs are porous crystalline polymeric materials constructed by covalently bonded organic building blocks with highly ordered and periodic network structures<sup>25,26</sup>. The extended  $\pi$ -conjugation ensures broad light absorption and high charge conductivity<sup>22</sup>. Equally important, the porous structure with the large surface area provides numerous active sites for CO<sub>2</sub> capture and catalytic reaction<sup>27,28</sup>. Recent studies reported high photocatalytic CO2 reduction activity on such Re-complex/COFs hybrid systems, which were rationalized by the efficient intramolecular charge transfer (ICT) from COF units to Re-complexes<sup>22,23</sup> However, the detailed charge transfer dynamics have not been thoroughtly understood. In fact, the charge transfer pathways in Re-complex/COFs hybrids can be complicated. Taking the two-dimensional (2D) donor-acceptor (2D D-A) COFs as an example, the high degree of  $\pi$ conjugation imparts a semiconducting behavior while the polaron formation reduces the exciton binding energy <sup>29,30</sup>. In addition, the early-time (i.e. subpicosecond to picosecond) excited state dynamics in COFs comprises multi-steps inter-unit charge transfer. Such process may compete or modulate the ICT, which should occur within a similar time scale<sup>29</sup>. energy-dependent photocatalytic reaction mechanism in such Recomplex/COFs hybrid system, which can be beneficial for future materials engineering towards optimal photocatalytic performance.

Another imperative topic worth investigating is the dynamics of the



Results

**Figure 1.** (a) Schematic structure of the Re-TpBpy; (b) FT-IR spectra of TpBpy, Re-TpBpy and their starting materials with the right panel showing the molecular structure of the corresponding unit.

hot carriers excited by the high energy photons above the bandgap of the COFs. In traditional semiconductors, the hot carriers quickly thermalize to the band edge. Harvesting the energy of the hot carriers without loosing it as thermal energy is a crucial step to break the 33% Shockley–Queisser thermodynamic efficiency limit of a standard single-junction solar cell<sup>31</sup>. The same gain in energy conversion efficiency can be expected in photocatalytic reactions <sup>31–35</sup>. Considering exsitance of inter-unit charge transfer during the excited state relaxation process in 2D D-A COFs which can be governed by the molecular assembly, the hot carrier collection should be feasible in Re-complex/COFs but requires experimental evidence.

Herein, taking a 2D COF (TpBpy) with 2,2'-bipyridine incorporating Re(CO)5Cl, named Re-TpBpy, as an example, we demonstrate the excited state dynamics and charge transfer process in the hybrid. The time-dependent density functional theory (TD-DFT) calculations first displays the available electronic transition after excitation of the hybrids. The femtosecond transient visible (fs-TA) and Time-resolved infrared (fs-TRIR) absorption spectroscopies provide complementary information for the charge transfer dyanmics. Photons with energy close to the bandgap of the COF directly excite the electron from ground state to the excited states of Bpy followed by sub-picosecond electron injection to Re(CO)<sub>3</sub>Cl. However, the injected electrons rapidly undergo geminated recombination with the residual holes in the COFs moiety within 13 ps. When the excitation is well above the band edge, the hot electrons and holes are initially generated evenly crosswise the entire COF. Hot electrons would directly inject into the higher energy orbital of Re(CO)<sub>3</sub>Cl within 2 ps and rebound to the Bpy within 24 ps. The hot holes slowly relax to the HOMO level of COFs (340 ps). The prolonged excited electron lifetime in Re(CO)<sub>3</sub>Cl and the higher energy levels, together with the additional long-lived free electrons in COF moiety contributes as merits for a two-electron transfer mediated CO<sub>2</sub> catalytic reaction. Our study rationalizes the excitation

#### Characterization of TpBpy and Re-TpBpy.

Re-TpBpy is constructed by long-range ordered 2D sheets through the layer to layer stacking as shown in Fig.1a. The characterization of TpBpy and Re-TpBpy was achieved by powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), and Fourier Transform Infrared (FT-IR). PXRD patterns of both TpBpy and Re-TpBpy match well with the simulated AA stacking structure in the hexagonal space group (P6). After Re-complex incorporation, the crystalline structure of TpBpy remains unchanged. The XPS spectra confirmed the anchoring of Re-complex to the host TpBpy only through its bipyridinic units<sup>24</sup> (for detailed XRD and XPS characterization, see Fig. S2 and S3 in the supporting information). The FT-IR spectrum (Fig. 1b) of Re-TpBpy manifest the preserved chemical functionalities of pristine TpBpy while two additional peaks arising at 2025 cm<sup>-1</sup> and 1887 cm<sup>-1</sup> can be attributed to the C=O stretching vibration in the Re(CO)<sub>3</sub>Cl moiety<sup>23</sup>. Additionally, compared with the FT-IR spectrum of Re(CO)5Cl and TpBpy, the C=O stretching bonds and the broadened C-N peak in the Re-TpBpy are slightly red-shifted, indicating the coordination of Re(CO)<sub>3</sub>Cl to the bipyridinic N atoms in the TpBpy. Our FT-IR result also excludes the existence of residual Tp and Bpy in both as-synthesized TpBpy and Re-TpBpy.

#### Steady-state spectroscopic study

Steady-state absorption and PL spectra first clarified the ground state features of the Re- TpBpy hybrid and its individual units (Fig. 2a). The absorption spectra of the pure Tp and Bpy both showed a single distinct absorption band of Tp (350-400 nm) and S1 of Bpy (380 nm). The absorption spectrum of Re-Bpy is identical to Bpy except for a subtle blue shift (maxima absorption at 360 nm) owing to the metal-to-ligand charge transfer (MLCT)  $[d(Re)-\pi^*(bpy)]^{36,37}$  On the contrary, the absorption spectrum of TpBpy exhibits dual



**Figure 2.** (a) Normalized UV–vis absorption (black) and steady-state photoluminescence spectra excited at 400 nm (red) and 530 nm (blue) of TpBpy, Re-TpBpy and their starting materials dispersed in Nafion (5% w/w in water and 1-propanol); (b) Tauc plots of the absorption spectra determining the optical band gap of TpBpy, Re-TpBpy, and their starting materials; (c) XPS VB spectra, and (d) band alignment established from XPS and UV-vis measurement of TpBpy, Re-TpBpy, and their starting materials.

absorption bands with a narrow bipyridine  $n-\pi^*$  transition band (324 nm) as well as a broad band at 508 nm for delocalized  $\pi$  electrons<sup>38</sup>. The similar absorption spectra between Re-TpBpy and TpBpy suggest the high ligand stability (i.e. chromophore function) after functionalization<sup>24</sup>. The slight blue shift of the spectrum for Re-TpBpy should be due to the metal-to-ligand charge transfer (MLCT) [d(Re)- $\pi^*$ (bpy)].

Fig. 2a also shows the emission spectra of all samples excited at the band edge(530 nm, blue curve) and well above the band edge (400 nm, red curve). Tp and Bpy share the same emission band at 500 nm upon the 400 nm excitation with moderate Stokes shift. In contrast, the emission spectrum of the Re-Bpy ( $\lambda em = 585 \text{ nm}$ ) is broad with large Stokes shift ( $\Delta\lambda$ =225 nm), which can be attributed to the existence of a triplet metal-to-ligand charge-transfer (3MLCT) states <sup>39</sup>. When excited at 530 nm, the emission spectra of TpBpy and Re-TpBpy are identical with emission bands at 620 nm. This indicates similar emissive states from delocalized  $\pi$  electrons in the two samples. When excited at higher energy (400 nm), the emission spectra of TpBpy and Re-TpBpy exhibit dual emission bands (i.e., 427 nm and 531 nm for TpBy, 431 nm, and 562 nm for Re-TpBpy). The origins of such multi-emission bands in COFs can be complicated where one hypnosis is the radiative recombination in the single units of the COF.<sup>40</sup> We can obtain the same conclusion in the following analysis of the excited states. In summary, the optical transitions of TpBpy and Re-TpBpy are distinct from the ones of their original building block units. We can further calculate the optical band gaps (E<sub>g</sub>) of Tp, Bpy, Re-Bpy, TpBpy and Re-TpBpy from the Tauc plots of the absorption spectra (Fig. 2b) to be 3.14 eV, 2.79 eV, 2.90eV, 2.26 eV, and 2.17 eV, respectively. The characterization with XPS determines the valence band maximum (VBM) position of Tp, Bpy, Re-Bpy, TpBpyand Re-TpBpy to be 1.43 eV, 1.99 eV, 0.96 eV, 1.89 eV, and 0.99 eV corresponding to the Fermi level, respectively (Fig. 2c). Based on such values, we can determine the band energy alignment of the samples, as shown in Fig. 2d.

#### Excited state structures

In order to obtain insight into the excited-state structure of the compounds, we used a triformylphloroglucinol (Tp) terminated bipyridine (Bpy) molecular fragment (Fig. 3) to represent the COF structure. The TD-DFT at the M06-L<sup>41-44</sup> /def 2 TZVP<sup>45,46</sup> level of theory has been employed to calculate the electronic structure and model the electronic transitions. Fig. 3 exhibits the calculated electronic excitation spectra of the TpBpy and Re-TpBpy (orange curves), which can resemble the experimental absorption spectra (red curves). The calculated spectrum of TpBpy mainly consists of two electronic excitation bands at 528 nm (S<sub>1</sub>) and 436 nm (S<sub>2</sub>), where high energy band  $S_2$  is equally contributed by the electronic transition (HOMO-3  $\rightarrow$  LUMO+1) and (HOMO  $\rightarrow$  LUMO+2). The low energy band S<sub>1</sub> is dominated by the electronic transition from HOMO to LUMO level as illustrated in Fig. 3a. The low energy optical transition only occurs at the Bpy moiety whereas the high energy transition involves the electron population at both Tp and Bpy in the COF moieties. The modeled spectrum of Re-TpBpy also shows two pronounced electronic excitation bands where the high energy band is contributed by two electronic transition S<sub>3</sub> (HOMO  $\rightarrow$  LUMO+2, 427 nm) and S<sub>2</sub> (HOMO-4  $\rightarrow$  LUMO+1, 441 nm) (Fig. 3b). The low energy band consists of one electronic transition  $S_1$  (HOMO-2  $\rightarrow$  LUMO+1, 558 nm). Compared with TpBpy, the low energy electronic transition in Re-TpBpy involves the excitation of the electron from the orbital in both Tp and Bpy moieties. The detailed calculated orbitals for both samples have been summarized in the supporting information.



**Figure 3.** UV-vis absorption spectra of a) TpBpy and b) Re-TpBpy compared with TD-DFT calculated fragment.

#### **Time-resolved Photoluminescence**

In the next step, we studied the photoluminescence (PL) dynamics of the samples. The steady-state PL spectra of TpBpy and Re-TpBpy are identical in terms of emission energy and spectral shapes (Fig. 4a). However, the relative PL quantum yield (extracted from absorption calibrated PL intensities) of Re-TpBpy is much lower. This should be attributed to the PL quenching by the integration of the Re-complex. The shorter PL lifetime of Re-TpBpy measured from time-correlated single-photon counting (TCSPC) verify the additional non-radiative process (Fig.4b). The exponential fitting can resolve two components with lifetimes of 1.1ns (91%), 19ns (9%) for TpBpy and 716ps (92%), 40ns (8%) for Re-TpBpy. However, the lifetime of the fast components (i.e. 1.1 ns for TpBpy and 716 ps for Re-TpBpy) are limited by the response function in the TCSPC measurement. Therefore streak camera technique was employed to explore the ultra-fast process. A similar faster PL decay of Re-TpBpy than TpBpy can be observed in Fig.4c. The PL decays can be fitted by tri-exponential functions. The two fast components can then be fitted as 106 ps (74%), 481 ps (24%) for TpBpy and 98 ps (66%), 340 ps (31%) for Re-TpBpy.

(A1) where the excitons are self-trapped within the local structure of the COF<sup>29</sup>. Such polaron formation also complies with the significant stokes shift from the PL spectra, as shown in Fig. 2a.



**Figure 4.** (a) Steady state PL emission spectra of TpBpy and Re-TpBpy normalized according to the absorbance at the excitation wavelength; (b) PL decays measured in TCSPC of the TpBpy and Re-TpBpy. Excitation wavelength=438 nm; (c) PL decays of the TpBpy and Re-TpBpy measured with streak camera excited at 400 nm.

#### Femtosecond transient visible absorption spectroscopy.

The excited-state dynamics of the samples were explored by transient absorption (TA) spectroscopy. We first excited the samples close to their band edge at 530 nm. In this case, all the excited species should populate the lowest excited states instantly. The TA spectra of TpBpy exhibit one broad negative band (B1) from 450 to 595 nm attributed to the band-edge ground state bleach (GSB) together with two positive excited state absorption bands (ESA, A1 and A2) from 600 nm to 700 nm (Fig. 5a). According to the above DFT calculation in Fig. 3a, 530 nm excitation will only trigger the transition to the lowest excited state (i.e. HOMO to LUMO) in TpBpy. Hence, A1 and A2 here should not be attributed to different levels of the excited state. One possible explanation is the excited state transform from a normal exciton state (A2) to a polaron state For Re-TpBpy, only one B1 can be observed with the absence of long-lived ESA (Fig. 5b). This already indicates the charge transfer from the excited states. A more quantitative analysis was then implemented using singular value decomposition (SVD) fitting (Fig. 5a&b, lower panel). The TA dynamics of TpBpy can be decomposed into four decay-associated components ( $t_1$ -  $t_4$ ). The first three components ( $t_1$ -  $t_3$ ) shared the same negative GSB signal with the identical position (B1), denoting the population of the lowest excited state. The difference between the first component ( $t_1 = 2$  ps) with the second and third components ( $t_2 = 70$  ps and  $t_3 = 4$  ns) appears as the blue-shifted ESA band from A2 to A1 by about 50 nm. TA kinetics at the A1 (Fig. 5d) and A2 (Fig. 5e) reveal the concurrent rising of A1 and decay of A2. This indicates the transformation of the lowest excited state (e.g. polaron formation) within 2 ps corresponding to the transition of ESA from A2 to A1



**Figure 5.** Transient absorption (TA) spectra under 530 nm excitation at the fluence of  $2 \times 10^{13}$  ph/cm<sup>2</sup> and the respective SVD fitting results of TpBpy (a), and Re-TpBpy (b). TA kinetics at some characteristic wavelength of B1 at 535 nm (c), A1 at 625 nm (d), and A2 at 675 nm (e). All the samples were measured in Nafion (5% w/w in water and 1-propanol) solution.

in TA spectra. Components 2 and 3 exhibits the same spectral feature corresponding to the depopulation dynamics of the same lowest excited state. The slowest component 4 featured as broad negative band with a lifetime exceeding the TA time window. This can also be visualized in the TA kinetics in Fig. 5c-e. After functionalization by the Re-complex, the TA dynamics of Re-TpBpy can also be decomposed into four components ( $t_1$ -  $t_4$ ) with lifetime of  $t_1$  = 990 fs,  $t_2$  = 13 ps,  $t_3$  = 262 ps accompany with one ultra-long component ((Fig. 5b). Component  $t_1$ -  $t_3$  of Re-TpBpy resembles the GSB feature as TpBpy but with shorter lifetimes as evidenced by the comparison of B1 kinetics in Fig. 5c. Most importantly, ESA bands are completely absent in components  $t_2$  and  $t_3$ . This suggest the ultrafast charge transfer from the lowest excited state. In addition, the longest component  $t_4$  also exhibits narrower GSB at the band edge position compared with GSB in component  $t_4$  of TpBpy. = 2 ps,  $t_2 = 24$  ps,  $t_3 = 340$  ps and one ultra-long component). The features of component  $t_1$  resemble those of TpBpy with a similar lifetime of 2 ps. Compared with 530 nm excitation, B2 with 400 nm excitation are long-lived in both  $t_1$ -  $t_3$  up to 340 ps. The prolonged B2 band in Re-TpBpy suggests that the long-lived high energy level population in contrast to TpBpy as further illustrated by the TA kinetics in Fig. 6d. Furthermore, A1 disappears in component  $t_2$  and reoccurs in  $t_3$ . This is consistent with the different A1 kinetics (Fig. 6e, red curve) from the B1 and B2 kinetics (Fig. 6c&d, red curve) especially at the timescale between 5 to 20 ps. The absence of A1 in component  $t_2$  can be induced by two possible scenarios: 1) there exist two pools of Re-TpBpy where electron transfer from TpBpy to Re<sup>I</sup> occurs in one pool and absent in the other. 2) the charge transfer of hot electrons from the COFs to Re<sup>I</sup> centers is followed by the back-transfer to the LUMO level. In the



**Figure 6.** Transient absorption (TA) spectra under 400 nm excitation at the fluence of  $2 \times 10^{13}$  ph/cm<sup>2</sup> and the respective SVD fitting results of TpBpy (a), and Re-TpBpy (b). ). TA kinetics of two samples at various emission wavelengths representing B1 (c), B2 (d), A1 (e), A2 (f). All spectra are recorded in Nafion (5% w/w in water and 1-propanol).

In order to monitor the dynamics of hot carriers, high energy excitation has also been employed in both samples. Compared with TA spectra excited at 530 nm, here the TA spectra of both TpBpy and Re-TpBpy (Fig.6a&b) exhibit one additional negative band (B2) around 450 nm (Fig. 6) with the slight red-shifted B1 to 515 nm. Since B2 appears in both TpBpy and Re-TpBpy, the additional bleach band should be attributed to the population of high energy/hot levels in the COFs unit. SVD fitting indicates that the dynamics of TpBpy can be described by four main components. The fastest component t1 (2 ps) consists of B1, B2, and A1. Component t<sub>2</sub> (34 ps) features the same B1 and B2 bands but the ESA is blueshifted to A2. The component t<sub>3</sub> (480 ps) lifetime shares almost the same spectral features of component 2 except for the absence of B2. A similar lifetime (481 ps) can also be extracted in the PL decay of TpBpy (Fig. 4c), manifesting the radiative recombination of the band-edge charge carriers. The component t4 only contains B1 but the contribution is negligible. The above SVD analysis indicates the long-lived B1 versus short-lived B2 as also evidenced by the extracted TA kinetics in Fig. 6c and d (blue curve).

On the other hand, both A1 and A2 appear instantaneously which is different from the one observed for 530 nm excitation. TA spectra of Re-TpBpy can also be fitted with four main components ( $t_1$  following, we will demonstrate the latter is more likely evidenced by time-resolved IR spectroscopy results, which probes the transient population of electrons at Re<sup>I</sup> centers. The lifetime  $t_3$  (340 ps) can be obtained from the TRPL decay in Fig. 4c, manifesting radiative recombination with hot carriers, which accounts for the high energy emission band in the steady-state PL spectrum (Fig. 2a). Identical to TpBpy, component 4 of Re-TpBpy comprises only B1 with negligible amplitude. In short, the additional B2 band and the wider ESA band when excited at 400 nm in components  $t_1$ ,  $t_3$  reflect the long-live hot excited level population. On the other hand, the absence of A1 in component  $t_2$  confirms the charge transfer of hot electrons to Re<sup>I</sup> centers within 2 ps.

#### Femtosecond transient infrared absorption spectroscopy

In order to further characterize the excited state dynamics at the two excitation wavelengths, we measured the time-resolved IR (TRIR) spectra of the samples. TRIR can probe photo-induced electronic transitions at low energy such as molecular vibrations or intraband free carriers<sup>47–51</sup>. No TRIR signal can be observed in neither TpBpy nor Re-Bpy when excited at 530 nm (Fig.7a and Fig. 7b). However, the TRIR spectrum of Re-TpBpy exhibits pronounced differential dips at 1850 cm<sup>-1</sup> and 2040 cm<sup>-1</sup> (Fig. 7c), resembling

the spectral feature of pure Re-Bpy excited at 400 nm (Fig.7f). Such differential dips are the fingerprint features of excited [Re<sup>I</sup>(bpy)(CO)3]\* as the C-O stretching vibration is perturbed due to the formation of Re radical species<sup>52</sup>. The TRIR kinetics in Fig. 7d suggests that the Re<sup>I</sup> radical is formed within 0.6 ps (rising time of the kinetics) together with 2 decay lifetimes (15 ps and 2.3 ns). Such formation time of the Re<sup>I</sup> radical is consistent with t<sub>1</sub> in TA components (0.99 ps) (Fig. 5b), confirming the sub-picosecond electron transfer from TpBpy to the Re<sup>I</sup> center after excitation. The 15 ps decay lifetime is identical to the component t<sub>3</sub> in TA (Fig. 5b). When excited at 400 nm, the TRIR spectra of both TpBpy and Re-TpBpy are dominated by the featureless positive absorption (Fig. 7 e&g), which is widely accepted as the sign of free carrier generation in semiconductor materials<sup>47,53,54</sup>. This means that the hot excited states reflected by the B2 and the broad A1 band in TA should all be populated by free carriers when excited at 400 nm. Moreover, the TRIR spectrum in Re-TpBpy features additional differential dips of the Re<sup>I</sup> radical, indicating the COFs-Re electron transfer occurs. We can decompose the dynamics of Re<sup>I</sup> radical (orange curve, Fig. 7h) by subtracting the TA kinetics at such mixed region (2040 cm<sup>-1</sup>, red curve, Fig. 7h) by the kinetics at the region only showing positive absorption (1850 cm<sup>-1</sup>, blue curve, Fig. 7h). Here the intensity of TA kinetics at 1850 cm<sup>-1</sup> is scaled up by the amplitude ratio between 1850 cm<sup>-1</sup> and 2040 cm<sup>-1</sup> as extracted in Fig. 7g ( $A_{2040 \text{ cm}-1}/A_{1850 \text{ cm}-1} = 1.9$ ) with only free carrier contribution in COFs. The deferential kinetics (i.e. the orange curve in Fig. 7H) shows a 0.8 ps building up time followed by a 26 ps decay, which is consistent with the above argumentation that the hot electrons are injected to Re<sup>I</sup> center within the picosecond and rebounce to the S1 level of TpBpy in 26 ps. We also notice that such kinetics is different from the depopulation of photo-excited pure [Re<sup>I</sup>(bpy)(CO)3]\* (green curve, Fig. 7h). This means the back transfer or geminate recombination of injected electrons in Re<sup>I</sup> center is faster than the electron-hole recombination in the Re<sup>I</sup>(bpy) moiety.

#### Discussion

#### **Cold Electron Injection**

The TD-DFT calculations indicate the 530 nm excitation can only generate an electronic transition from HOMO to LUMO (S1) in TpBpy, which merely locates at Bpy moiety (Fig. 3a). The TRIR results further suggest that the dominant excited species are excitons. Such bounded exciton formation is reasonable as the photogenerated electrons and holes are close in space in Bpy. The ESA transition from A2 to A1 in TA spectra in Fig. 5a should represent the formation of exciton polarons from initially generated excitons. The following up excited state depopulation at hundreds of ps can be observed in both the TA and TRPL results. We confirmed that the lifetime of such a process is highly dependent upon the excitation intensity (for details, see S8b). This indicates that the high order recombination of excited singlet excitons, which is often observed in conjugated polymers and semiconductor nanostructrues<sup>55-58</sup>. Previous research reports such ultrafast singlet-singlet exciton annihilation in COFs materials followed by the formation of ultra-long-lived specially separated charges<sup>30</sup>. However, the absence of free carriers over the whole time-window suggests that the residual excited state species are still excitons instead of free carriers in our COF. However, the lifetime of such excitons varies according to the relative spatial location. The short lifetime (4 ns) should refer to the excitonic recombination within the same COFs sheet, while the ultra-long lived exciton may contain the electrons



**Figure 7.** 7 TRIR spectra of TpBpy, Re-Bpy, and Re-TpBpy excited at 530 nm (a-c) and 400 nm (e-g). (d) TRIR kinetics at 2040 cm<sup>-1</sup> of Re-TpBpy excited at 530 nm. (h) TRIR kinetics at 2040 cm<sup>-1</sup> (red), 1850 cm<sup>-1</sup> (blue) and their differential curve (orange) of Re-TpBpy excited at 400 nm. The kinetics at 2040 cm<sup>-1</sup> of Re-Bpy excited at 400 nm is also presented (green). All spectra are recorded in Nafion (5% w/w in water and 1-propanol).

and holes at a different sheet of  $COFs^{30,59}$ . Fig. 8a summarizes the observed excited-state dynamics.

In Re-TpBpy, the electronic transition from the HOMO-2 to the LUMO (Fig. 3b) corresponds to a partial charge transfer state as the HOMO-2 locates at the orbitals over both Tp and Bpy moiety according to the calculation. The sub-picosecond depopulation of excited states in the TA spectra combined with rising of transient Re<sup>I\*</sup> radical formation spectra in TRIR can be unambiguously assigned to the electron transfer from the LUMO located at Bpy to the Re<sup>I</sup> center within 0.8-0.9 ps as shown in Fig. 8b. However, as holes can reside both at Tp and Bpy, we can expect different depopulation pathways of those holes after electron injection corresponding to two-lifetime components in TA (t2 and t3) (Fig. 5b). Holes at Bpy should undergo fast germinate recombination with electrons at Re<sup>I</sup> center due to the short distance between electrons and holes (13 ps), which is consistent with the same decay component (15 ps) in TRIR (Fig. 7d) demonstrating the concurrent depopulation of electrons. On the other hand, those holes at Tp should be implausible to recombine with remote electrons at Re<sup>I</sup> directly, instead, they will cool down to the HOMO level with relatively long time (262 ps) which is still strongly localized in Tp (for detailed electronic structure see Table S3). Such slow cooling time may be due to the necessary inter-unit (e.g. Tp to Bpy, or Bpy to Tp) charge transfer in the cooling pathway. Therefore recombination between those holes and electrons in Re<sup>I</sup> center will be inefficient, corresponding to the long component in both TA (Fig. 5b) and TRIR (Fig. 7d). The above analysis suggests the low energy excitation in Re-TpBpy is very close to the Re-COF interface, thus facilitating the electron injection from the COFs to the Re<sup>I</sup> center. However, geminate recombination is also efficient due to the close spacing between the injected electron and residual holes in COF moiety, as summarized in Fig. 8b.

TD-DFT calculation demonstrates at high-energy photon excitation condition, TpBpy will have a transition from HOMO→LUMO+2 and HOMO-3→LUMO+1 (Fig. 3a), while Re-TpBpy will exhibit an electronic transition from HOMO→LUMO+2 and HOMO- $4\rightarrow$ LUMO+1 (Fig. 3b). Compared with low energy excitation, the excited states are distributed more evenly through the Tp and Bpy. In addition, the TRIR results suggest that the initially excited species include free carriers resided at those high energy levels. The initial fastest component t1 in TA measurement (Fig. 6a) should be related to the partial polaron formation where some of the generated species also remain as free carriers as evidenced by the remaining A2 after 2 ps and the free carries absorption in the TRIR spectra. The dual emission band in steady state PL of Fig. 2a supports that the excited state depopulation should involve two parallel processes with radiative recombination from the higher level and lowest excited state. In TpBpy, the population of hot electrons at the LUMO+2 and the LUMO+1 as well as hot holes at the HOMO-3 contributed to the B2 in Fig. 6a while hole population at HOMO leads to the B1 consistent with the band edge GSB at 530 nm excitation. t<sub>2</sub> component in TA (Fig. 6a) features concurrent B1 and B2 should then be attributed to the radiative recombination between the electron at LUMO+1 and hole at HOMO-3 leading to the high energy PL emission. T<sub>3</sub> component, on the other hand, should be attributed to the recombiniation bewteen electrons and holes relaxed to the HOMO and LUMO level. Fig. 8c summarized the state dynamics.

As summarized in Fig. 8d, at Re-TpBpy, the excited electron at LUMO+2 and LUMO+1 would be injected to Re<sup>I</sup> center within 2 ps and then recombines to HOMO at Bpy within 24 ps resolved by the complementary dynamics observed in the TA and TRIR measurements, as shown in Fig. 8d. This can be due to either the hot electron injection through the higher excited states in Re<sup>I</sup> center or to the formation of a charge-transfer state (CTS) due to the Coloumbic attraction between injection electron in Re<sup>I</sup> and residual



Figure 8. Schematic diagram of the pathway and lifetime excited state dynamics of TpBpy and Re-TpBpy under a&b) 530 nm, and c&d) 400 nm excitation.

#### **Hot Electron Injection**

hole in COF followed by the dissociation of such CTS. Both pathways are well-observed in other molecular or semiconductor systems<sup>60,61</sup>. Such a 24 ps lifetime for such intermediate excited state can be a merit for hot-carrier harvesting. After hot carrier cooling, the depopulation of the excited states also depends on the spatial location of the charge carriers. If the hole locates at Bpy orbitals (HOMO-4 level at S<sub>2</sub> in Fig. 3b), the hot carrier emission will occur similarly to the case of TpBpy with lifetime of 340 ps corresponding to the t<sub>3</sub> component observed in TA (Fig. 6b), since the hot hole cooling to the HOMO in Re-TpBpy is hindered by the additional Bpy-to-Tp charge transfer. If hole locates at Tp orbitals in HOMO (S<sub>3</sub> in Fig. 3b), it will recombine with the relaxed electron at LUMO both radiatively and nonradiatively but with a longer lifetime as observed in both the TA and TRPL spectras. energy bands contributed by the transition from ground state to excited state barely in Bpy moiety and the high-energy bands features the unoccupied orbital is contributed evenly by the whole COFs moiety. Combining the observations of the excited dynamics resolved both in TA and TRIR, entirely different inter-unit charge transfer pathways in Re-TpBpy can be identified. Under band-edge excitation, the electrons excited at the HOMO level would quickly injected into Re<sup>I</sup>(bpy)(CO)<sub>3</sub>Cl within ps timescale and recombine within ns with the holes residing in Bpy close to Re center at about 13 ps. Under excitation with high energy photon, the photo-generated hot-electron is first injected into the highly excited level of Re<sup>I</sup>(bpy)(CO)<sub>3</sub> within 1-2 ps and recombine to the HOMO in COF within 24 ps. In addition, there remains long-lived free carriers in the COF moiety. This can rationalize the good photocatalytic CO<sub>2</sub> reduction performance of the obtained catalysts.



Figure 9. Photocatalytic evolutions of CO by Re-TpBpy under 520 nm and 440 nm excitation (a) and Schematic diagram to rationalize the catalytic performance under two excitation conditions (b).

#### Influence to the photocatalytic reaction:

The above analysis on the excited state dynamics of TpBpy and Re-TpBpy suggest that anchoring Re-complex into COFs structure does facilitate the charge separation for the photocatalytic reduction process. However, when high excitation photon energy is used, efficient hot electron injection would occur from TpBpy to higher energy orbital of Re-complex with the electron lifetime at Re<sup>I</sup> center almost doubled compared to the lifetime with 530 nm excitation. In contrast to the conventional semiconductor where the photo-generated hot electrons will quickly dissipate energy and relax to the lowest excited state, the unique electronic structure of the Re-TpBpy catalyst is expected to boost the photocatalytic performance from hot carriers. The following CO2 photocatalytic reduction experiment confirmed our assumption. The evolution of CO by our Re-COFs catalyst exhibit a much higher yield when 440 nm excitation is used compared with band-edge excitation at 520 nm (Fig. 9a), which should be attributed to 1) injected electrons are located at high energy levels in Re<sup>I</sup> centers with longer lifetime which favorable for the electron transfer process for the CO2 reduction, and 2) when excited with high energy besides the injected electrons to Re<sup>I</sup> center, there still remain long-lived electrons in COF moiety which is transferred back from Re<sup>I</sup>. This makes the two-electron reaction of CO2 conversion to CO to work as illustrated in Fig. 9b.

#### Conclusion

In this paper, we investigated the excited state dynamics with focus on the ultrafast charge transfer in Re<sup>I</sup>(bpy)(CO)<sub>3</sub>/TpBpy hybrid photocatalyst by complementary time-resolved laser spectroscopies and numerical methods. We first determine the electronic transition of the hybrid structure using time-dependent DFT calculations to model the optical absorption. We found that the absorption spectrum of Re-TpBpy mainly consists of two bands with the low

#### REFERENCES

1.Song, C. Global challenges and strategies for control, conversion and utilization of CO2 for sustainable development involving energy, catalysis, adsorption and chemical processing. *Catal. Today* **115**, 2–32 (2006).

2.Omae, I. Aspects of carbon dioxide utilization. *Catal. Today* **115**, 33–52 (2006).

3.Wu, J., Huang, Y., Ye, W. & Li, Y. CO2 Reduction: From the Electrochemical to Photochemical Approach. *Adv. Sci.* **4**, 1700194 (2017).

4.Tu, W., Zhou, Y. & Zou, Z. Photocatalytic Conversion of CO2 into Renewable Hydrocarbon Fuels: State-of-the-Art Accomplishment, Challenges, and Prospects. *Adv. Mater.* **26**, 4607–4626 (2014).

5.INOUE, T., FUJISHIMA, A., KONISHI, S. & HONDA, K. Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. *Nature* **277**, 637–638 (1979).

6.Wang, C., Sun, Z., Zheng, Y. & Hu, Y. H. Recent progress in visible light photocatalytic conversion of carbon dioxide. *J. Mater. Chem. A* **7**, 865–887 (2019).

7.Roy, S. C., Varghese, O. K., Paulose, M. & Grimes, C. A. Toward Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons. *ACS Nano* **4**, 1259–1278 (2010).

8. Takeda, H. & Ishitani, O. Development of efficient photocatalytic systems for CO2 reduction using mononuclear and multinuclear metal complexes based on mechanistic studies. *Coord. Chem. Rev.* **254**, 346–354 (2010).

9.Schneider, T. W., Ertem, M. Z., Muckerman, J. T. & Angeles-Boza, A. M. Mechanism of Photocatalytic Reduction of CO2 by Re(bpy)(CO)3C1 from Differences in Carbon Isotope Discrimination. *ACS Catal.* **6**, 5473–5481 (2016).

10.Yamazaki, Y., Takeda, H. & Ishitani, O. Photocatalytic

reduction of CO2 using metal complexes. *J. Photochem. Photobiol. C Photochem. Rev.* **25**, 106–137 (2015).

11.Hori, H., Johnson, F. P. A., Koike, K., Ishitani, O. & Ibusuki, T. Efficient photocatalytic CO2 reduction using [Re(bpy) (CO)3 {P(OEt)3}]+. *J. Photochem. Photobiol. A Chem.* **96**, 171–174 (1996).

12.Haweeker, J., Lehn, J.-M. & Ziessel, R. Efficient photochemical reduction of CO2 to CO by visible light irradiation of systems containing Re(bipy)(CO)3X or Ru(bipy)32+–Co2+ combinations as homogeneous catalysts. *J. Chem. Soc. Chem. Commun.* 536–538 (1983) doi:10.1039/C39830000536.

13.Takeda, H., Koike, K., Morimoto, T., Inumaru, H. & Ishitani, O. Photochemistry and photocatalysis of rhenium(I) diimine complexes. in *Inorganic Photochemistry* (eds. Eldik, R. van & Stochel, G. B. T.-A. in I. C.) vol. 63 137–186 (Academic Press, 2011).

14.Koike, K. *et al.* Key Process of the Photocatalytic Reduction of CO2 Using [Re(4,4'-X2-bipyridine)(CO)3PR3]+ (X = CH3, H, CF3; PR3 = Phosphorus Ligands): Dark Reaction of the One-Electron-Reduced Complexes with CO2. *Organometallics* **16**, 5724–5729 (1997).

15.Yamazaki, Y., Takeda, H. & Ishitani, O. Photocatalytic reduction of CO2 using metal complexes. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* vol. 25 106–137 (2015).

16.Vlček, A. Ultrafast Excited-State Processes in Re(I) Carbonyl-Diimine Complexes: From Excitation to Photochemistry BT -Photophysics of Organometallics. in (ed. Lees, A. J.) 115–158 (Springer Berlin Heidelberg, 2010). doi:10.1007/3418 2009 4.

17.Qiao, X. *et al.* Well-Defined Nanographene–Rhenium Complex as an Efficient Electrocatalyst and Photocatalyst for Selective CO2 Reduction. *J. Am. Chem. Soc.* **139**, 3934–3937 (2017).

18.Huang, R., Peng, Y., Wang, C., Shi, Z. & Lin, W. A Rhenium-Functionalized Metal–Organic Framework as a Single-Site Catalyst for Photochemical Reduction of Carbon Dioxide. *Eur. J. Inorg. Chem.* **2016**, 4358–4362 (2016).

19.Faustino, L. A. *et al.* Photocatalytic CO2 Reduction by Re(I) Polypyridyl Complexes Immobilized on Niobates Nanoscrolls. *ACS Sustain. Chem. Eng.* **6**, 6073–6083 (2018).

20.Windle, C. D. *et al.* Improving the Photocatalytic Reduction of CO2 to CO through Immobilisation of a Molecular Re Catalyst on TiO2. *Chem. – A Eur. J.* **21**, 3746–3754 (2015).

21.Xu, R. *et al.* Rhenium-modified porous covalent triazine framework for highly efficient photocatalytic carbon dioxide reduction in a solid-gas system. *Catal. Sci. Technol.* **8**, 2224–2230 (2018).

22.Yang, S. *et al.* 2D Covalent Organic Frameworks as Intrinsic Photocatalysts for Visible Light-Driven CO2 Reduction. *J. Am. Chem. Soc.* **140**, 14614–14618 (2018).

23.Fu, Z. *et al.* A stable covalent organic framework for photocatalytic carbon dioxide reduction. *Chem. Sci.* **11**, 543–550 (2020).

24.Li, S.-Y. *et al.* Rhenium-functionalized covalent organic framework photocatalyst for efficient CO2 reduction under visible light. *Microporous Mesoporous Mater.* **285**, 195–201 (2019).

25.Côté, A. P. *et al.* Porous, Crystalline, Covalent Organic Frameworks. *Science (80-. ).* **310**, 1166 LP – 1170 (2005).

26.Huang, N., Wang, P. & Jiang, D. Covalent organic frameworks: a materials platform for structural and functional designs. *Nat. Rev. Mater.* **1**, 16068 (2016).

27.Hu, X.-L., Li, H.-G. & Tan, B.-E. COFs-based Porous Materials for Photocatalytic Applications. *Chinese J. Polym. Sci.* **38**, 673–684 (2020).

28. Yang, Q., Luo, M., Liu, K., Cao, H. & Yan, H. Covalent organic

frameworks for photocatalytic applications. *Appl. Catal. B Environ.* **276**, 119174 (2020).

29.Kim, T. W. *et al.* Ultrafast charge transfer coupled with lattice phonons in two-dimensional covalent organic frameworks. *Nat. Commun.* **10**, 1873 (2019).

30.Jakowetz, A. C. *et al.* Excited-State Dynamics in Fully Conjugated 2D Covalent Organic Frameworks. *J. Am. Chem. Soc.* **141**, 11565–11571 (2019).

31.Nozik, A. J. Utilizing hot electrons. *Nat. Energy* **3**, 170–171 (2018).

32.Sun, Y. & Tang, Z. Photocatalytic hot-carrier chemistry. MRS Bull. 45, 20–25 (2020).

33.Nozik, A. J. Quantum dot solar cells. *Phys. E Low-dimensional Syst. Nanostructures* 14, 115–120 (2002).

34.Zhang, C. *et al.* Hot-carrier transfer at photocatalytic silicon/platinum interfaces. *J. Chem. Phys.* **152**, 144705 (2020).

35.Harutyunyan, H., Suchanek, F., Lemasters, R. & Foley, J. J. Hot-carrier dynamics in catalysis. *MRS Bull.* **45**, 32–36 (2020).

36.Zhao, W., Shao, H., Yu, G., Hou, Y. & Wang, S. The Coordination and Luminescence of the Eu(III) Complexes with the Polymers (PMMA, PVP). *Polymers* vol. 10 (2018).

37. Yang, L. *et al.* Theoretical Studies of Ground and Excited Electronic States in a Series of Halide Rhenium(I) Bipyridine Complexes. *J. Phys. Chem. A* **108**, 6797–6808 (2004).

38. Aiyappa, H. B., Thote, J., Shinde, D. B., Banerjee, R. & Kurungot, S. Cobalt-Modified Covalent Organic Framework as a Robust Water Oxidation Electrocatalyst. *Chem. Mater.* **28**, 4375–4379 (2016).

39.Knopf, K. M. *et al.* In Vitro Anticancer Activity and in Vivo Biodistribution of Rhenium(I) Tricarbonyl Aqua Complexes. *J. Am. Chem. Soc.* **139**, 14302–14314 (2017).

40.Haldar, S. *et al.* Anthracene-Resorcinol Derived Covalent Organic Framework as Flexible White Light Emitter. *J. Am. Chem. Soc.* **140**, 13367–13374 (2018).

41.Agarwal, J., Fujita, E., Schaefer, H. F. & Muckerman, J. T. Mechanisms for CO Production from CO2 Using Reduced Rhenium Tricarbonyl Catalysts. *J. Am. Chem. Soc.* **134**, 5180–5186 (2012).

42. Tao, Y., Zou, W., Luo, G.-G. & Kraka, E. Describing Polytopal Rearrangement Processes of Octacoordinate Structures. I. Renewed Insights into Fluxionality of the Rhenium Polyhydride Complex ReH5(PPh3)2(Pyridine). *Inorg. Chem.* **60**, 2492–2502 (2021).

43.Zhao, Y. & Truhlar, D. G. A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Chem. Phys.* **125**, 194101 (2006).

44.Zhao, Y. & Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other function. *Theor. Chem. Acc.* **120**, 215–241 (2008).

45.Weigend, F. & Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **7**, 3297–3305 (2005).

46.Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **8**, 1057–1065 (2006).

47.Paz, Y. Transient IR spectroscopy as a tool for studying photocatalytic materials. *J. Phys. Condens. Matter* **31**, 503004 (2019).

48.Furuhashi, K., Jia, Q., Kudo, A. & Onishi, H. Time-Resolved Infrared Absorption Study of SrTiO3 Photocatalysts Codoped with Rhodium and Antimony. J. Phys. Chem. C 117, 19101–19106 (2013).

49. Munson, K. T., Kennehan, E. R. & Asbury, J. B. Structural origins of the electronic properties of materials via time-resolved infrared spectroscopy. *J. Mater. Chem. C* **7**, 5889–5909 (2019).

50. Takeshita, K. *et al.* Effect of Annealing Temperature on Back Electron Transfer and Distribution of Deep Trap Sites in Dye-Sensitized TiO2, Studied by Time-Resolved Infrared Spectroscopy. *J. Phys. Chem. B* **108**, 2963–2969 (2004).

51.Heimer, T. A. & Heilweil, E. J. Direct Time-Resolved Infrared Measurement of Electron Injection in Dye-Sensitized Titanium Dioxide Films. *J. Phys. Chem. B* **101**, 10990–10993 (1997).

52. Abdellah, M. *et al.* Time-Resolved IR Spectroscopy Reveals a Mechanism with TiO2 as a Reversible Electron Acceptor in a TiO2–Re Catalyst System for CO2 Photoreduction. *J. Am. Chem. Soc.* **139**, 1226–1232 (2017).

53.Gaubas, E., Simoen, E. & Vanhellemont, J. Review—Carrier Lifetime Spectroscopy for Defect Characterization in Semiconductor Materials and Devices. *ECS J. Solid State Sci. Technol.* **5**, P3108–P3137 (2016).

54.Munson, K. T., Grieco, C., Kennehan, E. R., Stewart, R. J. & Asbury, J. B. Time-Resolved Infrared Spectroscopy Directly Probes Free and Trapped Carriers in Organo-Halide Perovskites. *ACS Energy Lett.* **2**, 651–658 (2017).

55.Sun, C., Figge, F., McGuire, J. A., Li, Q. & Li, L. Biexciton Auger Recombination in Colloidal Graphene Quantum Dots. *Phys. Rev. Lett.* **113**, 107401 (2014).

56.Makarov, N. S. *et al.* Spectral and Dynamical Properties of Single Excitons, Biexcitons, and Trions in Cesium–Lead-Halide Perovskite Quantum Dots. *Nano Lett.* **16**, 2349–2362 (2016).

57.Žídek, K. *et al.* Ultrafast Dynamics of Multiple Exciton Harvesting in the CdSe–ZnO System: Electron Injection versus Auger Recombination. *Nano Lett.* **12**, 6393–6399 (2012).

58.Brüggemann, B., Herek, J. L., Sundström, V., Pullerits, T. & May, V. Microscopic Theory of Exciton Annihilation: Application to the LH2 Antenna System. *J. Phys. Chem. B* **105**, 11391–11394 (2001).

59.Meng, Z., Stolz, R. M. & Mirica, K. A. Two-Dimensioal Chemiresistive Covalent Organic Framework with High Intrinsic Conductivity. *J. Am. Chem. Soc.* **141**, 11929–11937 (2019).

60.Židek, K., Abdellah, M., Zheng, K. & Pullerits, T. Electron relaxation in the CdSe quantum dot - ZnO composite: prospects for photovoltaic applications. *Sci. Rep.* **4**, 7244 (2014).

61.Žídek, K. *et al.* Electron Transfer in Quantum-Dot-Sensitized ZnO Nanowires: Ultrafast Time-Resolved Absorption and Terahertz Study. *J. Am. Chem. Soc.* **134**, 12110–12117 (2012).

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#### Notes

The authors declare no competing financial interests.

#### **Supplementary Information**

Supplementary Information: should be combined and supplied as a separate file, preferably in PDF format.
1	Ultrafast charge transfer dynamics in 2D Covalent Organic
2	Frameworks/Re-complex hybrid photocatalyst: Hot electrons vs. cold
3	electrons
4	
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## 39 Materials and methods

5,5'-diamino-2.2'-bipyridine (95%, Yuhao Chemical), Pentacarbonylchlororhenium (98%, Sigma-Aldrich), 40 2,2'-bipyridine ( $\geq$  99%, Sigma-Aldrich), Triformylphloroglucinol (95%, Yuhao Chemical), Mesitylene 41 42 (98%, Sigma-Aldrich), 1,4- Dioxane (anhydrous, 99.8%, Sigma-Aldrich), glacial acetic acid (ACS reagent, Aldrich), Nafion (10 wt% in H<sub>2</sub>O), 1-Propanol (for HPLC,  $\geq$  99.9%, Sigma-Aldrich), Toluene (for HPLC, 43 44 VWR Chemicals), Methanol (for HPLC, VWR Chemicals), Tetrahydrofuran (for HPLC, VWR Chemicals). Synthesis of Re(bpy)(CO)<sub>3</sub>Cl. This complex was prepared with slight modifications to literature 45 methods<sup>1,2</sup>. Re(CO)<sub>5</sub>Cl (0.3020 g, 0.83 mmol) was dissolved in 50 mL of hot toluene, then 2,2-bipyridine 46 (0.130 g, 0.83 mmol) was added, the mixture was stirred and reflux for 1h to get yellow product. Upon 47 cooling, the product was filtered, washed with methanol for 3 times, dried under vacuum at 60 °C overnight 48 and used without further purification. <sup>1</sup>H NMR ( $\delta$ , 400 MHz, DMSO-d<sub>6</sub>): 9.02 (d, 1H), 8.77 (d, 1H), 8.34(t, 49 50 1H), 7.76(t, 1H).

51 Synthesis of TpBpy. TpBpy was prepared according to literature methods with a little modification<sup>3</sup>. A 52 Pyrex tube (o.d.  $\times$  i.d. = 10  $\times$  8 mm<sup>2</sup> and length 25 cm)) was charged with triformylphloroglucinol (Tp) (21 mg, 0.10 mmol), 5,5'- diamino-2,2'- bipyridine (Bpy) (27.9 mg, 0.15 mmol), 0.5 mL 1,4-dioxane, 0.5 mL 53 mesitylene, 0.1mL 6 M aqueous acetic acid. This mixture was sonicated for 20 min in order to get a 54 55 homogeneous dispersion. The tube was flash-frozen in a liquid nitrogen bath, evacuated to an internal 56 pressure of ca.0.15 mmHg and flame-sealed. The tube was placed in an oven at 120 °C for 5 days upon 57 warming to room temperature to afford an orange-red precipitate. The precipitate was isolated by filtration 58 over a medium glass frit and washed with anhydrous tetrahydrofuran (THF, 20.0 mL). The product was 59 immersed in anhydrous THF (20.0 mL) for 8 h, during which the activation solvent was decanted and 60 freshly replenished four times. The solvent was removed by filtration and the precipitate dried under vacuum at 60 °C overnight to afford TpBpy (42 mg, 86%). 61

62 Synthesis of Re-TpBpy. The process of synthesis Re-TpBpy was similar to that of Re-Bpy. Re(CO)<sub>5</sub>Cl
63 (10 mg, 0.025 mmol) were dispersed in 10 mL hot toluene, then TpBpy (25 mg) was added, the mixture

was refluxed 40 min while stirring. The scarlet products were filtered, washed with methanol for 3 times,
dried under vacuum at 60 °C overnight and used without further purification.

**Photocatalytic Reduction of CO<sub>2</sub>.** The method of photocatalytic reduction of CO<sub>2</sub> was carried out according to literature methods with a little modification<sup>2</sup>. Re-TpBpy (1 mg) was dispersed in 3 mL of CH<sub>3</sub>CN and 0.2 mL of TEOA (triethanolamine) in 11 mL septum-sealed glass vials. The mixture was purged with Ar for 5 min and CO<sub>2</sub> for 15 min first, then irradiated by a LED lamp with 520 nm and 440 wavelengths for 8 h and kept stirring during the photocatalytic reaction. The amount of CO generated was quantified using Shimadzu gas chromatography (GC-2010) by analyzing 500  $\mu$ L of the headspace.

## 72 Computational methods

To investigate the relationship of the optical properties with molecular structures and electronic 73 structures, we used a triformylphloroglucinol (Tp) terminated bipyridine (Bpy) molecular 74 75 fragment (Fig. 3) to represent the COF structure. An implicit solvent model was used to reflect the solvation environment, and implemented using SMD solvation model<sup>4</sup> in Gaussian 16 package<sup>5</sup>. 76 Considering the transition metal complex in the fragment,  $M06-L^{6-11}$  was selected as the functional 77 and def 2-TZVP<sup>12,13</sup> was selected as the basis set for DFT calculations. N-propanol parameters 78 were used to represent the solvents in the SMD models<sup>14</sup>. Time-dependent density functional 79 theory (TD-DFT) calculations were also performed using these parameters. The UV-vis absorption 80 spectra and electron excitations were analyzed using the Multiwfn program<sup>15</sup>. 81

## 82 Characterization

Fourier-Transformed Infrared Spectroscopy (FT-IR) data were obtained by using ALPHA P FT-IR
spectrometer (Bruker). The samples just have to be brought into contact with the measurement interface.
The absorption spectra were measured in a UV-Vis absorption spectrophotometer from Agilent
Technologies (Santa Clara, USA). Photoluminescence (PL) was performed via Spex Fluorolog 1681
standard spectrofluorometer. Time-correlated single photon counting (TCSPC) was performed triggered

externally at 2.5 MHz to excite the sample at 438 nm. The emitted photons were detected by a fast avalanche
photodiode (SPAD, Micro Photon Device) with response time less than 50 ps after passing through a 470
nm long band pass filter. The Time-resolved Photoluminescence (TRPL) measurements were performed
by time-correlated single photon counting (Picoharp) using a pulsed diode laser (Wavelength: 438 nm;
Frequency: 2.5 MHz; Pulse duration: 40 ps; A long-pass filter from 450 nm) and a fast avalanche
photodiode. It is important to note that during all photophysical measurements the sample s were dispersed
in Nafion (5% w/w in water and 1-propanol) except Tp was dispersed in acetonitrile.

95 Nuclear Magnetic Resonance (NMR) spectroscopy were acquired on Bruker AVANCE 400 MHz
96 spectrometer with a 5 mm CryoProbe Prodigy using approximately 1 mg sample dissolved in 2 mL of
97 deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>).

Transient absorption (TA) spectroscopy measurements. Time-resolved experiments were carried out on 98 99 laser-based spectroscopy, with laser powers equating to less than one photon absorption per particle. 100 Samples for transient absorption experiments were kept in dark between each measurement. A Coherent 101 Legend Ti: Sapphire amplifier (800 nm,100 fs pulse length, 3 kHz repetition rate) was used. The output is 102 split to pump and probe beams. Excitation pulses at the wavelength of 450 nm were acquired using an 103 optical parametric amplifier (Topas C, Light Conversion). The probe pulses (a broad supercontinuum spectrum) were generated from the 800-nm pulses in a CaF<sub>2</sub> crystal and split by a beam splitter into a probe 104 pulse and a reference pulse. The probe pulse and the reference pulse were dispersed in a spectrograph and 105 106 detected by a diode array. Instrumental response time is  $\sim 100$  fs. Global SVD analysis was performed with 107 the Glotaran software package (http://glotaran.org).

Transient Mid-IR Absorption Spectroscopy.A frequency doubled Q-switched Nd:YAG laser (Quanta-Ray ProSeries, Spectra- Physics) was employed to obtain 400 nm and 530 nm pump light, 10 mJ/pulse with a fwhm of 10 ns. The 400 nm and 530 nm pump light was used through the MOPO crystal to generate ? nm light to pump the sample. Probing was done with the continuous wave quantum cascade (QC) IR laser with a tuning capability between 1960 and 2150 cm–1 (Daylight Solutions). For IR detection, a liquid nitrogencooled mercurycadmium- telluride (MCT) detector (KMPV10-1-J2, Kolmar Technologies, Inc.) was used. The IR probe light was overlapped with the pump beam in a quasi-co-linear arrangement at 25° angle.
Transient absorption traces were acquired with a Tektronix TDS 3052 500 MHz (5GS/s) oscilloscope in
connection with the L900 software (Edinburgh Instruments) and processed using Origin 9 software <sup>16,17</sup>.
Samples were kept in a modified Omni cell (Specac) with with O-ring sealed CaF2 windows and a path
lenth of 1 mm. All samples were prepared in an Ar filled glove box (Unilab, MBraun), and Nafion (5%
w/w in water and 1-propanol) was used as solvent in all experiments. All acids were dried overnight under
vacuum prior to use.



# 121 Supplementary Figures

122

**Supplementary Figure 1:** Emission spectra of TpBpy and Re-TpBpy calibrated by the absorption at the

124 400 nm excitation wavelength.

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**Supplementary Figure 2:** Two-dimensional transient absorption (TA) spectra under 530 nm 500 uW

129 excitation (a); TA kintees of TpBpy excited at different excitation intensity of representing B1 (b). All

130 spectra are recorded in Nafion (5% w/w in water and 1-propanol).



Supplementary Figure 3: Two-dimensional transient absorption (TA) spectra under 530 nm 100 uW (a)
and 400 nm 500 uW excitation and the respective SVD fittings of Re-Bpy (B). All spectra are recorded in
Nafion (5% w/w in water and 1-propanol).



**Supplementary Figure 4:** Crystalline Structures of TpBpy, top-view and side-view.

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# 150 Supplementary Tables

Orbital Name	Orobital Number	Energy (eV)	iso-surface images
LUMO+12	240	-0.96886231	
LUMO+11	239	-0.969700086	
LUMO+10	238	-0.972883907	
LUMO+9	237	-0.973715102	
LUMO+8	236	-1.068732822	
LUMO+7	235	-1.333214011	<b></b>
LUMO+6	234	-1.621848404	

# **Supplementary Table 1:** Calculated TD-DFT energy levels of TpBpy fragment.

LUMO+5	233	-1.995218628	
LUMO+4	232	-2.034934733	
LUMO+3	231	-2.035340048	
LUMO+2	230	-2.237486536	
LUMO+1	229	-2.576204276	
LUMO	228	-2.799618969	
НОМО	227	-5.045478166	· · · · · · · · · · · · · · · · · · ·
HOMO-1	226	-5.172556295	

НОМО-2	225	-5.172573899	
НОМО-3	224	-5.365218278	
НОМО-4	223	-5.670073594	
НОМО-5	222	-5.676649	
НОМО-6	221	-5.718600616	and the second s
НОМО-7	220	-5.940760198	A Constant
НОМО-8	219	-6.053834645	
НОМО-9	218	-6.200828562	

	HOMO-10	217	-6.205291056	
	HOMO-11	216	-6.22438551	
	НОМО-12	215	-6.279711603	
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**Supplementary Table 2:** Calculated TD-DFT energy levels of Re-TpBpy fragment.

Orbital Name	Orobital Number	Energy (eV)	iso-surface images
LUMO+12	277	-0.98413959	
LUMO+11	276	-0.986257352	
LUMO+10	275	-1.078184819	
LUMO+9	274	-1.283727355	
LUMO+8	273	-1.402089054	
LUMO+7	272	-1.867455072	
LUMO+6	271	-1.993478502	······································
LUMO+5	270	-2.067937563	

LUMO+4	269	-2.068107788	
LUMO+3	268	-2.196090793	\$382+180
LUMO+2	267	-2.455782405	
LUMO+1	266	-2.655408515	
LUMO	265	-3.092359577	Jorge Series
НОМО	264	-5.197598202	
HOMO-1	263	-5.19983685	
НОМО-2	262	-5.206329891	Stoth of States

НОМО-3	261	-5.429726984	
НОМО-4	260	-5.450935274	and the state
НОМО-5	259	-5.529614132	
НОМО-6	258	-5.724384074	
НОМО-7	257	-5.72505861	
НОМО-8	256	-5.811185661	Service -
НОМО-9	255	-5.893560943	
HOMO-10	254	-6.051646689	

	HOMO-11	253	-6.242005536	
				See 1
	HOMO-12	252	-6.242635938	ريكىش يحش
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<b>197</b> Table S3   Atomistic coordinates of TpBp-n	-propanol.
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Atom	x/a	<i>y/b</i>	z/c		
С	12.82607	8.28556	2.55511		
С	13.45496	7.06020	2.78772		
С	14.82914	6.98689	2.77993		
С	15.57025	8.13988	2.53708		
С	14.86423	9.32363	2.31420		
N	13.54423	9.39525	2.32468		
N	16.95759	8.05678	2.53155		
С	17.82925	9.04245	2.34057		
С	19.20221	8.90143	2.34951		
С	19.83544	7.61748	2.57592		
0	19.41644	11.21299	1.93258		
Н	17.39390	7.14591	2.69329		
С	11.35888	8.41665	2.55693		
N	10.84719	9.64553	2.72987		
С	9.53595	9.79424	2.73398		
С	8.63153	8.74398	2.56386		
С	9.15480	7.46825	2.37948		
С	10.52345	7.31106	2.37884		
N	7.27541	9.04021	2.58461		
С	6.26091	8.19419	2.43942		
С	4.92571	8.54401	2.45996		
С	4.50097	9.91679	2.65064		
0	4.35359	6.28294	2.11228		
Н	6.98782	10.01278	2.71924		
Н	12.87726	6.17008	2.99502		
Н	15.33747	6.04880	2.96769		
Н	15.38984	10.25146	2.11454		
Н	17.43134	10.03433	2.16596		
Н	9.15278	10.80138	2.88183		
Н	8.51277	6.61066	2.23157		
Н	10.93942	6.32606	2.21804		
Н	6.50186	7.14816	2.29282		
С	25.17733	2.46452	3.50020		
С	25.86933	3.63980	3.24436		
С	25.18371	4.82098	3.02469		
С	23.78974	4.83829	3.05894		
С	23.09088	3.66029	3.31675		
С	23.78958	2.48538	3.53452		
Ν	23.15734	6.06423	2.82988		
С	21.85689	6.31513	2.79629		
С	21.28822	7.55687	2.57191		

С	22.09939	8.73511	2.34742	
0	19.14747	6.58811	2.77095	
Н	23.74065	6.88773	2.66708	
Н	26.95160	3.64009	3.21484	
Н	25.71928	5.74115	2.82398	
Н	22.01009	3.65359	3.35105	
Н	21.18355	5.48187	2.95679	
С	0.04363	15.87067	3.39866	
С	-0.82902	14.80996	3.20089	
С	-0.34174	13.52688	3.02797	
С	1.03246	13.29143	3.05180	
С	1.91247	14.35353	3.25108	
С	1.41123	15.63239	3.42207	
N	1.46192	11.97301	2.87193	
С	2.70732	11.52291	2.83768	
С	3.07493	10.20092	2.65645	
С	2.08920	9.15531	2.48019	
0	5.34182	10.83295	2.80681	
Н	0.75538	11.24494	2.74837	
Н	-1.01779	12.69466	2.87235	
Н	2.98116	14.18948	3.27422	
Н	2.10149	16.45222	3.57633	
Н	3.50218	12.24865	2.96017	
С	-0.88193	2.37933	1.39553	
С	0.48865	2.16471	1.36233	
С	1.36591	3.21891	1.54322	
С	0.87717	4.50677	1.76077	
С	-0.49874	4.72642	1.79675	
С	-1.36508	3.66256	1.61334	
Ν	1.81513	5.52899	1.93622	
С	1.58419	6.82018	2.12301	
С	2.55698	7.78994	2.29141	
С	3.96579	7.46304	2.27749	
0	0.86382	9.41825	2.48944	
Н	2.80732	5.28467	1.92048	
Н	2.43699	3.05690	1.51728	
Н	-0.89682	5.71716	1.96830	
Н	-2.43249	3.84183	1.64282	
Н	0.55064	7.14407	2.14429	
С	23.98050	15.84298	0.99744	
С	22.59505	15.86256	1.07404	
С	21.89144	14.69437	1.30601	
С	22.57163	13.48768	1.46447	
С	23.96270	13.46287	1.38593	

С	24.65440	14.63928	1.15440
Ν	21.80353	12.34220	1.69475
С	22.23372	11.10816	1.91167
С	21.42496	10.00536	2.12426
С	19.98252	10.11167	2.12301
0	23.35077	8.66340	2.34530
Н	20.78577	12.43383	1.70162
Н	22.05530	16.79321	0.95291
Н	20.80989	14.70286	1.36812
Н	24.50650	12.53533	1.50045
Н	23.30532	10.94997	1.92505
Н	25.71343	1.54035	3.67234
Н	23.23899	1.57478	3.73477
Н	-0.33747	16.87448	3.53368
Н	-1.89803	14.98007	3.18032
Н	-1.56841	1.55483	1.25402
Н	0.88091	1.16969	1.19436
Н	24.53110	16.75672	0.81572
Н	25.73515	14.61171	1.09417

228	Table S4	Atomistic	coordinates	of Re-7	pB	py-n-	pro	panol	1.
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Atom	<i>x/a</i>	y/b	z/c
Re	11.90630	11.62434	2.51252
С	13.34728	12.87699	2.65634
С	10.70622	13.11024	2.63530
Cl	11.85313	11.15375	5.00108
С	11.93848	11.86514	0.62711
0	14.22872	13.62434	2.73320
0	11.95970	12.03195	-0.52248
С	12.36680	8.57097	2.46530
С	13.03362	7.34795	2.47652
С	14.40565	7.31227	2.47218
С	15.12441	8.50731	2.45467
С	14.40366	9.69781	2.44060
N	13.07256	9.72446	2.44783
N	16.50632	8.45742	2.44959
С	17.36165	9.48123	2.46355
С	18.73202	9.35907	2.44970
С	19.38389	8.06148	2.41564
0	18.91614	11.71015	2.50207
Н	16.96229	7.54094	2.43391
С	10.91775	8.69992	2.46339
Ν	10.42593	9.96032	2.43986
С	9.11168	10.15747	2.43069
С	8.19155	9.11228	2.44498
С	8.68571	7.80901	2.47030
С	10.04599	7.61402	2.47873
N	6.84848	9.43816	2.43322
С	5.81511	8.59586	2.46421
С	4.49171	8.97248	2.45092
С	4.09511	10.36854	2.39502
0	3.87220	6.69893	2.54400
Н	6.57596	10.42454	2.39973
Н	12.47678	6.42289	2.48958
Н	14.93470	6.36784	2.48236
Н	14.89880	10.65805	2.42199
Н	16.94924	10.48225	2.48916
Н	8.76698	11.18404	2.41323
Н	8.02260	6.95584	2.48210
Н	10.43444	6.60660	2.49837
Н	6.03485	7.53606	2.50520
С	24.76904	2.88971	2.22634
С	25.45391	4.09655	2.22124
С	24.76135	5.29355	2.25852

С	23.36784	5.29346	2.30188
С	22.67577	4.08401	2.30785
С	23.38128	2.89383	2.26999
Ν	22.72415	6.53444	2.33863
С	21.42157	6.76927	2.36306
С	20.83528	8.02333	2.39733
С	21.63021	9.23375	2.41268
0	18.70857	7.00644	2.40184
Н	23.29750	7.38084	2.34571
Н	26.53596	4.10934	2.18779
Н	25.29117	6.23856	2.25418
Н	21.59506	4.06587	2.34335
Н	20.76148	5.91038	2.35454
С	-0.27387	16.43984	2.20549
С	-1.15916	15.37166	2.23481
С	-0.68537	14.07275	2.27584
С	0.68756	13.82876	2.28802
С	1.58038	14.89849	2.25971
С	1.09234	16.19315	2.21842
Ν	1.09932	12.49278	2.32993
С	2.33579	12.02015	2.34076
С	2.67653	10.67841	2.38929
С	1.66925	9.63901	2.43575
0	4.95686	11.27640	2.35245
Н	0.38072	11.76636	2.35888
Н	-1.37126	13.23425	2.29864
Н	2.64848	14.73007	2.27035
Н	1.79204	17.01917	2.19666
Н	3.14639	12.73816	2.31010
С	-1.45038	2.85445	2.82253
С	-0.08566	2.60513	2.79391
С	0.81477	3.65284	2.72234
С	0.35515	4.96856	2.67863
С	-1.01454	5.22371	2.70831
С	-1.90435	4.16581	2.77945
Ν	1.31579	5.98285	2.60783
С	1.11268	7.29001	2.54923
С	2.10711	8.25181	2.49334
С	3.50695	7.89552	2.49855
0	0.44952	9.92515	2.42745
Н	2.30196	5.71531	2.60432
Н	1.88145	3.46366	2.69980
Н	-1.38992	6.23739	2.67764
Н	-2.96700	4.37220	2.80223

Н	0.08613	7.63581	2.54630
С	23.44139	16.48300	2.58323
С	22.05455	16.47459	2.62818
С	21.36202	15.27737	2.60302
С	22.05485	14.06960	2.53203
С	23.44789	14.07316	2.48661
С	24.12811	15.27837	2.51294
N	21.29573	12.89447	2.50883
С	21.73675	11.64677	2.46992
С	20.93991	10.51475	2.45098
С	19.49817	10.60264	2.47005
0	22.88169	9.17994	2.39436
Н	20.27761	12.97604	2.52581
Н	21.50479	17.40559	2.68345
Н	20.27934	15.26388	2.63921
Н	24.00313	13.14681	2.42971
Н	22.80950	11.49906	2.45347
Н	25.31104	1.95352	2.19736
Н	22.83649	1.95816	2.27540
Н	-0.64407	17.45620	2.17330
Н	-2.22727	15.54817	2.22568
Н	-2.15491	2.03494	2.87864
Н	0.28373	1.58804	2.82746
Н	23.98364	17.41931	2.60267
Н	25.21026	15.27308	2.47690
0	9.96839	14.00103	2.69623

## 237 **References**

- 238 1.Schneider, T. W., Ertem, M. Z., Muckerman, J. T. & Angeles-Boza, A. M. Mechanism of Photocatalytic
- 239 Reduction of CO2 by Re(bpy)(CO)3Cl from Differences in Carbon Isotope Discrimination. ACS Catal. 6,
- 240 5473–5481 (2016).
- 241 2.Yang, S. et al. 2D Covalent Organic Frameworks as Intrinsic Photocatalysts for Visible Light-Driven
- 242 CO2 Reduction. J. Am. Chem. Soc. 140, 14614–14618 (2018).
- 243 3.Zhong, W. et al. A Covalent Organic Framework Bearing Single Ni Sites as a Synergistic Photocatalyst
- 244 for Selective Photoreduction of CO2 to CO. J. Am. Chem. Soc. 141, 7615–7621 (2019).
- 245 4.Marenich, A. V, Cramer, C. J. & Truhlar, D. G. Universal Solvation Model Based on Solute Electron
- 246 Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic
- 247 Surface Tensions. J. Phys. Chem. B 113, 6378–6396 (2009).
- 248 5.Frisch, M. J. et al. G16\_C01. Gaussian 16, Revision C.01, Gaussian, Inc., Wallin (2016).
- 6.Zhao, Y. & Truhlar, D. G. A new local density functional for main-group thermochemistry, transition
  metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Chem. Phys.* 125, 194101 (2006).
- 251 7.Zhao, Y. & Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry,
- thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new
- functionals and systematic testing of four M06-class functionals and 12 other function. *Theor. Chem. Acc.*
- **120**, 215–241 (2008).
- 255 8.Tao, Y., Zou, W., Luo, G.-G. & Kraka, E. Describing Polytopal Rearrangement Processes of
- Octacoordinate Structures. I. Renewed Insights into Fluxionality of the Rhenium Polyhydride Complex
   ReH5(PPh3)2(Pyridine). *Inorg. Chem.* 60, 2492–2502 (2021).
- 257 Ref15(11115)2(1 yridine). *Thorg. Chem.* **60**, 2452-2502 (2021).
- 258 9.Agarwal, J., Fujita, E., Schaefer, H. F. & Muckerman, J. T. Mechanisms for CO Production from CO2
- Using Reduced Rhenium Tricarbonyl Catalysts. J. Am. Chem. Soc. 134, 5180–5186 (2012).
- 260 10.Dürr, A. B., Fisher, H. C., Kalvet, I., Truong, K.-N. & Schoenebeck, F. Divergent Reactivity of a
- 261 Dinuclear (NHC)Nickel(I) Catalyst versus Nickel(0) Enables Chemoselective Trifluoromethylselenolation.
- 262 Angew. Chem. Int. Ed. Engl. 56, 13431–13435 (2017).
- 263 11.Cammarota, R. C. et al. A Bimetallic Nickel-Gallium Complex Catalyzes CO2 Hydrogenation via the
- Intermediacy of an Anionic d10 Nickel Hydride. J. Am. Chem. Soc. 139, 14244–14250 (2017).
- 265 12.Weigend, F. & Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta
- valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* 7, 3297–3305
- 267 (2005).

- 13.Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* 8, 1057–1065
  (2006).
- 14.Borodin, O., Behl, W. & Jow, T. R. Oxidative Stability and Initial Decomposition Reactions of
  Carbonate, Sulfone, and Alkyl Phosphate-Based Electrolytes. *J. Phys. Chem. C* 117, 8661–8682 (2013).
- 15.Lu, T. & Chen, F. Multiwfn: A multifunctional wavefunction analyzer. J. Comput. Chem. 33, 580–592
- 273 (2012).
- 274 16.Mirmohades, M. et al. Direct Observation of Key Catalytic Intermediates in a Photoinduced Proton
- 275 Reduction Cycle with a Diiron Carbonyl Complex. J. Am. Chem. Soc. 136, 17366–17369 (2014).
- 276 17.Mirmohades, M. et al. Following [FeFe] Hydrogenase Active Site Intermediates by Time-Resolved
- 277 Mid-IR Spectroscopy. J. Phys. Chem. Lett. 7, 3290–3293 (2016).

#### caculated Uv-Vis-TpBpy-n-propanol

- # 1 2.3455 eV 528.60 nm f= 1.66360 Spin multiplicity= 1: H -> L 97.9%
- # 2 2.4172 eV 512.92 nm f= 0.02990 Spin multiplicity= 1:
- H-2 -> L 68.3%, H-1 -> L 22.8%, H-2 -> L+1 6.5%
- # 3 2.4260 eV 511.06 nm f= 0.03840 Spin multiplicity= 1:
- H-1 -> L 67.4%, H-2 -> L 22.5%, H-1 -> L+1 7.3%
- # 4 2.5128 eV 493.41 nm f= 0.00000 Spin multiplicity= 1:
- H -> L+1 70.7%, H-3 -> L 29.0%
- # 5 2.7021 eV 458.84 nm f= 0.16450 Spin multiplicity= 1:
- H-1 -> L+1 61.5%, H-2 -> L+1 21.2%, H-1 -> L+2 6.3%, H-1 -> L 5.6%
- # 6 2.7238 eV 455.19 nm f= 0.21360 Spin multiplicity= 1:
- H-2 -> L+1 61.4%, H-1 -> L+1 21.0%, H-2 -> L+2 6.6%, H-2 -> L 5.1%
- # 7 2.7423 eV 452.12 nm f= 0.00720 Spin multiplicity= 1:
  H-3 -> L 63.7%, H -> L+1 24.3%
- # 8 2.8424 eV 436.20 nm f= 0.78090 Spin multiplicity= 1:
- H-3 -> L+1 50.4%, H -> L+2 46.2%
- # 9 2.8714 eV 431.79 nm f= 0.00030 Spin multiplicity= 1:
- H-4 -> L 99.8%
- # 10 2.8780 eV 430.80 nm f= 0.00020 Spin multiplicity= 1:
- H-5 -> L 100.0%
- # 11 2.8904 eV 428.95 nm f= 0.02010 Spin multiplicity= 1:
  H-6 -> L 36.7%, H-3 -> L+1 33.4%, H -> L+2 27.6%
- # 12 2.9792 eV 416.17 nm f= 0.07450 Spin multiplicity= 1:
- H-2 -> L+2 47.6%, H -> L+4 30.9%, H-1 -> L+2 16.3%
- # 13 2.9877 eV 414.98 nm f= 0.06480 Spin multiplicity= 1:
- H -> L+3 45.0%, H-1 -> L+2 38.2%, H-2 -> L+2 12.9%
- # 14 3.0132 eV 411.47 nm f= 0.27840 Spin multiplicity= 1:
- H-6 -> L 50.5%, H -> L+2 17.6%, H-3 -> L+1 8.4%, H-2 -> L+4 8.2%, H-1 -> L+3 8.1%

- # 15 3.0648 eV 404.54 nm f= 0.16330 Spin multiplicity= 1:
- H -> L+4 58.7%, H-2 -> L+2 13.8%, H-2 -> L+5 13.0%
- # 16 3.0873 eV 401.59 nm f= 0.25710 Spin multiplicity= 1:
- H -> L+3 43.9%, H-1 -> L+2 20.5%, H-1 -> L+5 15.8%, H-2 -> L+2 7.1%
- # 17 3.0939 eV 400.74 nm f= 0.00000 Spin multiplicity= 1:

H-4 -> L+1 99.7%

- # 18 3.0990 eV 400.08 nm f= 0.00380 Spin multiplicity= 1:
- H -> L+5 59.0%, H-7 -> L 20.6%, H-3 -> L+2 12.6%
- # 19 3.1004 eV 399.90 nm f= 0.00000 Spin multiplicity= 1:

H-5 -> L+1 99.5%

- # 20 3.1374 eV 395.18 nm f= 0.00000 Spin multiplicity= 1:
- H-2 -> L+3 75.5%, H-1 -> L+3 24.4%

### caculated Uv-Vis-Re-TpBpy-n-propanol\_exc

# 1 2.1372 eV 580.12 nm f= 0.02050 Spin multiplicity= 1:

H-1 -> L 95.2%

# 2 2.1480 eV 577.21 nm f= 0.03070 Spin multiplicity= 1:

H -> L 88.0%, H-2 -> L 7.7%

- # 3 2.2232 eV 557.68 nm f= 1.60280 Spin multiplicity= 1:
- H-2 -> L 87.5%, H -> L 8.4%
- # 4 2.3480 eV 528.04 nm f= 0.14830 Spin multiplicity= 1:
- H-3 -> L 95.9%
- # 5 2.4190 eV 512.54 nm f= 0.01670 Spin multiplicity= 1:
  H-4 -> L 81.5%, H-2 -> L+1 7.6%, H-5 -> L 6.1%
- # 6 2.4827 eV 499.39 nm f= 0.02360 Spin multiplicity= 1:

H-5 -> L 90.9%

- # 7 2.5812 eV 480.34 nm f= 0.03390 Spin multiplicity= 1:
  H -> L+1 80.3%, H -> L+2 8.4%, H-2 -> L+1 7.4%
- # 8 2.6335 eV 470.80 nm f= 0.00020 Spin multiplicity= 1:

H-6 -> L 99.8%

- # 9 2.6347 eV 470.58 nm f= 0.00000 Spin multiplicity= 1:
- H-7 -> L 99.8%
- # 10 2.6563 eV 466.76 nm f= 0.12160 Spin multiplicity= 1:
- H-1 -> L+1 74.8%, H-1 -> L+2 17.4%
- # 11 2.6722 eV 463.98 nm f= 0.00080 Spin multiplicity= 1:
  H-2 -> L+1 67.4%, H-4 -> L 7.6%, H -> L+1 6.9%
- # 12 2.7690 eV 447.76 nm f= 0.11400 Spin multiplicity= 1:

H-8 -> L 44.0%, H-2 -> L+2 28.0%, H-3 -> L+1 19.4%

- # 13 2.7819 eV 445.68 nm f= 0.12630 Spin multiplicity= 1:
- H-3 -> L+1 67.6%, H-1 -> L+2 13.5%, H-8 -> L 10.2%
- # 14 2.7834 eV 445.44 nm f= 0.11580 Spin multiplicity= 1:
- H-1 -> L+2 62.2%, H-1 -> L+1 11.5%, H-3 -> L+1 10.2%, H-2 -> L+2 5.0%

- # 15 2.8025 eV 442.41 nm f= 0.00130 Spin multiplicity= 1:
- H-9 -> L 99.7%
- # 16 2.8132 eV 440.72 nm f= 0.44470 Spin multiplicity= 1:
- H-4 -> L+1 41.1%, H-2 -> L+2 25.6%, H-8 -> L 23.4%
- # 17 2.8790 eV 430.65 nm f= 0.00650 Spin multiplicity= 1: H-5 -> L+1 96.4%
- # 18 2.8979 eV 427.84 nm f= 0.36030 Spin multiplicity= 1:
- H -> L+2 70.4%, H-2 -> L+2 7.6%, H -> L+1 6.2%
- # 19 2.9265 eV 423.66 nm f= 0.02490 Spin multiplicity= 1:
- H-4 -> L+1 41.7%, H-2 -> L+2 19.0%, H-3 -> L+2 13.7%, H-8 -> L 7.3%
- # 20 2.9936 eV 414.16 nm f= 0.00540 Spin multiplicity= 1:
- H-3 -> L+2 77.3%, H-4 -> L+2 10.1%

# Ultrafast Excited-state Dynamics in a Ni-2,2'-Bipyridine Covalent Organic Framework Photocatalyst

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### Supporting Information Placeholder

**ABSTRACT:** Metalized covalent organic frameworks (COFs) have been recognized as emerging photocatalysts for CO<sub>2</sub> reduction due to their excellent photocatalytic activity and selectivity. However, the underlying photophysical mechanisms, especially the photo-induced charge transfer process, remain to be understood. Herein, we explored the excited-state dynamics of Ni metalized two-dimensional (2D) COFs (Ni-TpBpy) by time-resolved spectroscopy. The time-dependent density functional theory (TD-DFT) calculations first identified that the optical transition can lead to intramolecular charge transfer from the COFs to the Ni<sup>2+</sup> center. Experimentally we found that the excited-state dynamics are highly correlated to the excitation energy. Under band-edge excitation, the excited electrons are transferred from the COFs moiety into the Ni<sup>2+</sup> center followed by geminate recombination with holes residing at the COFs. Under high-energy excitation, the initial optical transition channel creates additional electrons and holes populations. While some electrons can still be directly excited to the Ni<sup>2+</sup> center, some hot electrons and holes remain in COFs moiety without an efficient cooling channel. This coexistence of hot and cold pools of electrons and holes can facilitate the two-electron injection process required by CO<sub>2</sub> reduction, which also rationalizes the enhanced catalytic performance at high excitation energy.

Photocatalytic reduction of CO2 that utilizes sunlight energy to convert CO2 into clean hydrocarbon fuel (such as carbon monoxide, methane, or methanol) is considered an effective solution to reduce air pollution and greenhouse gas emissions.<sup>1-6</sup> Therefore, looking for catalysts capable of achieving the efficient photocatalytic reduction of CO<sub>2</sub> becomes critical. Covalent organic frameworks (COFs) are ordered porous organic semiconductor materials composed of H, C, N, O, and other light elements connected by covalent bonds.<sup>7,8</sup> COFs-based heterogeneous materials have attracted particular attention for photocatalytic applications due to their unique structural advantages.9-14 The building units of the frameworks can undergo coordination reactions with metal ions to form and stabilize metal complex catalytic centers.<sup>15–18</sup> The high specific surface area increases the number of such catalytic active sites and, therefore, the CO<sub>2</sub> adsorption. In addition, the ordered conjugated structure promotes light absorption and electric conductivity.<sup>11,19</sup> Recent reports have revealed efficient CO<sub>2</sub> photocatalytic reduction in one of such photocatalysts, namely Re-TpBpy, which is constructed from Re(Bpy)(CO)5Cl and a two-dimensional (2D) COFs (TpBpy).<sup>20-22</sup> The efficient photo-induced charge separation has been confirmed to facilitate the photocatalytic reaction. However, to reduce the production cost, there is a great need to substitute noble metal with earth-abundant elements. Previous studies have demonstrated that nickel (Ni) complexes acting as active metal centers can also be integrated into COFs structures with moderate but promising photocatalytic activity for the reduction of CO2.23-25

However, such a system currently operates as a "black box" since neither the charge relaxation dynamics nor the charge transfer pathways are known for Ni-modified COFs hybrids.

In this work, we investigate the excited-state dynamics and photoinduced charge transfer process in a 2D 2, 2'-bipyridine-COFs (TpBpy) that incorporates Ni catalytic active sites to form Ni-TpBpy. Time-dependent density functional theory (TD-DFT) calculations first reveal its excited-state structures. Femtosecond transient absorption (fs-TA) spectroscopy is then employed to explore the excited-state charge transfer dynamics, which are highly dependent on the excitation wavelength. Finally, the pathways identified by combining experiment and theory are used to rationalize the CO<sub>2</sub> catalytic reaction mediated by a two-electron transfer process.

This study uses the prototypical COFs (TpBpy) with 2,2'-bipyridine.<sup>26</sup> A simple solution dipping method was employed to implant the Ni-complex into TpBpy in acetonitrile solution to yield the Ni-COFs hybrid, namely, Ni-TpBpy (for detailed synthesis information, see Fig. SI).<sup>23</sup> The structure of the as-obtained Ni-TpBpy is presented in Fig. 1a. The powder X-ray diffraction (PXRD) patterns of both TpBpy and Ni-TpBpy shown in Fig. S2 match well with the simulated AA stacking structure of COFs in the hexagonal space group (P6/m). This demonstrates that the crystalline structure



**Figure 1.** (a) Schematic structure of the Ni-TpBpy; (b) Normalized UV–vis absorption and steady-state photoluminescence spectra excited at 400 nm (pink) and 530 nm (blue) of TpBpy and Ni-TpBpy dispersed in Nafion (5% w/w in water and 1-propanol).

of TpBpy remains unchanged after incorporation of the Ni-complex. Fig. 1b displays the steady-state absorption and photoluminescence (PL) emission of TpBpy and Ni-TpBpy. The absorption spectrum of TpBpy exhibits a narrow  $n-\pi^*$  transition band (324) nm) ascribed to bipyridine, as well as a broad band at 508 nm ascribed to the  $\pi$  electrons delocalized within the COFs framework.  $^{\rm 18}$ The absorption spectrum of Ni-TpBpy shows the same shape as TpBpy except for a bathochromic shift in the bipyridine  $n-\pi^*$  transition (365 nm) and an increased absorbance in the 450-550 nm range, suggesting a strong charge-transfer character. The bathochromic- shift stems from a Stark effect on the bipyridine due to the charged central Ni<sup>2+</sup> ion.<sup>27</sup> Under band-edge excitation at 530 nm. TpBpv exhibits an emission band at 620 nm, with a Stokes shift of 90 nm. The emission band of Ni-TpBpy is at 580 nm with a smaller Stokes shift of 60 nm. Interestingly, the emission spectra of Ni-TpBpy exhibit one board band at 473 nm when excited at higher energy (i.e. 400 nm), which is different from the dual emission peak observed in TpBpy. (Fig. 1b).

To gain insight into the intrinsic electronic excited-state structure of the samples, we modeled and analyzed the electronic transitions of TpBpy and Ni-TpBpy via the time-dependent DFT (TD-DFT) at the M06-L<sup>28-31</sup> /def 2-TZVP<sup>32,33</sup> level of theory, which simplifies the COFs moiety as a triformylphloroglucinol (Tp) terminated bipyridine (Bpy) molecular fragment (Fig. 2). Such an approximation has already been successfully used in our previous work for carrying tractable calculations on COFs materials that deliver physical insights. It provides a simplified but compact visualization of the electronic structure able to guide the interpretation of the experimental observations.<sup>13,34,35</sup> Fig. 2 displays the calculated electronic excitation spectrum (blue curves) of TpBpy and Ni-TpBpy with the comparison to the experimental absorption spectra (purple curves). Open-shell calculations have been carried out using a spin-unrestricted formalism as Ni2+ is an open-shell system with a 3d8 ground state. Thus, the calculations deliver two sets of orbitals, corresponding to "spin-up" electrons (a orbitals) and spin-down electrons (b orbitals), respectively.

Two main electronic excitation bands at 528 nm (S<sub>1</sub>) and 436 nm (S<sub>2</sub>) have been identified in the calculated spectrum of TpBpy (Fig. 2a). The low energy band S<sub>1</sub> is dominated by the electronic transition from the HOMO to the LUMO level. The high energy band S<sub>2</sub> is equally contributed by the electronic transition (HOMO-3  $\rightarrow$  LUMO+1) and (HOMO  $\rightarrow$  LUMO+2). S1 mainly occurs within the Bpy moiety, whereas S2 involves electronic densities on both Bpy and Tp.

In the calculated spectrum of Ni-TpBpy, four pronounced electronic excitation bands can be extracted as shown in Fig. 2b, namely: S1 (HOMO<sub>b</sub>-2  $\rightarrow$  LUMO<sub>b</sub>, HOMO<sub>a</sub>-2  $\rightarrow$  LUMO<sub>a</sub>) at 554

nm; S<sub>2</sub> (HOMO<sub>b</sub>-6  $\rightarrow$  LUMO<sub>b</sub>, HOMO<sub>a</sub>-6  $\rightarrow$  LUMO<sub>a</sub>) at 446 nm; S<sub>3</sub> (HOMO<sub>b</sub>-3  $\rightarrow$  LUMO<sub>b</sub>+3, HOMO<sub>a</sub>-3  $\rightarrow$  LUMO<sub>a</sub>+1) at 439 nm; and S<sub>4</sub> (HOMO<sub>b</sub>  $\rightarrow$  LUMO<sub>b</sub>+4, HOMO<sub>a</sub>  $\rightarrow$  LUMO<sub>a</sub>+2) at 427 nm. Compared with TpBpy, S1 in Ni-TpBpy involves the promotion of electronic density to the Ni (II) center. The detailed calculated excited state structures for both samples have been summarized in the supporting information.

Next, we analyze the excited state dynamics of TpBpy and Ni-TpBpy by fs-TA using the excited-state calculations described above as references. We first excited the samples at 530 nm, which corresponds to energy close to their optical bandgap. In this case, the excited species are expected to relax to the lowest excited state very quickly.

From the TD-DFT calculations, the band edge excitation in TpBpy only triggers the S1 transition from the HOMO to the LUMO (Fig. 2a). As shown in Fig. 3a, the pseudo-color TA spectra of TpBpy exhibit the characteristic ground-state bleach (GSB, negative B1) from 450 to 595 nm due to the band-edge states filling after excitation, together with excited-state absorption (ESA) features at the red side from 600 nm to 700 nm. The singular value decomposition (SVD) fitting of the TA spectra (lower panel of the figure) leads to three decay-associated components t<sub>1</sub>, t<sub>2</sub>, t<sub>3</sub> with respective lifetimes of  $\tau_1 = 2.8$  ps,  $\tau_2 = 70$  ps,  $\tau_3 = 3.8$  ns, and a component with ultralong lifetime. Previous studies have shown that component t<sub>1</sub>, t<sub>2</sub>, t<sub>3</sub> correspond respectively to polaron formation, exciton-exciton annihilation, and band-edge single exciton recombination. The ultra-long component t<sub>4</sub> ( $\tau_4 = >> 10$  ns) represents the recombination of the delocalized free carrier after exciton annihilation.<sup>36</sup>

After loading the Ni-complex, the fs-TA spectrum (Fig. 3b) exhibits one additional negative band (B2) around 470 nm. The SVD fitting extracts three components with lifetime of  $\tau_1 = 5$  ps,  $\tau_2 = 68$  ps as well as an ultra-long lifetime (the lower panel of Fig. 3b). These three components share the same spectral feature of B1 and B2 but not A1 nor A2 as shown in Fig. 3b. According to the calculation, the band-edge electronic transition in Ni-TpBpy is more diverse since Ni<sup>2+</sup> cation possesses two vacuum orbital sets corresponding to spin-up and spin-down electrons (i.e. a and b). (Fig. 2b). Here B1 should be assigned to the bleach of the band-edge absorption



**Figure 2.** UV-vis absorption spectra of a) TpBpy and b) Ni-TpBpy compared with Calculated DFT fragment

transition S1, while B2 should be due to the bleach of S2, S3, or S4 transition. Since the band edge excitation only triggers e S1, the B2 signal observed in component  $t_1$  should be induced by the population of LUMO<sub>a</sub> or LUMO<sub>b</sub> orbitals by S1, thereby diminishing the probability of S2 transition as shown in Fig. 2b.

In contrast with the pure COFs,  $t_1$  of Ni-TpBp does not display any ESA (Fig. 3a). This absence can be attributed to charge transfer from COFs moiety to Ni<sup>2+</sup>. Such a charge transfer should occur prior to the formation of  $t_1$  with the IRF of the system (i.e., subpicosecond timescale). This point is examined in the light of the TD-DFT calculations. Since HOMO<sub>b</sub> is directly located at Ni<sup>2+</sup> and

HOMO<sub>a</sub> is located close to the  $Ni^{2+}$ , the charge transfer process is greatly facilitated (Fig.2b).

In component  $t_2$ , the amplitude ratio of B1 over B2 significantly decreases. This should be attributed to the relaxation of the hot holes from deeper levels (HOMO<sub>b-2</sub> and HOMO<sub>a-2</sub>) to the HOMOs levels (HOMO<sub>b</sub> and HOMO<sub>a</sub>). The populations of HOMO<sub>a</sub> and HOMO<sub>b</sub> cause the bleach of S4, which in turn induces B2, as discussed above (Fig. 2b).

The long-lived t<sub>3</sub> only exhibits a single band B1 without any B2, signaling hot holes remaining in the deep levels. Since HOMO<sub>b</sub> is located at Ni<sup>2+</sup>, while the deeper HOMO levels of the b orbitals set are on the COFs moieties, the holes are spatially far from the electrons. In this case, the relaxation from the HOMO<sub>b-2</sub> to the HOMO<sub>b</sub> is hampered due to the fact that it involves an inter-unit charge transfer from COFs to Ni<sup>2+</sup>. Therefore, it should be the hole residing at the HOMO<sub>b</sub> in TpBpy moiety that is long-lived. The t<sub>3</sub> component should then be attributed to the recombination of hot holes at HOMO<sub>b-2</sub> and electrons at LUMO<sub>b</sub>. Such a scenario accounts for the long recombination time. On the contrary, the holes at HOMO<sub>a-2</sub> should quickly relax to the lowest excited level (HOMO<sub>a</sub>) within the COFs moiety as shown in Fig. 2b.





**Figure 3.** Transient absorption (TA) spectra under 530 nm (a),(b) and 400 nm (c), (d) excitation at the fluence of 2×1013 ph/cm2 of TpBpy and Ni-TpBpy.

Following the above analysis, the origin of the  $t_2$  component (68 ps) with both B1 and B2 can now be attributed to the recombination of

electrons and holes in the a orbitals set (i.e. the hole at HOMO<sub>a</sub> and the electron at  $Ni^{2+}$ ), with the population at HOMO<sub>a</sub> leading to the bleach B2.

The above-excited state dynamics triggered with 530 nm excitation are illustrated in Fig. 4b. In summary, the component  $t_1$  combines multiple processes including the hot hole cooling and/or the polaron formation along with the charge transfer from the COFs to Ni<sup>2+</sup>. The component  $t_2$  refers to the geminate recombination of electron on the Ni<sup>2+</sup> and cold holes located on COFs. The component  $t_3$  refers to the recombination of electrons on the Ni<sup>2+</sup> and with long-living hot holes in the COFs.

When excited at 400 nm with a photon energy of 3.1 eV much larger than the band-gap, the excited state evolution becomes more complicated. According to the calculation, S2 in TpBpy contains two transitions (i.e. HOMO $\rightarrow$ LUMO+2 and HOMO-3 $\rightarrow$ LUMO+1) (Fig. 2a). These two transitions lead to the high energy GSB B2, while HOMO $\rightarrow$ LUMO+2 also triggers B1, as the HOMO participates in the band edge transition S1.

The fs-TA spectra of TpBpy can be decomposed into four components with lifetimes of  $\tau_1 = 2$  ps,  $\tau_2 = 34$  ps, and  $\tau_3 = 480$  ps, (Fig. 3c). The fast component (t<sub>1</sub>) with the appearance of B1, B2, A1, A2 can be assigned to the hot electron cooling from high energy levels to low energy levels and/or polaron formation. The second component (t<sub>2</sub>) featuring both B1, B2, and A1 exhibited a lifetime similar to the one observed in time-resolved photoluminescence (TRPL) decay measurement of the same sample, and therefore can be attributed to the radiative recombination process. The coexistence of B1 and B2 indicates the reduced probability of both S1 and S2 through the excited-state population (Fig. 2a). Therefore, the radiative recombination can only be assigned to hot electrons at LUMO+2 and holes at HOMO. The last component (t<sub>3</sub>) featuring B1 and A1 represents the typical recombination of the band-edge electrons and holes after cooling.

Considering now Ni-TpBpy excited at 400 nm, the fs-TA spectra can also be fitted by four components with lifetimes of  $\tau_1 = 4$  ps,  $\tau_2 = 59$  ps,  $\tau_3 = 517$  ps together with an ultra-long lifetime (Fig. 3d). According to the TD-DFT calculations, several electronic transitions can be excited, namely, S2 (HOMO<sub>b</sub>-6  $\rightarrow$  LUMO<sub>b</sub>, HOMO<sub>a</sub>-6  $\rightarrow$  LUMO<sub>a</sub>); S3 (HOMO<sub>b</sub>-3  $\rightarrow$  LUMO<sub>b</sub>+3, HOMO<sub>a</sub>-3  $\rightarrow$  LUMO<sub>a</sub>+1); S4 (HOMO<sub>b</sub>  $\rightarrow$  LUMO<sub>b</sub>+4, HOMO<sub>a</sub>  $\rightarrow$  LUMO<sub>a</sub>+2). All three transitions lead to B2 in TA spectra, while S2 also induces B1, since LUMO<sub>a</sub> and LUMO<sub>b</sub> participate in S1 transition (Fig. 2b).

In the SVD fitting results, components  $t_1$  and  $t_2$  exhibit characteristics similar to TpBpy but with longer lifetimes (Fig. 3c&d). Therefore,  $t_1$  should be attributed to the cooling of photo-generated hot electrons and hot holes at the deep levels and/or polaron formation (Fig. 3d). For the  $t_2$  component, the value of the lifetime and the spectral lineshape (i.e. the coexistence of B1 and B2) are all similar to the observations under 530 nm excitation (Fig. 3b). Therefore, the process should also be assigned to the recombination of the electrons initially transferred to Ni<sup>2+</sup> with the holes at HOMO<sub>a</sub> (Fig. 3d).

The appearance of A1, which is absent under 530 nm excitation, can be ascribed to the fact that in the b orbitals set, the deep hole levels are all located on the COFs unit, while the lowest HOMO<sub>b</sub> resides at Ni<sup>2+</sup> (for the detailed structure, see S.I.). This makes the cooling less efficient and consequently, intra-COFs excited populations remain.

The component  $t_3$  exhibits distinctive features, combining B2, A1 and a red-shifted B1. The band B2 indicates long-lived hot electrons and holes at deep levels up to 500 ps, in contrast to the TpBpy. The lifetime of  $t_3$  (517 ps) can also be observed in the TRPL decay (Figure S10), reflecting high-energy-level radiative recombination between hot electrons and hot holes. This also complies with the



Figure 4. Schematic diagram of the pathway and lifetime excited state dynamics of TpBpy and Ni-TpBpy under a&b) 530 nm, and c&d) 400 nm excitation.

appearance of the steady-state emission band above the absorption edge in Figure 1b. As the electrons and holes in the a orbitals set have already undergone fast geminate recombination in component t<sub>2</sub> as discussed above. We believe that component t<sub>3</sub> should be assigned to the radiative recombination between hot holes and hot electrons in the b orbitals set (Fig. 4d). Since the HOMO<sub>b</sub> and LUMO<sub>b</sub> are not located in the COFs but in Ni<sup>2+</sup>, hot electron cooling is spatially hindered, as shown in Fig. 2b). The ultra-long component t<sub>4</sub> features the single band B1. This should correspond to the recombination of electrons directly excited to Ni<sup>2+</sup> (from S2) and the hot holes remaining in the COFs moiety, following a scenario similar to the 530 nm excitation (Fig. 4b).



**Figure 5**. Photocatalytic evolutions of CO by Ni-TpBpy under 520 nm and 440 nm excitation (a) and Schematic diagram to rationalize the catalytic performance under the two excitation conditions (b).

Fig. 4c&d summarize the excited-state dynamics for TpBpy and Ni-TpBpy under 400 nm excitation. In short, in TpBpy the excited hot electrons and holes either undergo hot emission or relax to the band edge. In Ni-TpBpy, the excited state dynamics depend on the location of the initially excited orbitals compared to the location of the HOMO/LUMO levels. Efficient electron transfer from the COFs moiety to Ni<sup>2+</sup> can be observed, followed by fast geminate recombination (68 ps) if the initial excitation and the HOMO/LUMO levels all reside in the COFs unit (left panel of Fig. 4b). If the HOMO/LUMO levels are located at the Ni<sup>2+</sup>, the intra-COFs excitations of the deep levels are depopulated by hot emission (517 ps) while the COF to Ni<sup>2+</sup> excitation lead to ultra-long lived population (> 10 ns) with electrons at Ni<sup>2+</sup> and holes at COFs (left panel of Fig. 4b))

These excitation-wavelength-dependent excited-state dynamics in Ni-TpBpy significantly influence the photocatalytic reaction. The possibility of concurrent intra-COFs and COFs to Ni<sup>2+</sup> excitation at high-energy excitation in Ni-TpBpy leads to two pools of photogenerated electrons located either at the COFs or at the Ni<sup>2+</sup>. This enables the favorable donation of two electrons for CO<sub>2</sub> reduction, which improves photocatalytic performances at high energy excitation as shown in Fig. 5. In addition, long-lived holes can promote the hole injection to the scavengers to prevent the hole accumulation that irremediable leads to decreased photocatalytic performances via a photochemical degradation process. (for details, see SI).

In summary, We have elucidated the excited-state dynamics of a Ni-TpBpy hybrid photocatalyst by combining TD-DFT calculations and time-resolved laser spectroscopy. We first investigated the nature of the transition underlying the optical absorption of TpBpy and Ni-TpBpy using time-dependent DFT calculations. Based on the analysis, strongly excitation wavelengthdependent inter-unit charge transfer pathways can be identified in Ni-TpBpy from the TA measurements. Under band-edge excitation, the electrons are quickly injected at the Ni<sup>2+</sup> center within 5 ps but recombine with the holes residing in TpBpy within a short time (68 ps). Electrons can also recombine with hot holes localized in TpBpy on a much longer timescale. Under high-energy excitation, some of the hot electrons are generated, and they remain in COFs moiety. These favorable concurrent pathways can promote the twoelectron mediated process in CO<sub>2</sub> reduction, while preventing hole accumulation. Our findings pave the way to understanding the photocatalytic performances of metalized COFs catalysts and

provide the necessary guidance for future rational material engineering.

#### **Supporting Information**

Materials, methods, detailed characterization of TpBpy, Ni-TpBpy and DFT calculations (PDF), Uv-Vis calculated by TD-DFT calculations (txt). This material is available free of charge via the internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interests.

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#### REFERENCES

(1) Song, C. Global Challenges and Strategies for Control, Conversion and Utilization of CO2 for Sustainable Development Involving Energy, Catalysis, Adsorption and Chemical Processing. *Catal. Today* **2006**, *115*, 2–32.

(2) Miller, B. G. CHAPTER 4 - Coal-Fired Emissions and Legislative Action in the United States. In *Sustainable World*; Miller, B. G. B. T.-C. E. S., Ed.; Academic Press: Burlington, 2005; pp 123–194.

(3) Omae, I. Aspects of Carbon Dioxide Utilization. *Catal. Today* **2006**, *115*, 33–52.

(4) Wu, J.; Huang, Y.; Ye, W.; Li, Y. CO2 Reduction: From the Electrochemical to Photochemical Approach. *Adv. Sci.* **2017**, *4*, 1700194.

(5) Tu, W.; Zhou, Y.; Zou, Z. Photocatalytic Conversion of CO2 into Renewable Hydrocarbon Fuels: State-of-the-Art Accomplishment, Challenges, and Prospects. *Adv. Mater.* **2014**, *26*, 4607–4626.

(6) Roy, S. C.; Varghese, O. K.; Paulose, M.; Grimes, C. A. Toward Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons. *ACS Nano* **2010**, *4*, 1259–1278.

(7) Wan, S.; Guo, J.; Kim, J.; Ihee, H.; Jiang, D. A Belt-Shaped, Blue Luminescent, and Semiconducting Covalent Organic Framework. *Angew. Chemie Int. Ed.* **2008**, *47*, 8826–8830.

(8)Huang, W.; Luo, W.; Li, Y. Two-Dimensional Semiconducting Covalent Organic Frameworks for Photocatalytic Solar Fuel Production. *Mater. Today* **2020**, *40*, 160–172.

(9) Hu, X.-L.; Li, H.-G.; Tan, B.-E. COFs-Based Porous Materials for Photocatalytic Applications. *Chinese J. Polym. Sci.* **2020**, *38*, 673–684.

(10) Yang, Q.; Luo, M.; Liu, K.; Cao, H.; Yan, H. Covalent Organic Frameworks for Photocatalytic Applications. *Appl. Catal. B Environ.* **2020**, *276*, 119174.

(11) Li, J.; Zhao, D.; Liu, J.; Liu, A.; Ma, D. Covalent Organic Frameworks: A Promising Materials Platform for Photocatalytic CO2 Reductions. *Molecules*. 2020.

(12) Huang, W.; Li, Y. Semiconducting 2D Covalent Organic

Frameworks: A New Opportunity for Efficient Solar Fuel Production. *Chinese J. Chem.* **2019**, *37*, 1291–1292.

(13) Vyas, V. S.; Haase, F.; Stegbauer, L.; Savasci, G.; Podjaski, F.; Ochsenfeld, C.; Lotsch, B. V. A Tunable Azine Covalent Organic Framework Platform for Visible Light-Induced Hydrogen Generation. *Nat. Commun.* **2015**, *6*, 8508.

(14) Haug, W. K.; Moscarello, E. M.; Wolfson, E. R.; McGrier, P. L. The Luminescent and Photophysical Properties of Covalent Organic Frameworks. *Chem. Soc. Rev.* **2020**, *49*, 839–864.

(15) Fu, Z.; Wang, X.; Gardner, A. M.; Wang, X.; Chong, S. Y.; Neri, G.; Cowan, A. J.; Liu, L.; Li, X.; Vogel, A.; Clowes, R.; Bilton, M.; Chen, L.; Sprick, R. S.; Cooper, A. I. A Stable Covalent Organic Framework for Photocatalytic Carbon Dioxide Reduction. *Chem. Sci.* **2020**, *11*, 543–550.

(16) Guo, K.; Zhu, X.; Peng, L.; Fu, Y.; Ma, R.; Lu, X.; Zhang, F.; Zhu, W.; Fan, M. Boosting Photocatalytic CO2 Reduction over a Covalent Organic Framework Decorated with Ruthenium Nanoparticles. *Chem. Eng. J.* **2021**, *405*, 127011.

(17) Dong, Z.; Zhang, L.; Gong, J.; Zhao, Q. Covalent Organic Framework Nanorods Bearing Single Cu Sites for Efficient Photocatalysis. *Chem. Eng. J.* **2021**, *403*, 126383.

(18) Aiyappa, H. B.; Thote, J.; Shinde, D. B.; Banerjee, R.; Kurungot, S. Cobalt-Modified Covalent Organic Framework as a Robust Water Oxidation Electrocatalyst. *Chem. Mater.* **2016**, *28*, 4375–4379.

(19) Wang, G.-B.; Li, S.; Yan, C.-X.; Zhu, F.-C.; Lin, Q.-Q.; Xie, K.-H.; Geng, Y.; Dong, Y.-B. Covalent Organic Frameworks: Emerging High-Performance Platforms for Efficient Photocatalytic Applications. J. Mater. Chem. A **2020**, *8*, 6957–6983.

(20) Yang, S.; Hu, W.; Zhang, X.; He, P.; Pattengale, B.; Liu, C.; Cendejas, M.; Hermans, I.; Zhang, X.; Zhang, J.; Huang, J. 2D Covalent Organic Frameworks as Intrinsic Photocatalysts for Visible Light-Driven CO2 Reduction. *J. Am. Chem. Soc.* 2018, *140*, 14614–14618.

(21) Popov, D. A.; Luna, J. M.; Orchanian, N. M.; Haiges, R.; Downes, C. A.; Marinescu, S. C. A 2,2'-Bipyridine-Containing Covalent Organic Framework Bearing Rhenium(i) Tricarbonyl Moieties for CO2 Reduction. *Dalt. Trans.* **2018**, *47*, 17450–17460.

(22) Li, S.-Y.; Meng, S.; Zou, X.; El-Roz, M.; Telegeev, I.; Thili, O.; Liu, T. X.; Zhu, G. Rhenium-Functionalized Covalent Organic Framework Photocatalyst for Efficient CO2 Reduction under Visible Light. *Microporous Mesoporous Mater.* **2019**, *285*, 195–201.

(23) Zhong, W.; Sa, R.; Li, L.; He, Y.; Li, L.; Bi, J.; Zhuang, Z.; Yu, Y.; Zou, Z. A Covalent Organic Framework Bearing Single Ni Sites as a Synergistic Photocatalyst for Selective Photoreduction of CO2 to CO. J. Am. Chem. Soc. **2019**, *141*, 7615–7621.

(24) Do, J. Y.; Kwak, B. S.; Park, S.-M.; Kang, M. Effective Carbon Dioxide Photoreduction over Metals (Fe-, Co-, Ni-, and Cu-) Incorporated TiO2/Basalt Fiber Films. *Int. J. Photoenergy* **2016**, *2016*, 5195138.

(25) Gao, Y.; Qian, K.; Xu, B.; Li, Z.; Zheng, J.; Zhao, S.; Ding, F.; Sun, Y.; Xu, Z. Recent Advances in Visible-Light-Driven Conversion of CO2 by Photocatalysts into Fuels or Value-Added Chemicals. *Carbon Resour. Convers.* **2020**, *3*, 46–59.

(26) Shinde, D. B.; Aiyappa, H. B.; Bhadra, M.; Biswal, B. P.; Wadge, P.; Kandambeth, S.; Garai, B.; Kundu, T.; Kurungot, S.; Banerjee, R. A Mechanochemically Synthesized Covalent Organic Framework as a Proton-Conducting Solid Electrolyte. *J. Mater. Chem. A* **2016**, *4*, 2682–2690.

(27) Über Die UV-Absorptionsspektren von Komplexionen Mit  $\pi$ -Elektronensystemen Als Liganden. *Zeitschrift für Phys. Chemie* **1956**, *8*, 373–386.

(28) Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-Group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Phys.* **2006**, *125*, 194101. (29) Tao, Y.; Zou, W.; Luo, G.-G.; Kraka, E. Describing Polytopal Rearrangement Processes of Octacoordinate Structures. I. Renewed Insights into Fluxionality of the Rhenium Polyhydride Complex ReH5(PPh3)2(Pyridine). *Inorg. Chem.* **2021**, *60*, 2492– 2502.

(30) Agarwal, J.; Fujita, E.; Schaefer, H. F.; Muckerman, J. T. Mechanisms for CO Production from CO2 Using Reduced Rhenium Tricarbonyl Catalysts. *J. Am. Chem. Soc.* **2012**, *134*, 5180–5186.

(31) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Function. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(32) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(33) Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.

(34) Li, Z.; Sheng, L.; Wang, H.; Wang, X.; Li, M.; Xu, Y.; Cui, H.; Zhang, H.; Liang, H.; Xu, H.; He, X. Three-Dimensional Covalent Organic Framework with Ceq Topology. *J. Am. Chem. Soc.* **2021**, *143*, 92–96.

(35) Wu, C.; Liu, Y.; Liu, H.; Duan, C.; Pan, Q.; Zhu, J.; Hu, F.; Ma, X.; Jiu, T.; Li, Z.; Zhao, Y. Highly Conjugated Three-Dimensional Covalent Organic Frameworks Based on Spirobifluorene for Perovskite Solar Cell Enhancement. *J. Am. Chem. Soc.* **2018**, *140*, 10016–10024.

(36) Jakowetz, A. C.; Hinrichsen, T. F.; Ascherl, L.; Sick, T.; Calik, M.; Auras, F.; Medina, D. D.; Friend, R. H.; Rao, A.; Bein, T. Excited-State Dynamics in Fully Conjugated 2D Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2019**, *141*, 11565–11571.

1	Ultrafast excited-state dynamics in a Ni-2,2'-bipyridine covalent organic	
2	framework photocatalyst	
3		
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24	Supplementary Information	
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# 

## 41 Materials and methods

(TEOA) ( $\geq$  99.0 %, Sigma-Aldrich).

47

42 5,5'-diamino-2,2'-bipyridine (95%, Yuhao Chemical), Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O ( $\geq$  98.0 %, Sigma-

43 Aldrich), Triformylphloroglucinol (95%, Yuhao Chemical), Mesitylene (98%, Sigma-Aldrich),

44 1,4-Dioxane (anhydrous, 99.8%, Sigma-Aldrich), glacial acetic acid (ACS reagent, Aldrich),

45 Nafion (10 wt% in H<sub>2</sub>O), 1-Propanol (for HPLC,  $\geq$  99.9%, Sigma-Aldrich), Acetonitrile (for

46 HPLC, VWR Chemicals), Tetrahydrofuran (for HPLC, VWR Chemicals), Triethanolamine

Synthesis of TpBpy. TpBpy was prepared according to literature methods with a little 48 modification.<sup>1</sup> A Pyrex tube (o.d.  $\times$  i.d. = 10  $\times$  8 mm<sup>2</sup> and length 25 cm) was charged with 49 triformylphloroglucinol (Tp) (21 mg, 0.10 mmol), 5,5'- diamino-2,2'- bipyridine (Bpy) (27.9 mg, 50 51 0.15 mmol), 0.5 mL 1,4-dioxane, 0.5 mL mesitylene, 0.1mL 6 M aqueous acetic acid. This mixture was sonicated for 20 min to get a homogeneous dispersion. The tube was flash-frozen in a liquid 52 nitrogen bath, evacuated to an internal pressure of ca.0.15 mmHg, and flame-sealed. The tube was 53 54 placed in an oven at 120 °C for 5 days upon warming to room temperature to afford an orange-red 55 precipitate. The precipitate was isolated by filtration over a medium glass frit and washed with 56 anhydrous tetrahydrofuran (THF, 20.0 mL). The product was immersed in anhydrous THF (20.0 mL) for 8 h, during which the activation solvent was decanted and freshly replenished four times. 57 58 The solvent was removed by filtration and the precipitate dried under vacuum at 60 °C overnight 59 to afford TpBpy (42 mg, 86%).

Synthesis of Ni-TpBpy. Ni-TpBpy was prepared according to literature methods with a little
 modification.<sup>1</sup> Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (30 mg) were dispersed in 20 mL acetonitrile, then TpBpy (50 mg)
 was added, the mixture was stirred for 8 h at room temperature. The orange products were filtered,

washed with acetonitrile for 3 times, dried under vacuum at 60 °C overnight, and used without
further purification.

Photocatalytic Reduction of CO<sub>2</sub>. The method of photocatalytic reduction of CO<sub>2</sub> was carried out according to literature methods with a little modification. Ni-TpBpy (1 mg) was dispersed in 3 mL of CH<sub>3</sub>CN, and 0.2 mL of TEOA (triethanolamine) in 11 mL septum-sealed glass vials. The mixture was purged with Ar for 5 min and CO<sub>2</sub> for 15 min first, then irradiated by a LED lamp with 520 nm and 440 wavelengths for 8 h and kept stirring during the photocatalytic reaction. The amount of CO generated was quantified using Shimadzu gas chromatography (GC-2010) by analyzing 500  $\mu$ L of the headspace.

# 72 Computational methods

73 To investigate the relationship of the optical properties with molecular structures and electronic structures, we used a triformylphloroglucinol (Tp) terminated bipyridine (Bpy) molecular 74 fragment (Fig. S10) to represent the COFs structure. An implicit solvent model was used to reflect 75 76 the solvation environment, and implemented using SMD solvation model<sup>2</sup> in Gaussian 16 package<sup>3</sup>. Considering the transition metal complex in the fragment, M06-L<sup>4-9</sup> was selected as the 77 functional and def 2-TZVP<sup>10,11</sup> was selected as the basis set for DFT calculations. Water and *n*-78 propanol parameters were used to represent the solvents in the SMD models.<sup>12</sup> Time-dependent 79 density functional theory (TD-DFT) calculations were also performed using these parameters. The 80 UV-vis absorption spectra and electron excitations were analyzed using the Multiwfn program.<sup>13</sup> 81

## 82 Characterization

The absorption spectra were measured in a UV-Vis absorption spectrophotometer from Agilent Technologies (Santa Clara, USA). Photoluminescence (PL) was performed via Spex Fluorolog I681 standard spectrofluorometer. Time-correlated single-photon counting (TCSPC) was 86 performed with excitation laser pulse triggered externally at 2.5 MHz to excite the sample at 438 nm. The emitted photons were detected by a fast avalanche photodiode (SPAD, Micro Photon 87 Device) with a response time less than 50 ps after passing through a 470 nm long bandpass filter. 88 Time-resolved photoluminescence (TRPL) spectra at early time scale were also obtained using a 89 streakcamera (Hamamatsu, C6860). The laser source is an amplified titanium/sapphire laser 90 providing 800 nm 55-fs pulses at 80 MHz which is then frequency doubled for 400 nm excitation. 91 It is important to note that during all photophysical measurements, the sample material was 92 dispersed in Nafion (5% w/w in water and 1-propanol), except for Tp that was dispersed in 93 94 acetonitrile.

Transient absorption (TA) spectroscopy measurements. Time-resolved experiments were carried 95 out on a laser-based spectroscopy setup, with laser pulse fluence as low as  $2 \times 10^{13}$  ph/cm<sup>2</sup>. Samples 96 for transient absorption experiments were kept in the dark between each measurement. A Coherent 97 Legend Ti: Sapphire amplifier (800 nm, 100 fs pulse length, 3 kHz repetition rate) was used. The 98 output is split into pump and probe beams. Excitation pulses at the wavelength of 400 and 530 nm 99 were generated using an optical parametric amplifier (Topas C, Light Conversion). The probe 100 pulses (a broad supercontinuum spectrum) were generated from the 800-nm pulses in a CaF<sub>2</sub> 101 crystal and split by a beam splitter into a probe pulse and a reference pulse. The probe pulse and 102 the reference pulse were dispersed in a spectrograph and detected by a diode array. The 103 Instrumental response time is  $\sim 100$  fs. Global SVD analysis was performed with the Glotaran 104 105 software package (http://glotaran.org).

- 106
- 107
- 108



**Supplementary Figure 1:** Emission spectra of TpBpy and Ni-TpBpy calibrated by the

absorption at the 530 nm excitation wavelength.



**Supplementary Figure 2:** Emission spectra of TpBpy and Ni-TpBpy calibrated by the

absorption at the 400 nm excitation wavelength.



119

**Supplementary Figure 3:** PL decays measured in TCSPC of the TpBpy and Ni-TpBpy.

121 Excitation wavelength=438 nm;

122



**Supplementary Figure 4:** PL decays of the TpBpy and Ni-TpBpy measured in streak camera.

# 125 Supplementary Table

**Supplementary Table 1:** Calculated DFT energy levels of the Ni-TpBpy fragment.

Orbital Name	Energy (α, eV)	Energy (β, eV)	
LUMO+12	-1.06956757		
LUMO+11	-1.07187156		
LUMO+10	-1.089035329	-1.069567371	
LUMO+9	-1.094767652	-1.071870004	

LUMO+8	-1.531433704		-1.089034126	•••••
LUMO+7	-1.984508277		-1.094765431	388 - 28 - 28 - 28 - 28 - 28 - 28 - 28 -
LUMO+6	-2.124905123	·····	-1.526853453	·····
LUMO+5	-2.194679381		-1.959669452	
LUMO+4	-2.197352314		-2.121084823	
LUMO+3	-2.325792107	1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	-2.194578179	
LUMO+2	-2.566775883		-2.19726709	
LUMO+1	-2.78796781		-2.319494271	
LUMO	-3.228181285	in the second	-2.547119934	
НОМО	-5.315957294		-2.786374066	
HOMO-1	-5.320596762		-2.905893338	

НОМО-2	-5.348020088	14-15-19-19-19-19-19-19-19-19-19-19-19-19-19-	-3.183312593	
НОМО-3	-5.576774803	24	-3.209822426	
HOMO-4	-5.854922471		-5.315944179	1.000
HOMO-5	-5.857925693		-5.320529662	10-10-10-10-10-10-10-10-10-10-10-10-10-1
НОМО-6	-5.936980865	.a.00.a.	-5.346701437	
HOMO-7	-6.190476381		-5.577804783	
HOMO-8	-6.238877148		-5.856911739	\$*00.8·
НОМО-9	-6.365236443		-5.859383169	
НОМО-10	-6.374666558		-5.933789159	
HOMO-11	-6.43152705		-6.192317056	

HOMO-12	-6.455286332	-6.364460223	
		-6.371223677	
		-6.425666696	

# 128 Table S2 | Atomic coordinates of Ni-TpBpy-n-propanol.

Atom	x/a	y/b	z/c
С	12.94746	8.09021	2.47272
С	13.61448	6.86961	2.54285
С	14.98855	6.84320	2.52677
С	15.70264	8.03771	2.44028
С	14.97361	9.22457	2.36728
Ν	13.64959	9.23656	2.38457
Ν	17.08490	7.99144	2.43322
С	17.93661	9.01609	2.37275
С	19.30784	8.89854	2.39266
С	19.96293	7.60591	2.48625
0	19.48606	11.24520	2.23533
Н	17.54458	7.07852	2.49221
С	11.49334	8.22923	2.49012
Ν	11.01842	9.48982	2.43568
С	9.71536	9.71746	2.44364
С	8.77470	8.68901	2.50466
С	9.24950	7.37955	2.56346
С	10.60735	7.15677	2.55637
Ν	7.43620	9.03553	2.50345
С	6.38933	8.20970	2.49744
С	5.07199	8.60780	2.49479
С	4.69818	10.01117	2.50657
0	4.41538	6.34277	2.46253
Н	7.17927	10.02659	2.50013
Н	13.06193	5.94384	2.61123
Н	15.52336	5.90334	2.58256

Н	15.45469	10.19073	2.29004
Н	17.52029	10.01366	2.30737
Н	9.39813	10.75367	2.39907
Н	8.57098	6.53984	2.61738
Н	10.97815	6.14300	2.60307
Н	6.59253	7.14576	2.48954
С	25.36154	2.46709	2.97847
С	26.04080	3.67702	2.96338
С	25.34469	4.86822	2.86216
С	23.95326	4.85927	2.77440
С	23.26694	3.64657	2.78741
С	23.97593	2.46227	2.88975
N	23.30626	6.09502	2.67453
С	22.00348	6.32389	2.61876
С	21.41415	7.57327	2.52351
С	22.20574	8.78481	2.47030
0	19.29088	6.54962	2.53573
Н	23.87706	6.94266	2.64426
Н	27.12112	3.69676	3.03126
Н	25.86977	5.81583	2.85088
Н	22.18820	3.62118	2.71573
Н	21.34593	5.46366	2.65282
С	0.42315	16.15285	2.57674
С	-0.47819	15.09784	2.56687
С	-0.02407	13.79139	2.54999
С	1.34504	13.52654	2.54274
С	2.25394	14.58294	2.55205
С	1.78549	15.88537	2.56912
Ν	1.73658	12.18389	2.52574
С	2.96554	11.69218	2.52351
С	3.28500	10.34427	2.50596
С	2.26099	9.32045	2.48650
0	5.57495	10.90581	2.51785
Н	1.00697	11.46800	2.51338
Н	-0.72267	12.96313	2.54246
Н	3.31937	14.39833	2.54568
Н	2.49753	16.70102	2.57624
Н	3.78712	12.39816	2.53667
С	-0.97672	2.58641	2.25046
С	0.38274	2.31245	2.29698
С	1.30224	3.34468	2.34814
С	0.86747	4.66949	2.35307
С	-0.49695	4.94930	2.30544
С	-1.40604	3.90672	2.25508

Ν	1.84663	5.66743	2.40451
С	1.66631	6.97901	2.42866
С	2.67630	7.92527	2.46503
С	4.06996	7.54608	2.47434
0	1.04602	9.62636	2.48674
Н	2.82755	5.38210	2.42113
Н	2.36487	3.13616	2.38461
Н	-0.85357	5.97017	2.30597
Н	-2.46438	4.13228	2.21806
Н	0.64593	7.34221	2.41691
С	23.99339	16.03082	2.07293
С	22.60827	16.01382	1.99137
С	21.92012	14.81497	2.04382
С	22.61587	13.61449	2.17941
С	24.00703	13.62665	2.26288
С	24.68289	14.83337	2.20845
N	21.86115	12.43744	2.22748
С	22.30577	11.19403	2.32119
С	21.51233	10.06044	2.36980
С	20.07067	10.14225	2.32560
0	23.45707	8.73623	2.50921
Н	20.84327	12.51414	2.18693
Н	22.05661	16.93933	1.88585
Н	20.83887	14.79428	1.97973
Н	24.56365	12.70582	2.37227
Н	23.37858	11.05146	2.36225
Н	25.90609	1.53528	3.05759
Н	23.43565	1.52401	2.89868
Н	0.06837	17.17510	2.59002
Н	-1.54352	15.29056	2.57242
Н	-1.69618	1.77903	2.21020
Н	0.73312	1.28812	2.29358
Н	24.53210	16.96849	2.03220
Н	25.76362	14.83510	2.27466
Ni	12.48348	10.94177	2.30360
0	13.21995	13.02194	-1.27624
Cl	12.52279	14.13276	-0.65576
0	12.48407	15.24606	-1.55086
0	13.21457	14.49589	0.56449
0	11.17411	13.71405	-0.32381
0	14.11287	12.25809	2.11103
0	12.38233	10.75971	0.19319
Н	13.86137	13.02252	1.55802
Н	12.78738	11.47887	-0.32777

Н	14.32686	12.65507	2.97519
Н	11.46744	10.72846	-0.11473
0	12.33927	14.02936	5.99177
Cl	13.28376	14.39697	4.97430
0	14.00843	15.57250	5.34797
0	12.59286	14.62456	3.72081
0	14.22521	13.29108	4.78745
0	11.16604	12.57732	2.30874
0	12.52753	11.02109	4.43022
Н	11.57371	13.29112	2.83502
Н	11.67527	11.29214	4.79610
Н	11.07446	12.95991	1.41588
Н	13.16061	11.68643	4.75470

### 131 **References**

- 132 (1) Zhong, W.; Sa, R.; Li, L.; He, Y.; Li, L.; Bi, J.; Zhuang, Z.; Yu, Y.; Zou, Z. A Covalent Organic
- 133 Framework Bearing Single Ni Sites as a Synergistic Photocatalyst for Selective Photoreduction of
- 134 CO2 to CO. J. Am. Chem. Soc. 2019, 141, 7615–7621.
- 135 (2) Marenich, A. V; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute
- 136 Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric

137 Constant and Atomic Surface Tensions. J. Phys. Chem. B 2009, 113, 6378–6396.

- (3) Frisch, M. J.; Trucks, G. W. G16\_C01. 2016, p Gaussian 16, Revision C.01, Gaussian, Inc.,
  Wallin.
- 140 (4) Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-Group Thermochemistry,
- Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions. J. Chem. *Phys.* 2006, 125, 194101.
- (5) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group
  Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and
  Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class

- 146 Functionals and 12 Other Function. *Theor. Chem. Acc.* 2008, *120*, 215–241.
- 147 (6) Tao, Y.; Zou, W.; Luo, G.-G.; Kraka, E. Describing Polytopal Rearrangement Processes of
  148 Octacoordinate Structures. I. Renewed Insights into Fluxionality of the Rhenium Polyhydride
- 149 Complex ReH5(PPh3)2(Pyridine). *Inorg. Chem.* **2021**, *60*, 2492–2502.
- 150 (7) Agarwal, J.; Fujita, E.; Schaefer, H. F.; Muckerman, J. T. Mechanisms for CO Production from
- 151 CO2 Using Reduced Rhenium Tricarbonyl Catalysts. J. Am. Chem. Soc. 2012, 134, 5180–5186.
- 152 (8) Dürr, A. B.; Fisher, H. C.; Kalvet, I.; Truong, K.-N.; Schoenebeck, F. Divergent Reactivity of
- 153 a Dinuclear (NHC)Nickel(I) Catalyst versus Nickel(0) Enables Chemoselective
- 154 Trifluoromethylselenolation. Angew. Chem. Int. Ed. Engl. 2017, 56, 13431–13435.
- 155 (9) Cammarota, R. C.; Vollmer, M. V; Xie, J.; Ye, J.; Linehan, J. C.; Burgess, S. A.; Appel, A.
- 156 M.; Gagliardi, L.; Lu, C. C. A Bimetallic Nickel–Gallium Complex Catalyzes CO2 Hydrogenation
- via the Intermediacy of an Anionic D10 Nickel Hydride. J. Am. Chem. Soc. 2017, 139, 14244–
  14250.
- 159 (10) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and
- Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* 2005, 7, 3297–3305.
- 162 (11) Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.*163 2006, 8, 1057–1065.
- (12) Borodin, O.; Behl, W.; Jow, T. R. Oxidative Stability and Initial Decomposition Reactions of
  Carbonate, Sulfone, and Alkyl Phosphate-Based Electrolytes. *J. Phys. Chem. C* 2013, *117*, 8661–
  8682.
- 167 (13) Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. J. Comput. Chem.

168	<b>2012</b> , <i>33</i> , 580–592.

#### caculated Uv-Vis-TpBpy-n-propanol

- # 1 2.3446 eV 528.81 nm f= 1.65630 Spin multiplicity= 1: H -> L 97.9%
- # 2 2.4170 eV 512.97 nm f= 0.03010 Spin multiplicity= 1:
- H-2 -> L 68.3%, H-1 -> L 22.8%, H-2 -> L+1 6.4%
- # 3 2.4257 eV 511.13 nm f= 0.03890 Spin multiplicity= 1:
- H-1 -> L 67.4%, H-2 -> L 22.5%, H-1 -> L+1 7.2%
- # 4 2.5125 eV 493.47 nm f= 0.00000 Spin multiplicity= 1:
- H -> L+1 70.8%, H-3 -> L 28.9%
- # 5 2.7013 eV 458.98 nm f= 0.16470 Spin multiplicity= 1:
- H-1 -> L+1 61.6%, H-2 -> L+1 21.2%, H-1 -> L+2 6.2%, H-1 -> L 5.5%
- # 6 2.7231 eV 455.31 nm f= 0.21300 Spin multiplicity= 1:
- H-2 -> L+1 61.5%, H-1 -> L+1 21.0%, H-2 -> L+2 6.5%, H-2 -> L 5.0%
- # 7 2.7410 eV 452.33 nm f= 0.00680 Spin multiplicity= 1:
  H-3 -> L 63.9%, H -> L+1 24.3%
- # 8 2.8416 eV 436.32 nm f= 0.77120 Spin multiplicity= 1:
- H-3 -> L+1 50.6%, H -> L+2 46.0%
- # 9 2.8714 eV 431.79 nm f= 0.00030 Spin multiplicity= 1:
- H-4 -> L 99.8%
- # 10 2.8780 eV 430.80 nm f= 0.00020 Spin multiplicity= 1:
- H-5 -> L 100.0%
- # 11 2.8899 eV 429.03 nm f= 0.01950 Spin multiplicity= 1:
  H-6 -> L 36.5%, H-3 -> L+1 33.3%, H -> L+2 28.0%
- # 12 2.9789 eV 416.21 nm f= 0.07410 Spin multiplicity= 1:
- H-2 -> L+2 47.7%, H -> L+4 30.7%, H-1 -> L+2 16.3%
- # 13 2.9874 eV 415.02 nm f= 0.06460 Spin multiplicity= 1:
- H -> L+3 44.8%, H-1 -> L+2 38.3%, H-2 -> L+2 12.9%
- # 14 3.0126 eV 411.55 nm f= 0.27370 Spin multiplicity= 1:
- H-6 -> L 50.8%, H -> L+2 17.5%, H-3 -> L+1 8.3%, H-2 -> L+4 8.1%, H-1 -> L+3 8.0%

- # 15 3.0644 eV 404.60 nm f= 0.16160 Spin multiplicity= 1:
- H -> L+4 59.0%, H-2 -> L+2 13.8%, H-2 -> L+5 12.8%
- # 16 3.0870 eV 401.63 nm f= 0.25600 Spin multiplicity= 1:
- H -> L+3 44.1%, H-1 -> L+2 20.5%, H-1 -> L+5 15.7%, H-2 -> L+2 7.1%
- # 17 3.0938 eV 400.75 nm f= 0.00000 Spin multiplicity= 1:

H-4 -> L+1 99.7%

- # 18 3.0990 eV 400.08 nm f= 0.00380 Spin multiplicity= 1: H -> L+5 59.0%, H-7 -> L 20.6%, H-3 -> L+2 12.5%
- # 19 3.1004 eV 399.90 nm f= 0.00000 Spin multiplicity= 1:
- H-5 -> L+1 99.5%
- # 20 3.1374 eV 395.18 nm f= 0.00000 Spin multiplicity= 1:
- H-2 -> L+3 75.5%, H-1 -> L+3 24.4%
- # 21 3.1378 eV 395.13 nm f= 0.00010 Spin multiplicity= 1:
- H-1 -> L+4 75.5%, H-2 -> L+4 24.3%
- # 22 3.1448 eV 394.25 nm f= 0.00020 Spin multiplicity= 1:
- H-6 -> L+1 72.9%, H-3 -> L+2 21.9%
- # 23 3.1855 eV 389.21 nm f= 0.00060 Spin multiplicity= 1:
- H-7 -> L 48.2%, H-3 -> L+2 38.0%, H-6 -> L+1 8.8%
- # 24 3.2215 eV 384.86 nm f= 0.17070 Spin multiplicity= 1:
- H-1 -> L+5 52.8%, H-2 -> L+5 18.8%, H-3 -> L+3 15.4%, H -> L+3 5.6%
- # 25 3.2389 eV 382.80 nm f= 0.17830 Spin multiplicity= 1:
- H-2 -> L+5 50.1%, H-3 -> L+4 22.6%, H-1 -> L+5 17.6%
- # 26 3.2573 eV 380.63 nm f= 0.00020 Spin multiplicity= 1:
- H-8 -> L 99.9%
- # 27 3.3337 eV 371.91 nm f= 0.05850 Spin multiplicity= 1:

H-1 -> L+3 21.6%, H -> L+5 19.8%, H-7 -> L 10.9%, H-3 -> L+2 9.3%, H-2 -> L+3 7.6%, H-2 -> L+4 6.7%, H -> L+6 5.1%

# 28 3.3591 eV 369.10 nm f= 0.06840 Spin multiplicity= 1:

H-7 -> L+1 72.7%, H-3 -> L+5 8.7%, H-2 -> L+4 8.2%

- # 29 3.4020 eV 364.45 nm f= 0.00010 Spin multiplicity= 1: H-9 -> L 99.6%
- # 30 3.4062 eV 364.00 nm f= 0.00010 Spin multiplicity= 1: H-10 -> L 99.7%
- # 31 3.4141 eV 363.15 nm f= 0.51550 Spin multiplicity= 1: H-3 -> L+3 75.9%
- # 32 3.4278 eV 361.70 nm f= 0.00060 Spin multiplicity= 1: H-11 -> L 98.8%
- # 33 3.4313 eV 361.33 nm f= 0.83430 Spin multiplicity= 1: H-3 -> L+4 71.2%, H-2 -> L+5 9.4%
- # 34 3.4343 eV 361.02 nm f= 0.56630 Spin multiplicity= 1: H-3 -> L+5 57.2%, H-2 -> L+4 13.4%, H-6 -> L+2 9.5%
- # 35 3.4367 eV 360.77 nm f= 0.03360 Spin multiplicity= 1: H-4 -> L+2 93.3%
- # 36 3.4446 eV 359.94 nm f= 0.00060 Spin multiplicity= 1: H-5 -> L+2 97.9%
- # 37 3.4777 eV 356.51 nm f= 0.00010 Spin multiplicity= 1: H-8 -> L+1 95.1%
- # 38 3.4847 eV 355.80 nm f= 0.00010 Spin multiplicity= 1: H-12 -> L 95.0%
- # 39 3.5199 eV 352.24 nm f= 0.01200 Spin multiplicity= 1: H-6 -> L+2 53.7%, H -> L+6 28.7%
- # 40 3.5509 eV 349.16 nm f= 0.00020 Spin multiplicity= 1:
- H-2 -> L+6 75.3%, H-1 -> L+6 24.5%
- # 41 3.5664 eV 347.65 nm f= 0.11230 Spin multiplicity= 1:
- H -> L+6 47.2%, H-6 -> L+2 12.2%, H-1 -> L+3 12.1%
- # 42 3.5689 eV 347.40 nm f= 0.12510 Spin multiplicity= 1:
- H-1 -> L+6 67.4%, H-2 -> L+6 22.3%
- # 43 3.6253 eV 342.00 nm f= 0.00000 Spin multiplicity= 1:

H-9 -> L+1 97.8%

- # 44 3.6290 eV 341.65 nm f= 0.00000 Spin multiplicity= 1: H-10 -> L+1 93.2%, H-4 -> L+4 5.3%
- # 45 3.6355 eV 341.04 nm f= 0.00010 Spin multiplicity= 1:
- H-4 -> L+3 94.0%, H-5 -> L+3 5.3%
- # 46 3.6405 eV 340.57 nm f= 0.00000 Spin multiplicity= 1:
- H-5 -> L+4 68.3%, H-4 -> L+4 30.6%
- # 47 3.6449 eV 340.16 nm f= 0.00000 Spin multiplicity= 1: H-11 -> L+1 68.3%, H-5 -> L+3 29.6%
- # 48 3.6502 eV 339.66 nm f= 0.00000 Spin multiplicity= 1:
- H-4 -> L+4 62.2%, H-5 -> L+4 30.9%
- # 49 3.6579 eV 338.95 nm f= 0.00000 Spin multiplicity= 1:
- H-5 -> L+3 63.7%, H-11 -> L+1 30.5%
- # 50 3.6820 eV 336.73 nm f= 0.00000 Spin multiplicity= 1: H-4 -> L+5 91.4%, H-5 -> L+5 5.8%
- # 51 3.6871 eV 336.26 nm f= 0.00010 Spin multiplicity= 1: H-5 -> L+5 93.3%, H-4 -> L+5 5.5%
- # 52 3.7047 eV 334.67 nm f= 0.00000 Spin multiplicity= 1: H-12 -> L+1 97.4%
- # 53 3.7219 eV 333.12 nm f= 0.00140 Spin multiplicity= 1:
- H-7 -> L+2 62.3%, H-6 -> L+5 32.6%
- # 54 3.7415 eV 331.38 nm f= 0.11290 Spin multiplicity= 1: H-6 -> L+4 85.9%, H-7 -> L+4 9.6%
- # 55 3.7449 eV 331.07 nm f= 0.11030 Spin multiplicity= 1: H-6 -> L+3 47.1%, H-3 -> L+6 26.9%, H-7 -> L+3 6.3%
- # 56 3.7462 eV 330.96 nm f= 0.08450 Spin multiplicity= 1: H-6 -> L+3 38.4%, H-3 -> L+6 37.2%
- # 57 3.7515 eV 330.49 nm f= 0.00060 Spin multiplicity= 1:

H-13 -> L 97.8%

- # 58 3.7540 eV 330.27 nm f= 0.00560 Spin multiplicity= 1:
- H-14 -> L 96.8%
- # 59 3.7559 eV 330.11 nm f= 0.00240 Spin multiplicity= 1: H-15 -> L 97.9%
- # 60 3.7578 eV 329.94 nm f= 0.00060 Spin multiplicity= 1:
- H-16 -> L 97.4%
- # 61 3.7838 eV 327.67 nm f= 0.00340 Spin multiplicity= 1:
- H-17 -> L 79.6%, H-18 -> L 13.9%
- # 62 3.8077 eV 325.61 nm f= 0.03470 Spin multiplicity= 1:
- H-18 -> L 42.5%, H -> L+7 30.3%, H-6 -> L+2 5.2%
- # 63 3.8224 eV 324.36 nm f= 0.00010 Spin multiplicity= 1:

H-8 -> L+2 98.3%

- # 64 3.8287 eV 323.83 nm f= 0.02070 Spin multiplicity= 1:
- H-2 -> L+4 12.4%, H-1 -> L+7 12.3%, H-7 -> L+2 10.7%, H-7 -> L 9.7%, H -> L+5 7.3%, H-6 -> L+1 6.9%, H-6 -> L+5 6.9%, H-3 -> L+2 6.3%
- # 65 3.8394 eV 322.93 nm f= 0.00430 Spin multiplicity= 1:
- H-2 -> L+7 57.3%, H-1 -> L+7 26.8%, H -> L+7 5.8%
- # 66 3.8416 eV 322.74 nm f= 0.00160 Spin multiplicity= 1:
- H-2 -> L+7 39.3%, H-1 -> L+7 37.8%, H -> L+7 5.6%
- # 67 3.8431 eV 322.62 nm f= 0.00370 Spin multiplicity= 1:
- H-1 -> L+7 22.5%, H -> L+7 19.8%, H-6 -> L+5 18.5%, H-3 -> L+6 7.2%, H-7 -> L+2 6.2%
- # 68 3.8918 eV 318.58 nm f= 0.00920 Spin multiplicity= 1:

H-6 -> L+5 25.4%, H-3 -> L+6 13.2%, H-7 -> L+2 11.8%, H -> L+7 9.6%, H-19 -> L 8.9%, H-3 -> L+2 5.1%

- # 69 3.9034 eV 317.63 nm f= 0.04320 Spin multiplicity= 1:
- H-18 -> L 21.5%, H -> L+8 19.1%, H-20 -> L 9.9%, H-7 -> L+5 8.6%, H-17 -> L 7.8%
- # 70 3.9576 eV 313.28 nm f= 0.00830 Spin multiplicity= 1:
- H-20 -> L 64.5%, H-19 -> L 14.0%, H -> L+8 9.2%
- # 71 3.9623 eV 312.91 nm f= 0.00100 Spin multiplicity= 1:
- H-19 -> L 69.1%, H-20 -> L 14.8%

- # 72 3.9737 eV 312.01 nm f= 0.00000 Spin multiplicity= 1: H-9 -> L+2 95.3%
- # 73 3.9749 eV 311.92 nm f= 0.00000 Spin multiplicity= 1: H-10 -> L+2 95.4%
- # 74 3.9804 eV 311.49 nm f= 0.00100 Spin multiplicity= 1: H-14 -> L+1 94.5%
- # 75 3.9820 eV 311.36 nm f= 0.00070 Spin multiplicity= 1: H-13 -> L+1 94.0%
- # 76 3.9839 eV 311.21 nm f= 0.00080 Spin multiplicity= 1: H-16 -> L+1 93.9%
- # 77 3.9862 eV 311.03 nm f= 0.00120 Spin multiplicity= 1: H-15 -> L+1 92.3%
- # 78 3.9881 eV 310.89 nm f= 0.00000 Spin multiplicity= 1: H-11 -> L+2 99.6%
- # 79 3.9981 eV 310.11 nm f= 0.00070 Spin multiplicity= 1:
  H-22 -> L 84.6%, H-21 -> L 5.6%
- # 80 4.0008 eV 309.90 nm f= 0.00020 Spin multiplicity= 1: H-17 -> L+1 76.2%, H-18 -> L+1 20.4%
- # 81 4.0037 eV 309.67 nm f= 0.00140 Spin multiplicity= 1: H-21 -> L 85.9%, H-22 -> L 6.2%
- # 82 4.0184 eV 308.54 nm f= 0.00040 Spin multiplicity= 1: H-8 -> L+3 97.5%
- # 83 4.0237 eV 308.13 nm f= 0.00080 Spin multiplicity= 1: H-8 -> L+4 95.9%
- # 84 4.0334 eV 307.39 nm f= 0.01640 Spin multiplicity= 1:
- H-7 -> L+3 65.4%, H-1 -> L+8 14.3%, H-6 -> L+3 6.6%
- # 85 4.0339 eV 307.36 nm f= 0.02500 Spin multiplicity= 1:
- H-7 -> L+4 62.8%, H-2 -> L+8 16.7%, H-6 -> L+4 5.7%
- # 86 4.0396 eV 306.92 nm f= 0.05440 Spin multiplicity= 1:

H-7 -> L+5 39.5%, H-3 -> L+7 28.0%, H-18 -> L+1 9.8%, H-6 -> L+6 6.7% # 87 4.0461 eV 306.43 nm f= 0.00110 Spin multiplicity= 1: H-12 -> L+2 88.0%, H-4 -> L+6 6.2% # 88 4.0497 eV 306.16 nm f= 0.00000 Spin multiplicity= 1: H-4 -> L+6 90.2% # 89 4.0528 eV 305.92 nm f= 0.02410 Spin multiplicity= 1: H-3 -> L+7 32.1%, H-7 -> L+5 32.0%, H-18 -> L+1 18.6% # 90 4.0572 eV 305.59 nm f= 0.00000 Spin multiplicity= 1: H-5 -> L+6 97.7% # 91 4.0645 eV 305.04 nm f= 0.00060 Spin multiplicity= 1: H-8 -> L+5 89.5%, H-12 -> L+2 5.8% # 92 4.0724 eV 304.45 nm f= 0.00210 Spin multiplicity= 1: H-18 -> L+1 43.3%, H-3 -> L+7 33.1%, H-17 -> L+1 12.2% # 93 4.0784 eV 304.00 nm f= 0.00100 Spin multiplicity= 1: H -> L+9 94.8% # 94 4.0791 eV 303.95 nm f= 0.00050 Spin multiplicity= 1: H -> L+10 94.4% # 95 4.0822 eV 303.72 nm f= 0.00050 Spin multiplicity= 1: H -> L+11 95.4% # 96 4.0828 eV 303.67 nm f= 0.00090 Spin multiplicity= 1: H -> L+12 95.3% # 97 4.1306 eV 300.16 nm f= 0.00020 Spin multiplicity= 1: H-1 -> L+8 60.5%, H-2 -> L+8 19.2%, H-7 -> L+3 12.8% # 98 4.1367 eV 299.72 nm f= 0.00020 Spin multiplicity= 1: H-2 -> L+8 57.8%, H-1 -> L+8 18.6%, H-7 -> L+4 14.9% # 99 4.1628 eV 297.84 nm f= 0.00110 Spin multiplicity= 1: H-6 -> L+6 83.5% # 100 4.1669 eV 297.55 nm f= 0.00000 Spin multiplicity= 1: H-9 -> L+4 99.3%

- # 101 4.1701 eV 297.32 nm f= 0.00000 Spin multiplicity= 1:
- H-10 -> L+3 91.0%, H-9 -> L+3 8.7%
- # 102 4.1719 eV 297.19 nm f= 0.00000 Spin multiplicity= 1: H-9 -> L+3 88.0%, H-10 -> L+3 8.8%
- # 103 4.1804 eV 296.58 nm f= 0.00010 Spin multiplicity= 1: H-10 -> L+4 95.8%
- # 104 4.1899 eV 295.91 nm f= 0.00000 Spin multiplicity= 1: H-11 -> L+4 99.3%
- # 105 4.1990 eV 295.27 nm f= 0.00070 Spin multiplicity= 1: H-19 -> L+1 66.3%, H-20 -> L+1 21.2%
- # 106 4.1991 eV 295.26 nm f= 0.00000 Spin multiplicity= 1:
- H-2 -> L+9 74.7%, H-1 -> L+9 24.6%
- # 107 4.1999 eV 295.21 nm f= 0.00000 Spin multiplicity= 1:
- H-1 -> L+10 75.2%, H-2 -> L+10 24.6%
- # 108 4.2031 eV 294.98 nm f= 0.00000 Spin multiplicity= 1:
- H-2 -> L+11 75.6%, H-1 -> L+11 24.0%
- # 109 4.2039 eV 294.93 nm f= 0.00000 Spin multiplicity= 1: H-1 -> L+12 75.7%, H-2 -> L+12 24.0%
- # 110 4.2103 eV 294.48 nm f= 0.00000 Spin multiplicity= 1: H-11 -> L+3 95.2%
- # 111 4.2127 eV 294.31 nm f= 0.00020 Spin multiplicity= 1: H-20 -> L+1 68.4%, H-19 -> L+1 21.0%
- # 112 4.2131 eV 294.28 nm f= 0.00000 Spin multiplicity= 1: H-9 -> L+5 94.5%
- # 113 4.2219 eV 293.67 nm f= 0.00000 Spin multiplicity= 1: H-10 -> L+5 96.7%
- # 114 4.2327 eV 292.92 nm f= 0.00000 Spin multiplicity= 1: H-11 -> L+5 92.9%, H-12 -> L+3 5.0%
- # 115 4.2401 eV 292.41 nm f= 0.00310 Spin multiplicity= 1:

H -> L+8 32.3%, H-18 -> L+2 15.4%, H-17 -> L+2 14.3%, H-7 -> L+6 6.4%

# 116 4.2463 eV 291.98 nm f= 0.00000 Spin multiplicity= 1:

H-12 -> L+3 94.5%

# 117 4.2492 eV 291.78 nm f= 0.00650 Spin multiplicity= 1:

H-21 -> L+1 27.1%, H-1 -> L+9 23.8%, H-1 -> L+11 12.7%, H-16 -> L+2 10.8%, H-2 -> L+9 7.8%

# 118 4.2541 eV 291.45 nm f= 0.00220 Spin multiplicity= 1:

H-1 -> L+9 29.0%, H-21 -> L+1 19.2%, H-1 -> L+11 10.9%, H-2 -> L+9 9.4%, H-14 -> L+2 7.3%, H-16 -> L+2 6.2%

# 119 4.2549 eV 291.39 nm f= 0.01060 Spin multiplicity= 1:

H-2 -> L+10 33.1%, H-2 -> L+12 18.4%, H-15 -> L+2 12.7%, H-1 -> L+10 11.0%, H-1 -> L+12 5.9%, H-22 -> L+1 5.1%

# 120 4.2560 eV 291.32 nm f= 0.00000 Spin multiplicity= 1:

H-12 -> L+4 97.7%

# 121 4.2567 eV 291.27 nm f= 0.01260 Spin multiplicity= 1:

H-21 -> L+1 36.5%, H-1 -> L+11 28.2%, H-14 -> L+2 9.2%, H-2 -> L+11 8.3%

# 122 4.2576 eV 291.21 nm f= 0.00610 Spin multiplicity= 1:

H-2 -> L+12 30.4%, H-2 -> L+10 19.9%, H-13 -> L+2 14.9%, H-1 -> L+12 10.1%, H-1 -> L+10 6.6%

# 123 4.2685 eV 290.46 nm f= 0.00380 Spin multiplicity= 1:

H-22 -> L+1 76.4%

# 124 4.2902 eV 288.99 nm f= 0.00000 Spin multiplicity= 1:

H-12 -> L+5 98.4%

# 125 4.3251 eV 286.66 nm f= 0.00370 Spin multiplicity= 1:

H-13 -> L+2 73.7%, H-3 -> L+12 10.1%, H-2 -> L+12 7.8%

# 126 4.3269 eV 286.54 nm f= 0.00290 Spin multiplicity= 1:

H-15 -> L+2 76.0%, H-3 -> L+10 10.2%, H-2 -> L+10 6.0%

# 127 4.3317 eV 286.23 nm f= 0.00300 Spin multiplicity= 1:

H-14 -> L+2 69.7%, H-3 -> L+11 13.2%, H-1 -> L+11 7.9%

# 128 4.3334 eV 286.11 nm f= 0.00400 Spin multiplicity= 1:

H-16 -> L+2 71.2%, H-3 -> L+9 14.5%, H-1 -> L+9 6.2%

# 129 4.3374 eV 285.85 nm f= 0.00010 Spin multiplicity= 1:

H-4 -> L+7 95.4%

- # 130 4.3437 eV 285.43 nm f= 0.00000 Spin multiplicity= 1: H-5 -> L+7 98.9%
- # 131 4.3464 eV 285.26 nm f= 0.00320 Spin multiplicity= 1: H-17 -> L+2 53.3%, H-7 -> L+6 29.5%
- # 132 4.3570 eV 284.56 nm f= 0.00330 Spin multiplicity= 1: H-18 -> L+2 44.9%, H-7 -> L+6 32.7%, H-17 -> L+2 11.4%
- # 133 4.3757 eV 283.35 nm f= 0.00010 Spin multiplicity= 1: H-3 -> L+8 73.8%
- # 134 4.4180 eV 280.63 nm f= 0.00660 Spin multiplicity= 1:
- H-3 -> L+10 76.6%, H-15 -> L+4 12.4%
- # 135 4.4189 eV 280.58 nm f= 0.01090 Spin multiplicity= 1: H-3 -> L+9 66.5%, H-16 -> L+3 10.9%, H-3 -> L+11 6.7%
- # 136 4.4206 eV 280.47 nm f= 0.00420 Spin multiplicity= 1:
- H-3 -> L+11 68.1%, H-14 -> L+3 11.2%, H-3 -> L+9 6.0%
- # 137 4.4212 eV 280.43 nm f= 0.00580 Spin multiplicity= 1:
- H-3 -> L+12 75.2%, H-13 -> L+4 13.3%
- # 138 4.4281 eV 279.99 nm f= 0.01940 Spin multiplicity= 1:
- H-6 -> L+7 65.9%, H-7 -> L+6 15.3%
- # 139 4.4682 eV 277.48 nm f= 0.00010 Spin multiplicity= 1:
- H-8 -> L+6 97.4%
- # 140 4.5049 eV 275.22 nm f= 0.00270 Spin multiplicity= 1:
- H-20 -> L+2 17.9%, H-18 -> L+2 17.5%, H-6 -> L+8 17.0%, H-17 -> L+2 8.1%, H-6 -> L+7 6.7%, H -> L+8 5.4%
- # 141 4.5074 eV 275.07 nm f= 0.00000 Spin multiplicity= 1:
- H-13 -> L+3 99.6%
- # 142 4.5088 eV 274.98 nm f= 0.00000 Spin multiplicity= 1:
- H-14 -> L+4 99.5%

- # 143 4.5116 eV 274.81 nm f= 0.00000 Spin multiplicity= 1: H-15 -> L+3 98.8%
- # 144 4.5126 eV 274.75 nm f= 0.00000 Spin multiplicity= 1: H-16 -> L+4 98.9%
- # 145 4.5392 eV 273.14 nm f= 0.00100 Spin multiplicity= 1: H-13 -> L+5 58.3%, H-13 -> L+4 17.2%, H-19 -> L+2 6.9%
- # 146 4.5404 eV 273.07 nm f= 0.00030 Spin multiplicity= 1:
- H-17 -> L+3 79.2%, H-18 -> L+3 13.4%
- # 147 4.5415 eV 273.00 nm f= 0.00070 Spin multiplicity= 1:
- H-17 -> L+4 36.2%, H-15 -> L+5 29.1%, H-15 -> L+4 12.2%
- # 148 4.5429 eV 272.92 nm f= 0.00010 Spin multiplicity= 1:
- H-17 -> L+4 36.3%, H-14 -> L+5 17.0%, H-15 -> L+5 10.8%, H-13 -> L+5 7.9%, H-18 -> L+4 7.4%
- # 149 4.5438 eV 272.86 nm f= 0.00100 Spin multiplicity= 1:
- H-14 -> L+5 52.3%, H-15 -> L+5 18.6%, H-14 -> L+3 10.7%, H-15 -> L+4 6.2%, H-17 -> L+4 5.3%
- # 150 4.5469 eV 272.68 nm f= 0.00060 Spin multiplicity= 1:
- H-16 -> L+5 74.5%, H-16 -> L+3 16.9%
- # 151 4.5553 eV 272.18 nm f= 0.00620 Spin multiplicity= 1:
- H-19 -> L+2 35.4%, H-20 -> L+2 11.8%, H-20 -> L+5 7.6%, H-22 -> L+2 7.2%
- # 152 4.5563 eV 272.12 nm f= 0.00100 Spin multiplicity= 1:
- H-22 -> L+2 56.1%, H-18 -> L+4 18.2%
- # 153 4.5617 eV 271.79 nm f= 0.00520 Spin multiplicity= 1:
- H-21 -> L+2 48.8%, H-18 -> L+3 26.3%, H-19 -> L+3 5.4%
- # 154 4.5659 eV 271.54 nm f= 0.00170 Spin multiplicity= 1:
- H-23 -> L 48.1%, H-17 -> L+5 21.8%
- # 155 4.5820 eV 270.59 nm f= 0.00130 Spin multiplicity= 1:
- H-9 -> L+6 81.4%, H-17 -> L+5 6.5%
- # 156 4.5827 eV 270.55 nm f= 0.01140 Spin multiplicity= 1:

H-20 -> L+2 23.8%, H-19 -> L+2 14.0%, H-17 -> L+5 13.6%, H-9 -> L+6 13.2%, H-18 -> L+5 6.2%, H-19 -> L+5 6.0%

# 157 4.5837 eV 270.49 nm f= 0.00010 Spin multiplicity= 1:

H-10 -> L+6 97.8%

# 158 4.5876 eV 270.26 nm f= 0.00120 Spin multiplicity= 1:

H-17 -> L+5 34.4%, H-18 -> L+5 24.2%, H-7 -> L+7 8.6%, H-23 -> L 7.0%, H-24 -> L 5.1%

# 159 4.5973 eV 269.69 nm f= 0.01790 Spin multiplicity= 1:

H-14 -> L+3 49.1%, H-14 -> L+5 14.5%, H-6 -> L+11 11.9%

# 160 4.5997 eV 269.55 nm f= 0.00690 Spin multiplicity= 1:

H-16 -> L+3 45.6%, H-16 -> L+5 15.7%, H-6 -> L+9 11.9%

# 161 4.6028 eV 269.37 nm f= 0.00200 Spin multiplicity= 1:

H-4 -> L+8 74.1%, H-11 -> L+6 7.7%, H-13 -> L+4 6.9%

# 162 4.6031 eV 269.35 nm f= 0.01100 Spin multiplicity= 1:

H-13 -> L+4 33.4%, H-13 -> L+5 14.7%, H-4 -> L+8 14.3%, H-6 -> L+12 9.1%

# 163 4.6045 eV 269.27 nm f= 0.00000 Spin multiplicity= 1:

H-11 -> L+6 83.3%, H-4 -> L+8 10.9%, H-5 -> L+8 5.0%

# 164 4.6058 eV 269.19 nm f= 0.01000 Spin multiplicity= 1:

H-15 -> L+4 40.4%, H-15 -> L+5 22.0%, H-6 -> L+10 12.4%

# 165 4.6097 eV 268.96 nm f= 0.00000 Spin multiplicity= 1:

H-5 -> L+8 93.9%, H-11 -> L+6 5.5%

# 166 4.6148 eV 268.67 nm f= 0.02060 Spin multiplicity= 1:

H-18 -> L+4 24.5%, H-7 -> L+7 20.6%, H-24 -> L 7.0%, H-17 -> L+4 6.5%, H-22 -> L+2 5.9%, H -> L+14 5.4%, H-18 -> L+5 5.3%

# 167 4.6166 eV 268.56 nm f= 0.01460 Spin multiplicity= 1:

H-7 -> L+7 23.8%, H-18 -> L+4 21.8%, H-24 -> L 8.6%, H-18 -> L+5 6.5%, H-17 -> L+4 5.8%, H -> L+14 5.5%, H-22 -> L+2 5.0%

# 168 4.6221 eV 268.24 nm f= 0.03710 Spin multiplicity= 1:

H-18 -> L+3 40.6%, H-21 -> L+2 18.0%, H -> L+13 16.9%, H-17 -> L+3 11.5%

# 169 4.6743 eV 265.25 nm f= 0.00120 Spin multiplicity= 1:

H-12 -> L+6 96.7%

# 170 4.6877 eV 264.49 nm f= 0.00040 Spin multiplicity= 1:

H-19 -> L+4 51.4%, H-20 -> L+4 45.1%

- # 171 4.6879 eV 264.48 nm f= 0.00050 Spin multiplicity= 1: H-20 -> L+3 57.1%, H-19 -> L+3 38.9%
- # 172 4.6933 eV 264.17 nm f= 0.00740 Spin multiplicity= 1: H-24 -> L 45.0%, H-7 -> L+7 30.2%, H-6 -> L+8 5.2%
- # 173 4.6967 eV 263.98 nm f= 0.00000 Spin multiplicity= 1:

H-4 -> L+9 99.9%

- # 174 4.6975 eV 263.94 nm f= 0.00000 Spin multiplicity= 1: H-4 -> L+10 99.9%
- # 175 4.7007 eV 263.76 nm f= 0.00000 Spin multiplicity= 1: H-4 -> L+11 99.9%
- # 176 4.7015 eV 263.71 nm f= 0.00000 Spin multiplicity= 1:

H-4 -> L+12 99.9%

# 177 4.7032 eV 263.62 nm f= 0.00000 Spin multiplicity= 1:

H-5 -> L+9 99.9%

# 178 4.7040 eV 263.57 nm f= 0.00030 Spin multiplicity= 1:

H-5 -> L+10 98.6%

# 179 4.7042 eV 263.56 nm f= 0.01640 Spin multiplicity= 1:

H-18 -> L+5 26.0%, H-25 -> L 15.4%, H-17 -> L+5 12.6%, H-23 -> L 11.8%, H-7 -> L+8 7.5%, H-24 -> L 7.3%

# 180 4.7072 eV 263.39 nm f= 0.00000 Spin multiplicity= 1:

H-5 -> L+11 99.9%

# 181 4.7073 eV 263.39 nm f= 0.00030 Spin multiplicity= 1:

H -> L+14 74.9%, H-22 -> L+5 11.0%

# 182 4.7080 eV 263.35 nm f= 0.00000 Spin multiplicity= 1:

H-5 -> L+12 100.0%

# 183 4.7136 eV 263.04 nm f= 0.00190 Spin multiplicity= 1:

H -> L+13 67.1%, H-21 -> L+5 11.9%

# 184 4.7318 eV 262.02 nm f= 0.00000 Spin multiplicity= 1:

H-22 -> L+3 94.0%, H-21 -> L+3 5.8%

- # 185 4.7322 eV 262.00 nm f= 0.00000 Spin multiplicity= 1:
- H-21 -> L+4 94.0%, H-22 -> L+4 5.7%
- # 186 4.7372 eV 261.72 nm f= 0.01090 Spin multiplicity= 1:
- H-23 -> L+1 32.4%, H-8 -> L+7 30.7%, H-6 -> L+8 15.4%, H -> L+16 9.1%
- # 187 4.7456 eV 261.26 nm f= 0.00200 Spin multiplicity= 1:
- H-8 -> L+7 53.8%, H-23 -> L+1 29.1%
- # 188 4.7546 eV 260.77 nm f= 0.00030 Spin multiplicity= 1:
- H -> L+15 55.0%, H -> L+16 18.6%, H-20 -> L+5 10.3%
- # 189 4.7564 eV 260.67 nm f= 0.00020 Spin multiplicity= 1:
- H -> L+16 40.0%, H-23 -> L+1 21.1%, H -> L+15 20.2%
- # 190 4.7679 eV 260.04 nm f= 0.01040 Spin multiplicity= 1:
- H-24 -> L+1 34.3%, H-25 -> L 27.7%, H -> L+16 7.4%, H-19 -> L+5 6.5%
- # 191 4.7918 eV 258.74 nm f= 0.02170 Spin multiplicity= 1:
- H-19 -> L+5 20.3%, H-24 -> L+1 16.6%, H-21 -> L+3 9.4%, H-6 -> L+8 9.2%
- # 192 4.7999 eV 258.31 nm f= 0.03710 Spin multiplicity= 1:

H-21 -> L+5 70.4%

# 193 4.8099 eV 257.77 nm f= 0.02580 Spin multiplicity= 1:

H-6 -> L+10 60.2%, H-22 -> L+5 12.8%, H-7 -> L+10 5.5%

- # 194 4.8102 eV 257.75 nm f= 0.00010 Spin multiplicity= 1:
- H-2 -> L+13 74.3%, H-1 -> L+13 24.7%
- # 195 4.8109 eV 257.72 nm f= 0.00000 Spin multiplicity= 1:
- H-1 -> L+14 78.0%, H-2 -> L+14 20.6%
- # 196 4.8120 eV 257.66 nm f= 0.02820 Spin multiplicity= 1:
- H-22 -> L+5 21.7%, H-22 -> L+4 17.3%, H-2 -> L+14 12.5%, H-6 -> L+11 7.6%, H-20 -> L+5 6.6%
- # 197 4.8134 eV 257.58 nm f= 0.01400 Spin multiplicity= 1:
- H-6 -> L+9 67.4%, H-7 -> L+9 7.2%, H-16 -> L+3 5.2%
- # 198 4.8142 eV 257.54 nm f= 0.01600 Spin multiplicity= 1:
- H-6 -> L+12 67.9%, H-7 -> L+12 6.3%, H-6 -> L+11 5.2%

# 199 4.8159 eV 257.45 nm f= 0.01510 Spin multiplicity= 1:

H-6 -> L+11 41.0%, H-22 -> L+5 16.6%, H-6 -> L+12 5.2%

# 200 4.8222 eV 257.11 nm f= 0.01480 Spin multiplicity= 1:

H-22 -> L+5 14.7%, H-22 -> L+4 13.1%, H-6 -> L+11 13.1%, H-6 -> L+10 9.1%, H-2 -> L+14 6.5%

#### caculated Uv-Vis-Ni-TpBpy-n-propanol

- # 1 1.9834 eV 625.11 nm f= 0.00100 Spin multiplicity= ?:
- Ha-1 -> La 39.8%, Hb-1 -> Lb 39.2%, Ha-2 -> La 10.2%, Hb-2 -> Lb 6.2%
- # 2 2.0881 eV 593.77 nm f= 0.00010 Spin multiplicity= ?:
- Ha-2 -> La 43.2%, Hb-2 -> Lb 35.5%, Ha-1 -> La 11.2%, Hb-1 -> Lb 5.6%
- # 3 2.0903 eV 593.14 nm f= 0.00010 Spin multiplicity= ?:
- Ha -> La 56.4%, Hb -> Lb 38.8%
- # 4 2.1035 eV 589.42 nm f= 0.00010 Spin multiplicity= ?:
- Hb-9 -> Lb+1 41.8%, Hb-8 -> Lb+1 30.3%, Hb-9 -> Lb+3 11.4%, Hb-11 -> Lb+1 6.9%, Hb-8 -> Lb+3 6.7%
- # 5 2.1738 eV 570.36 nm f= 0.02180 Spin multiplicity= ?:
- Hb -> Lb 57.2%, Ha -> La 40.4%
- # 6 2.1905 eV 566.01 nm f= 0.00010 Spin multiplicity= ?:
- Hb-11 -> Lb+1 67.9%, Hb-9 -> Lb+1 15.6%, Hb-11 -> Lb+3 13.3%
- # 7 2.2003 eV 563.49 nm f= 0.03740 Spin multiplicity= ?:
- Hb-2 -> Lb 44.8%, Ha-2 -> La 31.0%, Ha-1 -> La 11.2%, Hb-1 -> Lb 10.2%
- # 8 2.2601 eV 548.58 nm f= 1.77040 Spin multiplicity= ?:
- Hb-1 -> Lb 41.2%, Ha-1 -> La 34.4%, Ha-2 -> La 12.2%, Hb-2 -> Lb 9.6%
- # 9 2.2833 eV 543.00 nm f= 0.00040 Spin multiplicity= ?:
- Ha-3 -> La 45.4%, Hb-3 -> Lb 38.5%, Hb-1 -> Lb+2 5.4%
- # 10 2.3915 eV 518.44 nm f= 0.00140 Spin multiplicity= ?:
- Hb-8 -> Lb+3 64.9%, Hb-9 -> Lb+3 30.8%, Hb-11 -> Lb+3 6.2%
- # 11 2.4081 eV 514.86 nm f= 0.00000 Spin multiplicity= ?: Hb -> Lb+1 98.1%
- # 12 2.4146 eV 513.48 nm f= 0.00000 Spin multiplicity= ?: Hb -> Lb+2 43.3%, Ha -> La+1 42.5%
- # 13 2.4195 eV 512.44 nm f= 0.00000 Spin multiplicity= ?: Hb-2 -> Lb+1 57.3%, Hb-1 -> Lb+1 42.0%
- # 14 2.4294 eV 510.35 nm f= 0.00010 Spin multiplicity= ?: Hb-1 -> Lb+1 52.3%, Hb-2 -> Lb+1 41.8%

# 15 2.4539 eV 505.25 nm f= 0.00680 Spin multiplicity= ?:

Ha-1 -> La+1 45.2%, Hb-1 -> Lb+2 25.8%, Ha-3 -> La 20.0%

# 16 2.4629 eV 503.41 nm f= 0.02110 Spin multiplicity= ?:

Hb-3 -> Lb 29.1%, Ha-3 -> La 19.2%, Hb-1 -> Lb+2 18.8%, Ha-2 -> La+1 17.3%, Hb-2 -> Lb+2 6.8%

# 17 2.4649 eV 503.00 nm f= 0.00920 Spin multiplicity= ?:

Hb-2 -> Lb+2 35.7%, Hb-3 -> Lb 21.3%, Ha-2 -> La+1 20.5%

# 18 2.5575 eV 484.79 nm f= 0.00000 Spin multiplicity= ?:

Ha-6 -> La 16.6%, Hb-6 -> Lb 15.7%, Hb-1 -> Lb+4 13.0%, Ha-1 -> La+2 12.6%, Hb-3 -> Lb+2 8.6%, Ha-3 -> La+1 8.2%

# 19 2.6120 eV 474.67 nm f= 0.05430 Spin multiplicity= ?:

Ha-2 -> La+1 36.0%, Hb-2 -> Lb+2 33.8%, Ha-1 -> La+1 11.7%, Hb-1 -> Lb+2 7.1%

# 20 2.6372 eV 470.14 nm f= 0.00000 Spin multiplicity= ?:

Ha-4 -> La 88.0%, Hb-4 -> Lb 10.9%

# 21 2.6531 eV 467.32 nm f= 0.00000 Spin multiplicity= ?:

Ha-5 -> La 76.4%, Hb-5 -> Lb 20.8%

# 22 2.6536 eV 467.23 nm f= 0.12340 Spin multiplicity= ?:

Ha -> La+1 41.5%, Hb -> Lb+2 40.9%, Ha -> La+2 7.5%, Hb -> Lb+4 6.3%

# 23 2.6652 eV 465.20 nm f= 0.00000 Spin multiplicity= ?:

Hb-3 -> Lb+1 99.9%

# 24 2.6688 eV 464.57 nm f= 0.00000 Spin multiplicity= ?:

Hb-4 -> Lb 86.6%, Ha-4 -> La 11.5%

# 25 2.6770 eV 463.15 nm f= 0.00130 Spin multiplicity= ?:

Ha-6 -> La 27.3%, Hb-6 -> Lb 23.2%, Ha-1 -> La+2 9.7%, Hb-3 -> Lb+2 7.7%, Hb-1 -> Lb+4 7.1%, Ha-3 -> La+1 6.4%

# 26 2.6858 eV 461.63 nm f= 0.00000 Spin multiplicity= ?:

Hb-5 -> Lb 77.8%, Ha-5 -> La 21.8%

# 27 2.6910 eV 460.74 nm f= 0.00020 Spin multiplicity= ?:

Ha-3 -> La+1 11.4%, Hb-3 -> Lb+2 10.1%, Ha -> La+5 9.7%, Hb -> Lb+7 9.4%, Hb-7 -> Lb 7.3%, Ha-8 -> La 7.3%

# 28 2.6940 eV 460.22 nm f= 0.00100 Spin multiplicity= ?:

Hb-2 -> Lb+4 31.0%, Ha-2 -> La+2 29.1%, Ha-1 -> La+2 7.6%, Hb-2 -> Lb+2 7.2%, Hb-1 -> Lb+4 5.1%, Ha-2 -> La+1 5.1% # 29 2.6941 eV 460.21 nm f= 0.00000 Spin multiplicity= ?: Hb -> Lb+3 99.2% # 30 2.6972 eV 459.68 nm f= 0.00010 Spin multiplicity= ?: Hb-1 -> Lb+3 56.4%, Ha-1 -> La+1 12.3%, Hb-1 -> Lb+2 10.0% # 31 2.6997 eV 459.25 nm f= 0.00070 Spin multiplicity= ?: Hb-1 -> Lb+3 37.3%, Hb-1 -> Lb+2 18.8%, Ha-1 -> La+1 16.0%, Ha-2 -> La+1 6.4% # 32 2.7080 eV 457.84 nm f= 0.00010 Spin multiplicity= ?: Hb-2 -> Lb+3 96.7% # 33 2.7432 eV 451.97 nm f= 0.00090 Spin multiplicity= ?: Ha -> La+2 48.0%, Hb -> Lb+4 36.7% # 34 2.7518 eV 450.56 nm f= 0.00020 Spin multiplicity= ?: Ha-1 -> La+2 17.9%, Ha-3 -> La+1 16.1%, Hb-3 -> Lb+2 14.4%, Hb-1 -> Lb+4 13.9%, Ha-2 -> La+2 7.2% # 35 2.7871 eV 444.85 nm f= 0.00100 Spin multiplicity= ?: Ha-7 -> La 98.7% # 36 2.7974 eV 443.21 nm f= 0.10810 Spin multiplicity= ?: Hb-6 -> Lb 34.3%, Ha-6 -> La 27.3%, Hb-1 -> Lb+4 17.3%, Ha-1 -> La+2 11.1% # 37 2.8298 eV 438.14 nm f= 0.26210 Spin multiplicity= ?: Hb-3 -> Lb+2 25.7%, Ha-6 -> La 11.9%, Ha-1 -> La+3 6.0%, Hb-1 -> Lb+5 5.9%, Ha-2 -> La+4 5.7% # 38 2.8344 eV 437.43 nm f= 0.20550 Spin multiplicity= ?: Hb -> Lb+4 27.1%, Ha -> La+2 23.1%, Ha-3 -> La+1 11.8% # 39 2.8354 eV 437.27 nm f= 0.26710 Spin multiplicity= ?: Ha-3 -> La+1 18.0%, Hb -> Lb+4 17.9%, Ha -> La+2 12.7%, Hb-6 -> Lb 6.3% # 40 2.9211 eV 424.44 nm f= 0.00030 Spin multiplicity= ?: Ha-8 -> La 31.1%, Hb-7 -> Lb 26.8%, Hb-2 -> Lb+6 5.8%, Ha-3 -> La+2 5.6%, Ha-2 -> La+4 5.1% # 41 2.9327 eV 422.76 nm f= 0.00040 Spin multiplicity= ?: Hb-4 -> Lb+1 98.9% # 42 2.9336 eV 422.63 nm f= 0.00010 Spin multiplicity= ?:

Hb -> Lb+5 32.9%, Ha -> La+3 32.0%, Hb -> Lb+4 5.2% # 43 2.9368 eV 422.17 nm f= 0.34780 Spin multiplicity= ?: Hb-2 -> Lb+4 33.0%, Ha-2 -> La+2 28.5%, Ha-1 -> La+2 9.7%, Hb-1 -> Lb+4 7.6% # 44 2.9405 eV 421.64 nm f= 0.00140 Spin multiplicity= ?: Hb -> Lb+7 20.5%, Ha -> La+5 16.9%, Hb-1 -> Lb+5 16.3%, Ha-1 -> La+3 16.2% # 45 2.9493 eV 420.39 nm f= 0.00010 Spin multiplicity= ?: Hb-5 -> Lb+1 99.8% # 46 2.9506 eV 420.20 nm f= 0.00020 Spin multiplicity= ?: Hb-3 -> Lb+3 98.3% # 47 2.9617 eV 418.63 nm f= 0.01020 Spin multiplicity= ?: Ha-3 -> La+1 15.3%, Hb-3 -> Lb+2 14.6%, Hb-1 -> Lb+4 13.2%, Ha-1 -> La+2 11.4%, Ha -> La+5 7.6%, Ha-2 -> La+2 5.3% # 48 2.9791 eV 416.18 nm f= 0.00050 Spin multiplicity= ?: Ha-3 -> La+2 32.5%, Hb-3 -> Lb+4 29.0%, Ha-2 -> La+4 11.6%, Hb-2 -> Lb+6 8.4% # 49 3.0203 eV 410.50 nm f= 0.00000 Spin multiplicity= ?: Hb-6 -> Lb+1 97.2% # 50 3.0363 eV 408.34 nm f= 0.00000 Spin multiplicity= ?: Ha-4 -> La+1 59.7%, Hb-4 -> Lb+2 38.1% # 51 3.0390 eV 407.98 nm f= 0.00110 Spin multiplicity= ?: Ha-2 -> La+3 74.5%, Ha-1 -> La+3 23.7% # 52 3.0468 eV 406.93 nm f= 0.00060 Spin multiplicity= ?: Hb-2 -> Lb+5 81.5%, Hb-1 -> Lb+5 17.0% # 53 3.0548 eV 405.87 nm f= 0.00420 Spin multiplicity= ?: Hb-8 -> Lb 98.2% # 54 3.0603 eV 405.14 nm f= 0.00000 Spin multiplicity= ?: Hb-1 -> Lb+6 34.6%, Ha-1 -> La+4 28.2%, Ha-2 -> La+4 8.3%, Ha-2 -> La+6 6.0%, Hb-2 -> Lb+6 5.4%, Hb-2 -> Lb+8 5.4% # 55 3.0662 eV 404.36 nm f= 0.00000 Spin multiplicity= ?: Hb-4 -> Lb+2 34.0%, Ha-4 -> La+1 25.3%, Ha-5 -> La+1 22.0%, Hb-5 -> Lb+2 17.7%

# 56 3.0694 eV 403.94 nm f= 0.00010 Spin multiplicity= ?:

Ha-5 -> La+1 30.6%, Hb-5 -> Lb+2 27.4%, Hb-4 -> Lb+2 26.7%, Ha-4 -> La+1 14.0%

- # 57 3.0728 eV 403.49 nm f= 0.01490 Spin multiplicity= ?:
- Ha-1 -> La+6 24.6%, Ha-8 -> La 12.9%, Hb-1 -> Lb+8 11.3%, Ha-6 -> La+1 8.6%, Ha-3 -> La+2 8.3%, Hb-2 -> Lb+6 6.1%
- # 58 3.0781 eV 402.79 nm f= 0.06620 Spin multiplicity= ?:
- Hb-7 -> Lb 25.4%, Hb-1 -> Lb+8 13.6%, Ha-8 -> La 10.5%, Hb-1 -> Lb+5 10.1%, Ha-1 -> La+3 8.5%
- # 59 3.0838 eV 402.05 nm f= 0.09240 Spin multiplicity= ?:
- Ha -> La+3 32.0%, Hb -> Lb+5 31.5%, Ha-1 -> La+5 14.4%, Hb-1 -> Lb+7 11.7%
- # 60 3.0865 eV 401.70 nm f= 0.00010 Spin multiplicity= ?:
- Hb-5 -> Lb+2 53.7%, Ha-5 -> La+1 45.9%
- # 61 3.0983 eV 400.17 nm f= 0.00230 Spin multiplicity= ?:
- Hb-9 -> Lb 68.4%, Hb-1 -> Lb+7 9.3%, Ha-1 -> La+5 7.5%
- # 62 3.0994 eV 400.03 nm f= 0.00030 Spin multiplicity= ?:
- Hb-1 -> Lb+7 29.7%, Ha-1 -> La+5 24.1%, Hb-9 -> Lb 22.7%, Hb -> Lb+5 5.4%, Ha-2 -> La+5 5.1%
- # 63 3.1060 eV 399.18 nm f= 0.00150 Spin multiplicity= ?:
- Hb-3 -> Lb+4 40.2%, Ha-3 -> La+2 31.1%
- # 64 3.1153 eV 397.98 nm f= 0.01590 Spin multiplicity= ?:
- Hb-6 -> Lb+2 49.2%, Hb-1 -> Lb+5 10.9%, Ha-1 -> La+6 5.8%, Ha-6 -> La+1 5.4%
- # 65 3.1170 eV 397.77 nm f= 0.00030 Spin multiplicity= ?:
- Ha -> La+4 66.9%, Hb -> Lb+6 31.8%
- # 66 3.1171 eV 397.75 nm f= 0.00010 Spin multiplicity= ?:
- Hb -> Lb+6 67.5%, Ha -> La+4 32.0%
- # 67 3.1192 eV 397.49 nm f= 0.02680 Spin multiplicity= ?:
- Ha-6 -> La+1 42.3%, Ha-1 -> La+3 15.2%, Hb-1 -> Lb+8 7.4%, Hb-1 -> Lb+5 7.2%, Ha-2 -> La+3 5.4%
- # 68 3.1440 eV 394.35 nm f= 0.00010 Spin multiplicity= ?:
- Ha-2 -> La+5 50.5%, Hb-2 -> Lb+7 26.4%, Ha-1 -> La+5 15.5%, Hb-1 -> Lb+7 5.8%
- # 69 3.1442 eV 394.33 nm f= 0.00000 Spin multiplicity= ?:

Hb-2 -> Lb+7 58.5%, Ha-2 -> La+5 27.1%, Hb-1 -> Lb+7 8.3%, Ha-1 -> La+5 5.6%

# 70 3.1550 eV 392.98 nm f= 0.07660 Spin multiplicity= ?:

Ha-1 -> La+4 32.4%, Hb-1 -> Lb+6 29.0%, Ha-2 -> La+4 9.5%, Ha-2 -> La+6 8.8%, Hb-2 -> Lb+8 5.3%, Hb-2 -> Lb+6 5.2%

# 71 3.1596 eV 392.40 nm f= 0.00060 Spin multiplicity= ?:

Hb-3 -> Lb+5 20.4%, Ha-3 -> La+3 20.3%

- # 72 3.1640 eV 391.86 nm f= 0.00000 Spin multiplicity= ?:
- Ha-9 -> La 80.2%, Hb-10 -> Lb 14.5%
- # 73 3.1761 eV 390.37 nm f= 0.00000 Spin multiplicity= ?:
- Ha-10 -> La 78.3%, Hb-12 -> Lb 16.7%
- # 74 3.1783 eV 390.10 nm f= 0.00140 Spin multiplicity= ?:
- Hb-2 -> Lb+8 36.3%, Ha-2 -> La+6 32.3%, Hb-1 -> Lb+6 8.0%, Ha-1 -> La+6 7.3%, Hb-1 -> Lb+8 6.1%
- # 75 3.1868 eV 389.06 nm f= 0.00040 Spin multiplicity= ?:
- Hb-10 -> Lb 50.0%, Ha-9 -> La 15.5%, Hb-11 -> Lb 9.2%, Ha-11 -> La 7.7%
- # 76 3.1878 eV 388.93 nm f= 0.00410 Spin multiplicity= ?:
- Hb-11 -> Lb 21.3%, Hb-10 -> Lb 20.8%, Ha-6 -> La+1 13.5%, Hb-6 -> Lb+2 11.0%
- # 77 3.1920 eV 388.42 nm f= 0.08280 Spin multiplicity= ?:
- Ha -> La+6 38.2%, Ha-1 -> La+5 13.7%, Hb -> Lb+8 12.2%, Hb-1 -> Lb+7 11.5%, Ha-2 -> La+5 5.5%
- # 78 3.1922 eV 388.40 nm f= 0.00820 Spin multiplicity= ?:
- Ha-12 -> La 24.1%, Ha-11 -> La 23.0%, Hb-14 -> Lb 15.5%, Hb-13 -> Lb 10.6%, Hb-10 -> Lb 9.1%
- # 79 3.1945 eV 388.12 nm f= 0.01510 Spin multiplicity= ?:
- Ha-12 -> La 29.0%, Hb-14 -> Lb 15.0%, Hb-11 -> Lb 14.5%, Ha-11 -> La 8.5%, Hb-13 -> Lb 7.6%
- # 80 3.1967 eV 387.85 nm f= 0.02510 Spin multiplicity= ?:
- Hb-11 -> Lb 43.6%, Ha-11 -> La 13.3%, Hb-13 -> Lb 8.2%, Ha-12 -> La 6.2%
- # 81 3.2035 eV 387.03 nm f= 0.00040 Spin multiplicity= ?:
- Hb-12 -> Lb 75.3%, Ha-10 -> La 17.1%
- # 82 3.2066 eV 386.65 nm f= 0.00640 Spin multiplicity= ?:

Hb -> Lb+8 59.4%, Ha -> La+6 34.8%

# 83 3.2169 eV 385.42 nm f= 0.00020 Spin multiplicity= ?:

Ha-7 -> La+1 96.1%
- # 84 3.2192 eV 385.14 nm f= 0.00110 Spin multiplicity= ?: Hb-4 -> Lb+3 99.3%
- # 85 3.2331 eV 383.48 nm f= 0.00020 Spin multiplicity= ?: Hb-13 -> Lb 62.3%, Ha-11 -> La 36.8%
- # 86 3.2354 eV 383.21 nm f= 0.00060 Spin multiplicity= ?: Hb-5 -> Lb+3 99.7%
- # 87 3.2508 eV 381.40 nm f= 0.00000 Spin multiplicity= ?:

Hb-14 -> Lb 63.3%, Ha-12 -> La 36.3%

# 88 3.2604 eV 380.27 nm f= 0.26100 Spin multiplicity= ?:

Hb -> Lb+8 24.3%, Ha -> La+6 21.3%, Hb-1 -> Lb+7 9.9%, Ha-1 -> La+5 9.4%, Ha-3 -> La+5 6.9%, Hb-3 -> Lb+7 6.7%, Hb -> Lb+5 6.3%, Ha -> La+3 6.2%

# 89 3.2638 eV 379.88 nm f= 0.00070 Spin multiplicity= ?:

Ha-1 -> La+7 28.3%, Hb-1 -> Lb+9 26.4%, Ha-2 -> La+7 7.3%

# 90 3.2644 eV 379.81 nm f= 0.00000 Spin multiplicity= ?:

Hb-7 -> Lb+1 95.2%

# 91 3.2748 eV 378.60 nm f= 0.00000 Spin multiplicity= ?:

Ha-5 -> La+2 48.7%, Hb-5 -> Lb+4 25.7%, Ha-4 -> La+2 21.4%

# 92 3.2795 eV 378.06 nm f= 0.00070 Spin multiplicity= ?:

Ha-3 -> La+3 24.4%, Hb-3 -> Lb+5 10.3%, Ha-6 -> La+2 9.4%, Ha-8 -> La+1 9.4%, Hb-7 -> Lb+2 9.0%, Hb-6 -> Lb+4 6.7%

# 93 3.2830 eV 377.66 nm f= 0.00000 Spin multiplicity= ?:

Ha-4 -> La+2 66.7%, Ha-5 -> La+2 16.1%, Hb-4 -> Lb+4 8.8%, Hb-5 -> Lb+4 5.6%

# 94 3.2910 eV 376.74 nm f= 0.16100 Spin multiplicity= ?:

Hb-2 -> Lb+8 29.1%, Ha-2 -> La+6 24.2%, Ha-3 -> La+4 10.6%, Hb-3 -> Lb+6 9.8%, Ha-1 -> La+6 8.1%, Hb-1 -> Lb+8 5.9%

# 95 3.2977 eV 375.97 nm f= 0.00010 Spin multiplicity= ?:

Hb-6 -> Lb+3 98.8%

# 96 3.3099 eV 374.59 nm f= 0.00050 Spin multiplicity= ?:

Hb-4 -> Lb+4 87.5%, Ha-4 -> La+2 10.2%

# 97 3.3102 eV 374.55 nm f= 0.10730 Spin multiplicity= ?:

Hb-3 -> Lb+5 34.7%, Ha-3 -> La+3 20.0%, Hb-1 -> Lb+8 13.0%, Ha-1 -> La+6 9.7%

# 98 3.3186 eV 373.60 nm f= 0.00010 Spin multiplicity= ?:

Hb-3 -> Lb+6 44.2%, Ha-3 -> La+4 44.1%

# 99 3.3269 eV 372.67 nm f= 0.00000 Spin multiplicity= ?:

Hb-5 -> Lb+4 66.0%, Ha-5 -> La+2 33.1%

# 100 3.3297 eV 372.36 nm f= 0.00000 Spin multiplicity= ?:

Hb-8 -> Lb+1 61.3%, Hb-9 -> Lb+1 29.5%, Hb-11 -> Lb+1 6.2%

# 101 3.3326 eV 372.03 nm f= 0.00000 Spin multiplicity= ?:

Ha-3 -> La+5 27.1%, Hb-3 -> Lb+7 26.7%, Ha-6 -> La+2 12.0%, Hb-6 -> Lb+4 10.1%, Ha-8 -> La+1 6.6%, Hb-7 -> Lb+2 6.1%

# 102 3.3331 eV 371.98 nm f= 0.00010 Spin multiplicity= ?:

Ha-6 -> La+2 19.3%, Ha-3 -> La+5 17.8%, Hb-3 -> Lb+7 17.6%, Hb-6 -> Lb+4 16.4%, Ha-8 -> La+1 9.8%, Hb-7 -> Lb+2 9.0%

# 103 3.3791 eV 366.91 nm f= 0.00230 Spin multiplicity= ?:

Ha-3 -> La+6 25.7%, Hb-3 -> Lb+8 21.0%, Ha-8 -> La+1 18.4%, Hb-7 -> Lb+2 9.7%, Ha-6 -> La+2 6.6%

# 104 3.3935 eV 365.36 nm f= 0.05420 Spin multiplicity= ?:

Hb -> Lb+7 13.6%, Ha -> La+5 13.5%, Hb-1 -> Lb+8 11.5%, Ha-1 -> La+6 10.9%, Hb-3 -> Lb+5 10.0%, Ha-3 -> La+3 8.8%

# 105 3.3964 eV 365.05 nm f= 0.15750 Spin multiplicity= ?:

Hb-7 -> Lb+2 24.4%, Ha-8 -> La+1 13.6%, Hb-6 -> Lb+4 11.8%, Ha-6 -> La+2 6.7%, Hb-3 -> Lb+8 5.5%

# 106 3.3991 eV 364.76 nm f= 0.00360 Spin multiplicity= ?:

Ha-13 -> La 97.3%

# 107 3.4015 eV 364.50 nm f= 0.00250 Spin multiplicity= ?:

Ha -> La+7 97.9%

# 108 3.4138 eV 363.19 nm f= 0.00110 Spin multiplicity= ?:

Ha-2 -> La+7 77.1%, Ha-1 -> La+7 21.5%

# 109 3.4241 eV 362.09 nm f= 0.03940 Spin multiplicity= ?:

Ha-7 -> La+2 62.8%, Hb-6 -> Lb+4 9.3%, Ha-6 -> La+2 7.7%, Ha-8 -> La+1 5.9%, Hb-7 -> Lb+2 5.8%

# 110 3.4249 eV 362.01 nm f= 0.00280 Spin multiplicity= ?:

Hb -> Lb+9 95.4%

- # 111 3.4255 eV 361.94 nm f= 0.08280 Spin multiplicity= ?:
- Ha-7 -> La+2 26.4%, Hb-6 -> Lb+4 22.2%, Ha-6 -> La+2 17.5%, Ha-8 -> La+1 12.2%, Hb-7 -> Lb+2 11.2%
- # 112 3.4371 eV 360.72 nm f= 0.00620 Spin multiplicity= ?:
- Hb-2 -> Lb+9 81.7%, Hb-1 -> Lb+9 15.5%
- # 113 3.4501 eV 359.36 nm f= 0.00000 Spin multiplicity= ?:

Hb-10 -> Lb+1 99.5%

- # 114 3.4521 eV 359.16 nm f= 0.00090 Spin multiplicity= ?:
- Hb-8 -> Lb+2 91.3%
- # 115 3.4547 eV 358.89 nm f= 0.00120 Spin multiplicity= ?:
- Ha-22 -> La 19.7%, Hb-23 -> Lb 17.6%, Ha-3 -> La+6 8.2%, Hb-3 -> Lb+8 5.7%, Hb-8 -> Lb+2 5.1%
- # 116 3.4602 eV 358.32 nm f= 0.00000 Spin multiplicity= ?:
- Ha-4 -> La+3 40.8%, Hb-4 -> Lb+5 33.3%, Hb-10 -> Lb+2 5.6%, Ha-9 -> La+1 5.6%
- # 117 3.4656 eV 357.76 nm f= 0.00190 Spin multiplicity= ?:
- Hb-12 -> Lb+1 99.3%
- # 118 3.4658 eV 357.74 nm f= 0.00200 Spin multiplicity= ?:

Ha-14 -> La 76.1%, Hb-15 -> Lb 15.5%

- # 119 3.4669 eV 357.62 nm f= 0.44660 Spin multiplicity= ?:
- Hb-3 -> Lb+6 34.8%, Ha-3 -> La+4 34.7%
- # 120 3.4720 eV 357.10 nm f= 0.84450 Spin multiplicity= ?:

Hb-3 -> Lb+7 38.4%, Ha-3 -> La+5 37.0%

- # 121 3.4753 eV 356.76 nm f= 0.00020 Spin multiplicity= ?: Ha-15 -> La 70.1%, Hb-16 -> Lb 22.6%
- # 122 3.4853 eV 355.73 nm f= 0.00180 Spin multiplicity= ?: Ha-16 -> La 63.6%, Hb-17 -> Lb 17.9%
- # 123 3.4888 eV 355.38 nm f= 0.00050 Spin multiplicity= ?:
- Ha-17 -> La 68.9%, Hb-18 -> Lb 21.8%
- # 124 3.4906 eV 355.19 nm f= 0.00320 Spin multiplicity= ?: Hb-15 -> Lb 63.2%, Ha-14 -> La 14.8%, Hb-9 -> Lb+2 13.4%
- # 125 3.4913 eV 355.12 nm f= 0.00310 Spin multiplicity= ?:

Hb-9 -> Lb+2 61.5%, Hb-13 -> Lb+1 16.7%, Hb-15 -> Lb 15.2%

- # 126 3.4944 eV 354.81 nm f= 0.00330 Spin multiplicity= ?:
- Hb-13 -> Lb+1 79.2%, Hb-9 -> Lb+2 18.6%
- # 127 3.5064 eV 353.59 nm f= 0.00310 Spin multiplicity= ?:
- Hb-16 -> Lb 71.7%, Ha-15 -> La 25.1%
- # 128 3.5120 eV 353.03 nm f= 0.00170 Spin multiplicity= ?:
- Hb-17 -> Lb 43.2%, Ha-16 -> La 26.2%, Hb-14 -> Lb+1 6.8%, Ha-6 -> La+3 5.6%, Hb-6 -> Lb+5 5.2%
- # 129 3.5121 eV 353.02 nm f= 0.00020 Spin multiplicity= ?:

Hb-14 -> Lb+1 93.1%

- # 130 3.5188 eV 352.35 nm f= 0.06590 Spin multiplicity= ?:
- Hb-1 -> Lb+9 28.9%, Ha-1 -> La+7 23.8%, Ha-2 -> La+7 8.2%, Hb-2 -> Lb+9 6.8%, Ha-3 -> La+6 6.6%, Hb-3 -> Lb+8 5.8%
- # 131 3.5189 eV 352.34 nm f= 0.00370 Spin multiplicity= ?:
- Hb-17 -> Lb 22.3%, Hb-18 -> Lb 14.3%, Hb-6 -> Lb+5 12.3%, Ha-6 -> La+3 12.0%, Ha-17 -> La 6.8%
- # 132 3.5198 eV 352.25 nm f= 0.00050 Spin multiplicity= ?:
- Ha-4 -> La+5 32.1%, Hb-4 -> Lb+7 31.1%, Hb-13 -> Lb+2 10.5%, Ha-11 -> La+1 8.9%
- # 133 3.5199 eV 352.24 nm f= 0.00370 Spin multiplicity= ?:
- Hb-18 -> Lb 55.8%, Ha-17 -> La 17.2%, Hb-17 -> Lb 6.7%
- # 134 3.5281 eV 351.42 nm f= 0.35620 Spin multiplicity= ?:
- Hb-3 -> Lb+8 25.5%, Ha-3 -> La+6 22.1%, Hb-2 -> Lb+6 9.0%, Ha-2 -> La+4 8.4%
- # 135 3.5394 eV 350.30 nm f= 0.00000 Spin multiplicity= ?:
- Hb-5 -> Lb+6 40.2%, Ha-5 -> La+4 39.6%, Hb-14 -> Lb+2 5.1%
- # 136 3.5472 eV 349.53 nm f= 0.00000 Spin multiplicity= ?:
- Hb-7 -> Lb+3 92.3%
- # 137 3.5552 eV 348.74 nm f= 0.00030 Spin multiplicity= ?:
- Ha-8 -> La+2 21.9%, Hb-7 -> Lb+4 17.0%, Ha-19 -> La 7.5%, Hb-20 -> Lb 7.2%, Ha-6 -> La+3 6.8%, Hb-6 -> Lb+5 6.2%
- # 138 3.5562 eV 348.64 nm f= 0.00000 Spin multiplicity= ?:
- Ha-4 -> La+3 45.1%, Hb-4 -> Lb+5 31.3%, Ha-5 -> La+3 6.4%, Ha-9 -> La+1 5.5%

- # 139 3.5658 eV 347.70 nm f= 0.00000 Spin multiplicity= ?: Ha-5 -> La+3 82.1%, Hb-4 -> Lb+5 7.7%
- # 140 3.5682 eV 347.47 nm f= 0.00000 Spin multiplicity= ?: Hb-6 -> Lb+6 26.8%, Ha-6 -> La+4 26.0%, Ha-21 -> La 5.1%
- # 141 3.5696 eV 347.33 nm f= 0.00000 Spin multiplicity= ?: Hb-10 -> Lb+2 40.4%, Ha-9 -> La+1 31.5%, Hb-4 -> Lb+5 18.3%
- # 142 3.5730 eV 347.00 nm f= 0.00000 Spin multiplicity= ?: Hb-12 -> Lb+2 32.4%, Ha-10 -> La+1 30.6%, Hb-5 -> Lb+5 7.6%
- # 143 3.5748 eV 346.83 nm f= 0.00010 Spin multiplicity= ?:
- Hb-9 -> Lb+3 36.5%, Hb-8 -> Lb+3 21.9%, Hb-9 -> Lb+1 8.7%
- # 144 3.5757 eV 346.74 nm f= 0.00000 Spin multiplicity= ?: Hb-6 -> Lb+7 27.1%, Ha-6 -> La+5 26.3%
- # 145 3.5760 eV 346.71 nm f= 0.00000 Spin multiplicity= ?: Hb-5 -> Lb+5 90.6%
- # 146 3.5896 eV 345.40 nm f= 0.00000 Spin multiplicity= ?: Ha-9 -> La+1 48.7%, Hb-10 -> Lb+2 47.1%
- # 147 3.5906 eV 345.30 nm f= 0.00030 Spin multiplicity= ?: Hb-11 -> Lb+2 92.9%
- # 148 3.6041 eV 344.01 nm f= 0.00000 Spin multiplicity= ?: Ha-10 -> La+1 51.0%, Hb-12 -> Lb+2 48.1%
- # 149 3.6143 eV 343.04 nm f= 0.00030 Spin multiplicity= ?:
- Ha-19 -> La 21.0%, Ha-3 -> La+7 17.7%, Hb-20 -> Lb 15.8%, Ha-8 -> La+2 12.0%, Hb-3 -> Lb+9 9.2%
- # 150 3.6192 eV 342.57 nm f= 0.00030 Spin multiplicity= ?:
- Ha-18 -> La 24.1%, Hb-19 -> Lb 17.1%, Ha-3 -> La+7 7.3%, Ha-8 -> La+2 6.8%
- # 151 3.6218 eV 342.33 nm f= 0.00000 Spin multiplicity= ?:
- Hb-13 -> Lb+2 49.3%, Ha-11 -> La+1 24.2%, Ha-4 -> La+5 11.8%, Hb-4 -> Lb+7 11.5%
- # 152 3.6299 eV 341.56 nm f= 0.00030 Spin multiplicity= ?:
- Ha-3 -> La+7 35.9%, Hb-3 -> Lb+9 14.8%, Ha-8 -> La+2 7.4%
- # 153 3.6333 eV 341.24 nm f= 0.00000 Spin multiplicity= ?:

- Ha-21 -> La 32.5%, Hb-22 -> Lb 26.3%, Hb-6 -> Lb+6 9.6%, Ha-6 -> La+4 9.3%
- # 154 3.6348 eV 341.10 nm f= 0.00000 Spin multiplicity= ?:
- Ha-4 -> La+4 96.2%
- # 155 3.6358 eV 341.01 nm f= 0.00000 Spin multiplicity= ?:

Ha-11 -> La+1 59.0%, Hb-13 -> Lb+2 33.8%

- # 156 3.6385 eV 340.76 nm f= 0.00000 Spin multiplicity= ?:
- Ha-20 -> La 30.1%, Hb-21 -> Lb 23.7%, Hb-6 -> Lb+7 8.5%, Ha-6 -> La+5 8.2%
- # 157 3.6408 eV 340.54 nm f= 0.00000 Spin multiplicity= ?:
- Hb-14 -> Lb+2 42.7%, Ha-12 -> La+1 41.2%, Ha-5 -> La+4 6.5%, Hb-5 -> Lb+6 5.8%
- # 158 3.6415 eV 340.48 nm f= 0.00000 Spin multiplicity= ?:

Hb-4 -> Lb+6 99.8%

- # 159 3.6496 eV 339.72 nm f= 0.00000 Spin multiplicity= ?:
- Ha-12 -> La+1 45.8%, Hb-14 -> Lb+2 45.1%
- # 160 3.6571 eV 339.02 nm f= 0.00760 Spin multiplicity= ?:
- Hb-7 -> Lb+4 52.2%, Ha-8 -> La+2 26.1%
- # 161 3.6622 eV 338.55 nm f= 0.00000 Spin multiplicity= ?:
- Hb-11 -> Lb+3 43.4%, Ha-7 -> La+3 26.2%, Hb-8 -> Lb+4 11.0%, Hb-11 -> Lb+1 8.1%
- # 162 3.6653 eV 338.26 nm f= 0.00000 Spin multiplicity= ?:
- Ha-4 -> La+5 39.6%, Hb-4 -> Lb+7 35.5%, Ha-5 -> La+5 15.4%
- # 163 3.6700 eV 337.83 nm f= 0.00000 Spin multiplicity= ?:
- Ha-5 -> La+5 21.8%, Hb-5 -> Lb+7 18.6%, Ha-5 -> La+6 16.0%, Hb-5 -> Lb+8 13.7%, Hb-4 -> Lb+7 8.1%
- # 164 3.6708 eV 337.76 nm f= 0.00000 Spin multiplicity= ?:
- Hb-5 -> Lb+6 44.6%, Ha-5 -> La+4 42.3%
- # 165 3.6725 eV 337.60 nm f= 0.00000 Spin multiplicity= ?:
- Ha-5 -> La+5 48.1%, Hb-5 -> Lb+7 41.8%
- # 166 3.6753 eV 337.34 nm f= 0.00000 Spin multiplicity= ?:
- Hb-5 -> Lb+7 37.6%, Ha-5 -> La+6 19.7%, Hb-5 -> Lb+8 17.0%, Ha-5 -> La+5 12.4%
- # 167 3.6771 eV 337.18 nm f= 0.00230 Spin multiplicity= ?:

Hb-3 -> Lb+9 22.9%, Hb-6 -> Lb+5 20.6%, Ha-6 -> La+3 17.4%, Hb-19 -> Lb 10.2%, Ha-3 -> La+7 10.1%, Ha-18 -> La 8.1%

- # 168 3.6954 eV 335.51 nm f= 0.02280 Spin multiplicity= ?:
- Hb-3 -> Lb+9 33.9%, Ha-3 -> La+7 18.5%, Ha-18 -> La 14.9%, Hb-19 -> Lb 13.5%
- # 169 3.6985 eV 335.23 nm f= 0.00060 Spin multiplicity= ?:
- Ha-7 -> La+3 46.2%, Hb-8 -> Lb+4 35.2%
- # 170 3.7062 eV 334.53 nm f= 0.00040 Spin multiplicity= ?:
- Hb-1 -> Lb+10 23.7%, Ha-1 -> La+8 21.3%, Ha-22 -> La 5.2%, Ha-2 -> La+8 5.1%
- # 171 3.7098 eV 334.21 nm f= 0.00060 Spin multiplicity= ?:
- Hb-8 -> Lb+4 45.3%, Hb-11 -> Lb+3 19.3%, Ha-7 -> La+3 12.3%
- # 172 3.7154 eV 333.70 nm f= 0.00100 Spin multiplicity= ?:
- Hb-19 -> Lb 23.5%, Ha-18 -> La 17.8%, Ha-6 -> La+3 16.5%, Hb-6 -> Lb+5 11.1%
- # 173 3.7213 eV 333.17 nm f= 0.00000 Spin multiplicity= ?:
- Ha-4 -> La+6 74.4%, Hb-4 -> Lb+8 16.0%
- # 174 3.7261 eV 332.75 nm f= 0.01960 Spin multiplicity= ?:
- Ha-19 -> La 42.3%, Hb-20 -> Lb 33.7%, Ha-6 -> La+6 9.4%
- # 175 3.7326 eV 332.17 nm f= 0.00250 Spin multiplicity= ?:
- Hb-6 -> Lb+8 35.2%, Ha-6 -> La+6 24.3%, Hb-20 -> Lb 14.0%, Hb-9 -> Lb+4 7.3%
- # 176 3.7361 eV 331.85 nm f= 0.00000 Spin multiplicity= ?:
- Hb-10 -> Lb+3 99.4%
- # 177 3.7413 eV 331.39 nm f= 0.00000 Spin multiplicity= ?:
- Hb-4 -> Lb+8 79.2%, Ha-4 -> La+6 18.6%
- # 178 3.7433 eV 331.22 nm f= 0.00150 Spin multiplicity= ?: Hb-9 -> Lb+4 81.7%
- # 179 3.7495 eV 330.67 nm f= 0.00090 Spin multiplicity= ?: Ha-20 -> La 48.0%, Hb-21 -> Lb 47.3%
- # 180 3.7502 eV 330.61 nm f= 0.00000 Spin multiplicity= ?: Hb-15 -> Lb+1 100.0%
- # 181 3.7516 eV 330.48 nm f= 0.00020 Spin multiplicity= ?:

Hb-12 -> Lb+3 98.4%

- # 182 3.7639 eV 329.40 nm f= 0.00000 Spin multiplicity= ?: Hb-5 -> Lb+8 49.5%, Ha-5 -> La+6 47.8%
- # 183 3.7650 eV 329.31 nm f= 0.00000 Spin multiplicity= ?: Hb-16 -> Lb+1 100.0%
- # 184 3.7673 eV 329.11 nm f= 0.00160 Spin multiplicity= ?: Hb-22 -> Lb 48.1%, Ha-21 -> La 46.6%
- # 185 3.7733 eV 328.58 nm f= 0.00000 Spin multiplicity= ?: Hb-17 -> Lb+1 99.9%
- # 186 3.7781 eV 328.17 nm f= 0.00000 Spin multiplicity= ?: Hb-18 -> Lb+1 100.0%
- # 187 3.7790 eV 328.09 nm f= 0.00990 Spin multiplicity= ?: Hb-13 -> Lb+3 67.5%
- # 188 3.7804 eV 327.97 nm f= 0.00270 Spin multiplicity= ?: Hb-13 -> Lb+3 25.1%, Hb-19 -> Lb 9.4%, Ha-14 -> La+1 7.5%, Hb-15 -> Lb+2 7.4%
- # 189 3.7882 eV 327.29 nm f= 0.10100 Spin multiplicity= ?:
- Ha-6 -> La+4 41.4%, Hb-6 -> Lb+6 41.4%
- # 190 3.7913 eV 327.02 nm f= 0.00110 Spin multiplicity= ?:

Ha-7 -> La+4 98.7%

- # 191 3.7928 eV 326.89 nm f= 0.00000 Spin multiplicity= ?:
- Ha-10 -> La+2 52.8%, Hb-12 -> Lb+4 31.0%, Hb-5 -> Lb+8 9.5%
- # 192 3.7980 eV 326.45 nm f= 0.00020 Spin multiplicity= ?:

Hb-14 -> Lb+3 99.6%

- # 193 3.8015 eV 326.15 nm f= 0.06970 Spin multiplicity= ?:
- Ha-7 -> La+5 28.0%, Ha-6 -> La+5 26.3%, Hb-6 -> Lb+7 23.4%, Ha -> La+8 8.1%
- # 194 3.8029 eV 326.03 nm f= 0.01580 Spin multiplicity= ?:
- Ha-9 -> La+2 57.2%, Hb-10 -> Lb+4 15.0%, Ha-7 -> La+5 5.5%, Ha-6 -> La+5 5.2%, Hb-6 -> Lb+7 5.1%
- # 195 3.8036 eV 325.97 nm f= 0.00270 Spin multiplicity= ?:
- Hb -> Lb+10 26.4%, Ha -> La+8 20.7%, Ha-14 -> La+1 7.9%, Hb-15 -> Lb+2 7.6%, Hb-21 -> Lb 6.7%

# 196 3.8046 eV 325.88 nm f= 0.02070 Spin multiplicity= ?:

Ha-7 -> La+5 65.1%, Ha-9 -> La+2 11.4%, Hb-6 -> Lb+7 7.5%, Ha-6 -> La+5 5.7%

# 197 3.8146 eV 325.03 nm f= 0.00010 Spin multiplicity= ?:

Ha -> La+8 23.5%, Hb -> Lb+10 16.7%, Ha-14 -> La+1 13.7%, Hb-15 -> Lb+2 13.4%

# 198 3.8181 eV 324.73 nm f= 0.07190 Spin multiplicity= ?:

Ha-13 -> La+1 34.5%, Hb-1 -> Lb+10 7.7%, Ha-1 -> La+8 7.0%, Ha -> La+5 5.3%, Hb -> Lb+7 5.1%

# 199 3.8185 eV 324.69 nm f= 0.03940 Spin multiplicity= ?:

Ha-13 -> La+1 64.3%

# 200 3.8218 eV 324.41 nm f= 0.00060 Spin multiplicity= ?:

Ha-8 -> La+3 16.1%, Hb-7 -> Lb+5 13.2%, Ha-16 -> La+1 12.5%, Hb-17 -> Lb+2 12.2%