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**ENGINEERING DUAL ACTIVE METAL SITES
ON METAL-ORGANIC FRAMEWORKS
FOR PHOTOCATALYTIC CO₂ REDUCTION**

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PhD

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**Engineering Dual Active Metal Sites on Metal-Organic
Frameworks for Photocatalytic CO₂ Reduction**

Lin Biyun

**A thesis submitted in partial fulfilment of the
requirements for the degree of Doctor of Philosophy**

August 2025

CERTIFICATE OF ORIGINALITY

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Abstract

Photocatalytic CO₂ reduction (CO₂RR) presents a promising strategy for addressing the global challenges of CO₂ emissions and renewable energy utilization. Metal-organic frameworks (MOFs) have received extensive research attention for their applications in CO₂RR due to their superior CO₂ capture capabilities, photochemical properties, and structural tunability. In this thesis, we investigated the atomic-level engineering of the dual metal active sites on metal-organic frameworks to optimize photocatalytic CO₂RR performance. We systemically evaluated how dual-atom catalysts (DACs), metal loading density, and bimetallic combinations (electronic structure tuning) influence the selectivity and efficiency of CO₂ conversion, particularly towards high-value multi-carbon (C₂₊) products. Combining experimental results with theoretical modeling, we established structure-activity relationships and developed rational design principles for optimizing MOF-based photocatalysts with tailored dual metal site. Advanced characterization techniques, including transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray absorption fine structure (XAFS) analysis, and photoluminescence (PL) were employed to probe the coordination environment and photoinduced charge transfer capability of catalysts.

List of Publication

Lin B, Lo T W B. Engineering isolated and paired active metal sites on MOFs for photocatalytic CO₂ reduction[J]. Coordination Chemistry Reviews, 2026, 549: 217329.

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Chapter 1 Introduction

Most of the content in this chapter has been published in a review recently [Engineering isolated and paired active metal sites on MOFs for photocatalytic CO₂ reduction. *Coordination Chemistry Reviews*, 2026, 549: 217329.]

1.1 Background

The accelerating anthropogenic CO₂ emissions from fossil fuel combustion have precipitated a dual crisis of climate destabilization and economic disruption, necessitating urgent development of carbon-neutral technologies¹⁻⁴. Photocatalytic CO₂ reduction reaction (CO₂RR) has consequently risen to the forefront of sustainable solutions, enabling the conversion of such greenhouse gas into chemical feedstocks while harnessing abundant solar energy⁵⁻⁸. However, the inherent thermodynamic stability of CO₂, characterized by its linear O=C=O configuration and requiring 750 kJ mol⁻¹ to dissociate the robust C=O bonds, presents fundamental kinetic barriers that necessitate sophisticated catalytic architectures⁹⁻¹². Since Halmann's pioneering photoelectrochemical demonstration in 1978, semiconductor-based photocatalysis has been established as a viable pathway for CO₂ conversion under ambient conditions^{13, 14, 15, 16}. Current advancements predominantly focus on optimizing catalytic interfaces that lead to the formation of C₁ products (such as CO, CH₄, and HCOOH) through strategies including defect engineering, heterojunction construction, and cocatalyst modification. Despite this progress, the photocatalytic synthesis of higher-value C₂₊ hydrocarbons and oxygenates (such as C₂H₄, C₂H₆, and CH₃COOH) is still considered much more challenging. This disparity originates primarily from the kinetic complexity of multi-electron transfer processes intrinsic of the formation of C₂₊ products, which requires a combined transfer of 8 – 12 electrons-and-protons compared to only 2 – 6 for C₁

products (**Table 1**)¹⁷⁻²⁰. Competing charge recombination and the thermodynamically favorable hydrogen evolution reaction (HER) disproportionately disrupt the critical C–C coupling steps necessary for chain growth²⁰⁻²².

Addressing this technological impasse demands a paradigm shift in photocatalyst design, moving beyond conventional optimization of light absorption and charge separation towards the atomic-level control of surface reaction dynamics. Emerging evidence suggests that the selective stabilization of critical intermediates (*COOH, *CHO) and precise spatial organization of active sites could circumvent traditional scaling relationships in CO₂RR²³⁻²⁷. Establishing detailed structure-activity relationships across atomic to microscopic scales is therefore essential for transforming photocatalytic systems into practical platforms for solar-driven synthesis of C₂₊ chemicals.

In general, the photocatalytic efficacy of semiconductor-based systems fundamentally depends on three kinetically coupled processes: (i) photon harvesting, (ii) charge carrier dynamics (separation/transport), and (iii) surface-mediated redox transformations²⁸⁻³¹. Concerted optimization of these synergistic processes is paramount for achieving selectivity towards C₂₊ products, precise control over multi-electron transfer cascades and intermediate stabilization energetics^{26-27, 32-33}. While significant progress over recent decades has expanded spectral response notably into the visible range, and mitigated bulk charge recombination through defect engineering and heterojunction design, the surface reaction dynamics governing C₂₊ selectivity remain inadequately addressed. These dynamics include CO₂ chemisorption energetics, *CO dimerization barriers, and C–C coupling transition states, generating diverse intermediate species whose stabilization dictates reaction pathways. These dynamics are exquisitely

sensitive to the atomic-scale electronic structure of catalytic metal sites. Subtle variations in oxidation state, coordination number, ligand field symmetry, and local charge density can alter C_{2+} selectivity by orders of magnitude³⁴⁻⁴⁰. Compounding these challenges, the thermodynamic proximity of CO_2RR and HER in aqueous systems creates an intrinsic selectivity conflict, drastically suppressing CO_2RR yields. Systematic atomic-level engineering of metal active sites is thus imperative to meet these critical needs. Such precise tailoring enables control over both surface chemistry and bulk characteristics to favor C_{2+} pathways. Crucially, this site-specific engineering often confers secondary benefits by extending light absorption spectra and enhancing charge separation efficiency, parameters intrinsically linked to overall photocatalytic performance through quantum yield relationships⁴¹⁻⁴³.

In this context, metal-organic frameworks (MOFs) have garnered significant attention as a tunable host domain for photocatalytic CO_2RR , offering distinct advantages over traditional semiconductor catalysts⁴⁴⁻⁴⁸. These crystalline porous materials, characterized by their high surface areas, tunable porosity, and modular compositions of metal clusters and organic linkers, enable precise atomic-level engineering of active sites and charge transport pathways. The well-defined coordination environments of metal clusters and organic linkers in MOFs facilitate the rational design of catalytic centers, optimizing CO_2 binding, activation and intermediate stabilization⁴⁹⁻⁵⁰. Additionally, the inherent porosity of MOFs enhances their capacity for CO_2 capture, a critical prerequisite for efficient reduction processes. Although a growing body of research and literature reviews on CO_2RR utilizing MOF-based photocatalysts, most studies have primarily focused on synthesis, modification methods, and general characterization^{27, 44, 47, 49, 51}. Comprehensive analyses specifically addressing the performance and engineering principles of metal-active sites within MOFs, particularly

at the atomic level and with a focus on C₂₊ selectivity, remain scarce. While some investigations explore atomic metal sites, detailed insights into tailoring selectivity for complex hydrocarbon products are often lacking^{44, 52-53}. This review intends to address this critical gap by highlighting the unique advantages of MOF-hosted metal sites for CO₂RR and systematically analyzing key engineering strategies targeting C₂₊ products. We will discuss some key metal-hosting engineering strategies, including metal atomicity (SACs versus DACs), coordination environment optimization, and spatial and distribution effects to enhance selectivity and activity in CO₂RR for high-value C₂₊ chemicals. By integrating advanced characterization, catalytic performance, and theoretical modeling, we will elucidate the mechanistic roles of these engineered sites in enhancing activity and selectivity. Ultimately, we will provide an outlook on the precise design of MOF photocatalysts with tailored metal active sites, underscoring their pivotal role in advancing CO₂RR towards selective C₂₊ synthesis.

1.2 Fundamentals of MOF-based photocatalysts for CO₂RR

1.2.1 Mechanism of Photocatalytic CO₂RR

CO₂ is a linear molecule (O=C=O) where each oxygen atom undergoes sp^2 hybridization. An sp^2 hybrid orbital from each oxygen forms a σ bond with the carbon sp hybrid orbital, while the remaining unhybridized $2p$ orbitals form two π bonds, resulting in stable C=O double bonds. This electronic configuration confers significant thermodynamic stability and kinetic inertness, rendering CO₂ activation and reduction energetically demanding. Consequently, the photocatalytic reduction of CO₂ is substantially constrained, necessitating meticulous catalyst design to enhance reactivity and selectivity, particularly for multi-carbon products requiring complex reaction pathways.

The active sites on these catalysts play a crucial role in the complex photocatalytic CO₂RR process, significantly enhancing the material's surface reactivity. The primary functions of these active sites include:

(1) CO₂ adsorption: CO₂RR initiates with the chemisorption of CO₂ onto active sites. Sites must exhibit strong affinity for CO₂ to maximize surface coverage and facilitate activation, often involving charge transfer from the catalyst to the CO₂ molecule, bending the linear O=C=O structure and lowering the energy barrier for subsequent reduction⁵⁴⁻⁵⁶.

(2) Light harvesting: While semiconductor catalysts possess intrinsic light absorption, metallic active sites can significantly broaden the absorption spectrum (e.g., via *d-d* transitions, ligand-to-metal charge transfer (LMCT), or metal-to-ligand charge transfer (MLCT)), enhancing solar energy utilization and exciton generation⁵⁷⁻⁵⁹.

(3) Charge separation: Following light absorption, photogenerated electrons and holes must be rapidly separated and transported to the catalyst surface. Metal sites can act as electron traps or facilitate directional charge transfer, suppressing recombination, which is critical for subsequent reactions^{35, 60}.

(4) Surface redox reactions: Surface-adsorbed CO₂ interacts with photogenerated charges (electrons and protons) to undergo stepwise reduction. This stage dictates catalytic performance and product selectivity. The multi-electron-multi-proton nature of CO₂RR generates a diverse range of intermediates (e.g., *COOH, *CO, *CHO, *CH₂O, *CH₃), whose relative stabilization energies determine branching points toward different products (**Table 1.1**)^{25, 27}. Crucially, C₂⁺ formation requires C–C coupling between adsorbed C₁ intermediates (e.g., *CO dimerization, *CO + *CHO coupling), demanding precise spatial and energetic control at the active site⁶¹⁻⁶³.

Competing HER, arising from water reduction, poses a significant challenge, often limiting CO₂RR efficiency and selectivity. Adsorbate binding strengths on the metal sites are paramount in steering reaction pathways towards either C₁, C₂₊, or H₂⁶².

Table 1.1. The photocatalytic CO₂ reduction potentials versus NHE at pH = 7 in aqueous solution[20, 25, 33].

Reaction	E ⁰ (V vs. NHE at pH = 7)
$CO_2 + e^- \rightarrow *CO_2^-$	-1.90
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.52
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0.61
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	-0.51
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + 2H_2O$	-0.38
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + H_2O$	-0.24
$2CO_2 + 8H^+ + 8e^- \rightarrow CH_3COOH + 2H_2O$	-0.30
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	-0.33
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	-0.34
$2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_6 + 4H_2O$	-0.27
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.42

1.2.2 MOFs as Photocatalysts

Metal-organic frameworks (MOFs), as an emerging class of compounds based upon reticular chemistry, exhibit exceptionally high specific surface areas and unprecedented structural programmability⁶⁴⁻⁶⁶. These crystalline materials are constructed through the

coordination of metal ions/clusters with organic ligands, interconnected via coordination bonds, van der Waals forces, or hydrogen bonds. This synthetic versatility allows for the combinatorial integration of diverse metal centers (such as main group metals, transition metals, and lanthanides) and organic linkers (such as carboxylates, azoles, phosphonates), making MOFs a versatile materials platform with near-infinite chemical permutations⁶⁷⁻⁶⁸. Since the early report of MOF-5, the research evolutionary trajectory of MOF has undergone an explosive diversification, encompassing applications ranging from gas absorption to catalysis⁶⁹. The metal ions or clusters within MOFs often exist in unsaturated forms, which can serve as metal active sites for catalytic reactions. While the structural diversity of MOFs is primarily engineered from the judicious selection of organic ligands, including aromatic dicarboxylic acids, nitrogen-containing heterocycles (such as pyridine and porphyrins), cyanides, crown ethers, phosphonates, and their functionalized derivatives. These ligands can be strategically modified at specific positions on the aromatic ring. For instance, functional groups (-NH₂, -OH, -SH) can be introduced in terephthalic acid ligands in the MOF matrix, which not only modulate the framework topology and morphology but also create additional ‘functional’ sites for various catalytic applications⁷⁰⁻⁷³. Furthermore, the presence of functional groups role as the anchoring sites to facilitate the anchoring of metal active sites^{71, 74-75}. Amino groups (-NH₂), for example, exhibit exceptional metal-anchoring capabilities through facile hydrogen dissociation, allowing for the precise immobilization of atomic-scale metal species via N–M coordination within the MOF matrix⁷⁴. This characteristic positions MOFs as excellent carriers for atomically dispersed metal sites.

From an electronic structure perspective, the periodic arrangement of metal-linker units in MOFs creates discrete semiconductor-like domains, facilitating efficient separation

and migration of photogenerated charge carriers. This unique characteristic, coupled with their ultrahigh surface areas and tunable pore architectures, makes MOFs as promising candidates for CO₂ capture and conversion applications⁷⁶⁻⁷⁷. When engineered for photocatalytic CO₂RR, the semiconductor properties of MOFs become particularly crucial. The bandgap energy, determined by the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), can be systematically modulated through the reticular arrangement between the preorganized metal clusters and organic linkers (**Fig. 1.1**)⁴⁷. For effective CO₂ reduction, it is essential that the LUMO level resides at a lower energy than the redox potential of CO₂ reduction. Moreover, through precise structural engineering, MOF photocatalysts enable fine-tuning of intermediate binding energies, potentially steering selectivity towards some more preferred products, such as high-value C₂₊ products. This capability is crucial for practical energy applications and underscores the unique potential of MOFs as modular platforms for mechanistic studies in the precise engineering of atomic metal sites in catalysts. We acknowledge the potential structural instability of MOFs in catalytic applications. Nevertheless, their reticular framework nature and tunable structure establish them as an ideal platform for investigating the solid-state chemistry and coordination chemistry of metal atom-supported catalysts.

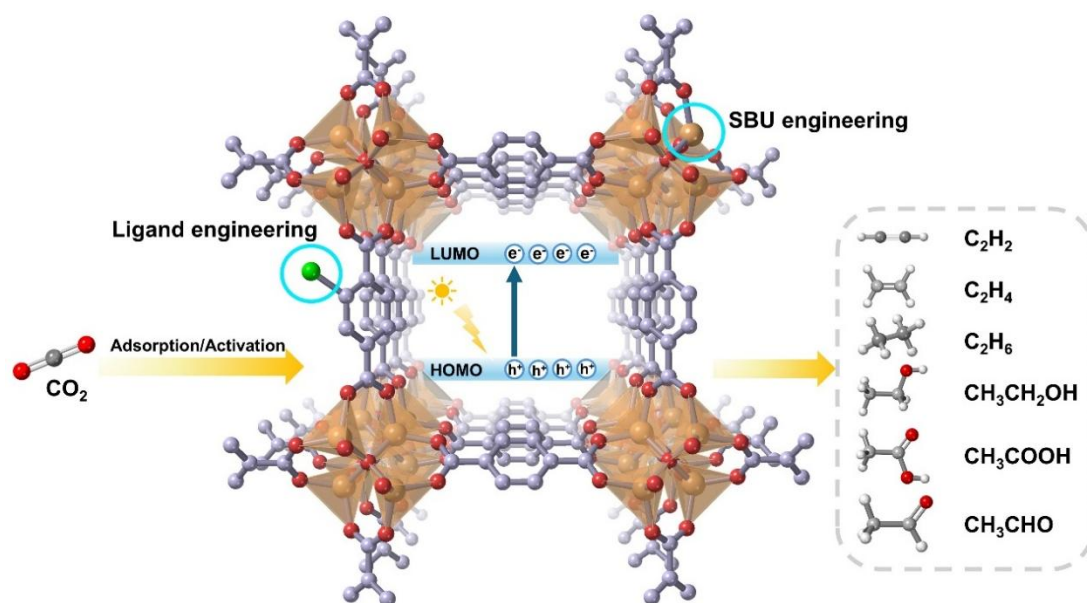


Fig. 1.1 Schematic representation of photocatalytic CO₂RR over MOF and the strategies to design active metal sites on MOFs for C₂₊ products.

1.3 Engineering Metal Active Sites in MOFs

Rational engineering of metal active sites on photocatalyst surfaces constitutes a cornerstone for advancing CO₂ photoreduction technologies^{51, 78}. These catalytic motifs govern three key processes: (1) CO₂ chemisorption and activation through orbital hybridization, (2) directional charge carrier transport and utilization, and (3) dynamic regulation of reaction intermediates. Crucially, metal active site engineering offers exceptional promise in tailoring the electronic structure of the catalytic microenvironment to favor specific reaction pathways, directly addressing the demand for selective C₂₊ hydrocarbon products⁷⁹⁻⁸⁰.

Currently, strategies for engineering metal active sites in MOFs can be categorized as follows: (1) defect engineering, which involves creating additional unsaturated metal sites of the SBUs⁸¹⁻⁸³; (2) post-synthetic modification (PSM) via grafting metal ions onto functionalized ligands^{74, 84}; (3) pre-synthetic exchange (PSE) of linkers anchored

with metal ions⁸⁵⁻⁸⁶; (4) creating MOF-derived catalysts (e.g., M-N-C materials)⁸⁷⁻⁸⁹. However, these conventional metal site deposition strategies often face inherent limitations that impede a comprehensive and deeper mechanistic understanding and hinder selectivity control to high-value chemicals from CO₂RR.

For instance, it is difficult to precisely control the microenvironment around the metal sites, as well as to accurately determine their valence state⁸⁹⁻⁹⁰. The inability to specifically analyze the role of individual metal active sites is further compounded by the influence of neighboring atoms on the metal center, which can alter the electron transfer pathways of reaction intermediates during CO₂RR⁹¹⁻⁹². Moreover, doping strategies often result in uncontrolled metal aggregation, leading to an uncontrollable metal center size and inconsistent metal valence states between the surface and interior of the cluster, thereby obscuring clear structure-property correlations^{80, 93-94}. Similarly, MOF-derived materials often suffer from ill-defined metal site locations and coordination environments, precluding accurate mechanistic analysis⁹⁵. In contrast, well-defined atomic-level metal site photocatalysts, particularly SACs and DACs within crystalline MOF matrices, offer structural simplicity and uniformity⁹⁶⁻⁹⁷. This enables the establishment of precise structure-activity relationships in CO₂RR, enhancing fundamental mechanistic understanding and facilitating the rational design of photocatalysts targeting C₂₊ products. Consequently, this review focuses on the engineering of isolated metal atom centers within MOFs, exploring their influence on CO₂RR and the strategy for enhancing C₂₊ product selectivity from an atomic-level perspective.

1.3.1 Single-Atom Catalysts (SACs) for CO₂RR

SACs, featuring isolated metal sites as active catalytic motifs meticulously anchored on

appropriate support materials, have garnered extensive research interest^{21, 98-99}. SACs theoretically achieve 100% atom utilization efficiency, as every metal atom is potentially accessible and participates in catalysis. This maximized atom efficiency provides an unparalleled platform for investigating the intrinsic function of metal active sites. Moreover, according to the distinctive properties and electronic structures of single atoms, the tailor-made catalysts can be designed with desired performance characteristics and selectivity for specific reactions. Yaghi and co-workers developed the strategic integration of amine-functionalized ligands into MOF architectures to synthesize single-metal-atom sites¹⁰⁰. They demonstrated that MOF's SBUs could be rationally engineered to host the transition metal active site with Ångström-level precision. This seminal research established a paradigm for creating atomically precise metal coordination sites within extended framework structures, a methodology widely adopted in subsequent MOF catalysis research.

Pyrazolate-based porphyrinic MOFs, such as the PCN and ZrPP series, have emerged as some promising scaffolds for anchoring metal sites due to their structurally well-defined N₄-coordination environments^{84, 101-102}. Notably, metalloporphyrin MOFs with well-defined single-atom architectures serve as exemplary systems for probing the structure-activity relationships of metal sites in CO₂RR (**Fig. 1.2a**). For example, Gong et al. employed Kohn-Sham density functional theory (DFT) calculations to systematically analyze metallic incorporated PCN-601 derivatives (M-PCN-601, M = various transition metals, as shown in **Fig. 1.2c – d**)¹⁰³. They evaluated the photocatalytic potential based on four critical parameters at metal centers: photoexcitation dynamics, visible-light absorption capacity, vacuum-aligned energy levels, and CO₂ adsorption configurations. Through comparative simulations, Ni and Co sites were identified as promising candidates within PCN-601 for CO₂RR. Zhou et

al. experimentally synthesized Ni-PCN-601 featuring Ni as the metal site and confirmed its enhancing CO₂RR performance, aligning with their theoretical prediction¹⁰⁴. Similarly, Lin and co-workers synthesized a series of porphyrinic-based Zr-MOFs (ZrPP-1) with modified isolated metal motifs (M = Zn, Cu, Fe, Co) exhibiting robust stability under alkaline conditions (**Fig. 1.2e – g**)¹⁰⁵. CO₂ adsorption measurements revealed that the metal ion incorporation significantly enhanced CO₂ adsorption capacity, with Co-functionalized ZrPP-1-Co exhibiting exceptional uptake (~90 cm³·g⁻¹ at 1 atm, 273 K). Subsequent photocatalytic CO₂RR testing demonstrated that ZrPP-1-Co outperformed both the pristine MOF and other metal variants, achieving a CO production rate of 14.0 mmol·g⁻¹·h⁻¹ with >96.4% selectivity. DFT calculations revealed that metal ion incorporation lowered the Fermi level, narrowed the bandgap, and enhanced charge carrier mobility. Additionally, partial charge density analysis further identified Co ions significantly contributed to the conduction band minimum, facilitating electron transfer from the benzene ring to the porphyrin ring. While highlighting the role of metal sites in charge dynamics, the study did not delve deeply into the origins of differing selectivity among metals.

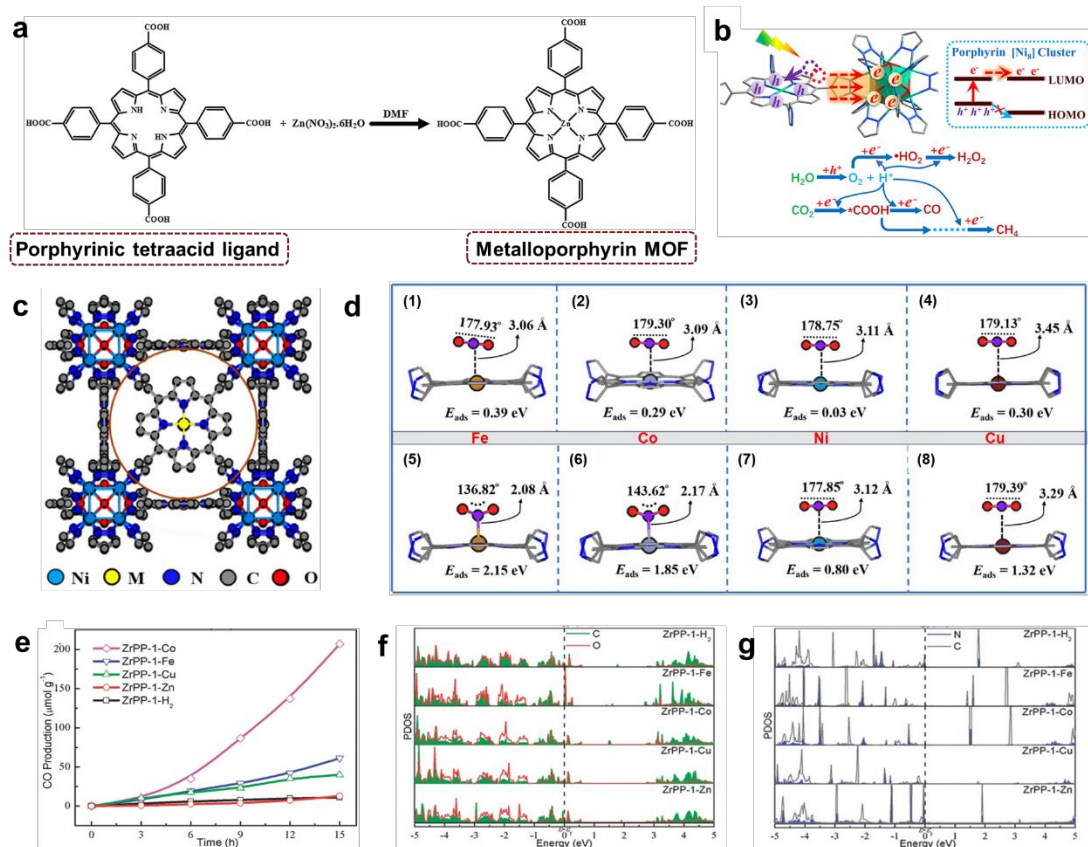


Fig. 1.2 (a) Synthetic reaction scheme for Zn/PMOF, Reproduced with permission¹⁰². Copyright 2016, Elsevier publication. **(b)** Charge separation and transfer through coordination sphere and related reaction pathways for the products, Reproduced with permission¹⁰⁴, Copyright 2024, ACS publication. **(c)** The isolated H₄MTPP (M = Fe, Co, Ni, or Cu) linker. **(d)** Optimized adsorption configurations of CO₂ on the metal^L of (1), (5) PCN-601(FeTPP), (2), (6) PCN-601(CoTPP), (3), (7) PCN-601(NiTPP), and (4), (8) PCN-601(CuTPP). For **d**(1)–(4), GS electron configuration is considered, while for **d**(5) – (8), CDFT-ES electron configuration is considered. Adsorption energies and key structural properties (i.e. O–C–O angles and metal^L–CO₂ distances) are also shown. Note that for each case only the metalloporphyrin linker and the adsorbed CO₂ are shown for clarity; the adsorbed CO₂ and the metal^L are represented by balls, and the organic moiety of the metalloporphyrin linker is simplified by lines. Color scheme: C of CO₂, purple; C of metalloporphyrin linker, gray; N, blue; O, red; Fe, orange; Co, light

purple; Ni, light blue; Cu, brown. Reproduced with permission¹⁰³, Copyright 2021, IOP publication. **(e)** Time courses of CO obtained from CO₂ photoreduction with catalysts of ZrPP-1-M under visible-light irradiation. **(f)** Partial density of states (PDOS) of C and O atoms, and **(g)** N and C atoms in ZrPP-1-M (M = H₂, Fe, Co, Cu, Zn). Reproduced with permission¹⁰⁵, Copyright 2018, Wiley publication.

Ye et al. engineered and synthesized MOF-525-Co, featuring unsaturated Co active sites within a porphyrinic framework, maximizing metal utilization and active site exposure, thereby improving CO₂ adsorption capacity, and facilitating efficient activation of CO₂¹⁰⁶. Catalytic performance evaluations revealed that MOF-525-Co achieved CO and CH₄ production rates of 200.6 and 36.76 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, representing increases of 3.13-fold and 5.93-fold over the unmodified MOF-525, respectively. Volumetric CO₂ adsorption measurements corroborated that the Co sites significantly enhance the catalyst's affinity for CO₂, thereby augmenting catalytic activity. To probe the mechanistic role of Co active sites in the CO₂RR, the authors synthesized a Zn-incorporated analog (MOF-525-Zn) as a control. Structural analysis revealed that Co atoms exist in an unsaturated coordination state within the MOF matrix, unlike Zn, providing more space for photon and intermediate to transfer/reactivity for carbon chain hydrogenation. Crucially, under visible-light irradiation, photogenerated electrons migrate from porphyrin ligands to Co centers, inducing a reversible light-driven spin-state transition from high-spin Co(II) to low-spin Co(I). This metastable Co(I) state facilitates CO₂ activation via electron transfer, regenerating Co(II) during the catalytic cycle. In contrast, the distinct product selectivity and significantly lower catalytic activity of MOF-525-Zn underscored the unique redox-active nature of cobalt centers in governing both catalytic activity and reaction pathways.

Although these systems primarily yield C₁ products, their insights remain crucial for the rational design of C₂₊ product-selective catalysts. Because the isolated metal anchoring structure is the ideal model for investigating the function of the metal sites. For example, Fe(II) (*d*⁶) displays strong oxygen affinity, potentially favoring oxygenates, Zn(II) (*d*¹⁰) enhances visible-light absorption due to its optically active *d*¹⁰ configuration though it often shows limited intrinsic catalytic activity, and Re(I) (*d*⁵) is known to suppress exciton recombination^{106, 107}. Kang et al. anchored Re(I) sites onto PCN-222 via post-synthetic modification, obtaining PCN-222-Re, which exhibited exceptional photocatalytic stability and CO production efficiency⁸⁴. This performance stemmed from the strong electron-accepting capability of the Re(I) sites, preventing charge recombination in adjacent porphyrin units.

To overcome limited light harvesting in intrinsic MOF semiconductors, photosensitizers (PS) are often incorporated into photocatalytic systems to initiate and sustain efficient reaction processes¹⁰⁸⁻¹⁰⁹. (3) Representative PS candidates often use metallic pyridine-based derivatives, such as [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine), which are widely employed for their exceptional light-absorption and electron-transfer properties^{98, 110}. Strategic integration of PS units as linkers within MOF frameworks provides optimized metal-active sites for photon capture and reduces reliance on external PS. Lin et al. employed a tetrapyrrole modification method to design various metal atom ligand derivatives based on a 2,2'-bipyridine ligand¹¹⁰. The designed ligand Re^I(CO)₃(dcbpy)Cl(H₂L₄) was successfully incorporated into the UiO-67 framework, creating well-defined Re SACs (**Fig. 1.3a – b**). This structural engineering endowed the material with exceptional photocatalytic activity for CO₂-to-CO conversion. Building on this success, Lin et al. further optimized the ligand environment by replacing the 2,2'-bipyridine unit with a more extended aromatic system, 4,4'-(2,2'-

bipyridine-5,5'-diyl)dibenzoic acid, resulting in the analogous single-atom site in UiO-69⁹⁸. The CO turnover number (TON) for MOF-1 in 6 hours (6.44) is more than double the performance of the unmodified MOF. While Li et al engineered a photosensitized MOF system (MOF-253-Ru(CO)₂Cl₂) by incorporating Ru centers into N, N'-chelating sites within the MOF-253 framework (**Fig. 1.3c – e**)⁶⁰. These Ru atoms acted as both photocatalytic active sites and stabilizers for photosensitizing moieties, boosting formate production TON from 2.9 to 35.8 h⁻¹, which is 12.3-fold enhancement attributed to optimized charge transfer and localized active-site engineering (**Fig. 1.3f**).

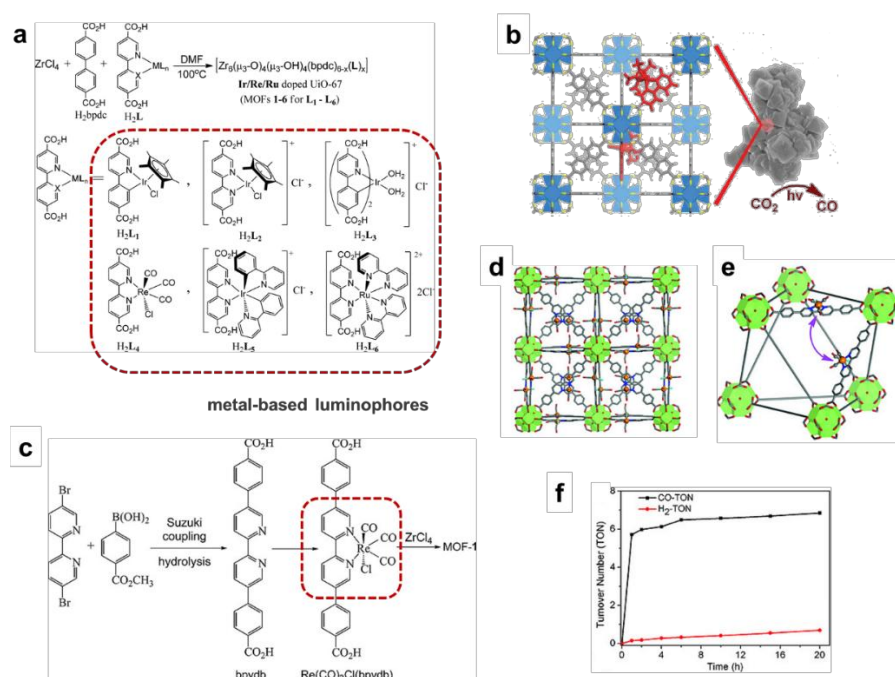


Fig. 1.3 (a) Synthesis of doped UiO-67. (b) Structural model of MOF-1 showing doping of the L1 ligand into the UiO-67 framework. Reproduced with permission¹¹⁰, Copyright 2011, ACS publication. (c) Synthesis of MOF-1. Crystal structure of MOF-1 (d) showing an octahedral cage and (e) viewed along the [100] direction of the unit cell. (f) CO and H₂ turnover number vs. time for MOF-1. Reproduced with permission⁹⁸, Copyright 2016, Wiley publication.

Beyond porphyrin and porphyrin-like structures, ligands functionalized with -NH₂, -SH

or other groups are also excellent platforms for immobilizing SACs¹¹¹⁻¹¹². This versatility enables rational catalyst design with enhanced flexibility. Critically, the synthetic methodology profoundly impacts the catalyst's structural architecture and consequent CO₂RR performance. This applies whether metal sites are first immobilized on functional groups prior to MOF assembly or introduced via post-synthetic modification, where functionalized ligands are grafted onto pre-formed MOF frameworks followed by metalation^{74, 84, 86, 96}. As shown in **Fig. 1.4a**, Zhou et al. constructed the Re-incorporated MOF via post-synthetic ligand exchange, where atomically dispersed Re centers function as highly active catalytic sites for the CO₂-to-CO reduction⁹⁶. Liu's team advanced this design by substituting Re centers in a UiO-67 type MOF by with Co, creating Co-UiO-67 (**Fig. 1.4b**)⁹³. This Co-SAC exhibited remarkable enhancement, achieving CO production rates 8 times higher (3292.5 vs. 412.5 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) and superior cycling stability compared to the Re analog (**Fig. 1.4c – d**). Theoretical analysis attributed this leap to the distinct electronic configuration of unsaturated Co *d*-orbitals, enabling stronger interfacial interactions with CO₂ molecules and lowering activation barriers (**Fig. 1.4e**).

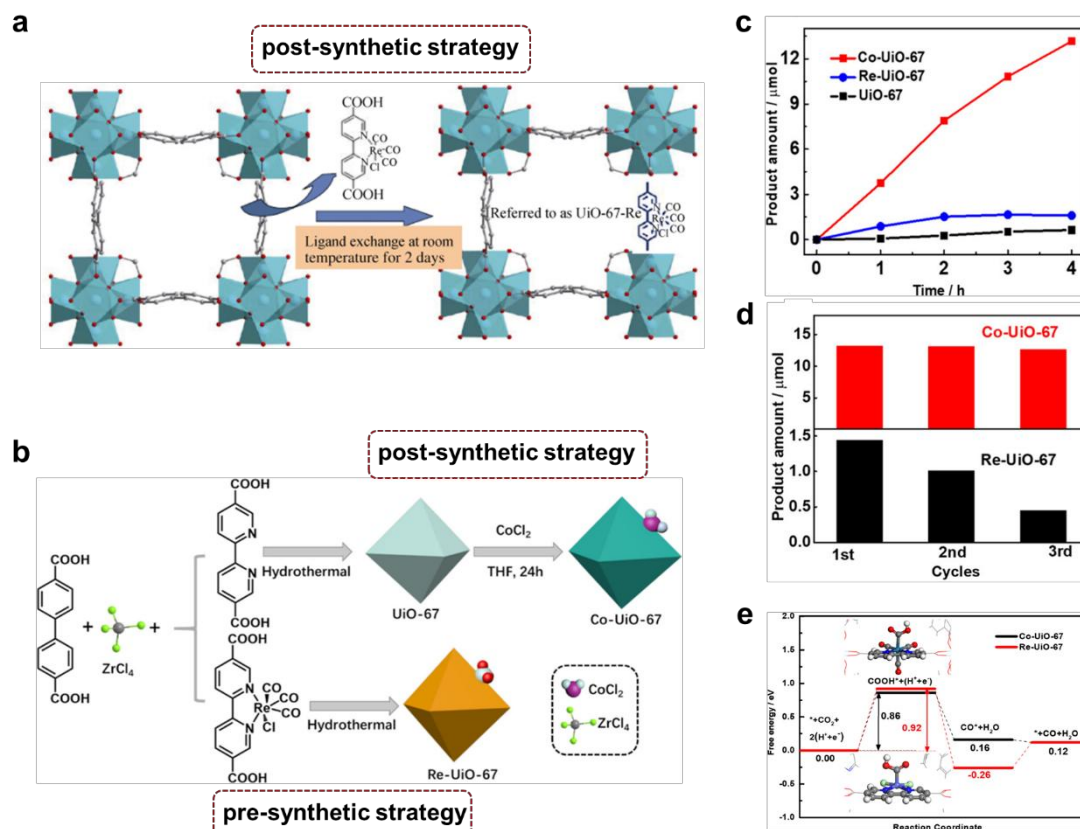


Fig. 1.4 (a) Schematic representation of post-synthetic exchange (PSE) of UiO-67-Re MOF. Reproduced with permission⁹⁶, Copyright 2019, Springer Nature Publication. **(b)** Synthetic Scheme of Co-UiO-67 (PSE) or Re-UiO-67 (PSM). **(c)** Evolution of CO under 300 W Xe lamp irradiation for 4 h with catalysts. **(d)** Production yields of CO over Co-UiO-67 and Re-UiO-67 in three repeated cycles. **(e)** Reaction free energy of CO₂ reduction to CO over Co-UiO-67 and Re-UiO-67. Reproduced with permission⁹³, Copyright 2020, ACS publication.

Despite many SACs tend to produce C₁ products, it has also been shown that some Cu SAs can yield C₂₊ products^{45, 79, 112-113}. Nevertheless, the underlying mechanisms driving this unique selectivity remain underexplored and are not yet fully understood. Li et al. showed that through light-driven synthesis, Cu SAs/UiO-66-NH₂ exhibits exceptional photocatalytic efficiency for the selective reduction of CO₂ to liquid

hydrocarbon products (**Fig. 1.5a, 1.5c, d**)¹¹². The evolution rates of CH₃OH and CH₃CH₂OH for Cu SAs/UiO-66-NH₂ were approximately 5.33 and 4.22 $\mu\text{mol h}^{-1} \text{g}^{-1}$, respectively, which are about two-fold and four-fold higher than those of Cu nanoparticles supported on the same MOF (Cu nanoparticles (Cu NPs)/UiO-66-NH₂) (**Fig. 1.5b**). DFT calculations rationalized this enhancement by identifying stabilized CO* and CHO* intermediates on Cu SAs sites, coupled with lower energy barriers for C–C coupling compared to Cu NPs, thereby favoring ethanol formation through kinetically accessible pathways (**Fig. 1.5e**).

Beyond conventional approaches utilizing strong coordinating ligands, defect engineering in the MOF matrix has emerged as a versatile strategy for immobilizing metal species within metal-oxide node architectures^{80, 114-116}. This methodology achieves dual functional optimization: (1) enhanced light-harvesting efficiency through defect-induced bandgap modulation or creation of mid-gap states, and (2) precise control over node chemical environments for targeted metal incorporation. This cooperative interplay facilitates electronic structure tuning of the anchored SACs, significantly boosting catalytic activity through optimized intermediate adsorption/desorption energetics. For example, Yan et al. engineered iridium SACs within defective UiO-66 membranes (Ir₁/A-aUiO), demonstrating outstandingly strong metal-support interactions (SMSI) that drive exceptional efficiency in CO₂-to-formic acid conversion (**Fig. 1.5f**)¹¹⁶. Comparative performance analysis revealed that the Ir-SAC system exhibits 6.5-fold and 338-fold higher formate production rates than Ir clusters (Ir_x/A-aUiO) and nanoparticles (Ir_{NPs}/A-aUiO) loaded on the same support, respectively (**Fig. 1.5g – h**). This enhancement originates from the atomic dispersion-induced electronic modulation, which simultaneously strengthens CO₂ chemisorption at metallic centers and reduces activation barriers for intermediate formation. In

contrast, Lercher et al. anchored Cu SACs onto zirconium clusters in UiO-66, achieving selective hydrogenation of CO₂ to methanol, showcasing different selectivity compared to Ir SACs⁸⁰.

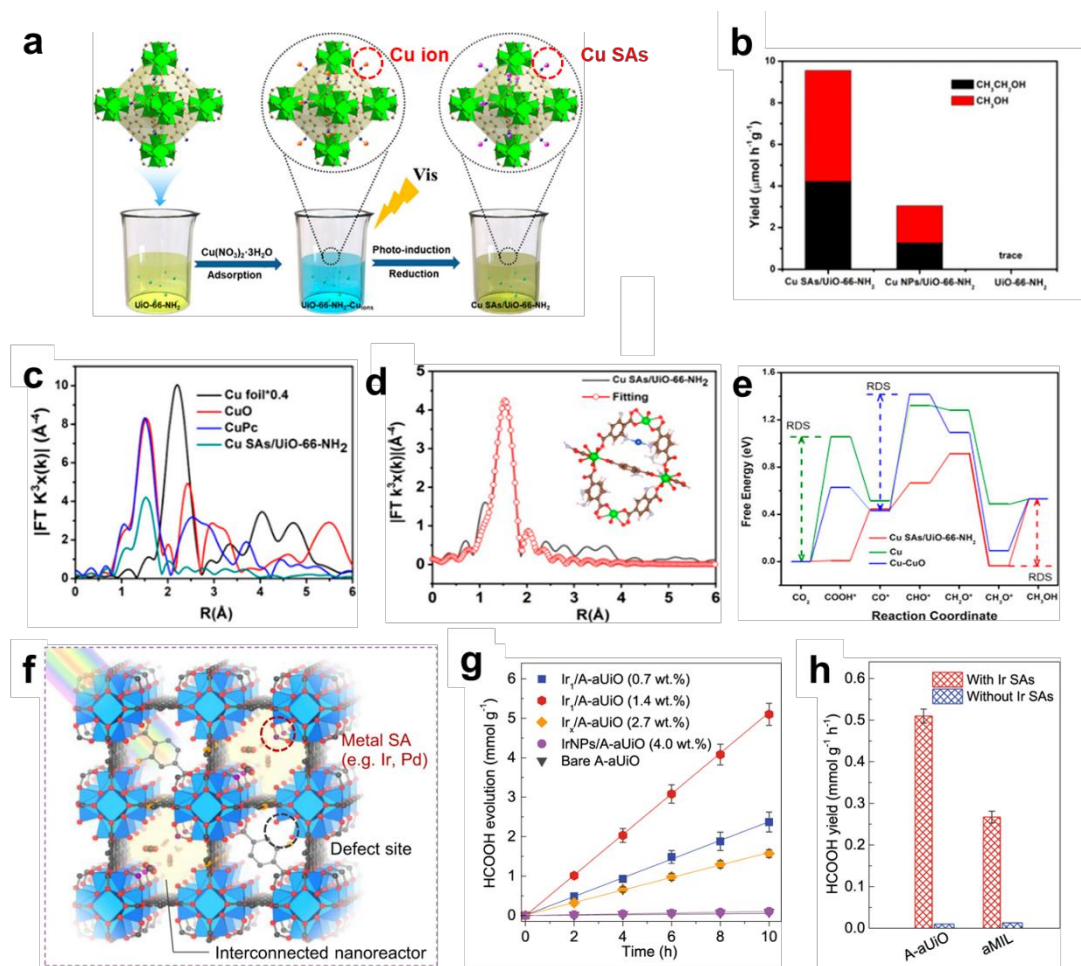


Fig. 1.5 (a) Synthesis process of the Cu SACs/UiO-66-NH₂ photocatalyst. C (gray), O (red), Zr–O clusters (green), N (blue), Cu ions (orange), and Cu SACs (purple). (b) Comparative rates of CH₃OH and CH₃CH₂OH formation of the UiO-66-NH₂, Cu SACs/UiO-66-NH₂, and Cu NPs/UiO-66-NH₂. (c) EXAFS results of the samples at the Cu K-edge. (d) EXAFS fitting curves of the Cu SACs/UiO-66-NH₂ at R space (inset, the corresponding structure model, C (brown), H (pink), O (red), N (light blue), Cu (blue), and Zr (green)). (e) Calculated free energy diagram of all steps for CO₂ reduction to

different intermediates on the samples. Reproduced with permission¹¹², Copyright 2020, ACS publication. **(f)** With controllable defect-engineering, specific metal SAs (e.g., Ir and Pd) can be precisely anchored on the edges of the $\text{Zr}_6\text{O}_4(\text{OH})_4(-\text{CO}_2)_{12-x}$ octahedral to act as programmable catalytic centers. **(g)** Time course of HCOOH evolution on A-aUiO, $\text{Ir}_1/\text{A-aUiO}$, $\text{Ir}_x/\text{A-aUiO}$ and $\text{Ir}_{\text{NPs}}/\text{A-aUiO}$ catalysts. **(h)** HCOOH yields on A-aUiO and aMIL catalysts with and without Ir SAs modification. Reproduced with permission¹¹⁶, Copyright 2021, Nature publication.

In brief, MOF-based SACs for CO_2RR have been extensively researched and developed. Leveraging the distinctive electronic properties of metals, SACs can be precisely tailored to enhance CO_2RR activity, product selectivity, and photostability. This is achieved by tuning the metal/support material properties and metal-support interactions to modulate light-harvesting capability, charge separation behavior, CO_2 adsorption and intermediates adsorption/desorption. Various noble metal-based SACs, such as porphyrin-like SACs (e.g., Ru, Rh, Ir), have been developed to improve light absorption and catalytic performance, though they primarily yield C_1 products. Additionally, certain 3d transition metal SACs exhibit excellent photocatalytic CO_2RR reduction performance. Notably, copper atoms demonstrate an exceptional capability for reducing CO_2 to high-value C_{2+} products, which is intrinsically linked to their electronic configuration. This configuration stabilizes key intermediates like $^*\text{CO}$ and multi-carbon species while lowering the energy barrier for intermediate polymerization. Consequently, Cu-based SACs show high activity, long-term stability, and C_{2+} product selectivity, positioning copper as the primary candidate for efficient conversion to multi-carbon products. However, further optimization of their coordination environments is essential to accommodate higher-order carbon products. Moreover, reports on MOF-based SACs producing C_{2+} products remain scarce, probably due to

the challenge of achieving C–C coupling at isolated single-atom sites where active centers are inherently distanced.

1.3.2 Dual-Atom Catalysts (DACs) for CO₂RR

In comparison to SACs with isolated metal sites in restricted reaction potential for developing long chain intermediate species from CO₂RR, DACs offer tunable metal selectivity with neighboring active motifs, enabling control over electronic and spatial properties, as well as subtle synergistic effects between different metal combinations^{35, 44, 78, 117-118}. This makes DACs particularly well-suited for multi-molecular catalytic reactions like C–C coupling⁴⁴. The complementary nature of the metal sites in DACs can provide differential capabilities for reactant activation, intermediate stabilization, and sequential reaction steps. Fundamentally, C₂₊ product formation in CO₂RR is governed by C–C coupling of carbon-containing intermediates, requiring an optimal balance between intermediate adsorption/desorption strength and stabilization of key transition states⁶¹. In essence, precisely designing DACs with tailored metal pairs and spatial arrangements holds promise for improving both the efficiency and selectivity of C₂₊ product formation, providing a means to overcome the hurdles associated with C–C coupling during CO₂RR⁹⁷. However, constructing a comprehensive library for precise selective control of metal pairs and regulating multi-step proton-coupled electron transfer (PCET) processes for complex intermediates remains challenging. Also, achieving selective target product formation without over-reduction or undesired side reactions is difficult to control. Consequently, studies on MOF-based DACs for CO₂RR applications, especially specifically targeting the formation of C₂₊ products, are still limited.

Computational studies by Guo et al. have delineated the structure-activity relationships

governing the photocatalytic CO₂RR performance of transition metals supported on Ti-BPDC, both as single atoms (M/Ti-BPDC, SACs)¹¹⁹ and diatomic pairs (Cu-M/Ti-BPDC, DACs)¹²⁰. Their analysis revealed that SACs are limited by the inability of an isolated metal site to manage complex multi-electron/proton transfers, primarily facilitating CO₂ reduction to HCOOH with insufficient activity or selectivity for C₂ products. The variability in activity and selectivity among SACs for C₁ products (CO and HCOOH) was elucidated with respect to metal-specific properties, including d-band center, electronegativity, and reducibility, which modulate the binding energies of the critical reaction intermediates. Based on this foundation, the authors extended their analysis to Cu-M/Ti-BPDC (M= Sc, Mn, Fe, Cu, Nb, Ru, Rh, Pd, Pt, Os, Ir, In, Sn, or Bi) to elucidate the bimetallic sites structure, active sites, and reactant interactions in DACs, with particular emphasis on synergistic effects between the metal pairs and their impact on photocatalytic CO₂RR to C₂ products. By correlating computed Gibbs free energies of pivotal intermediates in CO₂RR pathways with limiting energy changes, they established structure-activity relationships for DACs. Bader charge analysis indicated positive charge accumulation on Cu and In atoms, contrasted by negative charge on the bridging O₁ atom, signifying pronounced charge transfer within the Cu-O₁-In motif. This motif also exhibited marked charge redistribution with surrounding ligands, reflecting electron accumulation and depletion at metal-ligand interfaces. Later, they found the adsorption strength of the critical *COOH-*COOH intermediate directly influences CO₂RR activity. Thus, the authors linked its computed Gibbs free energy to limiting free energy changes to refine structure-activity correlations. As a result, Cu-In/Ti-BPDC displayed optimal adsorption and Gibbs free energies, rendering it the premier catalyst for CO₂ conversion to C₂ products, particularly C₂H₄. Extending this approach, free energy differences for other intermediates also served as descriptors,

revealing Cu-Sn/Ti-BPDC as optimal for CO₂ reduction to HCOOH and Cu-Os/Ti-BPDC for CH₃OH. These results underscore the strategic potential of rationally designed DACs. The introduction of a second metal center provides a powerful lever to precisely tailor the catalytic landscape, steering reaction pathways toward specific high-value products. Ultimately, rational design of the bimetallic composition and its electronic coupling with the support is paramount for achieving high activity and selectivity in the photocatalytic synthesis of C₂ products from CO₂.

DACs mirror the design logic of SACs by pairing photosensitizing noble metals complex (e.g., Ru(bpy)_n, Ir(ppy)_n) with reactive centers (e.g., Co, Re), creating light-harvesting/catalysis divisions^{90, 118, 119, 121-123}. Lu et al. exemplified this in engineering a dual-atom-functional photocatalyst (Co/Ru)_x-UiO-67(bpydc), where the Ru units absorb >600 nm light while Co SAs drive concurrent CO and H₂ production via CO₂ reduction (**Fig. 1.6**)¹¹⁹. This hybrid design leverages the complementary roles of Ru-site units and atomically dispersed Co catalytic centers, which demonstrated synergistic functionality unattainable in single-component systems. Similarly, Maji et al. emphasized that co-anchoring PS and effective catalytic metal active sites within the confined space of MOF can effectively facilitate electron transfer from the PS to the active metal sites (**Fig. 1.7**)¹²². Using sequential post-synthetic ligand exchange (PSE) and post-synthetic metalation (PSM), they constructed multifunctional Zr-MBA-Ru/Re-MOF assemblies. Starting with a Zr-MOF precursor, they immobilized [Ru(bpy)₂]²⁺ and [Re(CO)₅Cl] complexes on the ligands to obtain Zr-MBA-Ru/Re-MOF. This architecture achieved exceptional CO selectivity (99%) with a peak production rate of 440 mmol·g⁻¹·h⁻¹. Electron paramagnetic resonance (EPR) studies revealed excited-state electron transfer from Ru(II) to Re(I) moieties, confirming that the spatial proximity between Ru(II) and Re(I) sites within the MOF framework

promotes efficient charge transfer. Notably, the Ru(II) centers maintained their intrinsic photosensitizing functionality while integrating into the MOF matrix. Li et al. immobilized the same $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Re}(\text{CO})_5\text{Cl}]$ complexes within the MOF-253 framework, significantly enhancing both the photocatalytic yield and selectivity for photocatalytic CO_2 -to- HCOOH conversion⁹⁰.

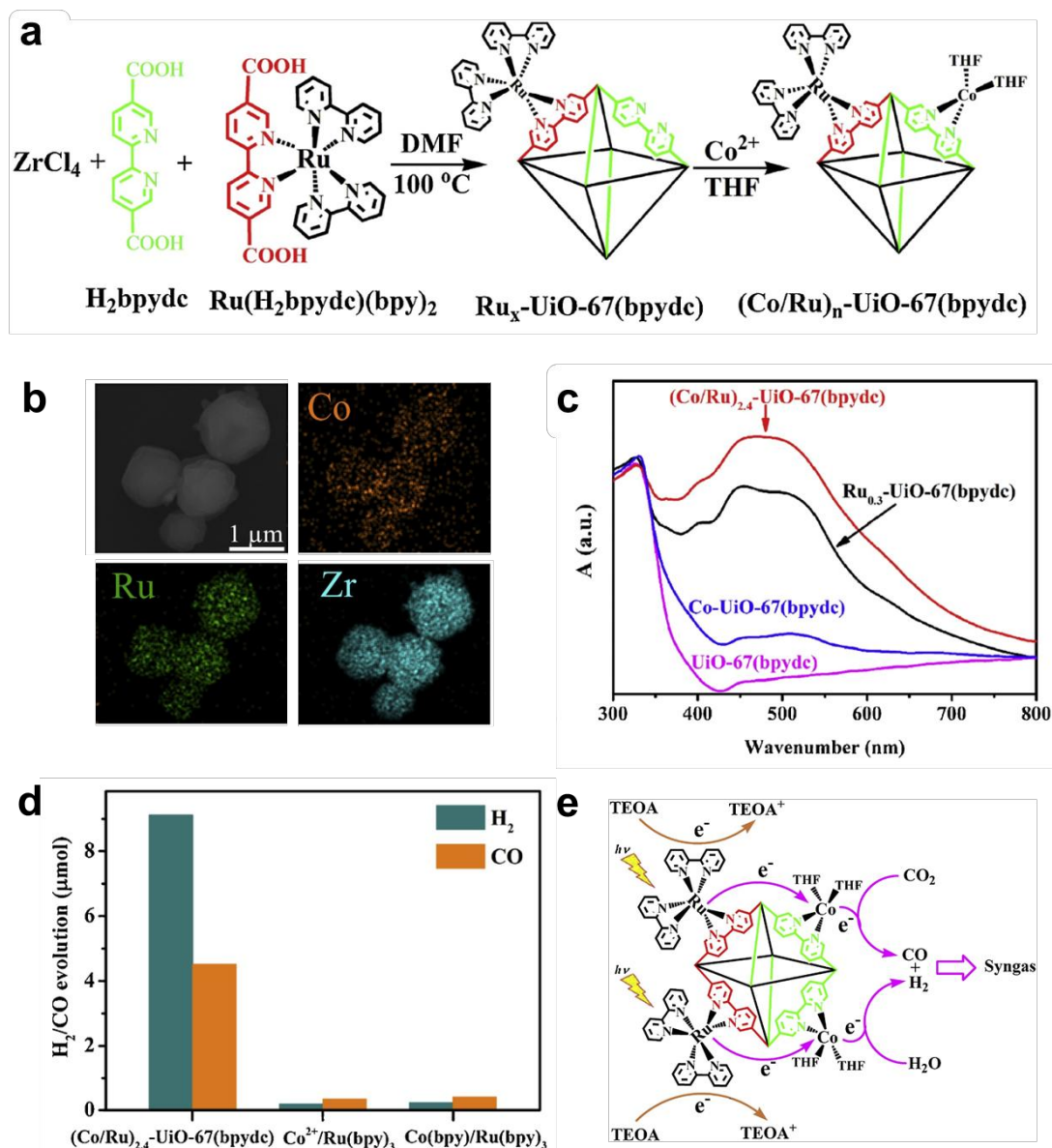


Fig. 1.6 (a) Schematic view of the synthetic process of $(\text{Co/Ru})_n\text{-UiO-67(bpydc)}$. (b) EDX mapping of $(\text{Co/Ru})_{2.4}\text{-UiO-67(bpydc)}$. (c) Normalized diffuse reflectance spectra for UiO-67(bpydc) , Co-UiO-67(bpydc) , $\text{Ru}_{0.3}\text{-UiO-67(bpydc)}$, and $(\text{Co/Ru})_{2.4}\text{-UiO-67(bpydc)}$.

67(bpydc). **(d)** H₂ and CO production in MOF and homogeneous catalytic system. **(e)** Proposed mechanism for photocatalytic syngas production with (Co/Ru)_n-UiO-67(bpydc) as the catalyst under the visible light irradiation. Reproduced with permission¹¹⁹, Copyright 2019, Elsevier publication.

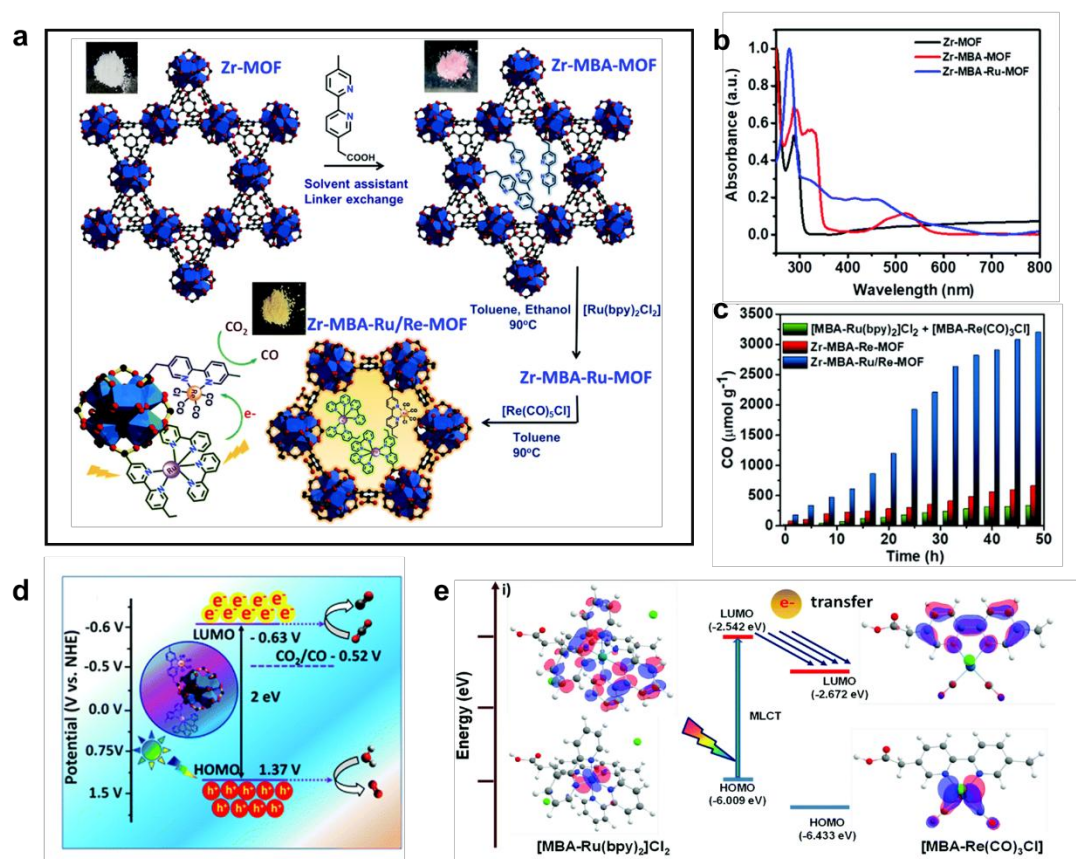


Fig. 1.7 **(a)** Schematic for the construction of Zr-MBA-Ru/Re-MOF *via* post-synthetic linker exchange and immobilization of the molecular photosensitizer and catalyst toward CO₂ reduction. **(b)** UV-vis spectra of Zr-MOF, Zr-MBA-MOF and Zr-MBA-Ru-MOF. **(c)** Comparison of photocatalytic CO formation of Zr-MBA-Ru/Re-MOF (blue), Zr-MBA-Re-MOF (red), and a homogeneous mixture of [MBA-Re(CO)₃Cl]/[MBA-Ru(bpy)₂]²⁺ (green) in mixed MeCN/H₂O solution along with BNAH and TEOA under visible light irradiation. **(d)** Energy diagram of the HOMO and LUMO levels of Zr-MBA-Ru/Re-MOF. **(e)** HOMO-LUMO positioning of the Ru-photosensitizer [MBA-Ru(bpy)₂]₂Cl₂ and Re-catalyst [MBA-Re(CO)₃Cl], showing the

possibility of charge transfer. Reproduced with permission¹²², Copyright 2021, Royal Society of Chemistry.

Apart from the PS-based metal site component, other transitional metals have also been employed in CO₂RR. Building upon extensive prior research on MOFs and metal photosensitizer design, Lin et al. developed a dual-atom-modified mPT-MOF featuring multifunctional sites through the stepwise introduction of Cu and Re atoms, as shown in **Fig. 1.8**¹²⁴. In this system, the Cu sites acted as PS enabling reductive quenching, subsequently injecting electrons into the Re catalytic centers for CO₂RR. The mPT-Cu/Re catalyst achieved a CO₂RR turnover number (TON) of 1328, nearly two orders of magnitude higher than pristine mPT-MOF. Photophysical and electrochemical studies elucidated the reductive quenching pathway in mPT-Cu/Re, confirming the role of Cu as a light-harvesting component for stabilizing the photocatalytic system. Furthermore, they substituted Re with Co to create distinct catalytic functionality, where Co centers favored the hydrogen evolution reaction (HER). This highlights how tuning the metal pair (e.g., Cu/Co vs. Cu/Re) enables precise control over reaction outcomes. Adjusting these bimetallic pairs offers a promising strategy for targeting specific reaction objectives, particularly in designing photocatalysts for targeted C₂₊ product synthesis. They also designed a two-step post-synthetic method for constructing the Cu-Zn dual metallic active sites in UiO-67-bpy matrix for other special needs of reaction¹²⁵.

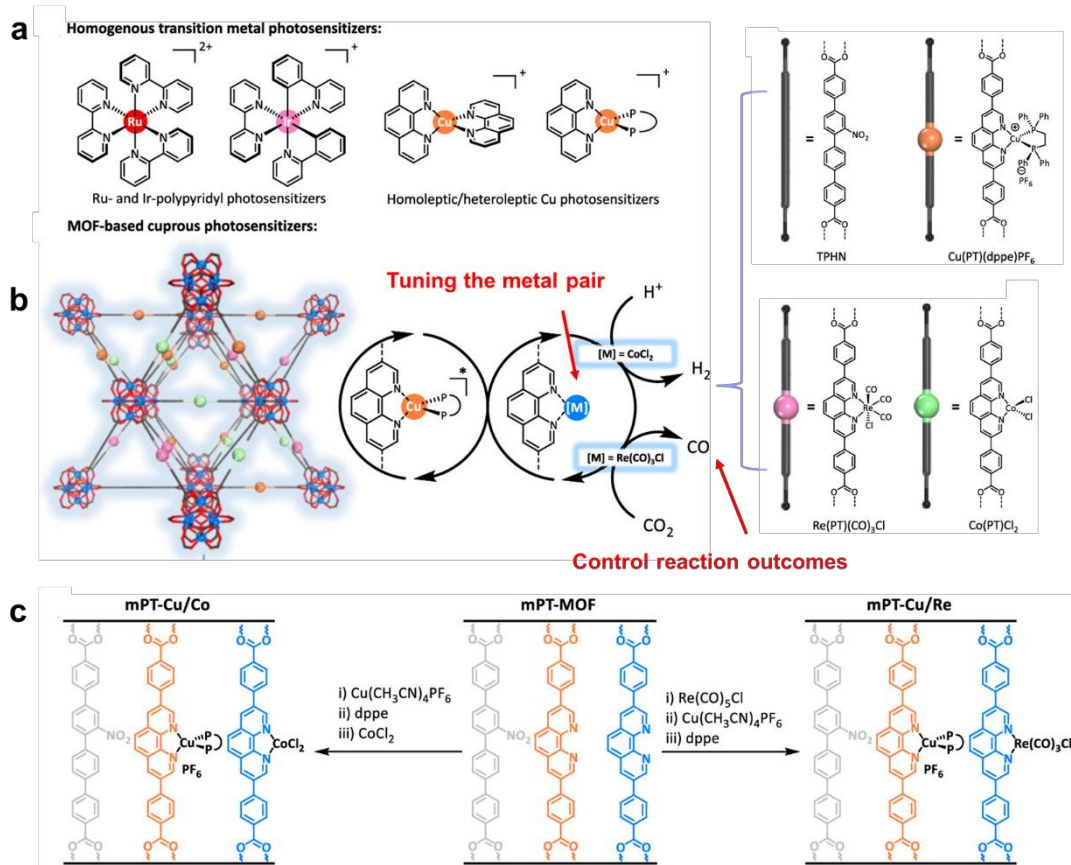


Fig. 1.8 (a) Molecular structures of transition metal photosensitizers. **(b)** Framework structures and bridging ligands of mPT-Cu/Co and mPT-Cu/Re MOFs. The proximity between Cu-PSs and molecular Co/Re catalysts in the MOFs enhances electron transfer and photocatalytic activities. **(c)** Post-synthetic modifications of mPT-MOF to afford mPT-Cu/Co and mPT-Cu/Re. Reproduced with permission¹²⁴, Copyright 2020, ACS publication.

Zhong et al. developed an innovative MOF-based catalytic platform centered on DACs, engineering a series of non-noble bimetallic MOF photocatalysts with precisely arranged atomic configurations⁹⁷. Among the DAC metal combinations (Cu/Ni, Mn/Co, Cu/Mn, and Ni/Co), the MOF-808-Cu/Ni system exhibited superior photocatalytic activity with a CH₄ production rate of 158.7 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ and 99.4% selectivity, which are 6.8 times and 2.8 times greater than those of the pure MOF-808-EDTA, respectively.

Crucially, this performance surpasses both single-atom counterparts (MOF-808-Cu: $62.1 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, 96.9%; MOF-808-Ni: $26.2 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, 48.1%), strongly indicating synergistic Cu-Ni site cooperativity that promotes CH_4 generation. DFT calculations reveals that this synergy originates from complementary roles between the Cu and Ni sites, which is particularly advantageous during the critical steps of $^*\text{CO}$ desorption or hydrogenation, collectively steering the pathway toward the formation of CH_4 . They revealed that the difference function in different metal sites affects the selectivity of CO_2RR . However, the study did not comprehensively address the performance variations among other DAC configurations or provide mechanistic insights into individual metal site contributions beyond the Cu/Ni system, leaving open questions about the generalizability of the observed cooperative effects.

Building on this foundation, Ma et al. conducted a study to further elucidate the distinct functions of individual metal site components in CO_2RR ¹²⁶. They engineered a UiO-66(Hf)-supported platform for anchoring bimetallic single-atom sites to investigate the synergistic effects of non-noble metal pairs (Co, Ni, Mn, Cu) on photocatalytic CO_2 -to-methanol conversion (**Fig. 1.9a – d**). During CO_2RR , Cu-containing DACs outperformed Cu-free counterparts in methanol production, with CuNi SACs/UiO-66(Hf) achieving the highest methanol yield. Indeed, methanol synthesis involves a six-electron transfer process, distinct from the two-electron CO formation pathway. Since Cu sites effectively stabilize CO intermediates, preventing premature desorption. Cu Sites have been revealed that they preferentially adsorbed CO_2 and lowered energy barriers for the initial three steps of C_1 intermediate formation ($^*\text{COOH} \rightarrow ^*\text{CO} \rightarrow ^*\text{CHO}$), leveraging the strong CO_2 affinity of Cu and orbital hybridization. The Ni sites dominate the subsequent protonation steps ($^*\text{CH}_2\text{O} \rightarrow ^*\text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH}$), utilizing the strong hydrogen adsorption property of Ni to accelerate proton-coupled electron

transfer. Ni atoms also occupied lower-energy molecular orbitals in the CuNi DAC system, narrowing the bandgap of UiO-66(Hf) by ~ 0.3 eV and enhancing charge separation efficiency. The electronic synergy and spatial proximity of Cu/Ni sites within the MOF pores enables efficient relay of intermediates, resolving kinetic bottlenecks in the six-electron reduction pathway. Extending this dual-site design philosophy, Xing et al. developed Fe/Ti bimetallic MOF systems for CO₂-to-methanol conversion¹²⁷. Unlike the approach by Ma et al., where bimetallic pairs are anchored to separate linkers¹²⁶, Xing et al. first synthesized MIL-125-NH₂ with engineered oxygen vacancies to expose abundant Ti active sites, then grafted Schiff-base moieties onto amino groups to introduce Fe single atoms (**Fig. 1.9e and f**). This strategy created Fe@MIL-OV-300 featuring oxygen-bridged Ti-O-Fe sites where the two metals are directly connected through atomic-scale linkages. This ultra-close proximity significantly enhanced methanol yield and selectivity compared to systems with distantly paired metals, demonstrating how tailored atomic connectivity can optimize catalytic cooperation for complex multi-step reactions (**Fig. 1.9g – i**).

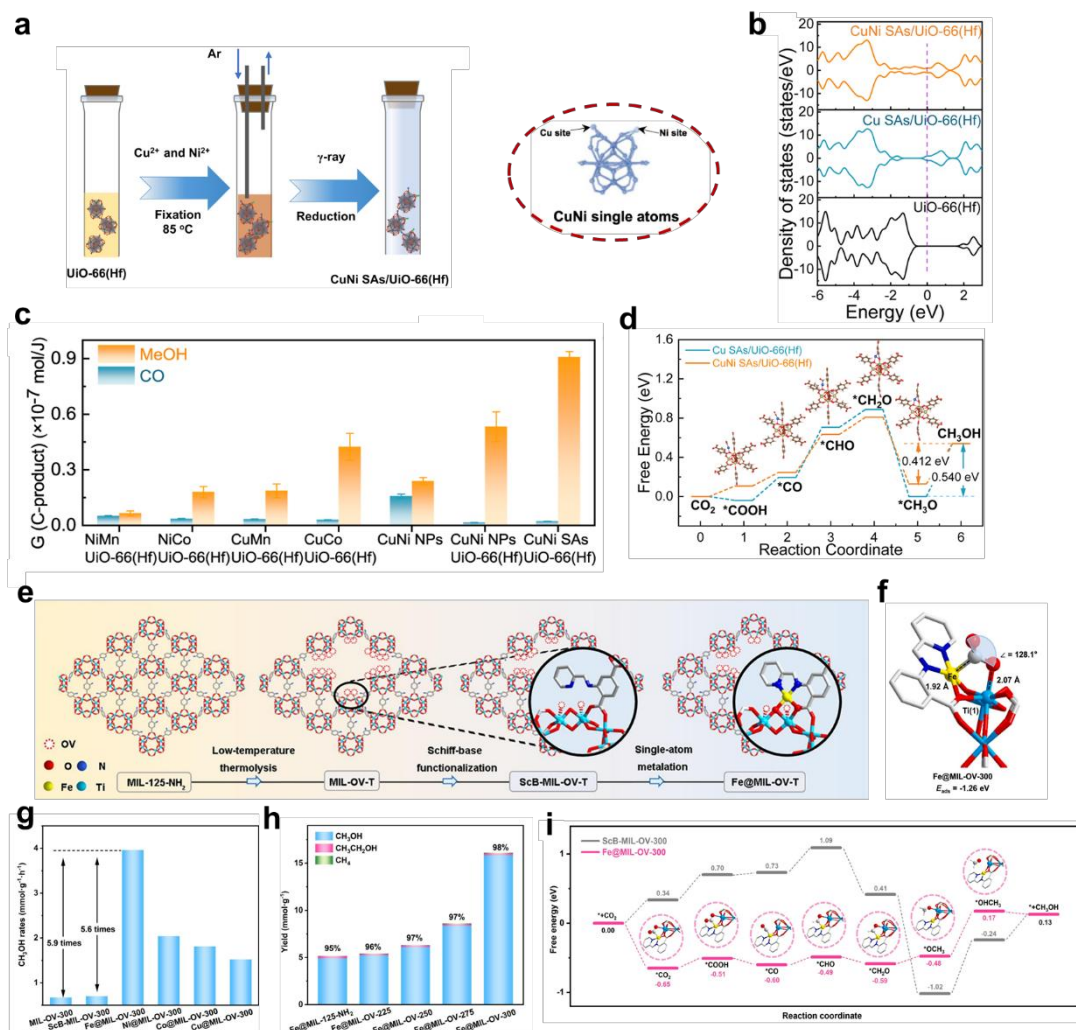


Fig. 1.9 (a) Synthesis scheme of CuNi SAs UiO-66(Hf). (b) Density of states for Cu-Ni SAs/UiO-66(Hf), Cu SAs/UiO-66(Hf), and UiO-66(Hf). (c) Catalytic activities comparison of various dual-metal-sites under identical condition. (d) Free energy profiles of CO_2 to CH_3OH . Reproduced with permission¹²⁶, Copyright 2023, Nature publication. (e) Synthetic diagram of Fe@MIL-OV-T. (f) Optimized structural model for CO_2 adsorption on Fe@MIL-OV-300. (g) Photocatalytic performances of CH_3OH generation using MIL-OV-300, and ScB-MIL-OV-300 and its derivatives containing metal SAs and (h) using Fe@MIL-125-NH₂ and Fe@MIL-OV-T with a reaction time of 4 h. (i) Calculated reaction pathways and intermediates to generate CH_3OH . Reproduced with permission¹²⁷, Copyright 2025, Elsevier publication.

Although some research exists on diatomic MOF catalysts applied to the CO₂RR, the discussions above have primarily focused on C₁ products. The generation of C₂₊ products involves more complex C–C coupling mechanisms, such as the dimerization of *CO, coupling between *CO and its hydrogenated intermediate *CHO, dimerization of *CHO, dimerization of *CH₃, and related asymmetric coupling of these intermediate species^{26, 61}. These C–C coupling processes typically require high energy barriers. Consequently, most DAC studies have focused on optimizing CO₂RR to achieve high selectivity for C₁ products, with few reports of achieving high yield and selectivity for C₂₊ products. Some studies have reported that C₁ intermediates experience electrostatic repulsion from adjacent homoatomic DAC sites with essentially identical charge distributions, which greatly hinders the formation of C₂₊ products¹²⁸⁻¹³⁰. In contrast, intermediates adsorbed on heteroatomic DACs often exhibit asymmetric charge distributions, effectively mitigating this repulsion. Moreover, different metal sites possess distinct preferences for stabilizing specific intermediate species, thereby increasing the probability of asymmetric C–C coupling to form C₂₊ intermediates. To explore the effect of diatomic configuration on CO₂RR, Kim et al. utilized COF as a research template to prepare heteroatomic DAC (ZnPor-RuCuDAC) along with homoatomic counterparts (ZnPor-Ru₂DAC and ZnPor-Cu₂DAC)¹²⁸. The photocatalytic CO₂RR results showed that the type of dual atoms combination significantly influences the selectivity toward acetic acid. When the Ru:Cu=0.5:0.5 COF, ZnPor-RuCuDAC exhibits the highest acetic acid production rate (400.5 μmol·g⁻¹·h⁻¹), along with the lowest activity for formate and CO. In comparison, the acetic acid selectivity for ZnPor-Cu₂DAC and ZnPor-Ru₂DAC were only 36.9% and 21.6%, respectively, with ZnPor-Cu₂DAC also showing the highest CO selectivity. This performance is attributed to the strong Ru 4*d*–Cu 3*d* gradient orbital coupling in the heteroatomic Ru–Cu pair acting as

the catalytic center. Charge distribution analysis from DFT calculations revealed that homoatomic Ru-Ru and Cu-Cu sites show balanced Bader charge distributions. In contrast, the Bader charge difference between Ru and Cu atoms at the Ru-Cu site is 4.71 in ZnPor-RuCuDAC, indicating enhanced asymmetry in electron delocalization. As a result, the Ru-Cu heteroatomic sites displayed lower adsorption energy for the $^*\text{CO}$ intermediate compared to Ru-Ru and Cu-Cu homoatomic sites. Furthermore, the asymmetric charge distribution on the Ru-Cu site surface also weakens the electrostatic repulsion between two adjacent $^*\text{CO}$ intermediates, resulting in reduced dipole-dipole interactions and a lower energy barrier for the C-C coupling process. In contrast, intermediates on the homoatomic ZnPor-Cu₂DAC tend to desorb as CO due to severe electrostatic repulsion.

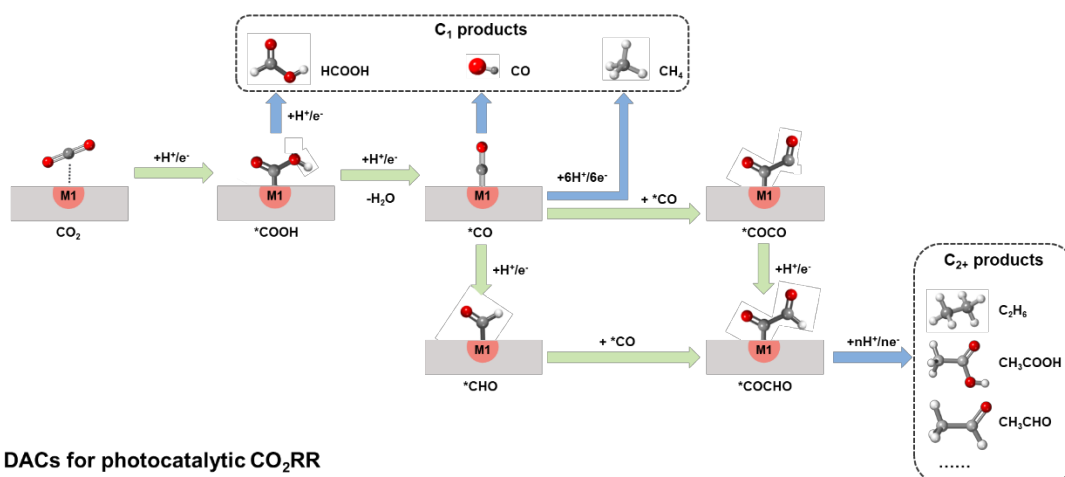
It has been shown that Cu SACs can effectively convert CO₂ into C₂₊ products through photocatalytic reduction^{36, 74, 79}. However, conventional Cu SACs often struggle with efficient $^*\text{CO}$ stabilization and C-C coupling, which hinders their practical utilization. To address this challenge, Huang et al. developed a Re/Cu DACs featuring synergistic C-C coupling for selective ethylene (C₂H₄) production¹¹⁸. Experimental results showed that the Re-bpy/PTF(Cu) catalyst achieved remarkable C₂H₄ generation at 73.2 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, whereas neither Cu nor Re SACs produced detectable C₂ product formation. Furthermore, control samples with H₂ (alternative of metal site), Ni or Co instead of Cu sites also failed to produce C₂H₄, confirming the indispensable role of Cu centers in ethylene synthesis. Mechanistic investigations revealed that Re sites preferentially facilitate CO generation, which subsequently migrates to adjacent Cu centers. This spatial organization enables the cooperative formation of critical Re-CO- $^*\text{CO}$ -Cu intermediates, effectively lowering the energy barrier for C-C bond formation. The complementary functions of the two metallic centers, which Re for $^*\text{CO}$ production and

Cu for coupling activation, create a synergistic platform that overcomes the intrinsic limitations of monometallic systems. Notably, this mechanism aligns with recent work by Zhang et al., who engineered a DAC featuring a Cu component as active centers to absorb $^*\text{CO}$ intermediate moved from Ir active sites and promote C–C coupling for C_2H_4 generation effectively¹³¹. Similarly, Song et al. utilized an up-bottom ion-cutting engineering approach for the synthesis of CuAu-DAs-TiO₂¹³⁰. In this system, Cu SAs serve as high-efficiency centers for $^*\text{CO}$ intermediate production, while Au SAs act as reaction centers that receive $^*\text{CO}$ intermediates from adjacent Cu SAs and drive C–C coupling. Owing to the synergistic interaction between Cu and Au SAs, which effectively reduce the energy barrier for the $^*\text{CO}$ –CO dicarbon intermediate, the CuAu-DAs-TiO₂ exhibits outstanding performance in converting CO₂ to C₂ products, achieving selectivity of 68.3% for C₂H₄ and 9.4% for C₂H₆. This enhanced performance is attributed to the effective reduction of the energy barrier associated with the $^*\text{CO}$ –CO dimerization intermediate. Collectively, these findings provide fundamental insights into the rational design of DACs targeting C₂₊ products in CO₂RR.

Therefore, the synergistic interplay between bimetallic sites in well-defined DACs renders them markedly superior to SACs for the photochemical conversion of CO₂ reduction to C₂₊ products (**Fig. 1.10**). Despite substantial research progress has been reported, most MOF materials featuring diatomic metal active centers focus on C₁ products, where one metal site often serves as the PS. However, the rational design for high-value C₂₊ products has been frequently overlooked. Achieving high selectivity for specific C₂₊ products involves navigating complex pathways of C–C coupling which is difficult to stabilize^{61, 63, 132}. Abundant research indicates that the C–C coupling process involves extensive competitive kinetics among numerous intermediates. For instance, it is challenging to stabilize intermediates like $^*\text{C}_2\text{H}_2$ and $^*\text{CH}_2\text{CO}$, as subsequent

hydrogenation reactions for these intermediate species exhibit relatively lower energy barriers, driving the CO₂RR process to continue beyond their formation rather than stopping there^{89, 132, 133}. Conversely, products like C₂H₆ generation require complete hydrogenation of CO₂, demanding the highest electron transfer among C₂ products^{31, 89}. Such extended reaction pathways offer more opportunities for side reactions, thereby reducing selectivity^{36, 118, 134}. Consequently, not only MOF-based DACs but also most current photocatalytic materials rarely achieve the mechanistic understanding and performance required for high-value C₂₊ products, highlighting a critical need for extensive research in this area. Precise site engineering inherent to MOFs holds immense promise for addressing this goal. By combining MOF design with theoretical calculations, it becomes possible to engineer bimetallic catalysts capable of precisely regulating the adsorption energetics and reaction pathways at each step for every active site. Within DACs, the coordination environment of each metal atom significantly influences the adsorption and desorption of reaction intermediates, ultimately dictating reaction selectivity.

SACs for photocatalytic CO₂RR



DACs for photocatalytic CO₂RR

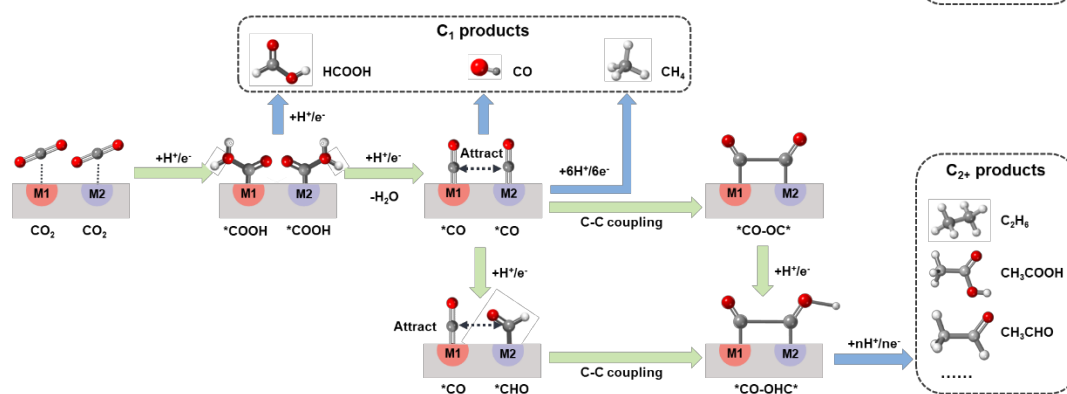


Fig. 1.10 Illustration of photocatalytic CO₂RR of some potential reaction pathways that govern C₁ and C₂₊ products formation over SACs and DACs.

1.3.3 Metal Loading Density

The concentration of metal atoms in SACs or DACs requires a delicate balance between achieving high dispersion (preventing aggregation) and ensuring sufficient active site density to drive reaction kinetics^{21, 27, 78}. Excessively high metal loading invariably induces unwanted atomic aggregation into clusters or nanoparticles, diminishing catalytic activity and often altering selectivity. Conversely, overly low concentrations risk limiting the number of available active sites, constraining overall reaction rates and potentially failing to provide the necessary site proximity for reactions requiring adjacent centers (e.g., C–C coupling)⁸⁰. Additionally, metal loading density

significantly influences the MOF's electronic structure and adsorption chemistry, thereby affecting its band structure and electron transport pathways, which further imparts catalytic activity and product selectivity¹³⁸⁻¹³⁹. Furthermore, the ratio of the photo-induced charge carrier generation rates to active site density must be optimized¹⁴⁰. An excessively high active site density can significantly affect the multi-electron transfer processes, thereby hindering the formation of C₂₊ products.

Yan et al. synthesized MOF-based photocatalysts by varying the loading of Ir SACs, identifying an optimal threshold beyond which aggregation occurred, compromising performance (**Fig. 1.5g and Fig. 1.11a**)¹¹⁶. The effect of metal loading can modulate intermediate adsorption strength by altering the local electronic density and coordination environment of the sites, thereby influencing the selectivity, particularly towards pathways requiring specific site densities like C₂₊ formation^{141, 142}. Duan et al. conducted a systematic investigation into the relationship between Cu SAC content and acetone productivity/selectivity in their catalytic system (**Fig. 1.11b**)⁷⁹. Their findings revealed a linear correlation between acetone yield and Cu site density, while product selectivity remained remarkably consistent across varying Cu loadings. Yaghi et al reported another example illustrating the impact of metal center density on photocatalytic CO₂ reduction performance¹⁴³. They designed a series of Re-MOFs (Re_n-MOF) by precisely incorporating varying densities of Re metal centers into a Zr-MOF matrix. Within a specific density range, the Re active sites effectively prevent dimerization of molecular catalysts and mitigate their deactivation.

Simultaneously, metal site density significantly impacts catalytic performance by modulating the host MOF's band structure, thereby optimizing it for the specific requirements of CO₂RR to high-value chemicals. Optimized density aligns bands to

favor the stabilization of critical intermediates like *CO (critical for C₂+) over competitive H⁺ reduction^{56, 138}. This effect arises from the unique electronic configurations of metal sites, typically featuring unpaired *d*-electrons or empty *d*-orbitals, which interact with CO₂ to form a modified energy band structure^{138, 144}. For example, Dong et al. demonstrated that tuning the Ni SAC content within NH₂-MIL-125 adjusts the overall electronic structure (**Fig. 1.11c**)¹³⁹. High-affinity metals at optimal density can extract photoelectrons from MOF linkers/clusters, suppressing recombination and delivering electrons to *CO intermediates. Additionally, metal loading density modulates the position of the *d*-band center relative to the Fermi level, critically influencing CO₂ and the adsorption of its intermediates, and thus affecting catalytic property¹³⁶. Ni SAC preferentially localizes near oxygen atoms in Ti-oxo clusters, exhibiting lower electron affinity than oxygen and altering the electron density of adjacent oxygen atoms. This enables more electrons to access the Ti-oxo clusters, enhancing the Ti⁴⁺/Ti³⁺ transition for efficient CO₂ conversion. Consequently, optimized Ni SAC doping can promote multi-electron transfer reaction pathways under sufficient electron supply. In contrast, Liu et al. exploited high-spin Co²⁺ properties by tuning Co SACs density to stabilize of COOH* intermediate and shift the rate-limiting step to CO* desorption, thereby enhancing CO₂-to-CO selectivity¹⁴⁶. Since the high-spin Co²⁺ with fully occupied *d*-electrons, readily excites the electron to unoccupied orbitals, modifying the potential energy of the catalyst surface and favoring CO adsorption.

The strategic optimization of metal site density in MOF-based SACs extends beyond preventing aggregation, critically influencing photonic and molecular interactions in photocatalytic CO₂RR. As highlighted by Zhang et al., active site concentration governs both light-harvesting efficiency and substrate collision frequency, necessitating

balanced tuning of photon absorption, reactant collision probability, and catalyst excited-state lifetime (**Fig. 1.11d and e**)¹⁴⁷. Guided by these principles, their Ru-embedded MOF design achieved optimized CO₂RR performance through precise metal loading. Concurrently, interfacial charge dynamics play a decisive role in CO₂RR. Carbon intermediates coordinate to metal sites while photogenerated oxygen species stabilize through Lewis's acid-base interactions with Zr⁴⁺ nodes. Lercher et al. found that direct ZrO₂-Cu bonding was mandatory for efficient CO₂ activation in UiO-66 systems (**Fig. 1.11f – k**)⁸⁰. Maintaining Cu as isolated SACs via concentration control instead of clusters enables optimal electron transfer from Cu centers to CO₂, lowering activation barriers. This mechanistic framework further extends to product distribution engineering. Targeted manipulation of metal site density, as reported by Lu et al. and Gao et al., enables precise regulation of syngas (CO/H₂) ratios in photocatalytic CO₂RR^{121, 148}. This highlights how deliberate adjustments in metal loading can steer reduction pathways toward specific chemical feedstocks. Furthermore, it is anticipated that adjusting the metal ratio in DACs allows for precise control over the production of targeted C₂₊ products to meet industrial requirements.

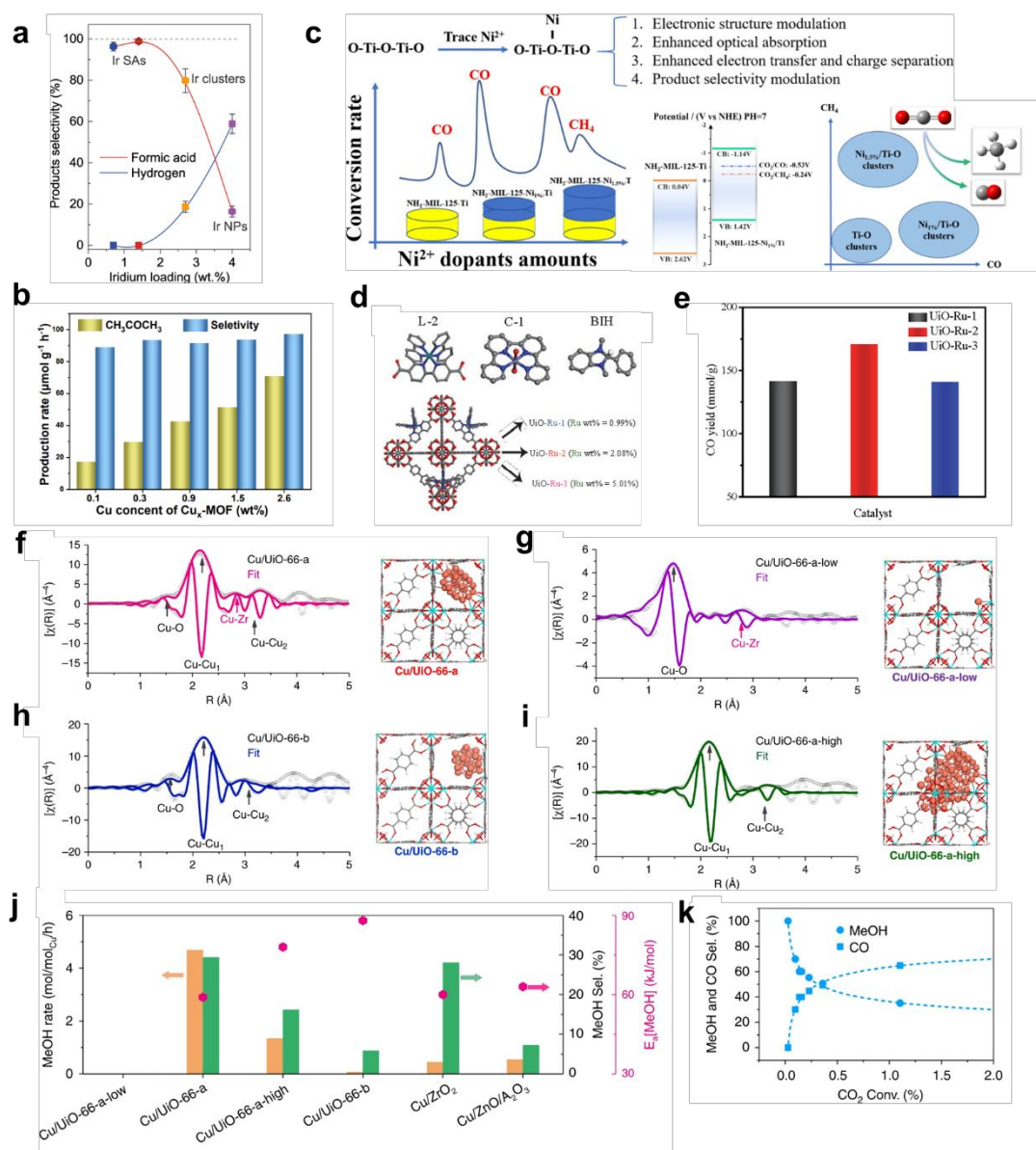


Fig. 1.10 (a) HCOOH and H₂ selectivity as a function of Ir loadings in Ir/A-aUiO catalysts. Reproduced with permission¹¹⁶, Copyright 2021, Nature publication. (b) The acetone production evolution of $\text{Cu}_x\text{-MOF}$ catalysts with different Cu contents. Reproduced with permission⁹⁷, Copyright 2021, Nature publication. (c) The calculated band structure of as-prepared samples and the Ni^{2+} dopants effect on the photocatalytic performance. Reproduced with permission¹³⁰, Copyright 2021, Elsevier publication. (d) Structures of L-2, C-1, BIH, and the L-2-doped MOF. (e) CO yield with UiO-Ru-1, UiO-Ru-2, and UiO-Ru-3 in 8 h with C-1 (50 μM). Reproduced with permission¹³⁸,

Copyright 2021, Elsevier publication. Cu K-edge k^3 -weighted EXAFS and Fourier-transform spectra with fitting lines of **(f)** Cu/UiO-66-a, **(g)** Cu/UiO-66-b, **(h)** Cu/UiO-66-a-low, and **(i)** Cu/UiO-66-a-high for which the Cu–Zr path is highlighted with red arrows and their deduced schematic structural models. **(j)** Rates of methanol (MeOH) production (orange bars), methanol selectivity (green bars) on selected catalysts at 250 °C and 32 bar, and activation energy (E_a , pink points). **(k)** The methanol and CO selectivity as functions of CO₂ conversion for Cu/UiO-66-a at 190 °C and 32 bar. The CO₂ conversion is varied by changing the gas space velocity. Reproduced with permission⁸⁰, Copyright 2020, Nature publication.

1.3.4 Spatial Architecture Design

The coordination environment of metal centers directly modulates their electronic structure and catalytic behavior. Subtle modifications to the spatial architecture of active sites can profoundly impact intermediate stabilization and reaction kinetics, particularly for C–C coupling^{91, 149-151}. Consequently, a detailed understanding of atomic-level catalyst structures, especially the spatial arrangement of active sites, is crucial. The synthesis of C₂₊ products presents fundamental challenges, as sequential carbon chain growth requiring multiple proton-coupled electron transfer steps. Furthermore, the increasing complexity of intermediate stabilization complicates the development of a comprehensive mechanism for spatial architecture design in metal active sites, accompanying by competing pathways leading to diverse byproducts.

Recent advances highlight that strategically designed bimetallic centers with optimal **interatomic distances** can effectively promote C–C coupling by facilitating the dimerization of C₁ intermediates (e.g., *CO) or coupling between C₁ and growing hydrocarbon chains¹⁵². Optimally spaced DACs not only facilitate intermediate

dimerization but also enhance electron transfer efficiency while suppressing charge carrier recombination¹²³. A notable example involves the work by Jiang et al. that utilizes Zr₆-oxo SBUs with adjacent surface -O/OH_x sites to immobilize Ni atom centers, significantly enhancing the photocatalytic activity by optimizing site proximity within the MOF matrix¹³¹.

Zhong et al. argued against a universal “ideal distance” for C–C coupling in CO₂RR, given the diverse intermediates and transition states involved (**Fig. 1.12a – f**)⁹⁷. They proposed engineering neighboring active sites with dynamic bond distances adaptable to different reaction steps. Leveraging MOF flexibility, they designed MOF-808-EDTA co-anchoring Cu and Ni SACs, creating spatially self-adaptive sites. Ab initio molecular dynamics simulations revealed dynamic fluctuations in the Cu-Ni distance ($d_{\text{Cu-Ni}}$: 4.250 - 5.036 Å) and the dihedral angle formed by the four N atoms in the EDTA ligand ($\theta_{\text{2N-N}}$: 12.419° - 90.114°). DFT calculations demonstrated that the high selectivity for the photocatalytic reduction of CO₂ to CH₄ observed in this material stemmed from the continuous adaptation of $d_{\text{Cu-Ni}}$ and $\theta_{\text{2N-N}}$ during intermediate formation and conversion. This dynamic adjustment ensures the active sites persistently reside at the optimal position for stabilizing intermediates and suppressing the desorption of byproducts. Besides, this MOF design strategy enables systematic modulation of the catalytic microenvironment to optimize active site interactions with substrates and intermediates. This exemplifies how MOF flexibility can be harnessed for dynamic site optimization.

Steric hindrance is an often-overlooked factor in stabilizing multi-carbon intermediates. Effective catalyst design must reconcile two competing requirements: (1) tailoring site geometry to enable bonding between C₁ intermediates (e.g., *CO) or C₁-C₂₊ intermediates without excessive steric repulsion; (2) optimizing ligand spatial

arrangements to reduce repulsion during intermediate adsorption. The steric effects arising from the spatial arrangement of coordinating ligands were shown to regulate intermediate adsorption/desorption equilibria, underscoring the multifaceted role of the coordination environment. This spatial dilemma is exemplified by the general inefficiency of CO–CH₃ coupling, where random active site distributions and bulky ligands often raise activation barriers. Duan et al. recently demonstrated a breakthrough in addressing this challenge through rational spatial design of planar triatomic NH₂–Cu–NH₂ sites within defective MOFs for acetone synthesis (**Fig. 1.12g – i**)⁷⁹. Specifically, the Cu sites act as electron reservoirs, channeling photogenerated electrons to drive sequential coupling of *CO and *CH₃ intermediates anchored on adjacent amino sites, culminating in acetone. Generally, coupling between *CO and *CH₃ intermediates or other high-carbon intermediates is challenging due to steric hindrance during adsorption at adjacent active sites. Key to this process was the planar arrangement of N–Cu–N motif, eliminating steric obstruction and significantly lowering the energy barrier for stabilizing the C₃ intermediate. This spatially optimized architecture achieved 97% acetone selectivity. Theoretical analysis further suggests that substituting nitrogen coordination sites with various metal atoms could enable precise regulation of multi-carbon product selectivity by controlling intermediate transformation pathways through tailored Cu–N synergies. It is to say that the specific geometric engineering is an effective way for controlling the selectivity and activity of CO₂RR to high-value chemicals. However, these studies explicitly targeting C₂₊ product selectivity via spatial design remain scarce.

The **coordination environment** of the metal center, such as the number, type, and geometry of coordinating atoms, profoundly dictates its electronic structure (oxidation state, *d*-band center, charge density) and consequently, its adsorption energetics and

catalytic pathway selectivity^{62, 150, 153}. Metals, particularly for transition metals, can adopt various coordination geometries due to their special electronic configurations, including tetrahedral (4-coordinate), square pyramidal (5-coordinate), and octahedral (6-coordinate) structures. These diverse geometries provide distinct catalytic dynamics. For example, tetrahedral Co ions have been shown to stabilize oxygen-containing intermediates more effectively than their octahedral configurations^{149, 154}.

Given that transition metal–nitrogen (TM–N) bonds are widely employed to functionalize and stabilize MOF-based photocatalysts, a deeper understanding of the metal center’s coordination environment, particularly the nitrogen coordination number, is essential. Jiang et al. systematically engineered three cobalt single-atom sites within UiO-67-bpy frameworks, featuring N coordination numbers of 2, 3, and 4 to probe this relationship (**Fig. 1.12j – k**)⁹¹. Photocatalytic CO₂RR evaluations revealed that the Co–N₃ configuration achieved optimal CO production rates, surpassing the Co–N₂ and Co–N₄ systems by factors of 1.5 and 3.7, respectively. This stark contrast highlights the critical influence of coordination geometry on catalytic functionality. DFT calculations further elucidated that nitrogen coordination number modulates both charge transfer dynamics and the electronic density distribution at the Co center, directly impacting the energy barriers for stabilizing critical reaction intermediates. Furthermore, the unsaturated Co–N₃ configuration provides adequate space for reactant access and interaction, unlike the potentially overcrowded N₄ site or the under-coordinated N₂ site. Also, low-coordination environments in metal SA offer significant advantages for CO₂ reduction¹⁵⁵. These configuration environments feature more unoccupied *d*-orbitals, which enhance the adsorption and activation of CO₂ while reducing the energy barriers of reaction intermediates. Additionally, they provide a broader reaction space, enabling the formation and stabilization of long carbon chain intermediates.

Substituting nitrogen atoms in metal coordination spheres with alternative heteroatoms modulates the electronic state of metal sites. This modification directly influences charge transfer dynamics within the MOF framework and at interfaces, ultimately governing catalytic performance. As an example, Pan et al. explored the adjustment of local coordination in Pt SACs by synthesizing two distinct configurations: Pt-C₂N and Pt-N₂¹⁵⁶. The Pt-C₂N configuration exhibits a shorter bonding distance compared to Pt-N₂, which improves the stabilization of Pt SA. Moreover, the distorted structure of Pt-C₂N disrupts the symmetric electron distribution of Pt-N₂, promoting efficient electron transfer to the Pt SA and thereby enhancing catalytic performance. Duan et al. used defect engineering in UiO-66 to create a Cu-N₂O₂ configuration serving as an electron-trapping site⁷⁹. This structure geometrically stabilizes the *CO intermediate and optimizes the pathway for symmetric acetone CH₃-C(O)-CH₃ formation. Nevertheless, systematic studies on how different coordinating atom types/numbers influence the CO₂RR performance and selectivity remain limited. It can be speculated that precise modulation of the metal-coordination (M-X) environment can regulate the local geometry and charge density of the metal, thereby optimizing the specific CO₂RR reaction pathways towards the targeted C₂₊ products at metal active sites.

Nature publication. **(g)** Illustration of the synthetic procedure for the Cu-MOF catalyst and the overall approach to reducing CO₂ into CH₃COCH₃ at CuN₂O₂ active sites under visible light irradiation. **(h)** Structural models of the Gibbs free energy calculations for CO₂ reduction on Cu-MOF. **(i)** Free-energy profile of the CO₂RR pathway on CuN₂O₂ sites in Cu-MOF. Reproduced with permission⁷⁹, Copyright 2024, Wiley publication. **(j)** Illustration of the stepwise synthetic strategies for UiO-Co-N_x (x = 2, 3, and 4) catalysts. **(k)** Free energy diagram describing the process of CO₂ reduction to CO via the COOH* intermediate over UiO-Co-N₂, UiO-Co-N₃, and UiO-Co-N₄ under visible light irradiation. Reproduced with permission⁹¹, Copyright 2023, Wiley publication.

However, current understanding of the coordination environment of metal centers, especially in the context of CO₂RR towards high-value C₂₊ chemicals, remains insufficient. Several critical aspects demand further investigation:

- (1) The influence of non-nitrogen coordinating atoms/anions (e.g., O, S, Cl⁻, -OH, carboxylates) on the electronic structure of metal site and intermediate binding for C₂₊ pathways.
- (2) For porphyrin-based SACs/DACs, the role of inter-ring π - π stacking interactions and potential π -bonding interactions with anchoring benzene rings in modulating charge transfer or intermediate stability.
- (3) The impact of asymmetric coordination environments (e.g., mixed N/O ligands) on breaking scaling relations and favoring C–C coupling steps.
- (4) The role of functional groups or pore environment near the primary coordination sphere in stabilizing polar intermediates or facilitating proton delivery during multi-step hydrogenation.

Advancing C₂₊ selectivity necessitates deliberate engineering of the metal coordination environment within MOFs to create sites that selectively stabilize key C–C coupling transition states while destabilizing pathways leading to C₁ products or HER.

1.4 Conclusion and Future Perspectives

The photocatalytic reduction of CO₂ to high-value C₂₊ products is highly sought after for sustainable energy and chemical production. MOFs, with their unparalleled structural and compositional tunability, have emerged as exceptional platforms for engineering catalytic metal active sites with atomic precision. This review has systematically analyzed the critical role of metal site engineering within MOFs, encompassing SACs, DACs, metal loading density optimization, and spatial architecture design (geometric control and coordination environment) to steer the activity and selectivity of CO₂RR, with a particular focus on the formidable challenge of C₂₊ synthesis. Because these factors are interrelated with each other, the discussion above maybe have overlapped in various sections.

SACs within MOFs provide an excellent chemical domain to elucidate intrinsic metal site properties and structure-activity relationships. While most MOF-based SACs primarily produce C₁ products, Cu SACs stand out due to their unique configuration, demonstrating tangible potential for C₂₊ liquid products (e.g., ethanol and acetic acid) by stabilizing *CO/*CHO intermediates and lowering C–C coupling barriers. The redox activity of certain metals (e.g., Co and Fe) and the ability to integrate PS metal centers directly into the framework further enhance design flexibility. DACs overcome limitations of isolated SACs by enabling synergistic effects between two distinct metal sites. Synergy can manifest as complementary functions (e.g., one site for CO generation, another for coupling/hydrogenation), enhanced charge transfer, or

optimized intermediate relay. Tuning the metal pair composition offers a powerful strategy to control reaction outcomes. Optimizing metal site density is essential to prevent aggregation, ensure sufficient site availability, and potentially enable site proximity for coupling reactions. Site density also influences the MOF's electronic structure (band alignment, charge separation) and can be tuned to favor stabilization of key C_{2+} intermediates like $^*CO$ over competitive HER. The geometric arrangement (distance, orientation) and the local coordination environment of metal sites are paramount determinants of selectivity, especially for C–C coupling. Precise control over inter-site distances can facilitate intermediate dimerization, while dynamic site adaptability within flexible MOFs offers a novel approach to optimize stabilization throughout complex reaction sequences. Steric effects, often neglected, can be mitigated through rational ligand design (e.g., planar sites and angular sites) to lower coupling barriers. The coordination number and ligand identity exert profound control over the metal's electronic structure and adsorption energetics; unsaturated sites often outperform their saturated counterparts. Deliberate engineering of the coordination environment, including beyond nitrogen-based ligands and secondary sphere effects, represents a largely untapped frontier for enhancing C_{2+} selectivity.

Despite the potential, experimentally demonstrated high-selectivity production of C_{2+} chemicals using MOF-based SACs/DACs remains scarce. Most reported systems still favor C_1 products. The multi-step, multi-intermediate nature of C_{2+} formation, involving complex C–C coupling mechanisms and extensive competitive kinetics, makes rational design exceptionally challenging. Stabilization of key intermediates like $^*C_2$ species is challenging. Suppressing HER remains a persistent challenge in aqueous CO_2RR , especially for pathways requiring high overpotentials like C_{2+} formation. Furthermore, the long-term stability of MOF photocatalysts, particularly those

incorporating reactive SACs/DACs, under harsh photocatalytic conditions (light, solvent, potential intermediates) also need to be further developed by scalable synthesis of MOFs with precisely controlled atomic sites. However, probing the dynamic structure of active sites under operando photocatalytic conditions, identifying true active species, and mapping reaction pathways with atomic precision remain significant challenges. Techniques like in-situ/operando XAS, FTIR, Raman, AP-XPS, and liquid-phase TEM need wider application. Bridging the gap between experimental realization and computational predictions (e.g., DFT screening of DAC pairs for C–C coupling) is crucial but often hampered by synthesis limitations and the complexity of modeling realistic MOF environments under reaction conditions.

Some future research directions and deployable solutions to overcome the ongoing challenges are also proposed as follows:

(1) Computational screening (e.g., DFT, AIMD) should be intensively employed to identify optimal homo- or hetero-bimetallic pairs and configurations (distance, angle) within MOF scaffolds that minimize energy barriers for specific C–C coupling steps (such as *CO dimerization and asymmetric coupling). Utilize machine learning models trained on experimental and high-quality computational datasets to predict promising MOF-metal site combinations, coordination environments, and reaction pathways for C₂₊ selectivity, guiding experimental efforts.

(2) Moving beyond standard N₄ porphyrin or N₂ bipyridine pockets. Deliberately design asymmetric coordination environments, incorporate strong-field ligands to modulate spin states, explore sulfur or oxygen coordination, and engineer the secondary coordination sphere (such as hydrogen-bonding networks and ionic functionalities) to stabilize polar C₂₊ intermediates or facilitate proton/electron transfer. Another method

is to explore other ligand classes (such as triazines, phenanthrolines, catecholates, phosphines, and carbenes) that offer unique coordination environments, redox activity, or light-harvesting capabilities for hosting active sites.

(3) Integrate atomic site control with mesoscopic MOF engineering. Design MOFs with spatially compartmentalized zones: one region optimized for CO₂ capture and initial reduction to *CO/C₁ intermediates, and adjacent zones featuring tailored DACs optimized for C–C coupling of those intermediates. Leverage MOF defects or multivariate systems to create these functional zones. Another strategy is exploring tandem systems or bifunctional sites where a first site reduces CO₂ efficiently to CO, and a nearby second site specializes in reducing CO to C₂₊ products, potentially simplifying the reaction network.

(4) Deploy advanced in-situ and operando characterization techniques to probe the dynamic evolution of metal active sites, identify true catalytic species, detect key intermediates, and map reaction pathways in real-time under working conditions.

In conclusion, the atomic-level engineering of metal active sites within MOFs presents a powerful and versatile strategy to tackle the formidable challenge of photocatalytic CO₂ reduction to C₂₊ products. While significant progress has been made in understanding fundamental principles and demonstrating potential, the field is still nascent, particularly concerning high-selective multi-carbon synthesis. By deepening our mechanistic understanding through advanced characterization and theory, and relentlessly pursuing innovative design strategies focused on spatial control, coordination engineering, and synergistic bimetallic sites, MOF-based photocatalysts hold immense promise for unlocking efficient and selective solar-driven carbon chain growth, paving the way towards a sustainable carbon-neutral future.

1.5 Aim and Objectives

Despite SACs/DACs having high structural regulatory diversity, challenges persist in achieving precise atom size control and synthetic repeatability. Moreover, the introduction of atoms often gives rise to the surface charge imbalance, leading to poor catalyst stability with the high surface energy, thereby promoting metal site aggregation. Limited by the comprehensive and advanced characterization techniques, the comprehensive structural characterization of active metal sites and their surrounding coordination environment in solid-state catalysts has remained a formidable task in the field of heterogeneous catalysis, impeding the establishment of structure-activity relationships. Therefore, it is crucial to design and construct a robust catalyst system as a research platform, enabling precise assembly of bimetallic active sites on supported catalysts, accompanied by state-of-the-art structural analysis techniques and diverse characterization approaches. By utilizing photocatalytic CO₂RR as a benchmark for catalytic performance, this platform aims to establish a novel theoretical framework to underpin the efficient and cost-effective utilization of bimetallic catalysis for high-value carbon products conversion.

This thesis aims to advance photocatalytic CO₂RR by engineering atomically precise dual-atom (Cu/Cu, 3d/3d, 3d/4d) catalysts within MOFs. Through controlled synthesis, characterization, and DFT calculations, we designed these catalysts to optimize spatial distribution and electronic structure, steering selectivity towards high-value C₂₊ products. We elucidated structure-activity relationships and developed a modular descriptor for tailoring the bimetallic active site in MOF-based photocatalysts with enhanced C₂₊ selectivity.

1.6 Thesis Overview

In **Chapter 1**, we briefly discussed and reviewed recent advancements in the atomic-level engineering of metal active sites in MOFs for photocatalytic CO₂RR, focusing on strategies to address the challenge of selective C₂₊ products. We systematically analyzed the critical role of metal site engineering within MOFs, encompassing SACs, DACs, optimized metal loading density optimization, and spatial architecture design to steer the activity and selectivity of CO₂RR, with a particular focus on the formidable challenge of C₂₊ synthesis. In **Chapter 2**, we detailed the characterization techniques and chemical utilized throughout the study.

In **Chapter 3**, we explored the design of supported atomic copper sites in MOF with controlled spatial distribution to direct CO₂RR toward C₁ or C₂₊ products. Integrated characterization and density functional theory (DFT) calculations revealed that low Cu concentrations favor isolated single-atom sites (SACs) that stabilize *COOH intermediate to promote C₁ products formation. Conversely, higher Cu loadings generate neighboring Cu···Cu dual atom motifs (DACs), which reduce the C–C coupling energy barrier via *OCCOH intermediates to selectively yield acetic acid.

Chapter 4 extends this work by developing 3d/3d bimetallic metal sites in DACs with precise spatial control using a stepwise synthesis strategy approach. Structural analyses confirmed bimetallic motifs (M_A···M_B) spaced approximately 5.3 Å apart on adjacent bpydc linkers. Optimal pairs (**FeFe**, **CoCu**, and **CuCu**) were identified as effective bimetallic pairs in UiO-M_AM_B for the selective production of acetic acid. **Cu** and **Fe** SA were identified for excelling at C–C coupling for C₂₊ products, unlike **Ni** and **Co** SA. This precise dual-atom design synergistically enhances C–C coupling and modulates the energy barrier of the potential-determining step (PDS), thereby steering CO₂RR selectivity.

Chapter 5 extends the investigation to 3d/4d bimetallic metal pairs within UiO-67. Leveraging the unique electronic configurations of 3d and 4d metals, along with advanced characterization techniques, we precisely identified the locations of specific metal sites as functional bimetallic motifs ($M_A\bullet\bullet M_B$), rather than random distributions ($M_A\bullet\bullet M_A$, and $M_B\bullet\bullet M_B$). Notably, **Ru** and **Pd** SA were identified as effective active sites for C-C coupling toward C_{2+} products, whereas **Rh** SA were less favorable for C_{2+} products formation. We determined that C_2 product efficiency and selectivity depend on the balance of CO_2 adsorption strength, intermediate stability, and the PDS energy barrier intrinsic to the metal combination. Consequently, we proposed key descriptors including ***d*-band center position**, **CO_2 /*CO adsorption energy**, and **ΔG differences for PDS** to evaluate catalytic performance and synergistic effects of the metal pairs in converting CO_2 -to- C_{2+} products.

In summary, this study advances photocatalytic CO_2 RR by demonstrating precise control over dual-atom catalysts. The precise spatial control over dual-metal sites offers an intriguing strategy for tailoring product selectivity in this process. We developed the modular descriptors, grounded in solid-state chemistry and coordination chemistry, to prepare a library of novel supported dual-atom catalysts. The findings contribute to our fundamental understanding of CO_2 activation and conversion, providing a foundation for the design and synthesis of highly efficient CO_2 photocatalysts with practical applications.

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Chapter 2 Experimental Section

This chapter details the information on the primary characterization techniques used in this thesis.

2.1 Characterization Techniques

2.1.1 Powder X-ray Diffraction

To determine the crystal structure and phase composition of the MOF, powder X-ray diffraction (PXRD) analysis was performed using a Rigaku SmartLab 9kW-Advance system. For more detailed characterization, high-resolution synchrotron PXRD was conducted on BL02B2 beamline at SPring-8, Japan, and TPS19A beamline at NSRRC, Taiwan.

On Beamline BL02B2, the incident X-rays with an energy of 16.99 keV and a wavelength of 0.729589 Å were used. A zero error of $-0.00019(1)^{\circ}$ was corrected using high-purity CeO₂ powder (NIST SRM674b). Samples were encapsulated in 0.5 mm borosilicate capillaries, and data were collected using a MYTHEN detector. Patterns were recorded over a 2θ range of $1.9\text{--}78^{\circ}$ with a data binning of 0.006° , and each pattern was acquired for at least 10 minutes to ensure high contrast and angular resolution.

On Beamline TPS19A, the incident X-rays with an energy of 16.00 keV and a wavelength of 0.77489 Å were used. A zero error of -0.000008° was corrected using high-purity CeO₂ powder (NIST SRM674b). Samples were encapsulated in 0.3 mm borosilicate capillaries, and data were collected using a MYTHEN detector. Patterns were recorded over a 2θ range of $0.934\text{--}91.048^{\circ}$ with a data binning of 0.003° .

It is important to note that the R-factors obtained using the MYTHEN detectors are artificially elevated. Thus, the quality of the Rietveld refinement was assessed by

examining the discrepancy between the fitted and observed data.

The obtained PXRD data were subsequently analyzed using the Rietveld refinement method with TOPAS v.6.0 software. Lattice parameters were determined, and the background was fitted using a Chebyshev polynomial with an average of 20 coefficients. The diffraction peaks were accurately modeled using the Thompson-Cox-Hastings (pseudo-Voigt) function. The final refined structural parameters for each data histogram were obtained through the Rietveld method, incorporating the fractional coordinates (x , y , z) and isotropic displacement factors (B_{eq}) for all atoms. Additionally, the weighted profile factor (R_{wp}) and goodness-of-fit values ($gof = R_{wp}/R_{exp}$) were calculated to assess the quality of fit, where R_{exp} represents the expected quality of the data.

2.1.2 Resonant X-ray Diffraction

Resonant X-ray diffraction (RXRD) is distinctively suited to synchrotron light sources, owing to the tunability of the incident beam's energy or wavelength. This technique enables the precise determination of crystallographic sites occupied by atoms with low electronic contrast. When the energy of X-rays matches or is close to the absorption edge of the target element in the material, this element absorbs X-rays and undergoes resonance. In the equation of the X-ray atomic scattering factor (f), it is primarily related to the number of electrons in the respective element (f_0) at most of the incident wavelengths. But when the incident wavelength is near the absorption edge, the f must be considered the factors of the real term (f') and imaginary term (f''), which are called anomalous scattering.

$$f = f_0 + f' + if'' \quad (1)$$

As a result, RXRD technology has been used to identify the atoms in the material. By analyzing resonant X-ray diffraction data, information about the lattice positions and

electronic states of specific elements can be obtained. In this work, this technique was used to differentiate the position of 3d and 4d transition metal sites in UiO-M_AM_B by tuning incident X-ray energies to the absorption edge of the 4d transition metal center.

The RXRD patterns of Rh-based UiO-M_AM_B were collected on Beamline BL13XU at SPring-8, Japan. The incident X-ray was set around the Rh K-edge at an energy level from 23069 eV to 23249 eV. All as-prepared samples were encapsulated in 0.3 mm borosilicate capillaries and scanned using the MYTHEN detector.

The RXRD patterns of Pd-based UiO-M_AM_B were collected on Beamline TPS19A at NSRRC, Taiwan. The incident X-ray was set around the Rh K-edge at an energy level from 24310 eV to 24340 eV. All as-prepared samples were encapsulated in 0.3 mm borosilicate capillaries and scanned using the MYTHEN detector.

2.1.3 Electron Microscopy

Scanning electron microscopy (SEM) images were acquired using TESCAN VEGA3, and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) with energy dispersive X-ray analysis (EDX) imaging and high-resolution iDPC-STEM images were conducted using a Cs-corrected STEM (Thermo Scientific Spectra 300 S/TEM) to investigate the surface morphology and assess particle size and elemental distribution within the MOF. All the datasets were acquired using a probe at 300 keV beam energy and 29.9 mrad probe-forming semi-angle. The electron-beam current was reduced to < 0.1 pA by an unfiltered monochromator. The dwell time was 2 μ s, and the electron dose was < 81 e⁻/Å².

2.1.4 Extended X-ray absorption fine structure spectroscopy

Extended X-ray absorption fine structure (EXAFS) spectroscopy data were collected

on Beamline TLS01C1 at NSRRC, Taiwan, employing a Si (111) double crystal monochromator to scan the photon energy. Artemis and Athena software were used for data treatment and analysis.

2.1.5 Other Characterization

The element composition was detected by X-ray fluorescence (XRF) spectrometers from Epsilon 4 (Malvern Panalytical). The surface Cu oxidation states of the constituent elements were analyzed by X-ray photoelectron spectroscopy (XPS) using Thermo Scientific Nexsa spectrometer. The optical properties of the as-prepared sample, including light absorption and bandgap energy, were studied using UV-visible spectroscopy (UV-vis) with PerkinElmer LAMBDA 1050, providing insights into the material's photon absorption capabilities and its potential for facilitating photocatalytic processes. Photoluminescence spectroscopy (PL) and time-resolved PL (TRPL) measurements, conducted with an Edinburgh FLS 1000 Photoluminescence Spectrometer, were used to evaluate the luminescent properties of the MOF, aiding in the understanding of charge carrier recombination processes and fluorescent lifetime critical for efficient photocatalysis. The average lifetime ($\tau_{\text{eff}} = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$) is extracted from the TRPL spectra by fitting with a biexponential function. The mechanism and intermediates of the photocatalytic CO₂ reduction reaction were explored using *in-situ* Fourier-transform infrared spectroscopy (DRIFTS) using Bruker Vertex-70 FTIR. The thermogravimetric analysis (TGA) measurements of as-synthesized samples were performed in air (40 mL min⁻¹) up to a certain temperature using Thermogravimetric Analyzer/Differential Scanning Calorimeter (Mettler Toledo TGA/DSC3+).

2.2 Photocatalytic CO₂ Reduction Reaction Performance

The photocatalytic CO₂ reduction reaction (CO₂RR) activity was evaluated using a closed reaction system. A 300 W Xe light source (GLORIA-X500A, Zolix Instruments Co., Ltd.) served as the illumination source. In a typical experimental procedure, 30 mg of the synthesized photocatalyst was added to a quartz reactor containing 50 mL of deionized water and 0.1 mL of triethanolamine (TEOA) as a sacrificial agent. Prior to initiating the reaction, the closed reaction system containing the solution was degassed for 30 minutes, followed by CO₂ bubbling for an additional 30 minutes. This process was repeated to ensure the complete removal of residual gases from the system. The gaseous and liquid products were subsequently analyzed using a gas chromatography system (GC 2060, Shanghai Ruimin Instruments Co., Ltd.) and ¹H NMR spectroscopy (Bruker Advance-III 400 MHz FT-NMR System), respectively.

The selectivity of acetic acid was calculated according to the following equation:

$$\text{Selectivity of } CH_3COOH(\%) = \frac{\text{mol of } CH_3COOH \times 2}{\text{mol of total carbon of products}} \quad (2)$$

Based on the metal active sites in the catalyst, the turnover number (TON) and turnover frequency (TOF) are calculated using the following equations:

$$TON = \frac{\text{moles of total products}}{\text{moles of active sites}} \quad (3)$$

While,

$$\begin{aligned} \text{Mol of total carbon of products} = & \text{mole of } CO + \text{mole of } CH_4 + \\ & \text{mole of } HCOOH + \text{mole of } CH_3COOH \times 2 \end{aligned} \quad (4)$$

$$\begin{aligned} \text{Mol of total products} = & \text{mole of } CO + \text{mole of } CH_4 + \text{mole of } HCOOH + \\ & \text{mole of } CH_3COOH \end{aligned} \quad (5)$$

2.3 Photoelectrochemical Properties

The photoelectrochemical properties were assessed using CHI760E setup in a standard three-electrode configuration. The electrolyte used was 0.5 M Na₂SO₄, with an Ag/AgCl electrode functioning as the reference electrode and a platinum electrode serving as the counter electrode. For the preparation of the working electrodes, 10 mg of the sample was dispersed in 1 mL of a mixed solution with an anhydrous ethanol to Nafion volume ratio of 50:1. Then, 10 µL of the suspension was deposited onto a 1×1 cm² SnO₂:F (FTO) electrode, followed by solvent evaporation through heating at 150 °C for 2 hours. A 300 W Xe lamp, providing an illumination intensity of 100 mW·cm⁻², was used as the light source.

The conversion between potential versus the reversible hydrogen electrode (RHE) and versus Ag/AgCl was calculated using the following formula:

$$E_{RHE} = 0.197 + 0.059 * pH + E_{Ag/AgCl}^o \quad (6)$$

The band gap of the as-prepared samples was calculated using the Kubelka-Munk equation, based on data obtained from UV-visible diffuse reflectance spectroscopy, as illustrated below.

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (7)$$

where α , h , ν , A , and E_g represent the absorption coefficient, Planck constant, frequency of light, constant, and band gap, respectively.

The conduction band (CB) was determined through Mott-Schottky (M-S) analysis conducted on an electrochemical workstation to measure the flat-band potential. The corresponding equations are presented as follows.

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 e N_D} \left(E - E_{fb} - \frac{kT}{e} \right) \quad (\text{for n-type semiconductor}) \quad (8)$$

where C represents the interfacial capacitance, ϵ is the relative dielectric constant, ϵ_0 denotes the vacuum permittivity, e is the elementary charge, N_D is the carrier concentration, k is the Boltzmann constant, T is the absolute room temperature, and E_{fb} is the flat-band potential. For n-type semiconductors, the flat-band potential is typically 0.1 to 0.3 V more positive than the conduction band potential.

According to the following equation, the valence band potentials of the as-prepared sample were further obtained.

$$E_{VB} = E_g - E_{CB} \quad (9)$$

where E_{VB} is the valence band potential, E_g is the band gap, and E_{CB} is the conduction band potential.

2.4 Theoretical Calculation

Density functional theory (DFT) calculations were carried out in the Vienna ab initio simulation package (VASP) based on the plane-wave basis sets with the projector augmented-wave method¹⁻⁴. The exchange-correlation potential was treated by using a generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) parametrization⁵. The van der Waals correction of Grimme's DFT-D3 model was also used⁶⁻⁷. In order to sample the k -space within the Brillouin zone, the Γ -centered Monkhorst-Pack grids were used⁷ along with a plane-wave cutoff energy of 450 eV. For structural optimizations, the atomic positions were allowed to relax in all three directions, while the shape and volume of the supercell were fixed until the convergence criteria for energy and force were set to 1×10^{-5} eV and 0.02 eV/Å, respectively.

2.5 References

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Chapter 3 Optimizing Copper-Copper Bimetallic Site in Metal-Organic Framework for Photocatalytic CO₂ Reduction to Acetic Acid

3.1 Introduction

Artificial photosynthesis, specifically the photocatalytic CO₂ reduction reaction (CO₂RR) to multi-carbon (C₂₊) products, has attracted significant and sustained research interest since Halmann's groundbreaking demonstration in 1978¹⁻³. Mimicking natural photosynthesis, this approach offers a dual strategy for greenhouse gas mitigation and renewable fuel production by harnessing solar energy⁴⁻⁵. While extensive efforts have focused on converting CO₂ into value-added C₂₊ chemicals, such as ethanol and acetic acid, low yields and insufficient control over product selectivity necessitate further advancements⁶⁻⁷. Over the past few decades, significant strides have been made in improving CO₂ conversion efficiency, approaching industrially relevant benchmarks. However, efforts to improve selectivity, especially toward value-added C₂₊ products, have been limited. The volume of recent studies focusing on low-value C₁ products poses a significant economic barrier to the widespread adoption of this technology. Consequently, it is essential to enhance both photoconversion efficiency and selectivity toward value-added C₂₊ products to advance the practical applications of photocatalytic CO₂ conversion.

The photocatalytic conversion of CO₂ to C₂₊ products is an inherently complex process⁸⁻⁹. Recent investigations suggest that achieving high selectivity toward C₂₊ products necessitates more than conventional photocatalytic attributes, such as efficient light harvesting, charge carrier separation, and favorable band alignment. Subtle variations in the molecular microenvironment, including the strategic incorporation of synergistic moieties to stabilize key intermediate species or transition states associated

with C₂₊ product formation, play a pivotal role in dictating specific reaction pathways¹⁰⁻¹¹.

A prominent trend in catalysis involves the utilization of supported SACs to maximize atom efficiency for cost-effectiveness and enhanced sustainability¹²⁻¹⁴. SACs, characterized by their site-specific activity in a variety of reactions, are currently a central focus in numerous atom-efficient catalytic processes. In comparison to SACs with isolated metal sites that lack neighboring active motifs, DACs offer tunable metal selectivity, enabling control over electronic and spatial properties, as well as subtle synergistic effects between different metal combinations. This makes DACs particularly well-suited for multi-molecular catalytic reactions. However, achieving high selectivity toward C₂₊ products in CO₂RR remains a challenge for DACs, primarily due to the limited control over the microenvironment required for the concerted activation of CO* and subsequent complex reactions essential for carbon-carbon (C–C) coupling¹⁵⁻¹⁶. There are still ongoing debates on the molecular-level mechanisms by which local electronic structures are modified and specific intermediates/transition states for C₂₊ product formation are stabilized within this class of heterogeneous atomic catalysts.

In this work, we utilize UiO-67, a Zr-based metal-organic framework (MOF), with a controlled ratio of 2,2'-bipyridine-5,5'-dicarboxylic acid (H₂bpydc) exchanged for the standard biphenyl-4,4'-dicarboxylic acid (H₂bpdc) ligand, as the domain matrix for grafting atomic Cu sites. Our objective is to investigate the impact of atomic site distribution on the selectivity of C₁ and C₂₊ products in photocatalytic CO₂RR. We synthesized a series of Cu-containing UiO-67 samples with Cu SA weight percentages ranging from 0.67 wt% to 2.0 wt%. Excitingly, we found that varying the Cu

concentration subtly steered product selectivity. At low Cu concentrations, the samples predominantly produced C₁ products. Conversely, at high Cu concentrations, the selectivity shifted toward C₂₊ products, with UiO-Cu-1.0 achieving a remarkable acetic acid selectivity of approximately 89%. Through a combination of photoelectrochemical measurements and density functional theory (DFT) calculations, we identified two distinct regimes: (i) at low Cu content, isolated Cu sites preferentially stabilize *COOH intermediates, favoring the formation of C₁ products; (ii) at elevated Cu loadings, neighboring Cu···Cu dual atom motifs facilitate C–C coupling via the *OCCOH step, significantly reducing the activation energy and achieving high selectivity for acetic acid. This work establishes a quantitative chemical model that directly correlates the metal site microenvironment, in terms of site distribution, with C₂₊ chemical production in photocatalytic CO₂RR. Our findings provide a transferable engineering strategy for steering CO₂ photoreduction selectivity and offer fundamental insights into synergistic cooperativity between moieties within a confined spatial regime in photocatalytic multi-carbon synthesis.

3.2 Experimental Procedures

3.2.1 Synthesis of UiO-67

A mixture of 120 mg ZrCl₄, 126 mg H₂bpdC, and 1.88 g benzoic acid were prepared in a 100 mL beaker by adding 20 mL of a solvent composed of DMF and ethanol in a 4:1 volume ratio. The resulting solution was ultrasonicated for 30 minutes to achieve a homogeneous dispersion, then transferred to an autoclave and heated at 120 °C for 24 hours. The suspension was subsequently washed three times with DMF and methanol, respectively. The final UiO-67 product was collected after being dried under vacuum.

3.2.2 Synthesis of UiO-Cu-x

A mixture of 120 mg ZrCl_4 , 101 mg biphenyl-4,4'-dicarboxylic acid (H_2bpdc , $\text{C}_{14}\text{H}_{10}\text{O}_4$), and 21 mg 2,2'-bipyridine-5,5'-dicarboxylic acid (H_2bpydc , $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4$) (with a molar ratio of H_2bpdc to H_2bpydc of 5:1) were combined with 1.88 g of benzoic acid and 20 mL of a solvent mixture (DMF to ethanol ratio of 4:1). The resulting mixture was ultrasonicated for 30 minutes to ensure proper dispersion, then transferred to an autoclave and heated at 120 °C for 24 hours. Afterward, the suspension was washed three times with DMF and methanol, respectively. The UiO-67-bpy was collected following vacuum drying. Its theoretical molecular formula is $\text{C}_{82}\text{H}_{52}\text{O}_{32}\text{Zr}_6\text{N}_2$, with a theoretical molecular weight of 2124.63 g/mol ($[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpydc})(\text{bpdc})_5]$).

UiO-Cu was synthesized by the following processes: 1 mmol of UiO-67-bpy and a certain amount of copper(II) acetylacetonate were mixed into 15 mL of methanol for vigorously stirring at 55 °C for 24 h. The suspension was washed three times to wipe off the remaining chemicals. The final UiO-Cu was collected after vacuum drying. The UiO-Cu were labeled as UiO-Cu-x (where $x = 0.25, 0.50, 0.75, 1.0$), representing the theoretical molarity ratio of Cu atom to H_2bpydc in UiO-Cu-x.

3.3 Results and Discussion

3.3.1 Characterization and Atomic Structure of UiO-Cu-x

The synthesized procedure for UiO-Cu-x is illustrated in **Fig. 3.1**. We first prepared UiO-67-bpy by partially substituting the original H_2bpdc linkers with the bipyridine-containing H_2bpydc linkers, resulting in the UiO-67-bpy precursor with a molar ratio of H_2bpdc to H_2bpydc of 5:1. Subsequently, copper atoms were integrated into the MOF

through the impregnation method, yielding the UiO-Cu-x catalyst with the desired single-atom configuration.

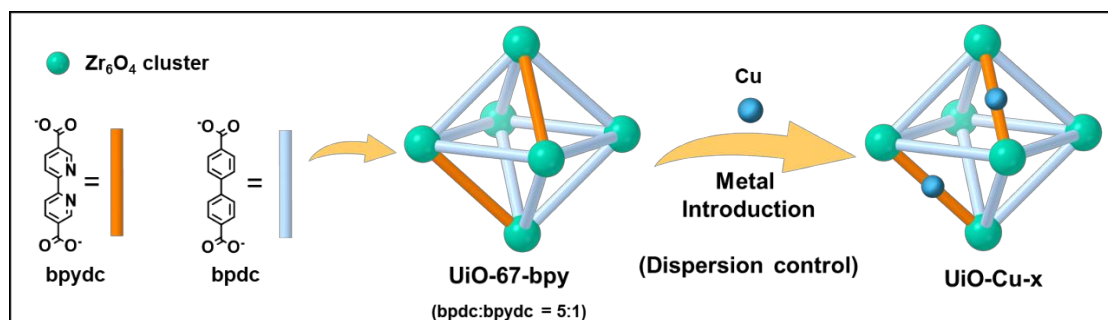


Fig. 3.1 Schematic representation of the synthetic process for UiO-Cu-x.

Coordination with the bpydc linkers was confirmed through PXRD analysis, which demonstrates the structural integrity and high crystallinity of the samples following metalation (**Fig. 3.2**). All synthesized samples exhibit a cubic lattice with the space group of $Fm\bar{3}m$. The crystallographic parameters are summarized in **Table 3.1** and **3.2**, indicating that the lattice parameter remained relatively unchanged at *ca.* 26.8 Å, with an insignificant fluctuation of ~0.01% upon the incorporation of Cu species. This suggests that the introduction of copper did not alter the crystal structure of UiO-67. Furthermore, no additional Bragg peaks corresponding to elemental Cu or Cu oxides were observed, indicating the absence of crystalline aggregates formed.

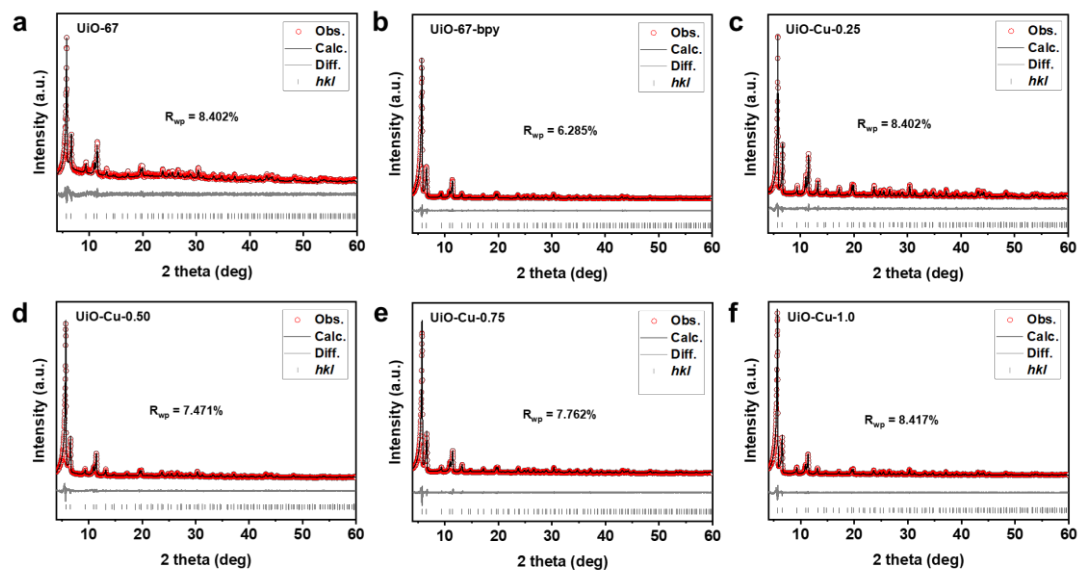


Fig. 3.2 PXRD pattern and the Pawley refinement profile of (a) UiO-67, (b) UiO-67-bpy, (c) UiO-Cu-0.25, (d) UiO-Cu-0.50, (e) UiO-Cu-0.75, and (f) UiO-Cu-1.0.

Table 3.1. Crystallographic parameters derived from the PXRD measurements of UiO-67, UiO-67-bpy and UiO-Cu-0.25.

	UiO-67	UiO-67-bpy	UiO-Cu-0.25
Radiation type	Cu K α	Cu K α	Cu K α
(Å)	(1.5418)	(1.5418)	(1.5418)
2 θ range for refinement (°)	4-60	4-60	4-60
Space group	<i>Fm$\bar{3}m$</i>	<i>Fm$\bar{3}m$</i>	<i>Fm$\bar{3}m$</i>
Crystal system	Cubic	Cubic	Cubic
a (Å)	26.8524	26.8147	26.7943
Cell volume (Å ³)	19362.0	19280.7	19236.6
Number of parameters	26	28	26
Number of <i>hkl</i> s	181	184	181
Refinement method	Le Bail	Le Bail	Le Bail
R _{wp} /R _{exp} /R _p (%)	8.402/2.318/6.622	6.285/1.873/4.502	8.417/2.428/6.372
<i>Gof</i>	3.624	3.356	3.467

Table 3.2. Crystallographic parameters derived from the PXRD measurements of UiO-Cu-0.50, UiO-Cu-0.75 and UiO-Cu-1.0.

	UiO-Cu-0.50	UiO-Cu-0.75	UiO-Cu-1.0
Radiation type	Cu K α	Cu K α	Cu K α
(Å)	(1.5418)	(1.5418)	(1.5418)
2 θ range for refinement (°)	4-60	4-60	4-60
Space group	<i>Fm$\bar{3}m$</i>	<i>Fm$\bar{3}m$</i>	<i>Fm$\bar{3}m$</i>
Crystal system	Cubic	Cubic	Cubic
a (Å)	26.8135	26.7984	26.8277
Cell volume (Å ³)	19278.0	19245.4	19308.6
Number of parameters	26	26	19
Number of <i>hkl</i> s	182	182	184
Refinement method	Le Bail	Le Bail	Le Bail
R _{wp} /R _{exp} /R _p (%)	7.471/2.001/5.716	7.762/1.999/5.856	8.417/2.428/6.372
<i>Gof</i>	3.732	3.883	3.467

SEM further supports this finding, as the nanocrystallites of the metalated samples maintain a well-defined octahedral morphology (**Fig. 3.3**). All UiO-67 and UiO-Cu-x samples kept at an average particle size of approximately 200 nm, without metal aggregation appearing on the catalyst's surface. Elemental analysis revealed the copper atomic percentages in UiO-Cu-x, as detailed in **Table 3.3**. The atomic ratio of Cu to Zr increased linearly from 0.048:1 to 0.088:1, 0.124:1, and 0.149:1 for UiO-Cu-x (with x = 0.25, 0.50, 0.75, and 1.0). We will subsequently employ UiO-Cu-1.0 as the primary case for the discussion of material characterization, as it better demonstrates the catalytic chemistry of interest in this work.

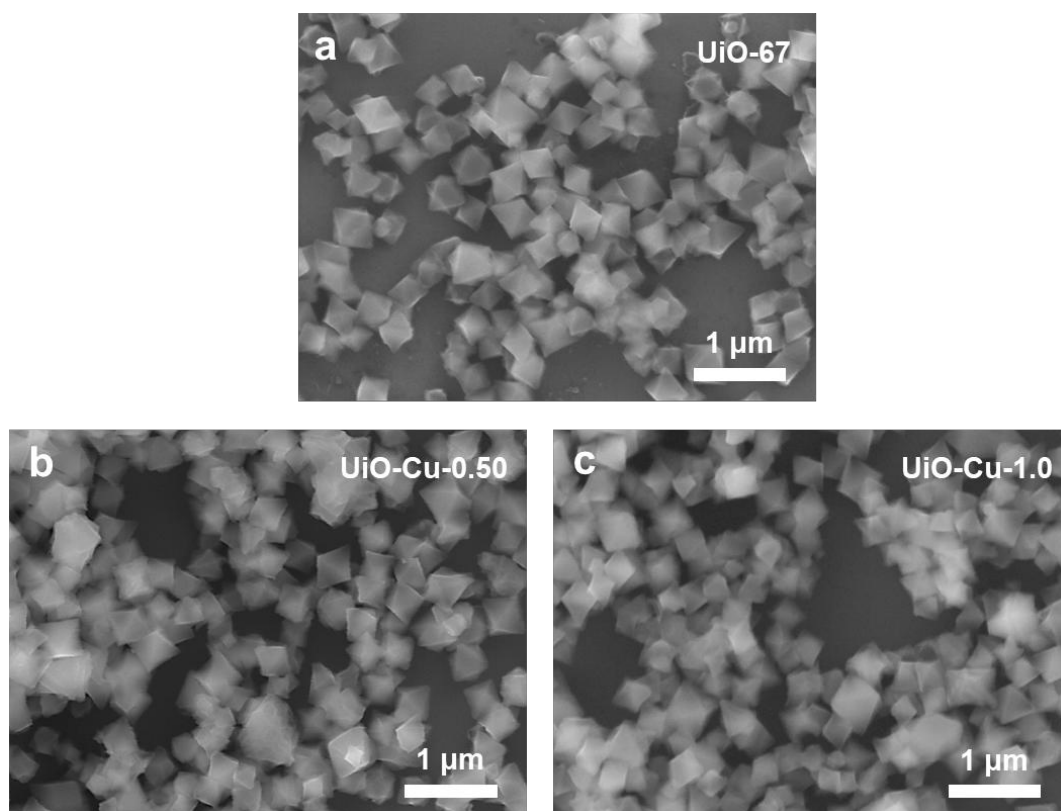


Fig. 3.3 SEM images of (a) UiO-67, (b) UiO-Cu-0.50, and (c) UiO-Cu-1.0.

Table 3.3. Elemental analysis of UiO-Cu-x by ICP-OES measurement.

	Cu content (wt %)	Zr content (wt %)	Atomic ratio Cu : Zr
UiO-Cu-0.25	0.67	24.53	0.048:1
UiO-Cu-0.50	1.38	22.49	0.088:1
UiO-Cu-0.75	1.69	19.59	0.124:1
UiO-Cu-1.0	2.00	19.38	0.149:1

HAADF-STEM was utilized to visualize the copper atoms within UiO-Cu-x. As shown in the EDX color mappings (**Fig. 3.4b**), UiO-Cu-1.0 exhibits a homogeneous copper distribution, confirming the atomic-level incorporation of copper within the MOF. We further applied the iDPC technique, which enables atomic-resolution imaging of

materials sensitive to electron beams, to enhance our understanding of the arrangement and interactions of copper atoms within the UiO-67 domain (**Fig. 3.4c – f**). Structural differences between pristine UiO-67 and UiO-Cu-1.0 are evident when viewed along the [110] crystal direction. Notably, we do not observe significant distortion or contrast differences of the Zr_6O_4 secondary building units in either pristine UiO-67 and UiO-Cu-1.0, where they remain well organized. Regarding the linker morphology, the phenyl rings oriented parallel to [110] in UiO-67 are arranged linearly, with the carbon atoms of the linkers distinguishable. In contrast, upon copper incorporation, the phenyl rings appeared blurred and broadened, likely due to the torsion of Cu-complexed bpydc linkers. Additionally, we observed the emergence of some bright atomic dots adjacent to the phenyl rings, indicating that the copper atoms are anchored onto the bpydc linkers rather than grafted onto the Zr_6O_4 secondary building units. Overall, our investigations confirm the successful synthesis of UiO-67-supported copper atomic sites with high atomic definition and dispersion.

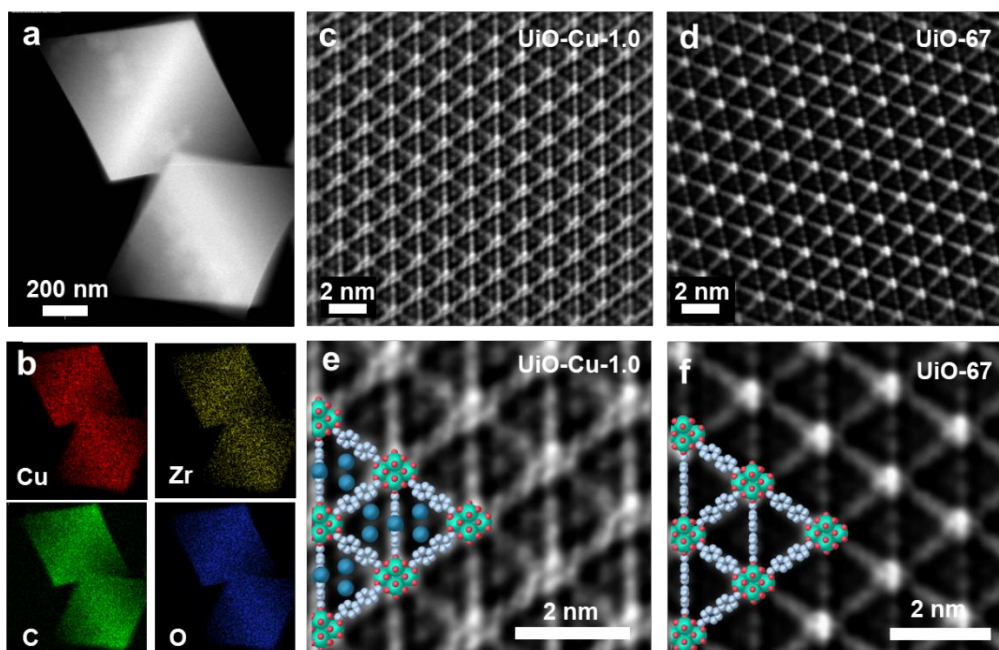


Fig. 3.4 (a) High-resolution HAADF-STEM image and (b) EDX elemental mapping of

UiO-Cu-1.0. iDPC-STEM images of (c) UiO-Cu-1.0 and (d) UiO-67, and structural models with magnified iDPC-STEM images of (f) UiO-Cu-1.0 and (g) UiO-67 viewing along [110] crystal direction.

We then employed synchrotron X-ray absorption spectroscopy to investigate the chemical coordination environment of the copper sites in UiO-Cu-x. As illustrated in the Cu K-edge XANES spectra (**Fig. 3.5a**), the pre-edge features of UiO-Cu-0.5 and UiO-Cu-1.0 closely align and are consistent with the spectral signature of Cu(II) species. Our analysis of the EXAFS spectroscopy data (**Fig. 3.5b** and **3.5c**) provides insight into the coordination information of the copper centers. A prominent peak at *ca.* 1.5 Å is attributed to the Cu–N backscattering path. As summarized in **Table 3.4**, the quantitative curve fitting results indicate consistent Cu–N bond lengths of *ca.* 1.95 Å, with a coordination number of *ca.* 4. This suggests that these Cu-containing MOFs possess analogous coordination geometries, with copper atoms primarily bound to the nitrogen motifs of the bpydc linkers and two coordinate water/hydroxyl species.

We also employed wavelet transform analysis to enhance correlation between the k- and R-space data (**Fig. 3.5d – f**), utilizing the software package developed by Funke and Chukalina, with a Morlet wavelet configured at $\kappa = 10$ and $\sigma = 1$. The highest intensity is observed at the lobe centered at $k = 6.5 \text{ Å}^{-1}$, and $R = 1.5 \text{ Å}$, which corresponds to the N atoms surrounding the Cu centers. We did not observe a noticeable peak corresponding to Cu–Cu backscattering in either UiO-Cu-0.5 or UiO-Cu-1.0, indicating that copper species exist as dispersed atomic species within the UiO-67 framework, thereby ruling out the presence of metallic clusters or alloys. These results suggest that both materials share analogous coordination geometries, with copper atoms primarily bound to two nitrogen sites from the bpydc linkers. Given the similar electron

densities of nitrogen and oxygen, the presence of the additional two nitrogen atoms in the pathway may indicate potential interactions with hydroxyl groups during synthesis¹⁷. This conclusion is further supported by XPS data, which corroborates the electronic and chemical state of copper in our samples, as depicted in **Fig. 3.6** and **Table 3.5**. The oxidation state of +2 for Cu has been observed in UiO-Cu.

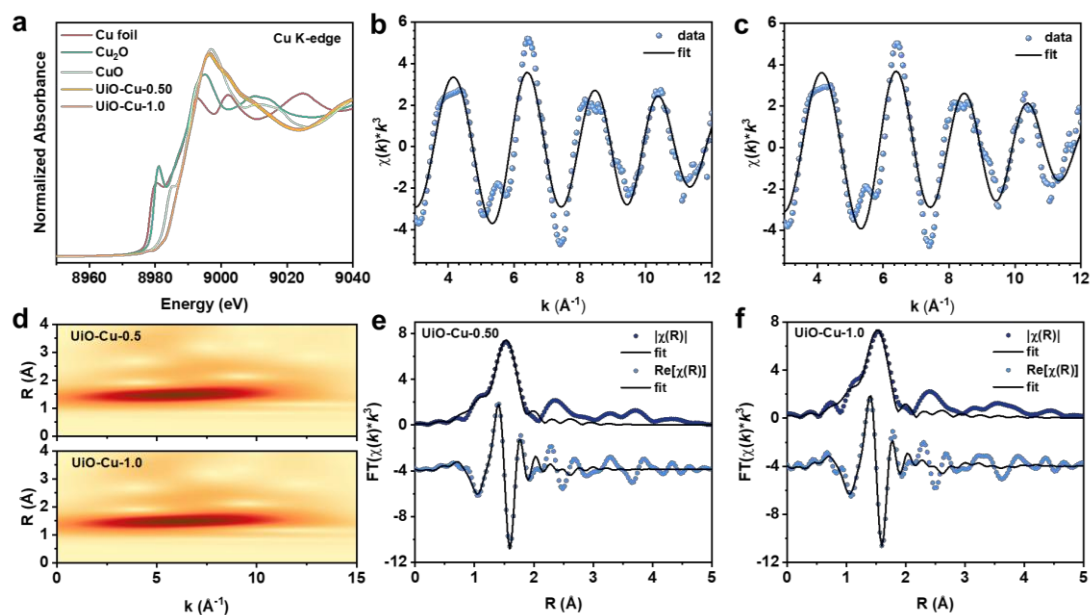


Fig. 3.5 (a) Cu K-edge XANES spectra of Cu standards and UiO-Cu-x (where x = 0.50 and 1.0). EXAFS in k-space for (b) UiO-Cu-0.50, and (c) UiO-Cu-1.0. Wavelet transform analysis of the Cu K-edge for (d) UiO-Cu-0.50 (top) and UiO-Cu-1.0 (bottom). R-space representations ($|\chi(R)|$ and $\text{Re}[\chi(R)]$ parts) for (e) UiO-Cu-0.50 and (f) UiO-Cu-1.0.

Table 3.4. Curve fitting parameters for Cu K-edge EXAFS for UiO-Cu-0.50 and UiO-Cu-1.0.

Sample	Path	N	R / Å	σ^2 / Å ²	ΔE_0	R-factor	k range
UiO-Cu-0.50	Cu-N/O	4.0(6)	1.94(1)	0.004(2)	-4.7(21)	0.015	3-13
UiO-Cu-1.0	Cu-N/O	3.4(3)	1.95(1)	0.003(1)	-3.3(13)	0.009	3-13

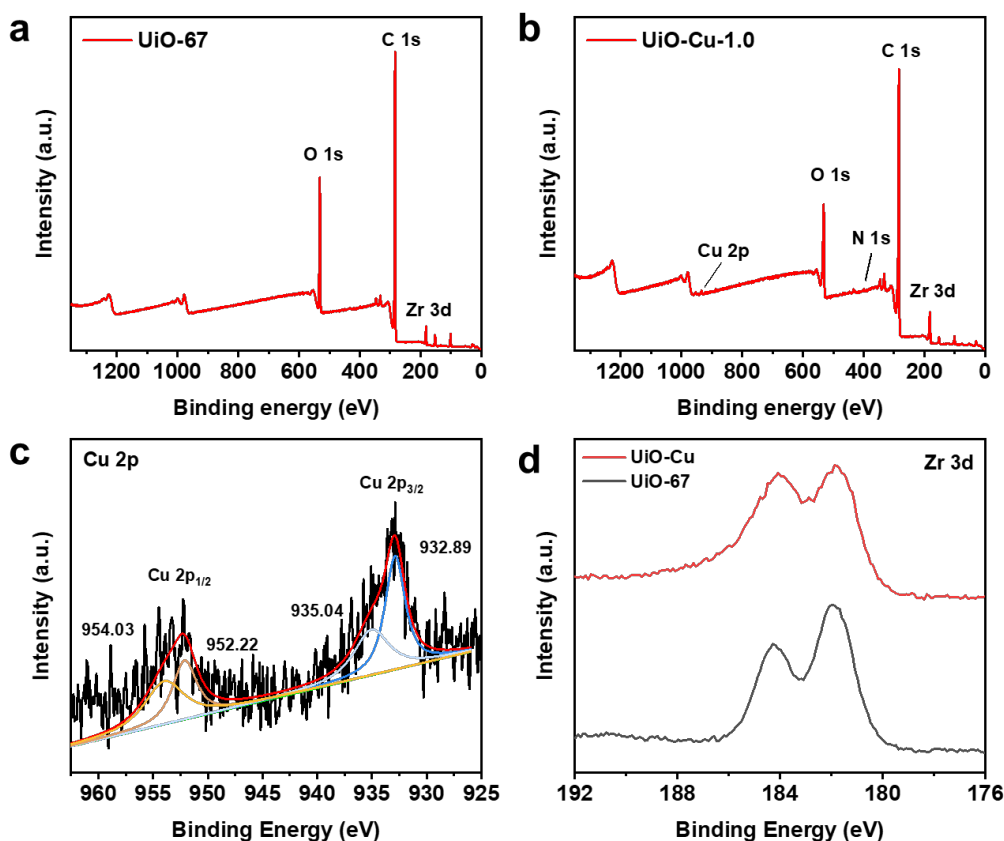


Fig. 3.6 XPS full spectrum of (a) UiO-67 and (b) UiO-Cu-1.0, and (c) element spectrum of Cu 2p in UiO-Cu-1.0, and (d) Zr 3d in UiO-67 and UiO-Cu-1.0.

Table 3.5. Elemental analysis of UiO-Cu-1.0 by XPS measurement.

UiO-Cu-1.0					
Element	Cu 2p	O 1s	N 1s	C 1s	Zr 3d
Atomic %	0.21	15.88	0.89	81.94	1.09

The atomic configuration of the copper sites was further resolved using high-resolution synchrotron PXRD combined with Rietveld refinement¹⁷⁻¹⁹. Whereas the positions of the Bragg peaks remained relatively unchanged, notable variations in the intensities of these peaks are evident. Specifically, the apparent changes in Bragg peak intensities in

the higher 2θ regime upon metalation can be attributed to the significant alterations in the scattering factors resulting from heavier copper atoms. Quantitative analysis of the PXRD patterns provides insights into the distribution of copper species. As presented in **Fig. 3.7** and **Table 3.6**, the Bragg peaks remain highly symmetrical across all samples, suggesting that the metalation process is highly homogeneous. Considering the (111) reflection ($2\theta \approx 2.71^\circ$) as a representative example, theoretical considerations suggest that if copper species were incorporated in a disordered fashion within the MOF structure, incoherent diffraction would arise. This would manifest as a shift in peak position and the emergence of asymmetric peaks. However, the Bragg peaks observed for UiO-67, UiO-Cu-0.50, and UiO-Cu-1.0 exhibit symmetrical profiles (as indicated by asymmetry parameters of 0.0001 in **Table 3.6**), demonstrating a high degree of homogeneity within the samples. This observation implies that the metalation processes proceed uniformly throughout the MOF framework, resulting in a consistent distribution of copper active sites. Further quantitative analysis of the synchrotron PXRD patterns (**Table 3.6**) yielded volume-weighted mean column heights (LVol) calculated from both the full width at half maximum (FWHM) and integral breadth (IB) values, assuming an intermediate crystallite size broadening described by a Voigt function. Similarly, the micro-strain, ϵ_0 , indicative of lattice imperfections such as dislocations and vacancies, was derived from the FWHMs. The preservation of symmetry observed in UiO-67 (peak asymmetry parameter of 0.0001) following copper metalation in UiO-Cu-0.50 and UiO-Cu-1.0 reinforces the conclusion that Cu sites are homogeneously and orderly dispersed within the MOF structure.

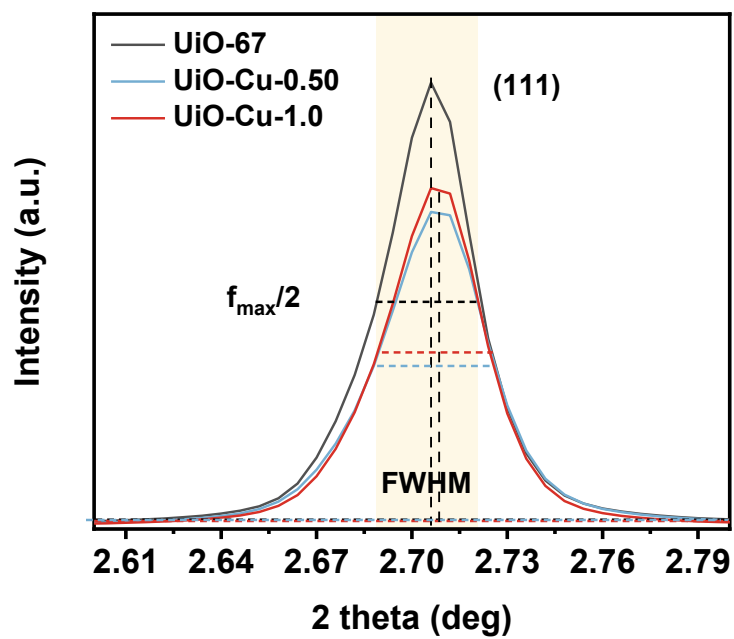


Fig. 3.7 Comparison of the Bragg peak (111) over UiO-67, UiO-Cu-0.50, and UiO-Cu-1.0. The synchrotron PXRD data were collected on Beamline BL02B2 at SPring-8.

Table 3.6. Quantitative peak parameters of samples from synchrotron PXRD.

	UiO-67	UiO-Cu-0.50	UiO-Cu-1.0
Peak asymmetry parameter	0.0001	0.0001	0.0001
LVol-Integral breadths	113.9	157.8	104.4
LVol-FWHM	148.0	167.5	124.8
Microstrain (ϵ_0) *	0.02279	0.02347	0.01096
Strain (Gaussian)	0.0911	0.0938	0.0438
Strain (Lorentzian)	0.0001	0.0001	0.0001

LVol - Volume weighted mean column heights.

ϵ_0 - dislocations, vacancies, and other defects, calculated from FWHMs.

The Rietveld refined crystal structures of the samples, guided by the above structural analyses, are depicted in **Fig. 3.8 – 3.10**. High-quality Rietveld refinement can be confirmed by a low R-weighted pattern (R_{wp}) value and a small difference between the experimental data and the refinement profiles. The site occupancy factors of the Cu sites have been fixed on the basis of the elemental analysis results to ensure the refinement reliability. It is evident that the Cu atoms interact with the N moieties of the bpydc linkers, indicating Cu–N coordination within the UiO-67 domain (**Tables 3.7 – 3.10**). Given that the highly symmetrical peaks observed in our PXRD data set, the bpydc linkers and Cu sites are homogeneously distributed and fully unbiased within the UiO domain.

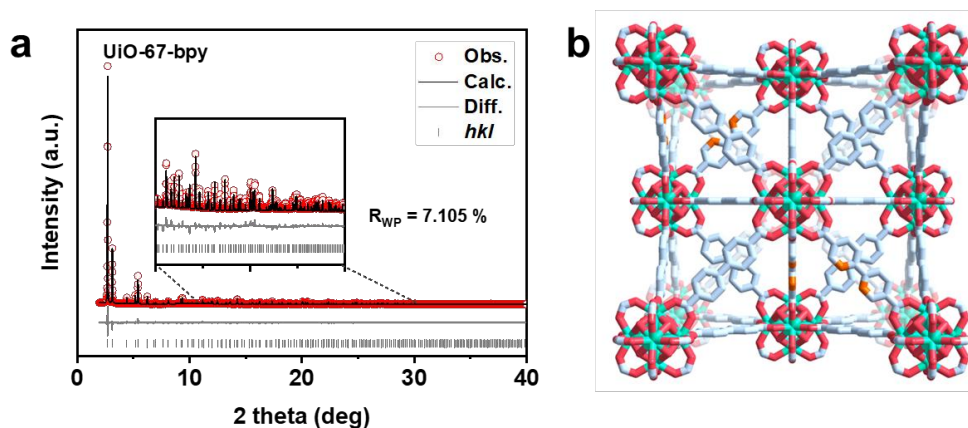


Fig. 3.8 High-resolution synchrotron PXRD patterns collected on Beanline BL02B2 at SPring-8 ($\lambda = 0.729589 \text{ \AA}$) and the corresponding Rietveld refinement profiles of **(a)** UiO-67-bpy. **(b)** Panels present their respective Rietveld refined crystal structures.

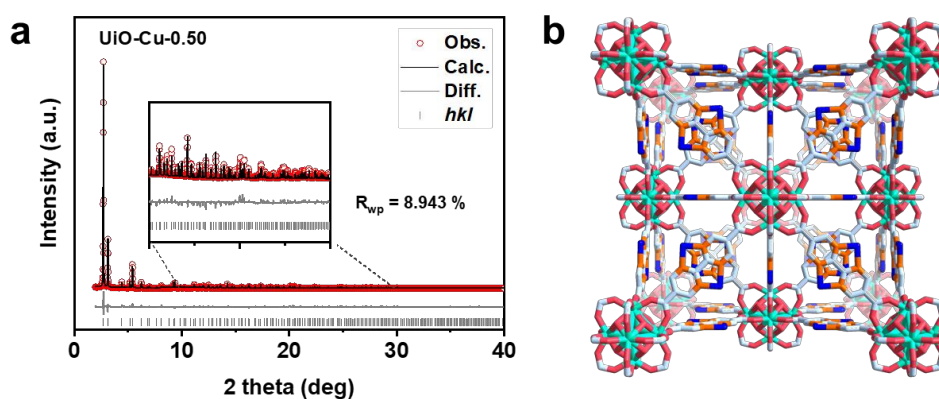


Fig. 3.9 High-resolution synchrotron PXRD patterns collected on Beanline BL02B2 at SPring-8 ($\lambda = 0.729589 \text{ \AA}$) and the corresponding Rietveld refinement profiles of **(a)** UiO-Cu-0.50, **(b)** Panels present their respective Rietveld refined crystal structures.

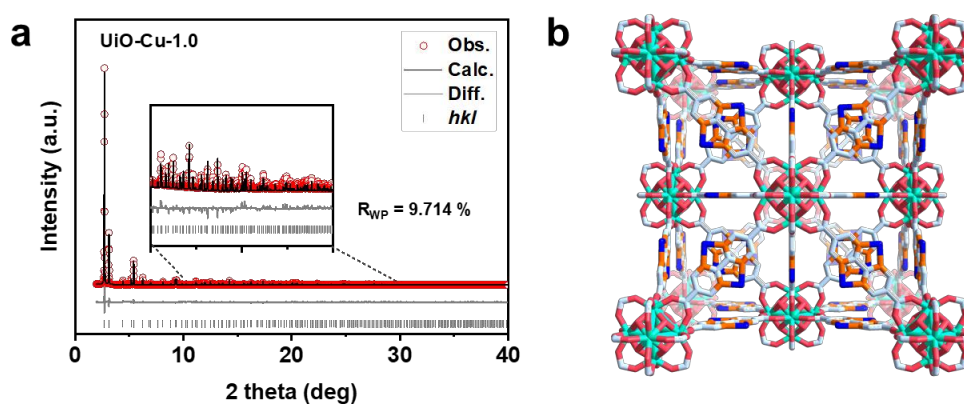


Fig. 3.10 High-resolution synchrotron PXRD patterns collected on Beanline BL02B2 at SPring-8 ($\lambda = 0.729589 \text{ \AA}$) and the corresponding Rietveld refinement profiles of **(a)** UiO-Cu-1.0, **(b)** Panels present their respective Rietveld refined crystal structures.

Table 3.7. Crystallographic data of the synchrotron PXRD measurements of UiO-67-bpy, UiO-Cu-0.50, and UiO-Cu-1.0.

	UiO-67-bpy	UiO-Cu-0.50	UiO-Cu-1.0
X-ray energy (keV)	16.99	16.99	16.99
Beamline	BL02B2	BL02B2	BL02B2
Detector	MYTHEN	MYTHEN	MYTHEN
Wavelength (Å)	0.7296	0.7296	0.7296
2 θ -zero point (°)	-0.00019	-0.00019	-0.00019
Space group	<i>Fm$\bar{3}m$</i>	<i>Fm$\bar{3}m$</i>	<i>Fm$\bar{3}m$</i>
Crystal system	Cubic	Cubic	Cubic
Cell volume (Å ³)	19279.613	19283.350	19280.761
a (Å)	26.8143	26.8160	26.8148
2 θ range for refinement (°)	1.95-78.00	1.95-78.00	1.95-78.00
Number of parameters	49	42	43
Number of <i>hkl</i> s	2617	2621	2617
Refinement methods	Rietveld	Rietveld	Rietveld
R _{wp} /R _{exp} /R _p (%)	7.105/0.765/5.336	8.943/0.884/6.279	9.714/0.895/6.491

Table 3.8. Atomic parameters of UiO-67-bpy from Rietveld refinement.

Atom	x	y	z	SOF	Beq ($\text{\AA}^2$)	Wyckoff letter
Zr1	-0.09195	0	0	1	1	24e
O1	0.12815	0	0.06626	1	1.5	96j
O2	0.06234	0.06234	0.06234	1	1.5	32f
C1	0.11680	0	0.11680	1	10	48h
C2	0.15662	0	0.15662	1	10	48h
C3	0.20633	0	0.14330	1	10	96j
C4	0.24272	0	0.17969	1	10	96j
C5	0.22940	0	0.22940	1	10	48h
C6	0.17969	0	0.24272	1	10	96j
C7	0.14330	0	0.20633	1	10	96j

Table 3.9. Atomic parameters of UiO-Cu-0.50 from Rietveld refinement.

Atom	x	y	z	SOF	Beq ($\text{\AA}^2$)	Wyckoff letter
Zr1	-0.08977	0	0	1	1	24e
O1	0.12877	0	0.06298	1	1.5	96j
O2	0.06234	0.06234	0.06234	1	1.5	32f
C1	0.11670	0	0.11670	1	10	48h
C2	0.15656	0	0.15652	1	10	48h
C3	0.20587	0	0.14329	1	10	96j
C4	0.24199	0	0.17942	1	10	96j
C5	0.22877	0	0.22877	1	10	48h
C6	0.17942	0	0.24199	1	10	96j
C7	0.14329	0	0.20587	1	10	96j
Cu	0.31647	0	0.17552	0.07	10	96j

Table 3.10. Atomic parameters of UiO-Cu-1.0 from Rietveld refinement.

Atom	x	y	z	SOF	Beq (Å ²)	Wyckoff letter
Zr1	-0.09007	0	0	1	1	24e
O1	0.12729	0	0.06948	1	1.5	96j
O2	0.06234	0.06234	0.06234	1	1.5	32f
C1	0.11670	0	0.11670	1	10	48h
C2	0.15652	0	0.15652	1	10	48h
C3	0.20587	0	0.14330	1	10	96j
C4	0.24200	0	0.17942	1	10	96j
C5	0.22877	0	0.22877	1	10	48h
C6	0.17942	0	0.24200	1	10	96j
C7	0.14330	0	0.20587	1	10	96j
Cu	0.31648	0	0.17552	0.15	10	96j

According to the above analysis, we present the schematic illustration of the crystal structure from a molecular perspective, revealing the UiO-Cu-x models with varying copper concentrations (**Fig. 3.11**). Statistically, at $x \leq 0.5$, where x denotes the theoretical molar Cu-to-bpydc ratio in UiO-Cu-x, it suggests that each theoretical structural formula unit, $C_8H_{52}O_{32}Zr_6N_2$, can accommodate at most half a copper atom, as the bpydc linker is shared between two units. This gives a maximum Cu-to-linker ratio of 0.5:6. In contrast, at $0.5 < x \leq 1$, each unit can accommodate at most one copper atom, rendering a maximum Cu-to-linker ratio of 1:6. As illustrated in the scheme, the presence of ‘neighboring Cu motifs’ between two units only becomes apparent (with a Cu···Cu distance ~ 5.22 Å) when the Cu-to-linker ratio exceeds 0.5:6.

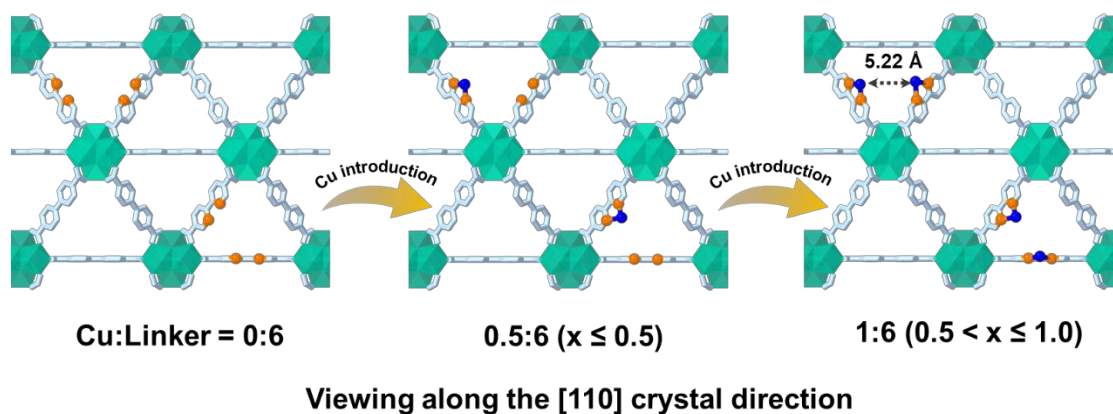


Fig. 3.11 Schematic illustration depicting the copper distribution within the UiO domain, based on homogeneous and unbiased distribution of linkers and Cu sites.

3.3.2 Photocatalytic CO₂RR Performance

In light of the well-dispersed nature of the copper single-atom within the UiO domain, we aimed to evaluate their photocatalytic CO₂RR activity. Briefly, CO₂-saturated deionized water with triethanolamine (TEOA) as a sacrificial agent with our catalysts was illuminated under a 300 W Xe light. As illustrated in **Fig. 3.12a** and **Table 3.11**, UiO-67 and UiO-67-bpy produced HCOOH, at rates of 41.5 and 14.7 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively, with negligible CO production. UiO-Cu-0.25 and UiO-Cu-0.50 maintained HCOOH as the dominant product, achieving yields of 47.2 and 62.9 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively, while also producing CO. UiO-Cu-0.75 and UiO-Cu-1.0 exhibited a shift in selectivity toward acetic acid (CH₃COOH), with UiO-Cu-0.75 achieving a rate of 10.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ at 46% selectivity, and UiO-Cu-1.0 reaching 48.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ at 89% selectivity. This transition from predominantly only C₁ to C₂₊ chemicals implies that product distribution is critically dependent on copper site density, with higher Cu concentrations favoring C–C coupling for CH₃COOH formation. As shown in **Fig. 3.12b**, we also conducted a series of control experiments to confirm the role of our catalysts for photocatalytic CO₂RR. Specifically, we observed nil activity in the absence

of CO₂, light, sacrificial reagent (TEOA), photocatalyst, or light. To assess catalytic stability, UiO-Cu-1.0 was subjected to five consecutive photocatalytic cycles, during which we noted gradual degradation (**Fig. 3.12c**, and **Table 3.12**). Although PXRD analysis revealed a gradual loss of crystallinity, indicating framework instability under prolonged operation (**Fig. 3.12d**), HAADF-STEM and corresponding EDX elemental mapping confirmed that Cu species remained atomically dispersed without aggregation (**Fig. 3.13-14**). Collectively, these results suggest that the observed activity retention is attributable to the intact single-atom sites, while the overall activity decay is likely due to the partial collapse of the MOF matrix.

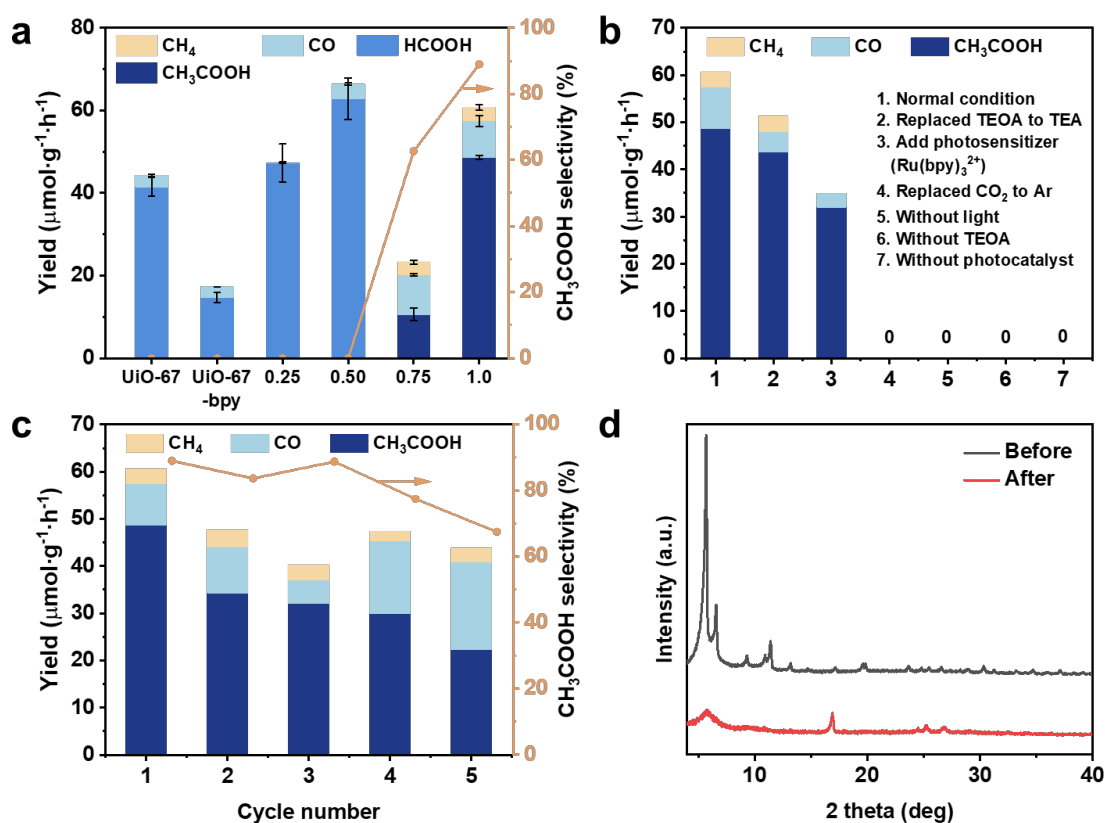


Fig. 3.12 (a) CO₂RR performance of UiO-67, UiO-67-bpy, and UiO-Cu-x under Xe light illumination using TEOA as the sacrificial agent. (b) Control experiments under different reaction conditions. (c) Photocatalytic stability assessment of UiO-Cu-1.0. (d)

Comparison of the PXRD patterns of UiO-Cu-1.0 before and after five catalytic cycles.

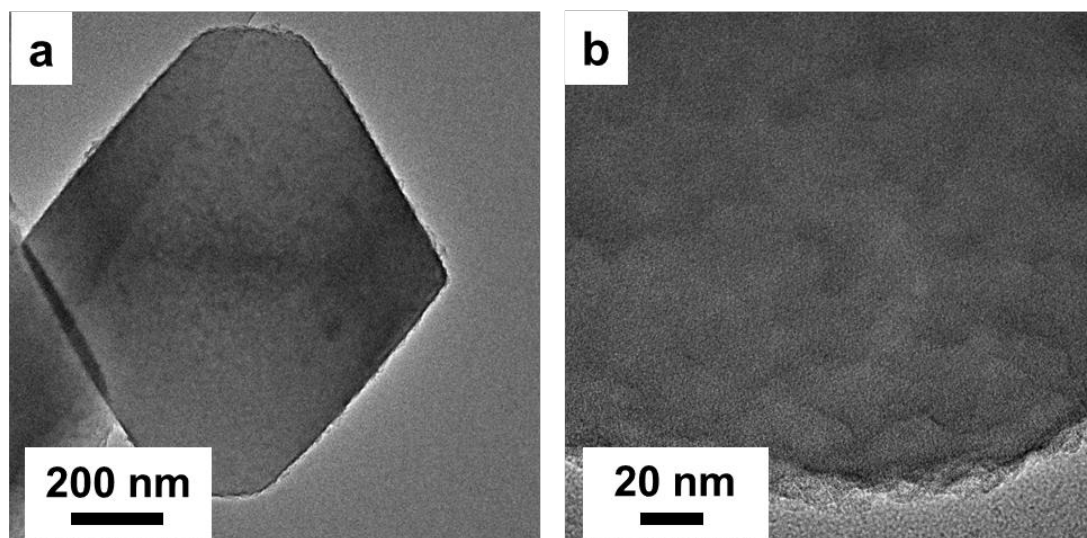


Fig. 3.13 (a, b) Representative TEM images of UiO-Cu-1.0 after five catalytic cycles.

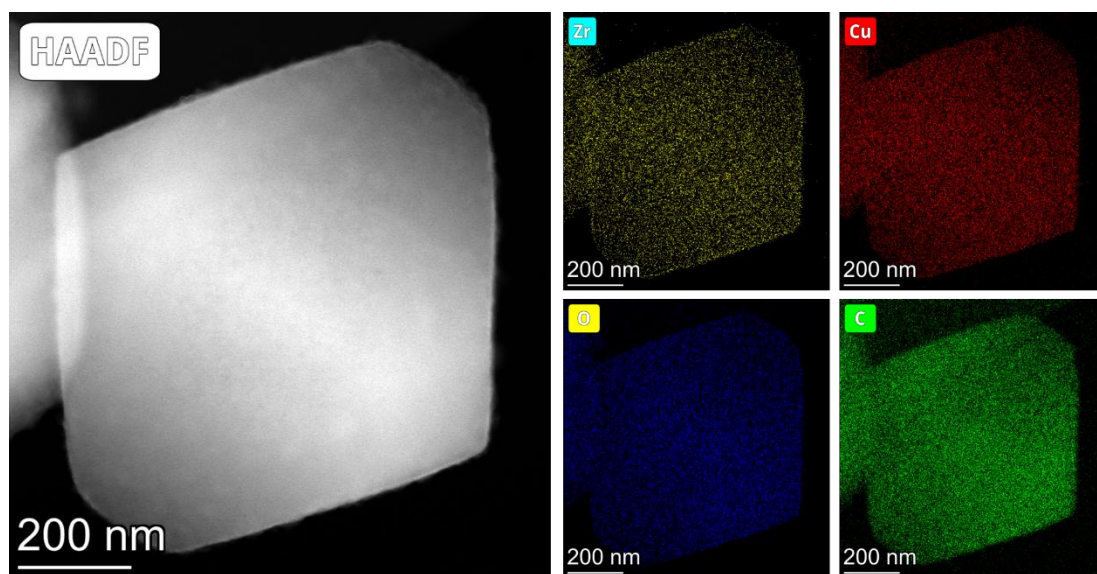


Fig. 3.14 Corresponding EDX element mapping of UiO-Cu-1.0 after five catalytic cycles.

Table 3.11. TON value for the total product of catalysts in different Cu concentrations.

Catalyst	TON _{total} *	TON _{acetic acid}
UiO-Cu-0.25	75.05	0
UiO-Cu-0.50	50.97	0
UiO-Cu-0.75	14.53	6.62
UiO-Cu-1.0	32.13	25.74

* TON was calculated using 30 mg of catalyst with 5 hours of illumination.

Table 3.12. Elemental analysis of UiO-Cu-1.0 after CO₂RR from ICP-OES measurement.

Sample	Test element	Leaching concentration (ppm)	Leaching content (mg for Cu)	Leaching percentage (%)
UiO-Cu-1.0	Cu	0.5453	0.0273	4.54%

3.3.3 Photophysical Properties of UiO-Cu-x

The photophysical properties of UiO-Cu-x were analyzed to elucidate its electronic structure and charge transfer dynamics. UV-visible diffuse reflectance spectroscopy (UV-vis) revealed a broad absorption band in the 500–800 nm range for UiO-Cu-x (**Fig. 3.15a**), attributable to Cu(II) *d-d* transitions²⁰. Enhanced light absorption intensity across a broader wavelength range correlates with improved photocatalytic activity, suggesting that copper incorporation improves light-harvesting efficiency. To further investigate the electronic landscape, we extrapolated the bandgap of the synthesized materials using the Kubelka-Munk-transformed UV-vis data²¹. As illustrated in **Fig. 3.15b**, the synthesized materials exhibit comparable energy structures. The bandgap of UiO-67-bpy (3.72 eV) is marginally wider than that of pristine UiO-67 (3.68 eV), due to partial linker substitution. In contrast, introducing copper species slightly reduces the bandgap of the UiO-Cu-x series to approximately 3.50 eV. The insignificant differences

in the apparent bandgap of the Cu-modified samples (ranging from 3.47 eV to 3.56 eV) suggest that the superior catalytic reactivity originates from the local structures. Also, Mott-Schottky analysis provided conduction band (CB) positions, with the valence band (VB) energies derived computationally (**Fig. 3.16** and **Table 3.13**). The band structure of UiO-67-bpy closely matched that of UiO-67, consistent with prior studies²². Notably, UiO-Cu-x exhibited electronic parameters nearly identical to those of UiO-67, indicating that copper incorporation only marginally perturbs the electronic landscape of UiO-67 domain. Therefore, the calculated band structure of the MOF aligns well with the formation of the target product, CH₃COOH, during CO₂RR, underscoring its suitability for this catalytic process^{23, 24}.

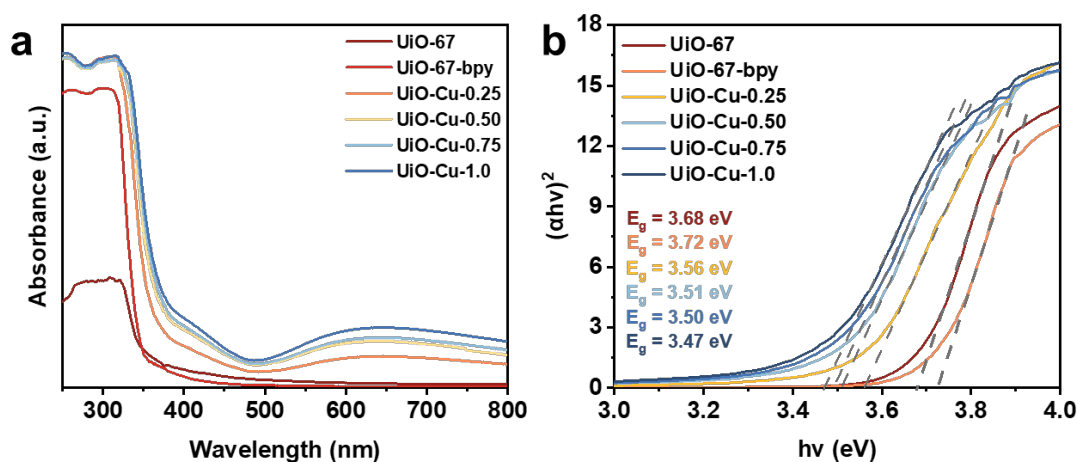


Fig. 3.15 (a) UV-vis spectra and (b) plots of $(\alpha h\nu)^2$ vs. photon energy for UiO-67, UiO-67-bpy, and UiO-Cu-x (where x = 0.25, 0.50, 0.75, and 1.0).

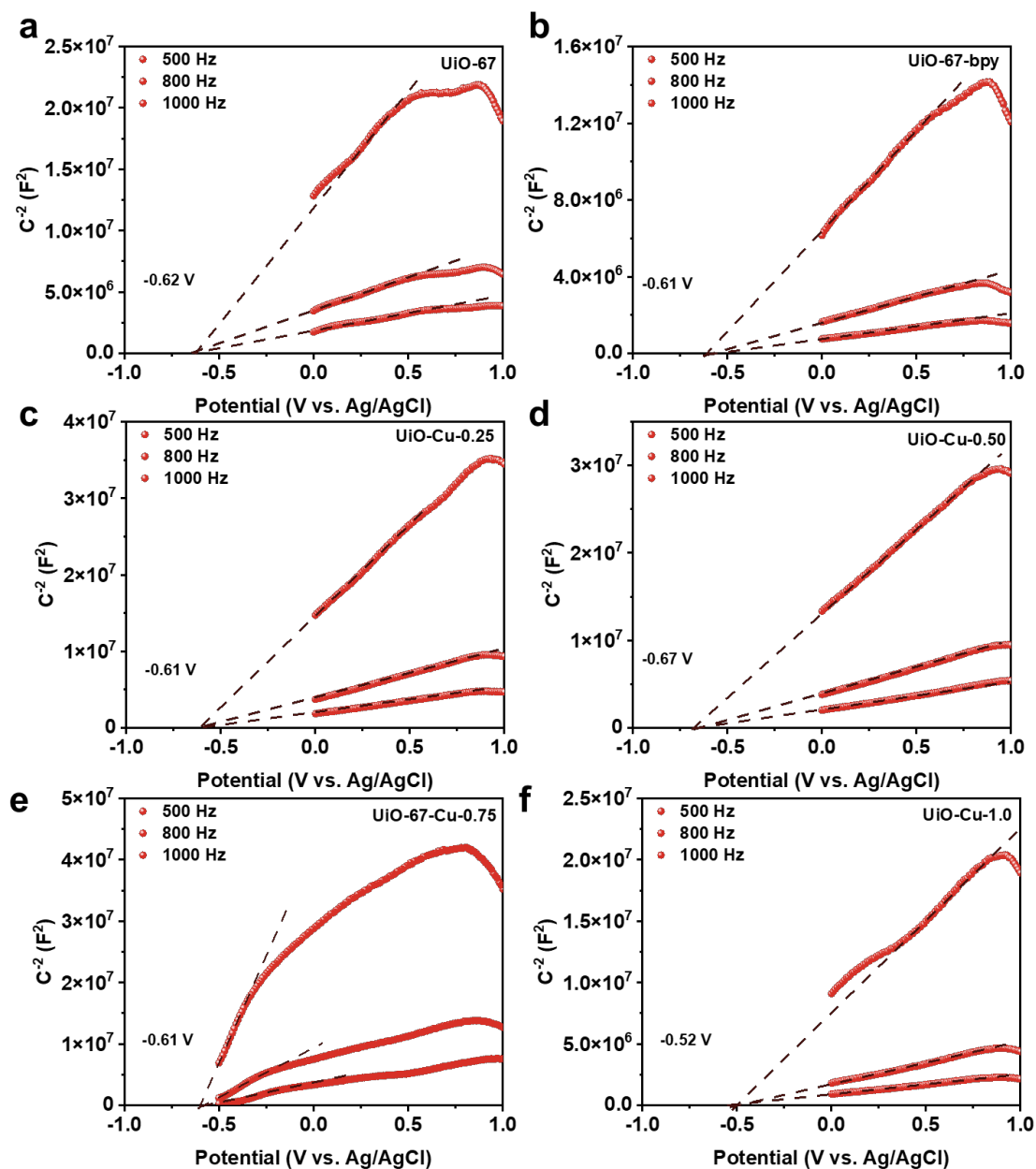
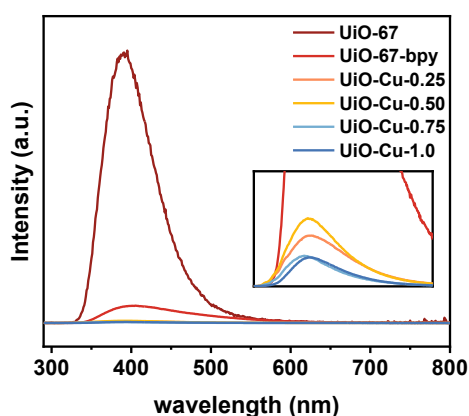


Fig. 3.16 Mott-Schottky plots of (a) UiO-67, (b) UiO-67-bpy, (c) UiO-Cu-0.25, (d) UiO-Cu-0.50, (e) UiO-Cu-0.75, and (f) UiO-Cu-1.0 measured at 500, 800, and 1000 Hz in 0.1 M Na₂SO₄ electrolyte (pH = 7).

Table 3.13. Band positions of the as-prepared samples vs. NHE.

Sample	Bandgap (eV)	Valence band (eV)	Conduction band (eV)
UiO-67	3.68	3.47	-0.21
UiO-67-bpy	3.72	3.52	-0.20
UiO-Cu-0.25	3.56	3.36	-0.20
UiO-Cu-0.50	3.51	3.25	-0.26
UiO-Cu-0.75	3.50	3.30	-0.20
UiO-Cu-1.0	3.47	3.36	-0.11

We subsequently employed PL spectroscopy to elucidate the recombination dynamics of the photo-induced electron-hole pairs within our catalysts. As shown in **Fig. 3.17**, UiO-67 exhibits the highest PL intensity, indicating rapid electron-hole recombination. In contrast, UiO-67-bpy and UiO-Cu-x display significantly lower PL intensity. The incorporation of single-atom copper further reduces PL intensity, signifying diminished charge recombination due to the supported copper motifs on the UiO framework. This enhancement indicates improved charge separation via linker-to-metal charge transfer (LMCT).

**Fig. 3.17** PL spectra of UiO-67, UiO-67-bpy, and UiO-Cu-x (where x = 0.25, 0.50, 0.75, and 1.0).

To further explore the charge carrier dynamics, we employed TRPL spectroscopy (**Fig. 3.18**). All decay profiles were fitted using a bi-exponential function $y = A_1 \exp(-\frac{t}{\tau_1}) + A_2 \exp(-\frac{t}{\tau_2})$, yielding two distinct lifetime components (τ_1 and τ_2). The effective lifetime is ($\tau_{\text{eff}} = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$) which is extracted from the TRPL spectra by fitting with a biexponential function (**Table 3.14**). TRPL lifetime reflects the average survival time of photogenerated electron-hole pairs. UiO-67, UiO-67-bpy, and UiO-Cu-x ($x = 0.25, 0.50, 0.75$ and 1.00); $\tau_{\text{eff}} = 1.808, 1.350, 1.000, 1.069, 1.006$ and 1.026 ns, respectively. This trend aligns with enhanced charge separation and migration to catalytic sites, rather than detrimental recombination within the bulk structure. The shortened TRPL lifetimes, coupled with reduced steady-state PL intensity in UiO-Cu-x catalysts, strongly correlate with the introduction of copper species. These dual observations with shorter TRPL lifetimes and lower PL intensity suggest that copper incorporation promotes efficient extraction of carriers for surface redox reactions, suppressing self-recombination. Further analysis of the biexponential fitting reveals two recombination pathways: the faster decay component (τ_1) relates to non-radiative recombination mediated by trap states, while the slower decay component (τ_2) reflects intrinsic radiative recombination of free carriers. Pristine UiO-67 exhibits the longest τ_1 (0.965 ns), attributed to ligand-to-cluster charge transfer (LCCT) processes²⁵. Substitution with bipyridine ligands in UiO-67-bpy reduces τ_1 to 0.767 ns, likely due to nitrogen-induced charge delocalization. Remarkably, UiO-Cu-x catalysts display the shortest τ_1 values (0.633-0.691 ns) and the highest contribution of the fast-decay component (A_1), consistent with LMCT dynamics²⁶. This LMCT behavior, facilitated by the rigid metal-organic framework, promotes rapid exciton quenching through directional charge migration. The controlled integration of copper into the UiO-67 framework likely induces localized charge asymmetry, driving spatial separation of

electrons and holes toward active catalytic sites. This mechanistic framework explains the superior photocatalytic CO₂ reduction performance of UiO-Cu-x, where optimized carrier utilization outweighs the reduced bulk recombination lifetime.

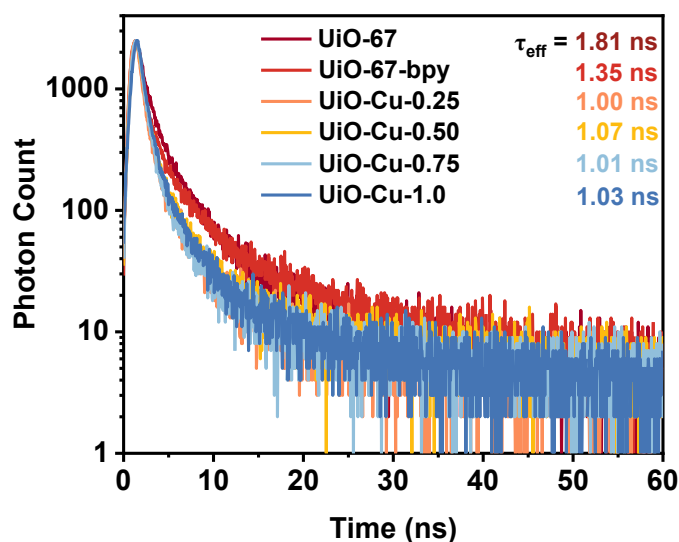


Fig. 3.18 TRPL spectra of UiO-67, UiO-67-bpy, and UiO-Cu-x (where x = 0.25, 0.50, 0.75, and 1.0).

Table 3.14. Lifetime components in TRPL decay fitted by double exponential components.

Sample	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	T_{eff}
UiO-67	0.965	73.51	4.145	26.49	1.808
UiO-67-bpy	0.767	85.01	4.660	14.99	1.350
UiO-Cu-0.25	0.691	88.04	3.268	11.96	1.000
UiO-Cu-0.50	0.689	85.99	3.404	14.01	1.069
UiO-Cu-0.75	0.679	87.99	3.396	12.01	1.006
UiO-Cu-1.0	0.633	85.64	3.369	14.36	1.026

We also investigated the charge transfer dynamics using electrochemical impedance

spectroscopy (EIS) and transient photocurrent responses. The Nyquist plots from the EIS analysis (**Fig. 3.19a**) reflect the charge transfer resistance, with UiO-Cu-1.0 displaying the smallest curvature radius, indicative of rapid charge transfer at the surface. The photocurrent generated signifies charge transfer from the catalyst to the external circuit; thus, a higher photocurrent density reflects faster charge separation within the catalyst. As depicted in **Fig. 3.19b**, UiO-Cu-1.0 demonstrates the highest photocurrent density compared to UiO-67 and other UiO-Cu-x analogs, providing compelling evidence that copper introduction significantly accelerates charge transfer at the surface of the UiO-67 domain.

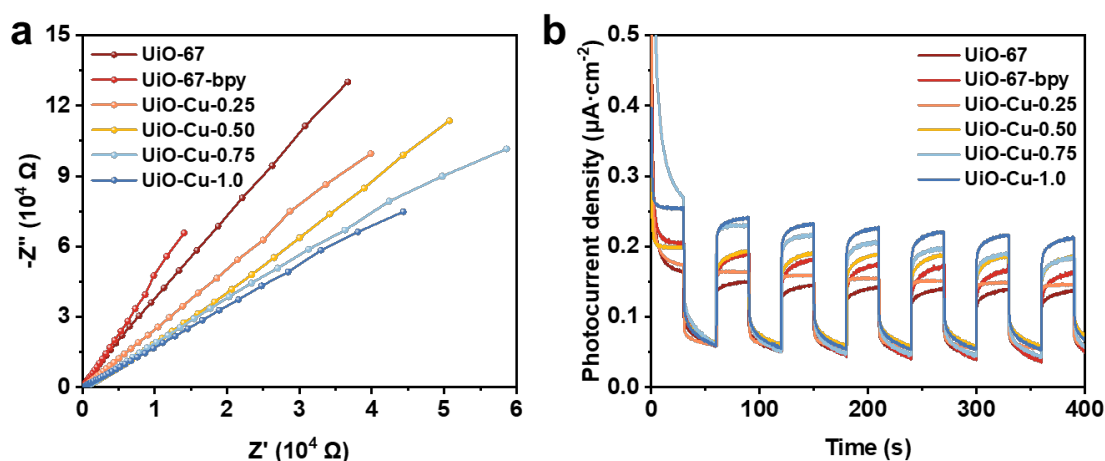


Fig. 3.19 (a) Nyquist plots from the EIS analysis, and (b) transient photocurrent responses of UiO-67, UiO-67-bpy, and UiO-Cu-x (where x = 0.25, 0.50, 0.75, and 1.0).

3.3.4 CO_2RR Mechanism of UiO-Cu-x

Despite our above photophysical characterization revealing substantially improved photochemical properties with increasing copper loading, a core question still remains here: Why is the product selectivity steered from C_1 to C_{2+} products? To address this, we employed *in-situ* DRIFTS to probe the presence of intermediate species during the reaction. The *in-situ* spectroscopic data of UiO-67, UiO-Cu-0.50, and UiO-Cu-1.0

reveal distinct spectral features indicative of specific chemical species (**Fig. 3.20**). First, both datasets exhibit IR peaks at 1084 and 1302 cm^{-1} , characteristic of *CHO and $\text{*COOH}_{\text{stretching}}$ stretching vibrations^{27, 28}, respectively, confirming the formation of C_1 products. Conversely, UiO-Cu-0.50 and UiO-Cu-1.0 display unique spectral features with an IR peak at 1714 cm^{-1} , corresponding to carbonyl stretching vibrations ($\text{*CO}_{\text{stretching}}$). This suggests that the CO species are adsorbed in bridging configurations between adjacent metal sites (M-CO), a configuration crucial for activating CO intermediates during photocatalytic CO_2RR ^{29, 30}. The absence of comparable IR peaks in UiO-67 suggests that the ‘neighboring $\text{Cu}\cdots\text{Cu}$ motifs’ in UiO-Cu-1.0 can better facilitate CO binding, providing a key mechanistic advantage for selective CO_2 conversion. Furthermore, we also observed additional IR peaks characteristic of intermediate species in UiO-Cu-1.0, including *OC-CO at 1480 cm^{-1} and *HOC-CO at 1225 and 1514 cm^{-1} ^{31, 32}. These observations provide strong evidence into the formation of intermediates involved in C–C coupling, indicative of a potential reaction pathway: $\text{CO}_2 \rightarrow \text{M-CO}^* \rightarrow \text{*OC-CO} \rightarrow \text{*HOC-CO}$ over UiO-Cu-1.0.

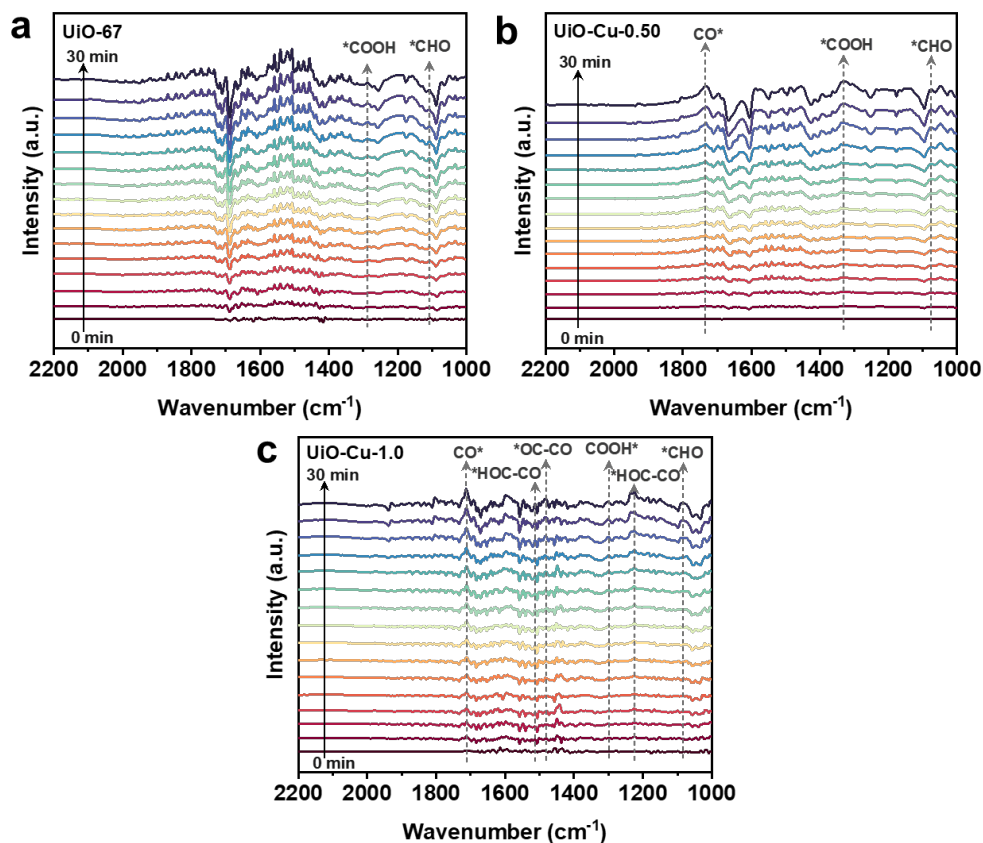


Fig. 3.20 *In-situ* DRIFTS spectra for CO₂RR over (a) UiO-67, (b) UiO-Cu-0.50, and (c) UiO-Cu-1.0.

We have accordingly chosen UiO-Cu-0.50 and UiO-Cu-1.0 as the representative examples on the production of C₁ and C₂₊ products from CO₂RR by DFT calculation investigation. Note that these samples correspond to one and two copper motifs per two C₈₂H₅₂O₃₂Zr₆N₂ units based on the statistical distribution analysis of copper discussed above. Previous studies have shown that the hydrogenation of CO₂ at either C or the O motifs can lead to the formation of C–H or C–O bonds, yielding distinct intermediates: *OCHO and *OCOH. These intermediates are crucial in the formation of *HCOOH and *CO products, respectively^{33, 34}, with *CO serving as a key coupling intermediate for the subsequent production of C₂₊ products³⁵.

As shown in **Fig. 3.21a**, UiO-Cu-0.50 favors the CO₂ hydrogenation at the C motif,

promoting the formation of HCOOH, which aligns with our experimental catalysis observations. Similarly, **Fig. 3.21b** presents the complete reaction pathway for CO₂RR leading to the formation of CH₃COOH over UiO-Cu-1.0. The PDS for the *HCOOH product is *CO₂ → *OCHO, with a potential barrier of 1.29 eV. In contrast, the PDS for the CH₃COOH pathway is *CO–*CO → *CO–*COH, with a lower potential barrier of 0.95 eV. This reduced energy barrier suggests that the UiO-Cu-1.0 structure is more favorable for catalyzing CH₃COOH formation via CO₂RR. The comparison of reaction pathway energies highlights how varying copper concentrations modulate product selectivity between C₁ and C₂₊ species, warranting further investigation of the underlying electronic structure differences.

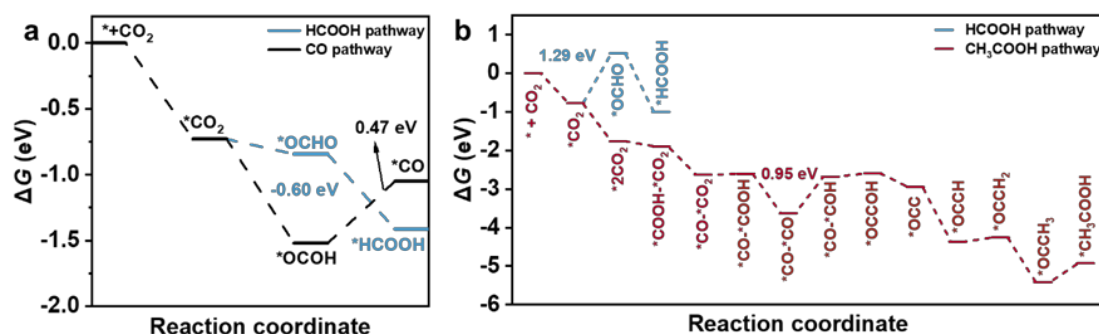


Fig. 3.21 Calculated Gibbs free energy profiles for the CO₂RR steps over (a) UiO-Cu-0.50 and (b) UiO-Cu-1.0.

To analyze the bonding interactions and electronic structure, we employed the crystal orbital Hamilton population (COHP) analysis to examine bonding/antibonding contributions, orbital participation, and bond strength variations³⁶. We focused on *HCOOH and *CO in the context of CO₂RR over UiO-Cu-0.50, as these intermediates represent C₁ products and the potential C₂₊ products, respectively. As shown in **Fig. 3.21**, the integrated COHP (ICOHP) values reveal that the Cu–O bond in *HCOOH is

stronger than the Cu–C bond in $^*\text{CO}$, indicating that the adsorption of HCOOH is more favorable in UiO-Cu-0.50 , promoting the generation of C_1 products.

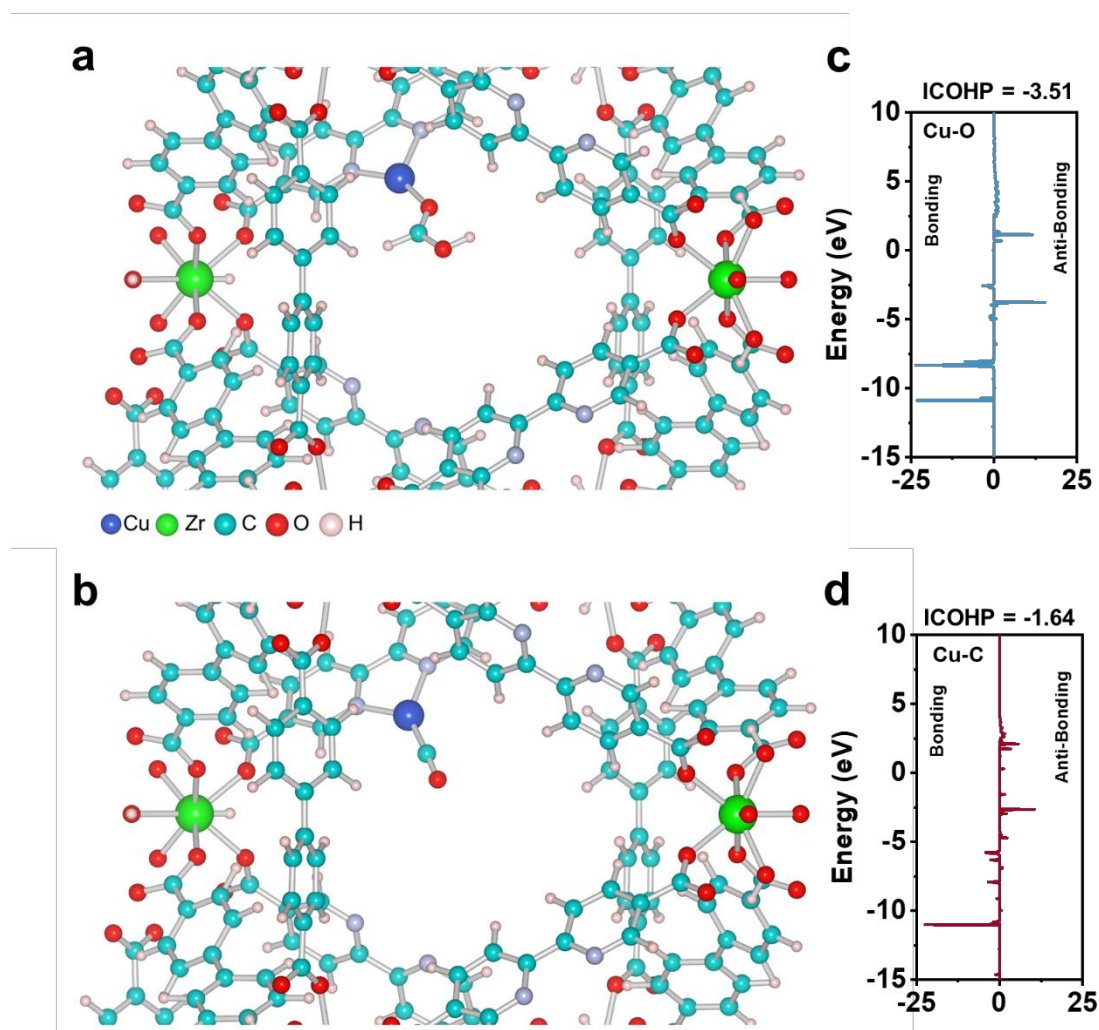


Fig. 3.22 DFT-optimized structures of (a) $^*\text{HCOOH-}^*\square$ and (b) $^*\text{CO-}^*\square$ in the UiO-Cu-0.50 . Corresponding COHP analysis of (c) Cu–O bond of the $^*\text{HCOOH-}^*\square$, (d) Cu–C bond of the $^*\text{CO-}^*\square$ in UiO-Cu-0.5 . All DFT calculations were performed at GGA/PBE level.

For UiO-Cu-1.0 , we considered two different adsorption scenarios. Initially, we calculated the bond strengths for one Cu site occupied by either $^*\text{HCOOH}$ or $^*\text{CO}$ intermediate, while the other site remains vacant ($^*\square$) (**Fig. 3.22**). The analysis reveals that the Cu–O bond in $^*\text{HCOOH}$ ($\text{ICOHP} = -3.55$) is stronger than the Cu–C bond in

*CO (ICOHP = -1.66). This suggests that neglecting the intermediate adsorption at neighboring Cu sites may hinder the generation of C_{2+} products.

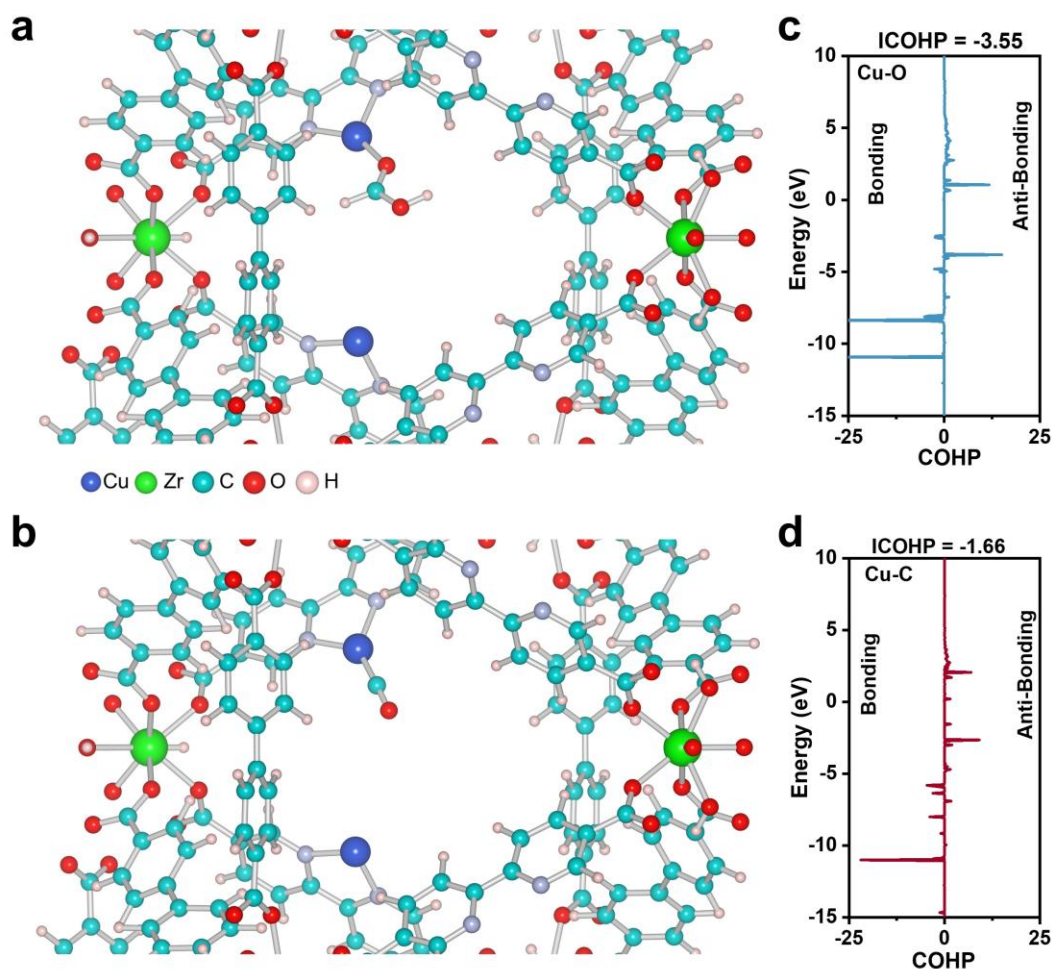


Fig. 3.23 DFT-optimized structures of (a) $*HCOOH$ -*□ and (b) $*CO$ -*□ in the UiO-Cu-1.0. Corresponding COHP analysis of (c) Cu-O bond of the $*HCOOH$ -*□, (d) Cu-C bond of the $*CO$ -*□ in UiO-Cu-1.0.

Consequently, we established a $*HCOOH$ - $*CO_2$ and CO - $*CO_2$ model (Fig. 3.24). In this configuration, when a Cu site is occupied by CO_2 , the other Cu site will exhibit stronger Cu-C bond characteristics compared to the Cu-O bond, indicating that the adsorption of CO_2 on a Cu site enhances $*CO$ adsorption at the neighboring $Cu \cdots Cu$ motifs in UiO-Cu-1.0 through a synergistic interaction.

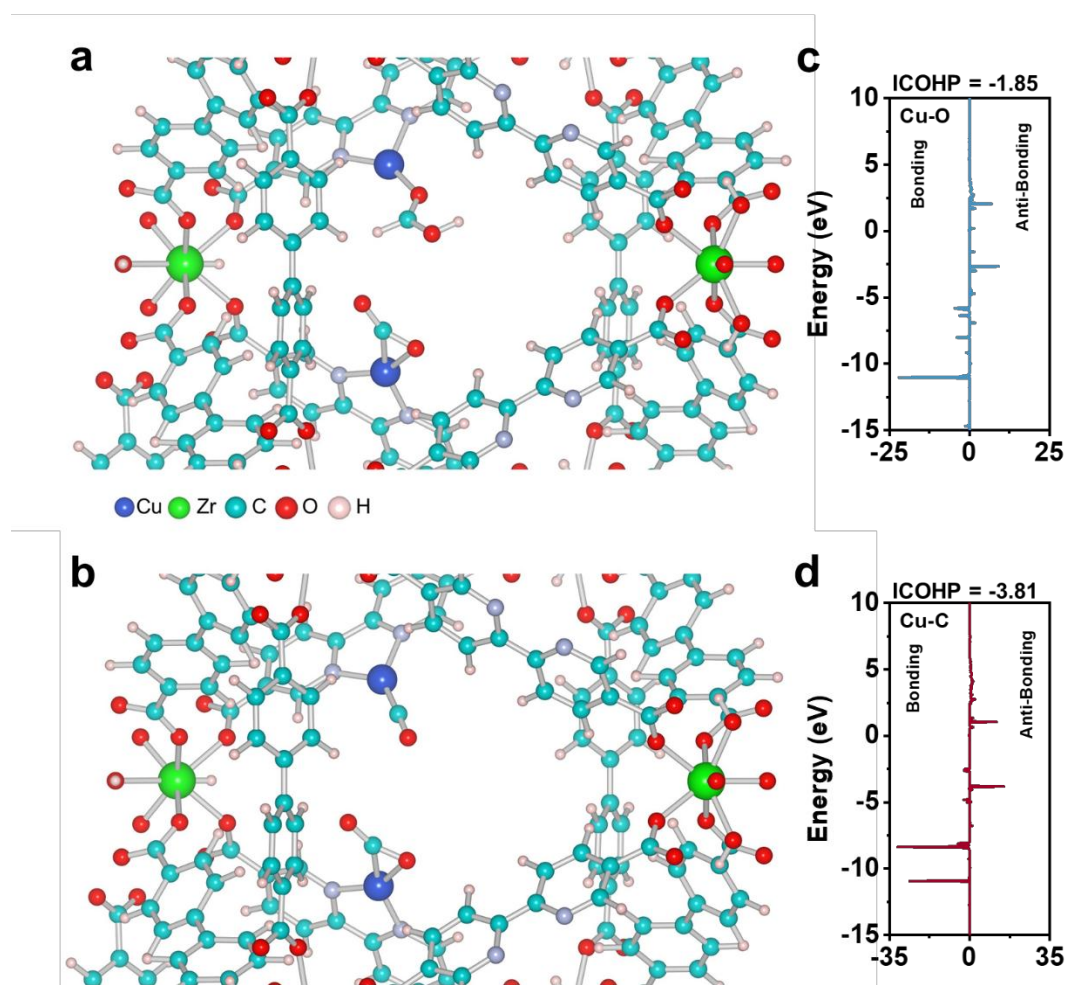


Fig. 3.24 DFT-optimized structures of (a) $^*\text{HCOOH}-^*\text{CO}_2$ and (b) $^*\text{CO}-^*\text{CO}_2$ on the UiO-Cu-1.0. Corresponding COHP analysis of (c) Cu-O bond for $^*\text{HCOOH}$ in $^*\text{HCOOH}-^*\text{CO}_2$, (d) Cu-C bond for $^*\text{CO}$ on $^*\text{CO}-^*\text{CO}_2$ in UiO-Cu-1.0.

We further analyzed the projected density of states (PDOS) of the orbitals involved in this synergistic cooperation between the two neighboring $\text{Cu}\cdots\text{Cu}$ motifs in UiO-Cu-1.0, as shown in **Fig. 3.25**. For UiO-Cu-0.50 (only 1 copper site, **Fig. 3.25a**), Cu exhibits greater orbital overlap with $^*\text{HCOOH}$ than with $^*\text{CO}$. Conversely, for UiO-Cu-1.0 (**Fig. 3.25b**), the PDOS reveals reduced overlap with $^*\text{HCOOH}$ orbital and enhanced overlap with $^*\text{CO}$ in the $^*\text{HCOOH}-^*\text{CO}_2$ and $^*\text{CO}-^*\text{CO}_2$ configurations. This observation confirms that the presence of adsorbed CO_2 enhances the interaction between $^*\text{CO}$ and the Cu site, thereby promoting the adsorption of $^*\text{CO}$. It is

noteworthy that $^*\text{CO}$ is a key coupling intermediate for the generation of C_{2+} products as discussed above. The charge density difference (**Fig. 3.26**) for $^*\text{CO}$ – $^*\text{CO}_2$ and $^*\text{CO}$ – $^*\text{COH}$ on UiO-Cu-1.0 further demonstrated significant electron transfer from CO_2 to the Cu sites, increasing the site's electron density. Both $^*\text{CO}$ and $^*\text{COH}$ intermediates exhibit notable electron-withdrawing behavior, promoting their adsorption and coupling, and thereby enhancing the generation of C_{2+} products.

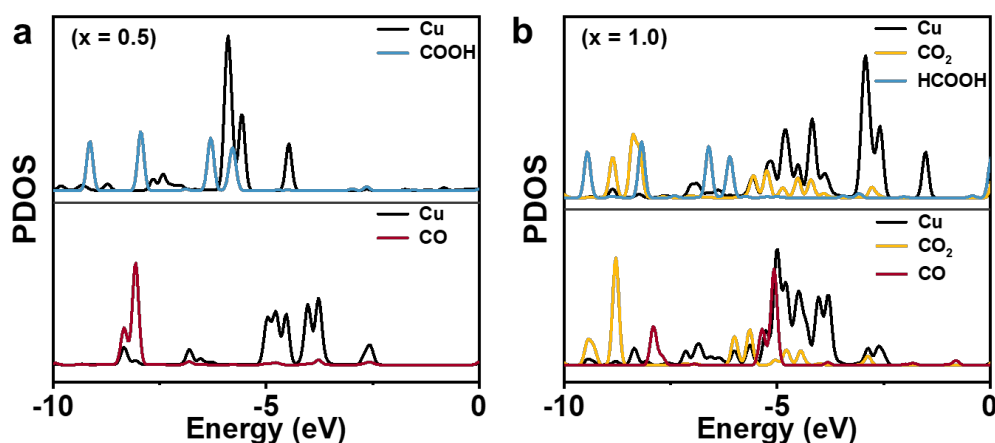


Fig. 3.25 PDOS analysis for (a) $^*\text{HCOOH}$ (top) and $^*\text{CO}$ (bottom) in UiO-Cu-0.50, (b) $^*\text{HCOOH}$ – $^*\text{CO}_2$ (top) and $^*\text{CO}$ – $^*\text{CO}_2$ (bottom) in UiO-Cu-1.0.

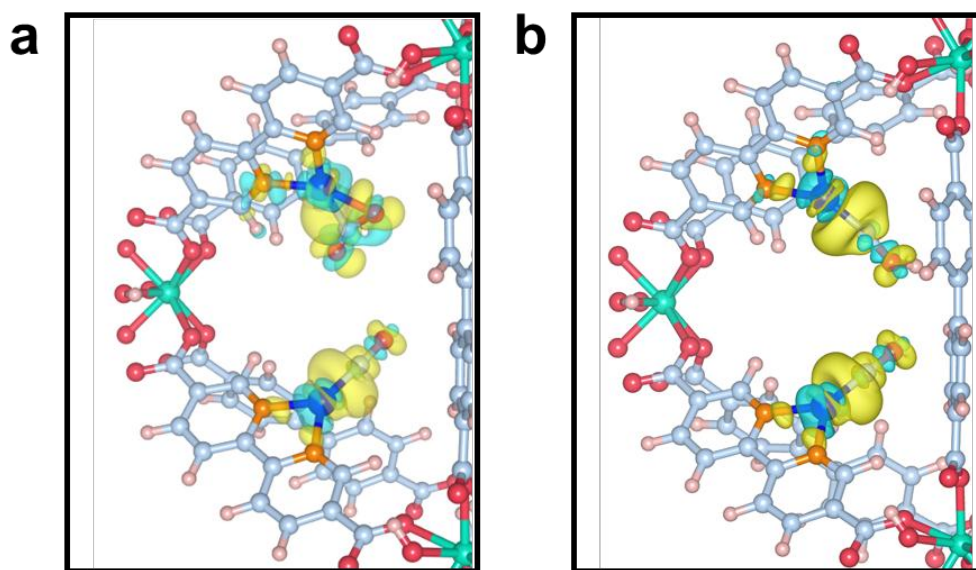


Fig. 3.26 Charge density difference illustration for (a) $^*\text{CO}$ – $^*\text{CO}_2$ and (b) $^*\text{CO}$ – $^*\text{COH}$

in UiO-Cu-1.0. The green area indicates a decrease in charge density, while the yellow area indicates an increase. Atoms are represented in the ball-and-stick model, with green, red, light blue, pink, and blue balls corresponding to Zr, O, C, H, and Cu, respectively.

By integrating our *in-situ* DRIFTS analysis and DFT calculation, we accordingly propose the following CO₂RR pathway (**Fig. 3.27**): Under light irradiation, UiO-Cu-*x* efficiently adsorbs CO₂, facilitating its activation into *CO₂ species. The *CO₂ species demonstrate enhanced stability in systems with higher copper distribution ($0.5 < x \leq 1.0$) compared to those with lower distribution ($x < 0.5$), thereby favoring its subsequent conversion to *COOH intermediates. It hence favors the subsequent C–C coupling step, likely progressing through key reaction steps: *HOOC–*CO₂, *OC–*CO₂, *OC–*COOH, and *OC–*CO, ultimately driving the selective formation of CH₃COOH. These results elucidate the mechanistic role of single-atomic copper distribution in directing reaction pathways, underscoring the importance of precisely engineered metal sites and their spatial distribution for optimizing C–C coupling efficiency and steering CO₂ conversion toward value-added C₂⁺ chemical products.

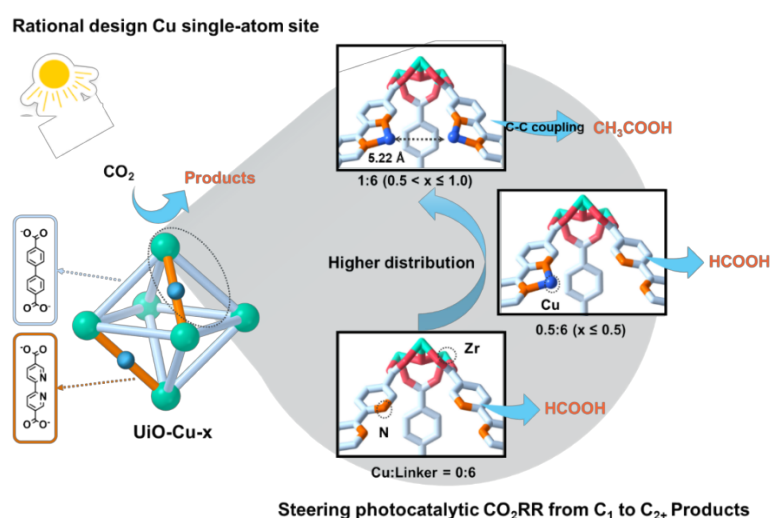


Fig. 3.27 Proposed CO₂RR mechanism on UiO-Cu-*x* catalysts.

3.4 Conclusion

In conclusion, we have successfully engineered a series of supported atomic copper sites catalyst (DACs) with well-controlled site distribution, enabling the selective steering between single-carbon and multi-carbon products from photocatalytic CO₂RR. This work ultimately enables the identification of UiO-Cu-1.0 as an effective catalyst for the selective production of CH₃COOH. Using UiO-67 as the support domain, our work underscores the pivotal role of **dual-atomic copper site** in dictating product selectivity. Both experimental and theoretical investigations reveal that an optimal concentration of copper for DACs formation not only promotes the C–C coupling pathway but also substantially reduces the energy barrier for the potential-determining step. The integration of copper sites into the UiO-67 domain advances our understanding of the mechanisms underlying CO₂ reduction and establishes a foundation for future research for designing supported DACs with diverse metal sites and support domain matrices. This study offers valuable insights into the development of advanced photocatalysts, enabling precise control over product selectivity through fine-tuning of metal site concentrations and leveraging the unique photochemical properties of MOFs.

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Chapter 4 Precise Modulation of 3d/3d Bimetallic Sites in Metal-Organic Framework for Photocatalytic CO₂ Reduction to Acetic Acid

4.1 Introduction

Carbon neutrality has emerged as a prominent social issue that has attracted widespread attention and intensive research interest. In recent years, significant progress has been made in the exploration and development of various techniques for the utilization and conversion of CO₂ into valuable carbonaceous products¹⁻³. Among these innovative strategies, photocatalytic CO₂RR has been considered as a highly promising and transformative technology for the efficient utilization of CO₂⁴⁻⁵. However, achieving high selectivity of high-value C₂₊ chemicals (such as CH₃COOH, CH₃CH₂OH etc.) over simple C₁ chemicals (e.g., CO, CH₄) remains a fundamental challenge, limiting the utility of this technique⁶⁻⁷. Thus, it is imperative to promote the design and development of state-of-the-art photocatalysts with exceptional selectivity, thereby expanding the frontiers and applications of CO₂RR.

Metal atom catalysts have become an emerging trend for the use of supported metal atom catalysts in energy conversion and chemical transformations due to their surface effects, and optimal atom utilization⁸⁻⁹. DACs represent an up-and-coming leading-edge technology in this field, offering synergistic effects, tailored electronic structures, and enhanced control over multi-step reactions¹⁰⁻¹¹. Unlike SACs, DACs offer tunable metal selectivity through adjacent metal sites, enabling precise modulation of reactant activation and intermediate absorption/desorption. This makes DACs particularly well-suited for multimolecular catalytic reactions. Precise design and control of the type and distribution of bimetallic sites is expected to improve both the efficiency and selectivity of C₂₊ product formation, providing a means to overcome the barriers associated with

C-C coupling in CO₂ reduction reactions.

3d transition metals (TMs) are uniquely suited for this role. Their distinctive electronic configurations ([Ar]3d^x4s²) provide variable oxidation states and exposed *d*-orbitals, facilitating dynamic redox behavior and diverse coordination environments, which are essential for catalytic versatility¹²⁻¹³. Despite their outstanding roles as active sites in 3d-TM-based CO₂RR systems, the mechanistic interaction between these metals and multi-electron pathways, especially for C₂₊ chemical selectivity, in particular, has still been under-explored.

To address this gap, we further engineered 3d-TM bimetallic sites within the UiO-67 matrix based on our work as described in **Chapter 3**, strategically pairing different metals to optimize acetate selectivity. We demonstrated that Cu-based DACs exhibit exceptional activity and selectivity for the photocatalytic reduction of CO₂ to acetate. In particular, UiO-FeFe, UiO-FeCu, UiO-CoCu, and UiO-CuCu bimetallic systems show the ability to convert CO₂ to acetic acid. While Co/Cu and Cu/Cu bimetallic system achieves remarkable selectivity for acetate (up to 90%) in the photocatalytic CO₂RR process. Through *in-situ* FTIR spectroscopy and DFT calculations, we found that synergistic interaction between metal site A and metal site B modulates the microenvironment of the catalyst, steering the electronic structure to optimize CO₂ adsorption and activation towards specific pathways. **Cu** and **Fe** SA are effective active sites for C–C coupling for C₂₊ products, whereas **Ni** and **Co** SA are less favorable for C₂₊ products formation. This work establishes a novel pathway for rational DAC design, advancing selective CO₂-to-acetate conversion.

4.2 Experimental Procedures

All of the reagents were purchased from Dieckmann Company (Acros, Macklin, Alfa

Aesar, and others) without further purification.

4.2.1 Synthesis of Metal-Bipyridine Complexes (Metal-bpy)

Complexes of Cu(II), Fe(III), and Co(II) with 2,2'-bipyridine-5,5'-dicarboxylic acid (H₂bpydc) were prepared as follows:

Metal precursor (1.1 mmol; copper(II) acetylacetonate, iron(III) acetylacetonate or cobalt(II) chloride hexahydrate) and H₂bpydc (1mmol) were dissolved methanol (50 mL) in a round-bottom flask. The mixture was stirred at 60 °C for 24 h. The resulting precipitate was isolated by centrifugation, washed sequentially with methanol and ethanol three times, and vacuum-dried overnight to yield the complexes denoted as Cu-bpy, Fe-bpy, and Co-bpy.

4.2.2 Attempted Synthesis of Ni-bpy

Synthesis of an analogous Ni(II)-bpy complex was attempted using nickel(II) nitrate (both anhydrous and hexahydrate), nickel(II) chloride (both anhydrous and hexahydrate), and nickel(II) bis(acetylacetonate) as metal precursors, following identical reaction conditions (1.1 mmol metal salt, 1 mmol H₂bpydc, 50 mL methanol, 60 °C, 24 h). However, X-ray fluorescence (XRF) elemental analysis of all resulting solids consistently revealed nickel content below 0.1 wt%. This indicates unsuccessful quantitative complexation of Ni(II) with the H₂bpydc ligand under these conditions.

4.2.3 Synthesis of UiO-M_A (Primary Metal Incorporation)

Zr-based MOFs with primary 3d-TM sites (UiO-M_A, M = Cu, Fe, or Co) were synthesized via a modified literature procedure:

ZrCl₄ (120 mg), biphenyl-4,4'-dicarboxylic acid (H₂bpdcc, 106 mg), H₂bpydc (11 mg), M-bpy complex (Cu-bpy: 22 mg; Fe-bpy: 21 mg; Co-bpy: 14 mg), and benzoic acid

(1.88 g) were dispersed in N,N-dimethylformamide (DMF, 16 mL) and ethanol (4 mL). The resulting mixture was ultrasonicated for 30 mins to ensure proper dispersion and then transferred to autoclave and heated at 120 °C for 24 h. The product was isolated by centrifugation, washed sequentially with DMF and methanol three times, and vacuum-dried overnight. Its theoretical molecular formula is $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpydc})(\text{bpdc})_5\text{M}_\text{A}$.

4.2.4 Synthesis of UiO- $\text{M}_\text{A}\text{M}_\text{B}$ (Secondary Metal Incorporation)

Dual-metal catalysts (UiO- $\text{M}_\text{A}\text{M}_\text{B}$, 3d-3d pairs) were prepared by anchoring secondary metals onto UiO- M_A as follows.

UiO- M_A (1 mmol) and a secondary metal salt (1 mmol; nickel(II) bis(acetylacetonate), copper(II) acetylacetonate, iron(III) acetylacetonate, or cobalt(II) chloride hexahydrate) were dispersed in 15 mL methanol. The suspension was stirred vigorously at 55 °C for 24 h. The product was isolated by centrifugation, washed with methanol three times, and vacuum-dried overnight. Its theoretical molecular formula is $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpydc})(\text{bpdc})_5\text{M}_\text{A}\text{M}_\text{B}$.

4.2.5 Synthesis of UiO-67 and UiO-67-bpy

The pristine UiO-67 framework was synthesized according to the procedure detailed in **Chapter 3.2**.

UiO-67-bpy was prepared analogously to UiO- M_A but without metal complexes: ZrCl_4 (120 mg), H_2bpdc (105.8 mg), H_2bpydc (21.2 mg), and benzoic acid (1.88 g) were dispersed in DMF/ethanol (16:4 v/v). Subsequent procedures (ultrasonication, heating, washing, drying) followed identical conditions to UiO- M_A synthesis.

4.3 Results and Discussion

4.3.1 Characterization and Atomic Structure of $\text{UiO-M}_\text{A}\text{M}_\text{B}$

$\text{UiO-M}_\text{A}\text{M}_\text{B}$ diatomic catalysts synthesis process is engineered through a sequential metal introduction strategy to precisely incorporate two distinct metal species into the UiO-67 matrix, as shown in **Fig. 4.1**. Briefly, we first tried to prepare metal-bipyridine complexes for immobilizing metal A (M_A) into the H_2bpydc via wet impregnation. This approach has successfully incorporated Fe, Co, and Cu metal atoms into the linkers' structure. However, attempts to introduce Ni have proven consistently unsuccessful. We made extensive efforts to overcome this limitation, including testing various nickel metal salts with different oxidation states, and modifying synthetic conditions (e.g., solvent, temperature, reaction time). Despite these optimizations, Ni incorporation remained unachievable. This persistent failure is possibly related to the electronic configuration of the Ni atom itself. The successful metal-bipyridine complexes will combine with other precursors to form single-atom catalysts (SACs, UiO-M_A) with atomically dispersed metal A sites by hydrothermal synthesis. At the same time, the UiO-M_A incorporates bipyridine-containing H_2bpydc linkers, partially substituted for the original H_2bpdc linker, resulting in the UiO-M_A with a molar ratio of $\text{M}_\text{A}\text{-bpy}$ to H_2bpydc of 1:1. Subsequently, metal B was anchored to the bpydc linker via secondary impregnation, forming the target $\text{UiO-M}_\text{A}\text{M}_\text{B}$ dual-atom system (DACs) with precise spatial separation of metallic components.

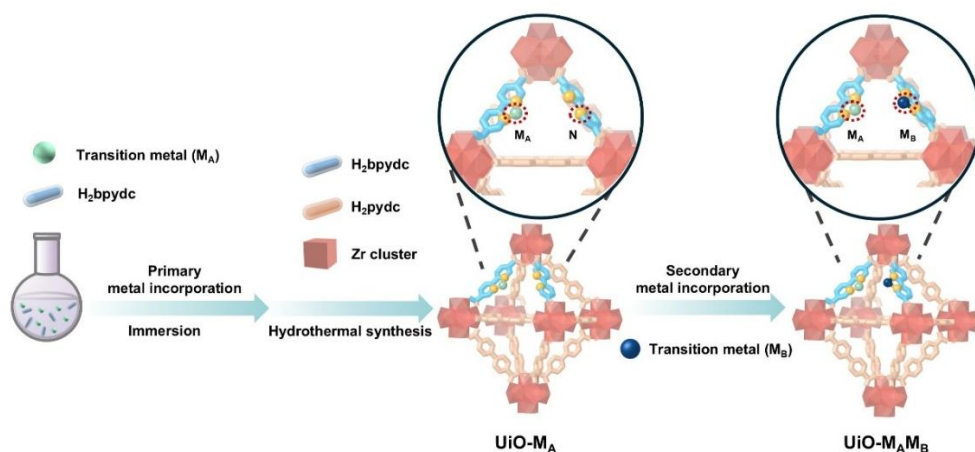


Fig. 4.1 Schematic representation of the synthetic process for UiO-M_AM_B.

We first conducted morphological analysis of UiO-M_AM_B using SEM and TEM technology. As shown in **Fig. 4.2** and **Fig. 4.3**, the metalated samples retain a uniform octahedral structure, indicating that metal incorporation does not destroy the framework of UiO-67. The pristine UiO-67, UiO-FeM_B, UiO-CuM_B exhibit an average particle size of approximately 300 nm, whereas UiO-CoM_B has an average size of only approximately 100 nm, with particle size inhomogeneity accompanying. This size discrepancy likely arises because Co-bpy influences UiO-Co hydrothermal crystal growth, favoring the formation of additional crystal nuclei over growth on existing crystals. Both SEM and TEM images revealed no metal aggregation on the catalyst's surface. Furthermore, TEM coupled with elemental mapping confirmed homogeneous metal distribution within the framework, revealing the successful bimetallic incorporation (**Fig. 4.4-4.6**).

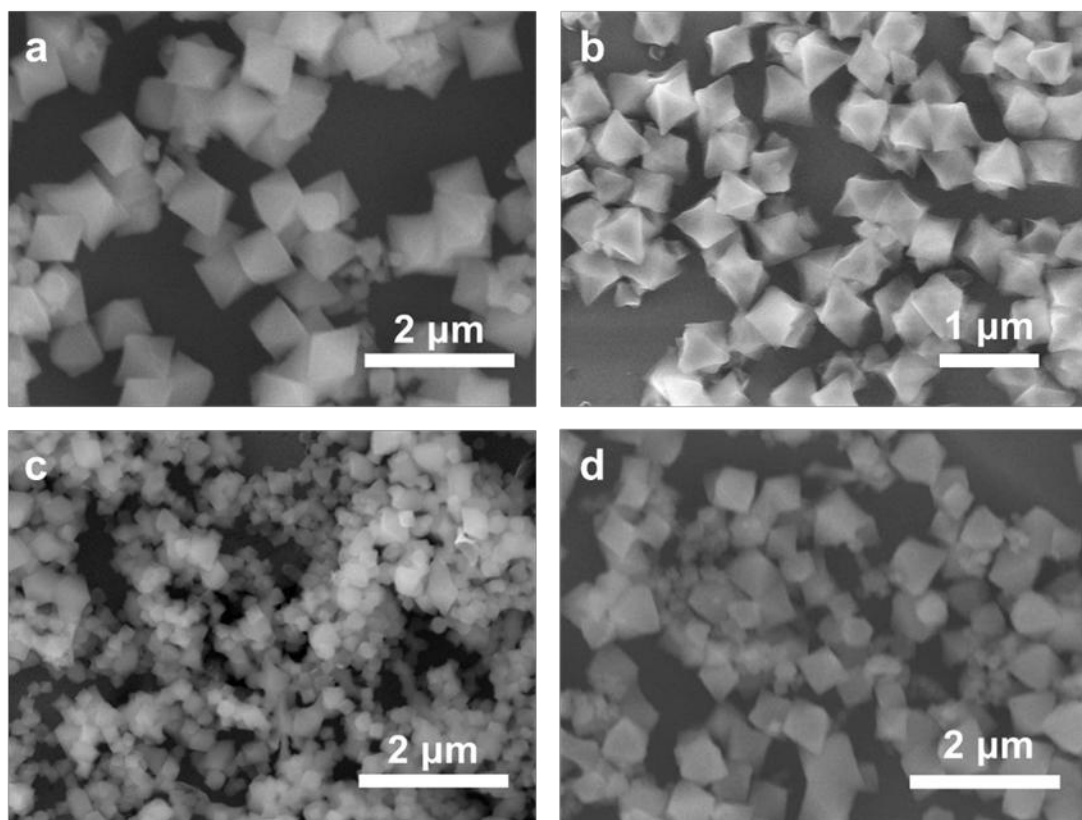


Fig. 4.2 SEM images of (a) UiO-67, (b) UiO-Fe, (c) UiO-Co, and (d) UiO-Cu.

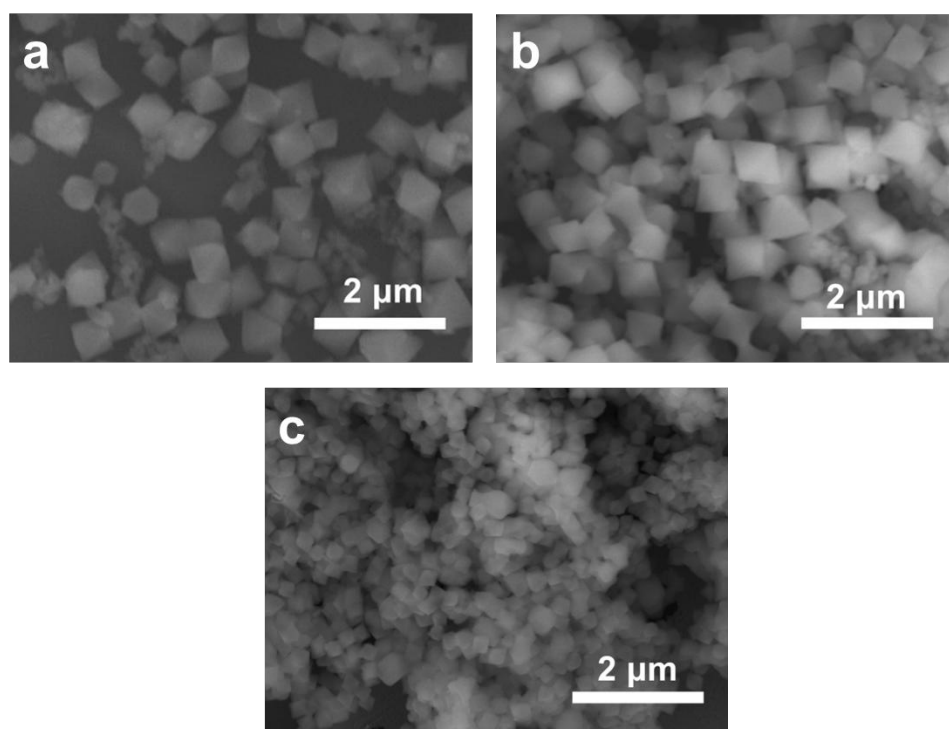


Fig. 4.3 SEM images of (a) UiO-FeCu, (b) UiO-CuNi, and (c) UiO-CoFe.

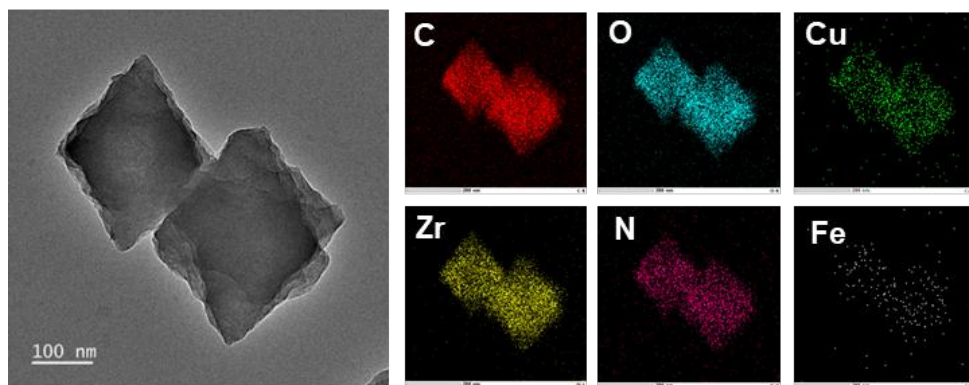


Fig. 4.4 TEM images and their element mapping of UiO-FeCu.

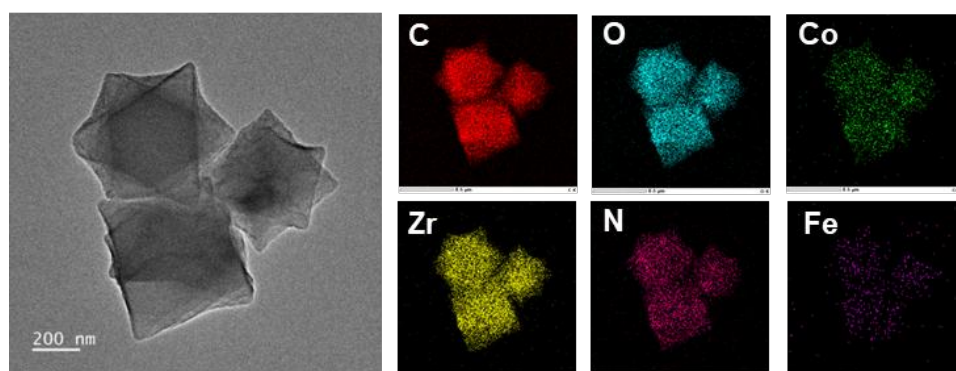


Fig. 4.5 TEM images and their element mapping of UiO-CoFe.

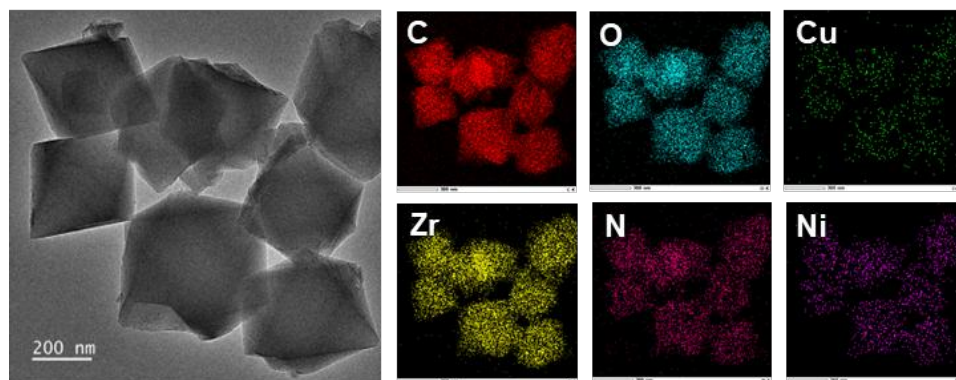


Fig. 4.6 TEM images and their element mapping of UiO-CuNi.

The PXRD analysis (**Fig. 4.7**) further confirmed the structural integrity and high crystallinity of all synthesized samples. Detailed crystallographic parameters will be analyzed in the subsequent synchrotron XRD section. XRF quantification (**Table 4.1**) demonstrated tunable metal A/B ratios ranging between 30% and 70%, consistent with the intended design.

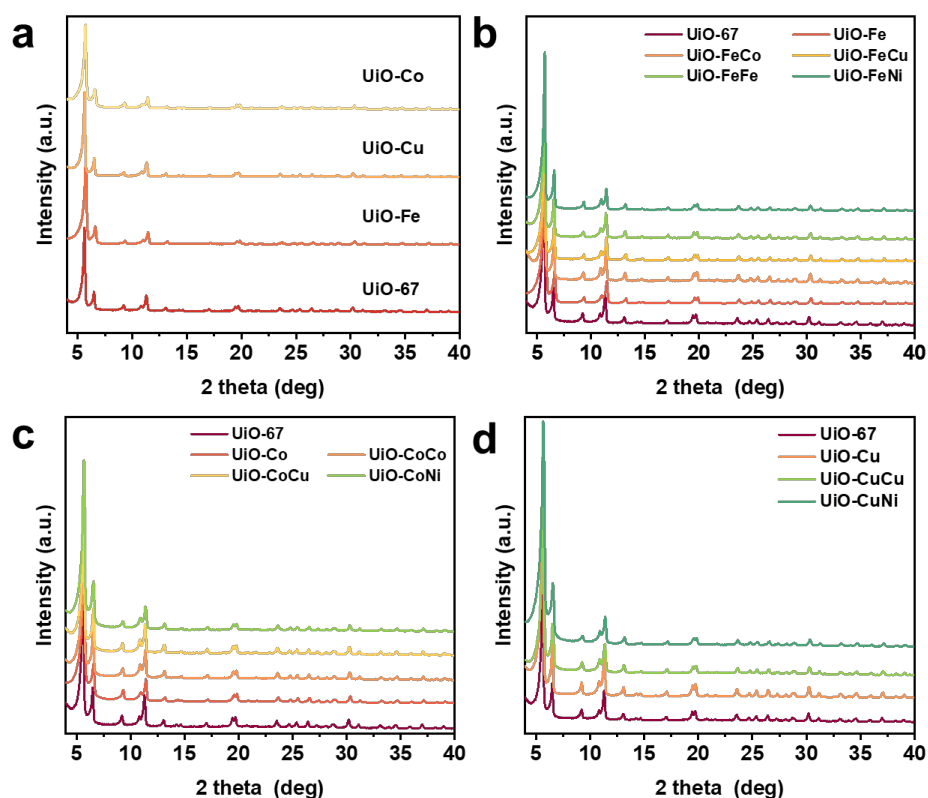


Fig. 4.7 XRD patterns for (a) UiO-67, UiO-Fe, UiO-Cu and UiO-Co, (b) UiO-FeM_B series, (c) UiO-CoM_B series, and (d) UiO-CuM_B series.

Table 4.1. Element contents of as-prepared samples from XRF analysis.

Sample (UiO-M _A M _B)	element			Atomic ratio Zr : M _A : M _B
	Zr (weight%)	M _A (weight%)	M _B (weight%)	
UiO-Fe	23.35	1.39	-	1:0.10
UiO-Cu	25.33	1.53	-	1:0.09
UiO-Co	32.87	1.46	-	1:0.07
UiO-FeCu	34.42	1.02	0.76	1:0.05:0.03
UiO-CoCu	38.76	1.27	3.76	1:0.07:0.07
UiO-CoNi	37.42	1.39	2.00	1:0.06:0.08
UiO-CuNi	36.62	1.07	2.59	1:0.05:0.10

The chemical composition and surface chemical state of the as-prepared sample were investigated by XPS (**Fig. 4.8**). Using UiO-CoCu as a representative UiO-M_AM_B, XPS survey spectra were collected for UiO-67, UiO-Fe, UiO-Co, UiO-Cu and UiO-CoCu. All spectra align well with previously reported patterns^{14, 15}. However, due to the extremely low content of metal elements, characteristic binding energy signals for metals were not detectable in the elemental spectra. Analysis of other elements revealed no significant shifts in the Zr 3*d*, O 1*s*, or C 1*s* characteristic peaks, confirming the structural integrity of the UiO-67 matrix. It is observed that a slight positive increase peak (~ 400 eV) in N 1*s* characteristic peak, attributed to electrons transfer toward the anchored metal sites (**Fig. 4.8d**)^{16, 17}. This observation of electron transfer confirms the successful metal introduction into the bpydc linker of the UiO-67 matrix.

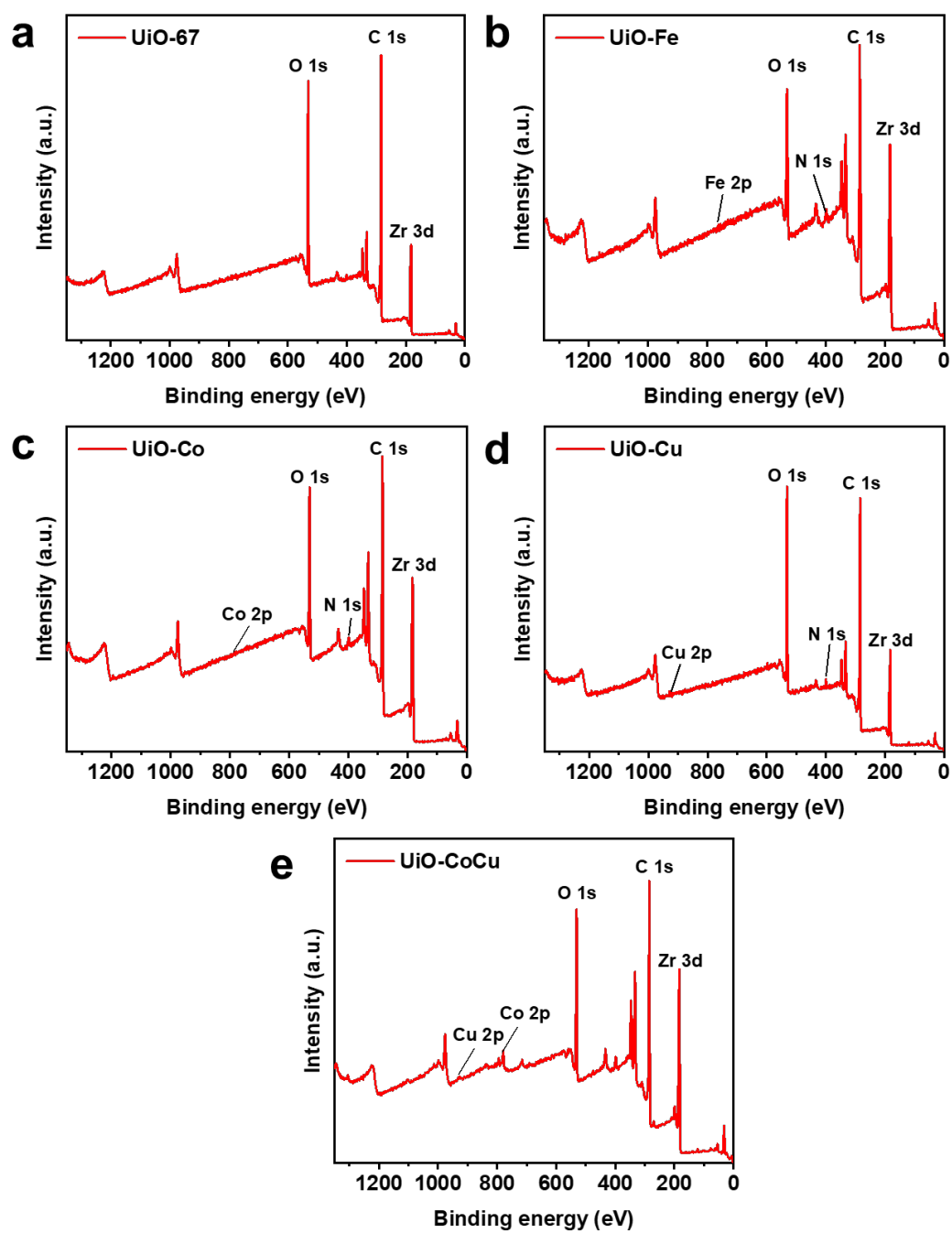


Fig. 4.8 XPS survey spectrum of (a) UiO-67, (b) UiO-Fe, (c) UiO-Co, (d) UiO-Cu, and (e) UiO-CoCu.

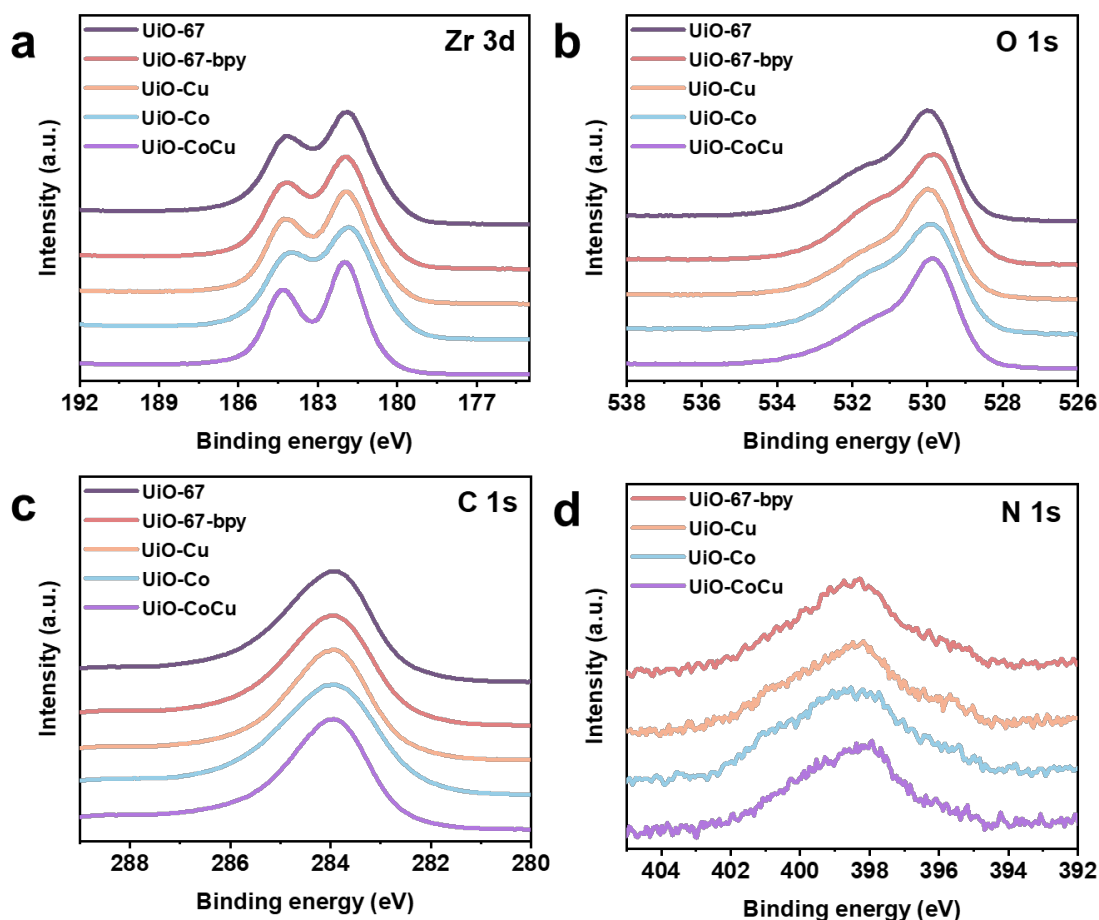


Fig. 4.9 Element spectrum of XPS (a) Zr 3d, (b) O 1s, (c) C 1s, and (d) N 1s of UiO-67, UiO-bpy, UiO-Cu, UiO-Co, and UiO-CoCu.

The thermal stability of the UiO-M_AM_B was evaluated by TGA. As shown in **Fig. 4.10**, pristine UiO-67 exhibited a broad decomposition peak at 140 °C, attributed to solvent release from hydrothermal synthesis¹⁸⁻¹⁹. UiO-Fe displayed a similar profile, while UiO-Cu showed a slight shift to higher temperature (~145 °C), likely due to stronger solvent affinity at Cu sites. In contrast, bimetallic UiO-FeCu revealed two distinct decomposition peaks at approximately 170 °C and 260 °C. Combined with mass loss analysis, these two decomposition peaks probably arise from the solvent affinity at the bimetallic active site and slowed solvent release kinetics due to metal-metal interactions. In addition, we pretreated the UiO-FeCu by heating at 120 °C under vacuum for 24 hours to remove all the solvent from the framework. Subsequently, the pre-treated

sample was exposed to CO₂. Finally, both samples were analyzed using TGA to investigate the thermal stability of CO₂ (Fig. 4.11). Compared to the pristine and CO₂-pre-adsorbed UiO-FeCu and the sample, the TGA decomposition profile of pre-treated UiO-FeCu showed minimal fluctuations, with the derivative weight percentage remaining below 1%. After CO₂ absorption, the TGA decomposition profile of UiO-FeCu also exhibited two decomposition peaks at approximately 100 and 225 °C, corresponding to the release of CO₂. These results demonstrate the framework's thermal stability and reveal enhanced affinity at bimetallic sites.

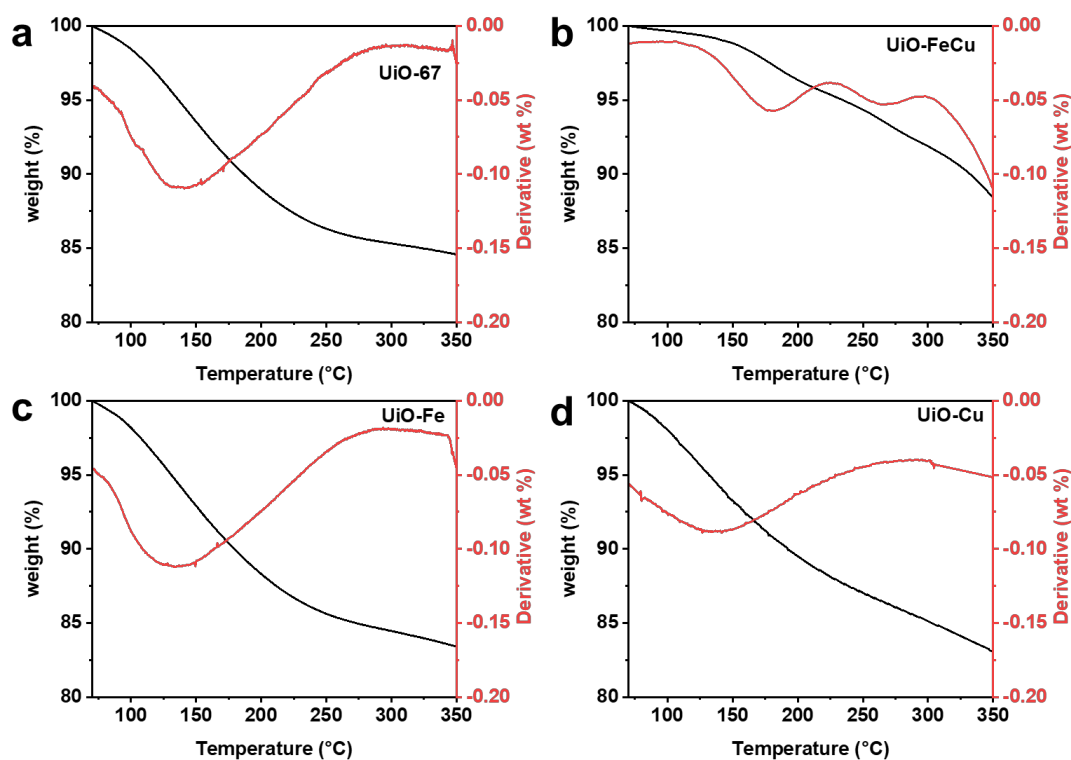


Fig. 4.10 TGA profiles of (a) UiO-67, (b) UiO-FeCu, (c) UiO-Fe, and (d) UiO-Cu.

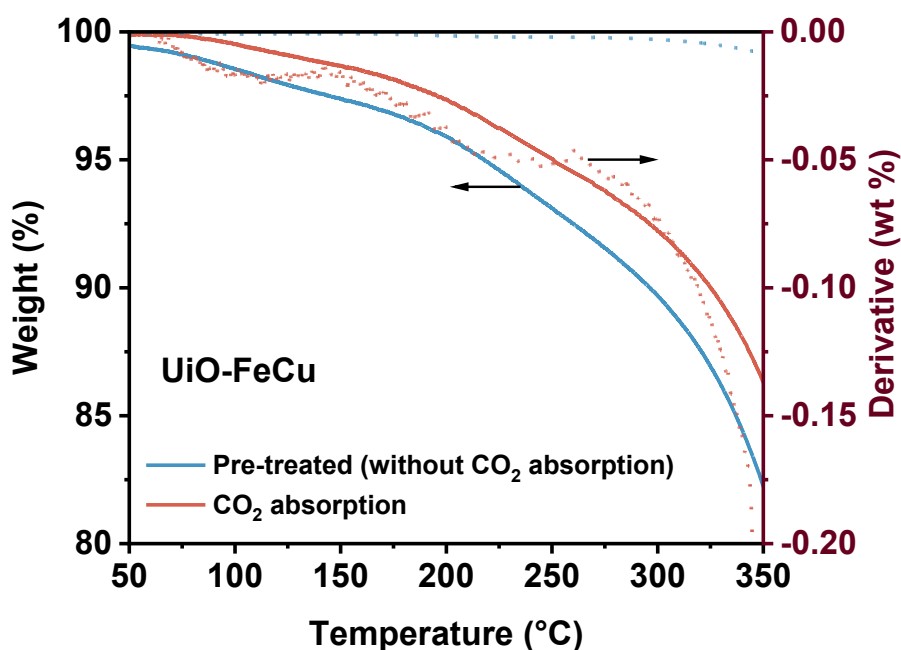


Fig. 4.11 TGA profiles of pristine UiO-FeCu and with CO₂ adsorption.

The location coordination environment of metal centers in UiO-M_AM_B was investigated using EXAFS spectra. To distinguish different atoms within the atomic shell, WT analysis was applied. This method correlates k- and R-space data to identify the centers of backscattering wavefunctions, as shown in **Fig. 4.12-4.14**. For both metal elements, the WT-EXAFS data displayed a dominant lobe centered at $k \approx 6.0 \text{ \AA}^{-1}$, $R \approx 1.6 \text{ \AA}$, corresponding to the M–N(O) backscattering paths. Crucially, no WT intensity was observed for M–M backscattering paths (expected at $k > 10.0 \text{ \AA}^{-1}$, $R > 2.5 \text{ \AA}$) in any samples. This absence indicates that the metal species within UiO-67 exist as dispersed single atoms, without forming metallic clusters or alloys. The R-space Fourier transforms of the metal K-edge EXAFS spectra also support this result, showing distinct peaks at approximately $1.7 \text{ \AA}$, attributable to the M–N/O bond distance, as illustrated in **Fig. 4.12c,d-4.14c,d**. Due to the similar electron densities of nitrogen and oxygen atoms, distinguishing their respective bonds in the EXAFS spectrum proved challenging. To further analyze the metal coordination environment, quantitative fitting

of the EXAFS data was performed, with results summarized in **Table 4.2**. For UiO-FeCu, the Fe–N(O) pathway has a bond length of approximately 2.01 Å with a coordination number of 5.4, while the Cu–N(O) pathway has a bond length of about 1.97 Å with a coordination number of 4.1. These results suggest that both Fe and Cu atoms are anchored to nitrogen sites on the H₂bpydc ligand, with additional coordination to water or hydroxyl species, where the Fe center exhibits four coordination numbers and the Cu center shows two coordination numbers to these species. Similarly, for UiO-CoCu and UiO-CoNi, the Co centers have coordination numbers of 4.8 and 5.0, respectively, and the Ni center in UiO-CoNi has a coordination number of 5.9, indicating the presence of four coordination numbers to water/hydroxyl species at these metal centers, which is influenced by the electronic configurations of the respective metal elements.

We utilized the quantitative fitting of the EXAFS data for further analysis of the metal coordination environment (**Table 4. 2**). Using UiO-FeCu as example, quantitative curve fitting results indicate consistent Fe–N(O) and Cu–N(O) path lengths of *ca.* 2.01 Å and 1.97 Å, with a coordination number of 5.4 and 4.1. It is supposed that Fe and Cu anchor with N site on the H₂bpydc and with certain coordinated water/hydroxyl species, which is four coordination in the Fe center and two coordination in the Cu center. For the Co center in UiO-CoCu and UiO-CoNi, and the Ni center in UiO-CoNi, the coordination number is 5.5, 5.0, and 5.9, which also revealed the extra four-coordinate water/hydroxyl species in the metal center. The specific coordination number for each metal is probably related to its electronic configuration. Collectively, these atomic-resolution structural results provide compelling evidence that the introduced metals exist as isolated single atoms within the UiO-67 matrix, consistent with the findings above.

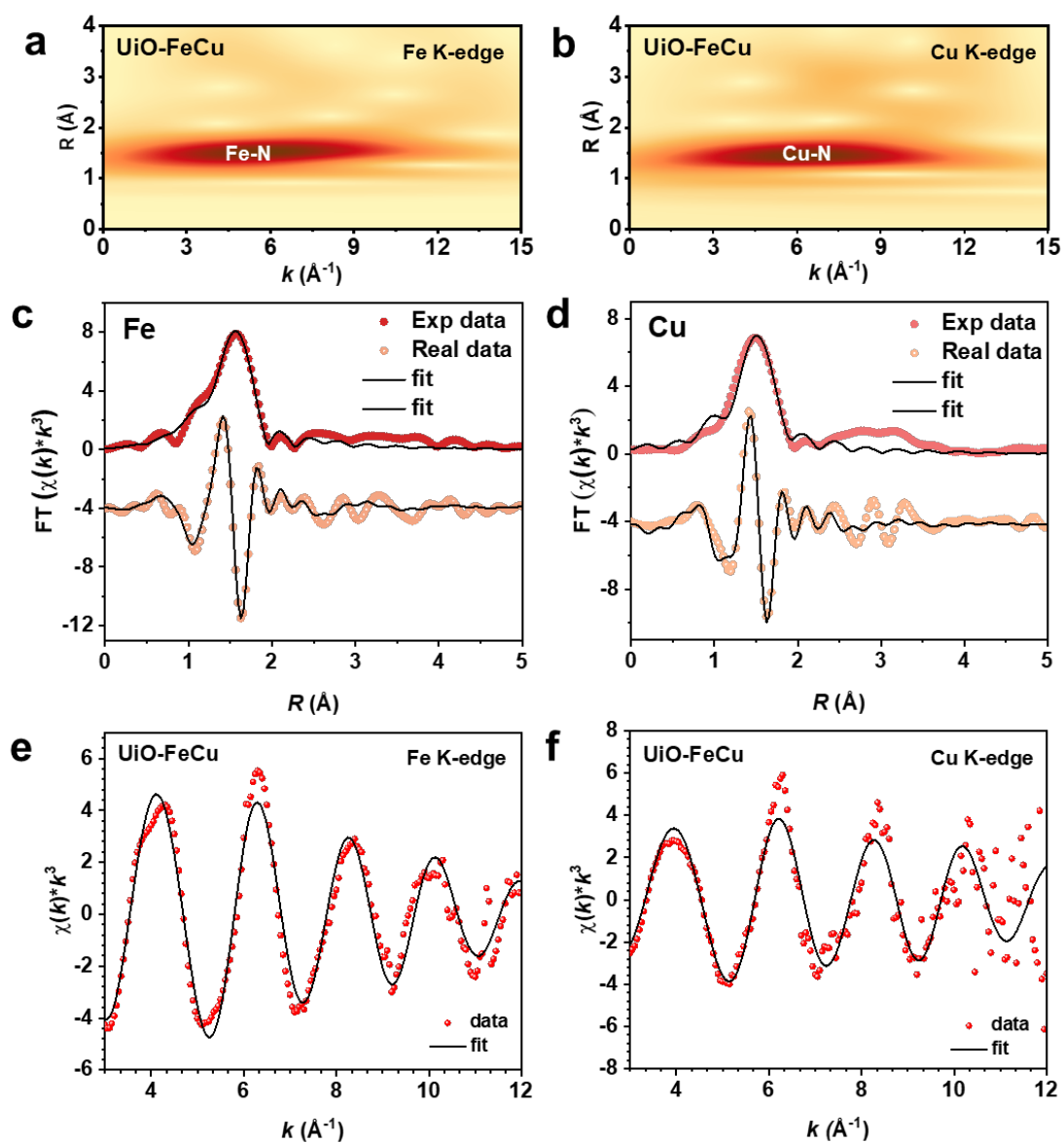


Fig. 4.12 (a, b) Wavelet transform plots of k^3 weighted EXAFS signal, using Morlet wavelet with $\kappa = 10$, $\sigma = 1$, (c, d) EXAFS in R-space representations ($|\chi(R)|$ and $\text{Re}[\chi(R)]$ parts) and (e, f) in k-space of the Fe and Cu K-edge of UiO-FeCu.

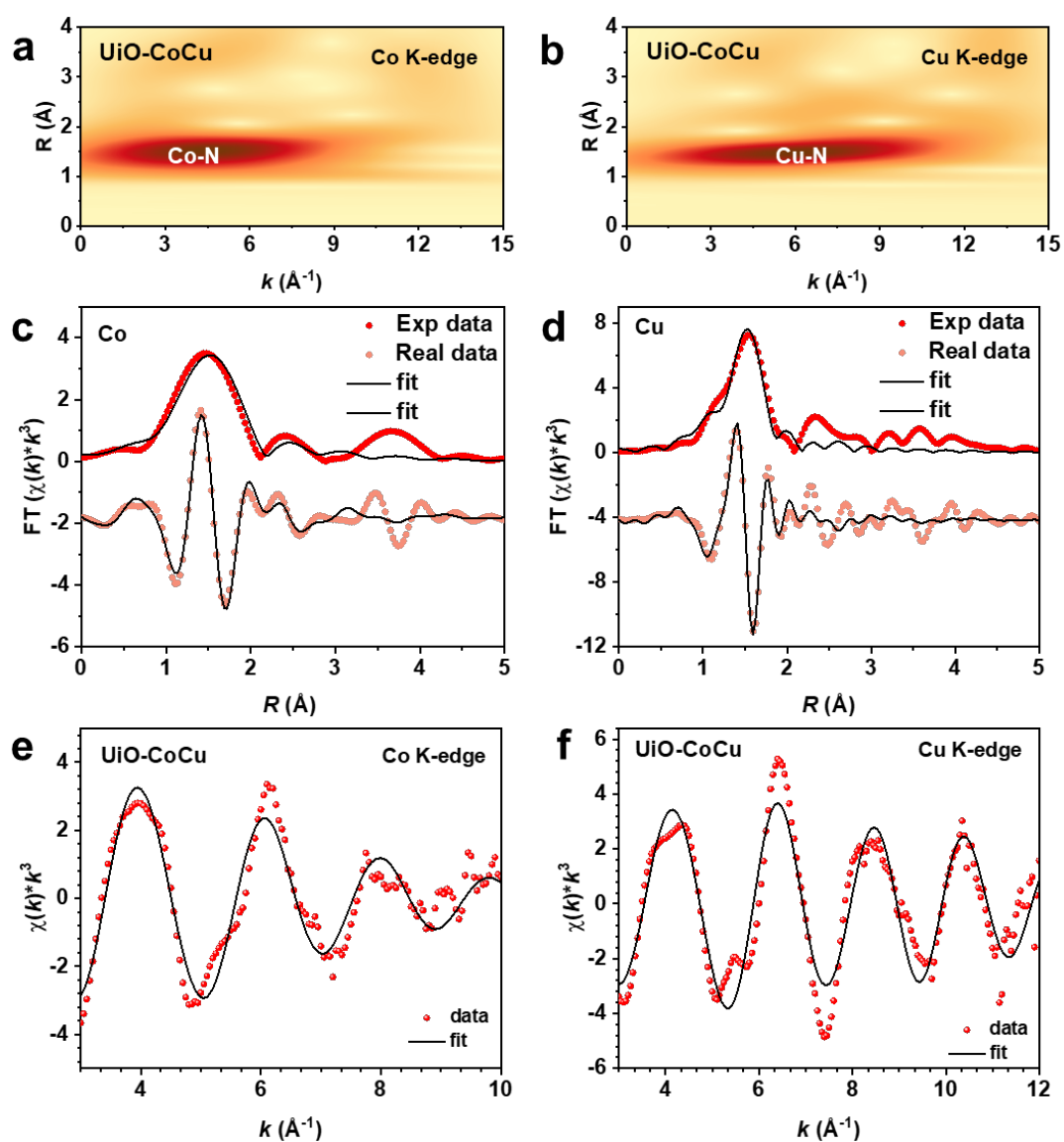


Fig. 4.13 (a, b) Wavelet transform plots of k^3 weighted EXAFS signal, using Morlet wavelet with $\kappa = 10$, $\sigma = 1$, (c, d) EXAFS in R-space representations ($|\chi(R)|$ and $\text{Re}[\chi(R)]$ parts) and (e, f) in k-space of the Co and Cu K-edge of UiO-CoCu.

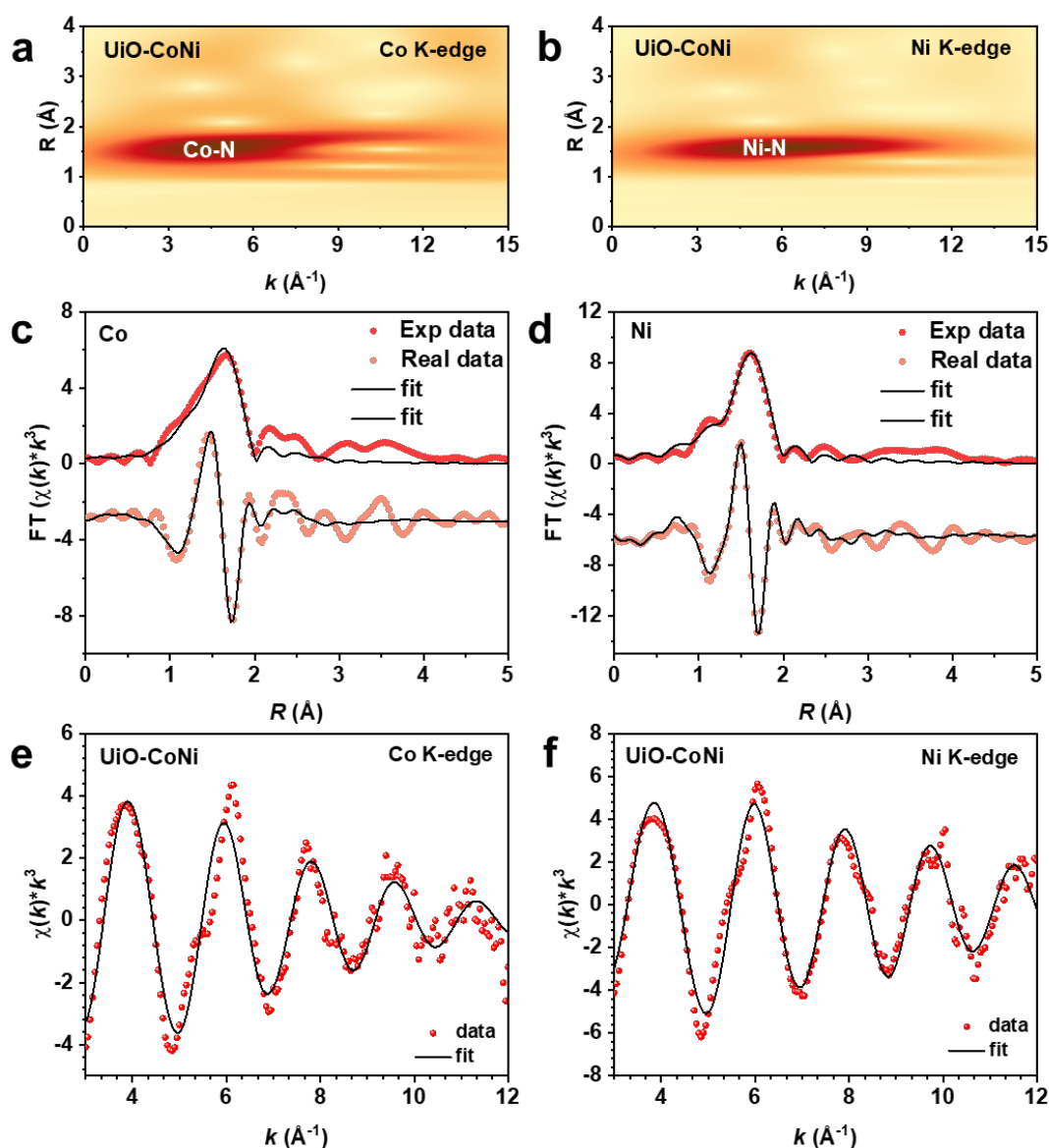


Fig. 4.14 (a, b) Wavelet transform plots of k^3 weighted EXAFS signal, using Morlet wavelet with $\kappa = 10$, $\sigma = 1$, (c, d) EXAFS in R-space representations ($|\chi(R)|$ and $\text{Re}[\chi(R)]$ parts) and (e, f) in k-space of the Co and Ni K-edge of UiO-CoNi.

Table 4.2. Curve fitting parameters for metal K-edge EXAFS for UiO-M_AM_B.

Sample	Path	<i>N</i>	<i>R</i> / Å	σ^2 / Å ²	ΔE_0	R-factor	k range
UiO-FeCu	Fe–N(O)	5.4(4)	2.01(1)	0.006(1)	-5.7(8)	0.007	3-12.0
	Cu–N(O)	4.1(5)	1.97(1)	0.003(1)	-8.1(16)	0.020	3-11.4
UiO-CoCu	Cu–N(O)	3.6(4)	1.94(1)	0.003(1)	-4.3(17)	0.015	3-13
	Co–N(O)	5.5(2)	2.04(1)	0.011(3)	-7.3(4)	0.011	3-8
UiO-CoNi	Co–N(O)	5.0(4)	2.12(1)	0.008(2)	-2.5(7)	0.008	3-12
	Ni–N(O)	5.9(1)	2.06(1)	0.005(1)	-7.1(2)	0.002	3-12

S_0^2 was fixed as 0.9. ΔE_0 is refined as a global fit parameter.

Data range: $1.0 \leq R \leq 2.5$ -3.0 Å.

σ^2 is the Debye-Waller factor (a measure of thermal/lattice vibrations of atoms).

High-resolution synchrotron PXRD analysis was employed to further investigate the atomic crystal structures of the samples. The crystallographic parameters, along with their refinement profiles for the as-prepared samples, are displayed in **Fig. 4.15 – 4.20 and Table 4.3 – 4.10**. All synthesized samples exhibit a cubic lattice with the space group of $Fm\bar{3}m$. The lattice parameter remained relatively constant at *ca.* 26.8 Å, showing insignificant fluctuations ($\sim 0.01\%$) upon incorporation of 3d transition metal species. It is confirmed that the introduction of metal species has marginal effect on the framework of UiO-67. Furthermore, no additional Bragg peaks corresponding to elemental metal or metal oxides were observed, indicating the absence of crystalline aggregates, consistent with the above studies.

The intensity and position of Bragg peaks in PXRD are usually used to estimate the crystallization of samples. As a representative example, the (111) reflection ($2\theta \approx 2.71^\circ$) in **Fig. 4.15** shows the variation in their intensities, attributed to the significant alterations in the scattering factors resulting from different metal atom pairs. For the

position of the Bragg peak, it is related to the symmetry peaks of the MOF structure²⁰. Most samples maintain high symmetry (peak asymmetry parameter of 0.0001), indicating a high degree of homogeneity²¹. In contrast, UiO-FeCo exhibits a slight peak shift toward the higher 2θ regime, causing the increasing value of the peak asymmetry parameter, likely due to metal effects or material instability. These findings suggest that metalation proceeds uniformly throughout the MOF framework, yielding consistent distributions of metal-active sites. Quantitative analysis of the synchrotron PXRD data further provided LVol, micro-strain, and ϵ_0 . These were calculated from FWHM and IB values using a Voigt function to model intermediate crystallite size broadening, ensuring reliable data for refinement.

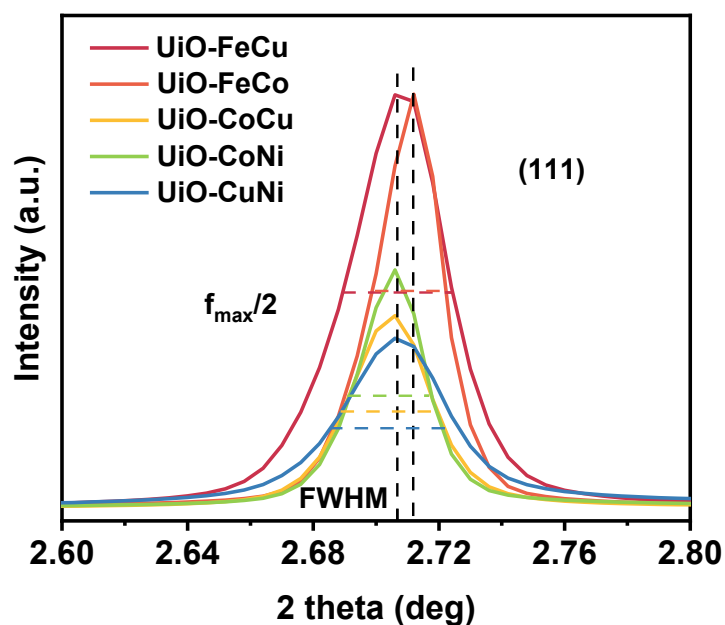


Fig. 4.15 Comparison of the Bragg peak (111) over UiO-FeCu, UiO-FeCo, UiO-CoCu, UiO-CoNi and UiO-CuNi. The synchrotron PXRD data were collected on Beamline BL02B2 at SPring-8.

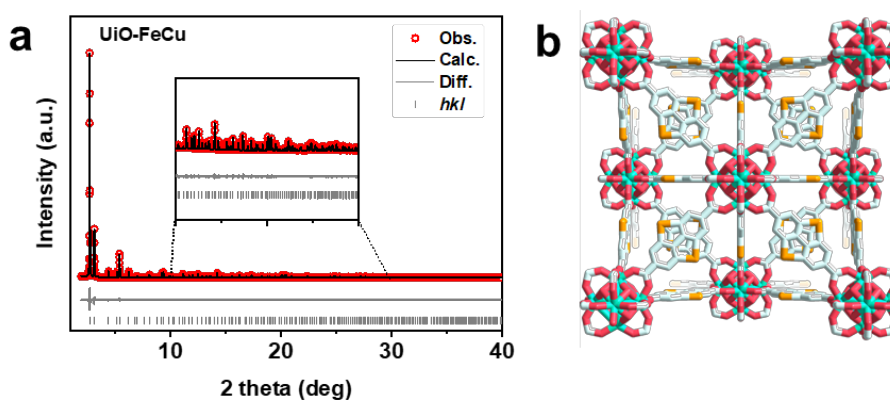
Table 4.3. Quantitative peak parameters of samples from synchrotron PXRD.

	UiO- FeCu	UiO- FeCo	UiO- CoCu	UiO- CoNi	UiO- CuNi
Peak asymmetry parameter	0.0001	0.0001	0.0001	0.0001	0.0001
LVol-Integral breadths	87.4	258.8	184.8	150.7	111.3
LVol-FWHM	103.1	360.8	206.2	197.6	155.3
Microstrain (ϵ_0) *	0.00004	0.00070	0.00004	0.00004	0.00004
Strain (Gaussian)	0.00010	0.00010	0.00010	0.00010	0.00010
Strain (Lorentzian)	0.00010	0.00282	0.00010	0.00010	0.00010

LVol – Volume weighted mean column heights.

ϵ_0 – dislocations, vacancies, and other defects, calculated from FWHMs.

The Rietveld refined crystal structures of the samples, guided by the above structural analyses, are depicted in **Fig. 4.16 – 4.20** and **Table 4.4 – 4.10**. The low R_{wp} value and a small difference between the experimental data and the refinement profiles were used to decide the quality of Rietveld refinement²². To ensure refinement reliability, the SOF of the metal sites was fixed based on the XRF elemental analysis results. In the simulated Rietveld-refined crystal structures, the metal atoms were anchored to the N moieties of the bpydc linkers, with SOF values ranging from 0.13 to 0.15.

**Fig. 4.16** (a) High-resolution synchrotron PXRD patterns collected on Beamlane

BL02B2 at SPring-8 ($\lambda = 0.729589 \text{ \AA}$) and the corresponding Rietveld refinement profiles of UiO-FeCu, and **(b)** the respective Rietveld refined crystal structure.

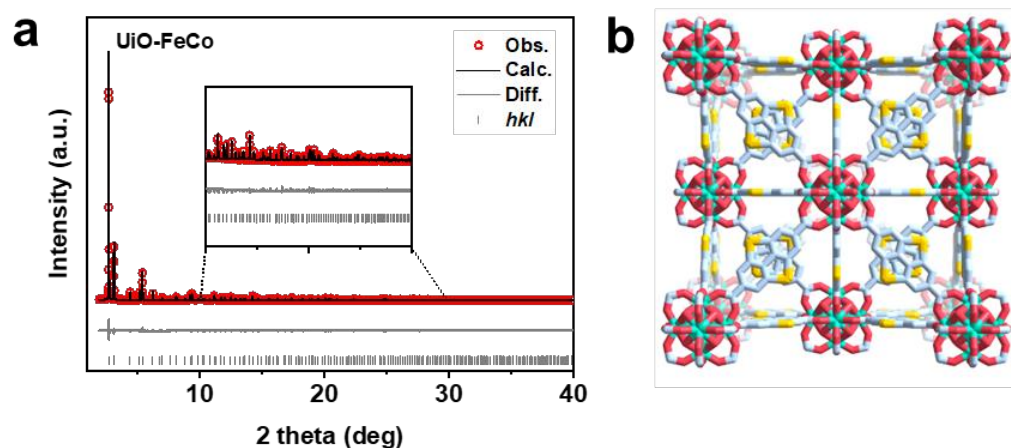


Fig. 4.17 (a) High-resolution synchrotron PXRD patterns collected on Beanline BL02B2 at SPring-8 ($\lambda = 0.729589 \text{ \AA}$) and the corresponding Rietveld refinement profiles of UiO-FeCo, and **(b)** the respective Rietveld refined crystal structure.

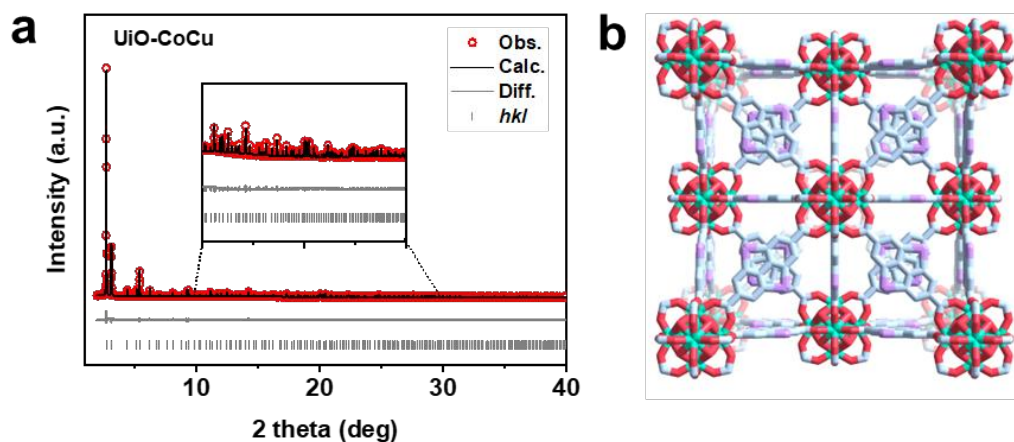


Fig. 4.18 (a) High-resolution synchrotron PXRD patterns collected on Beanline BL02B2 at SPring-8 ($\lambda = 0.729589 \text{ \AA}$) and the corresponding Rietveld refinement profiles of UiO-CoCu, and **(b)** the respective Rietveld refined crystal structure.

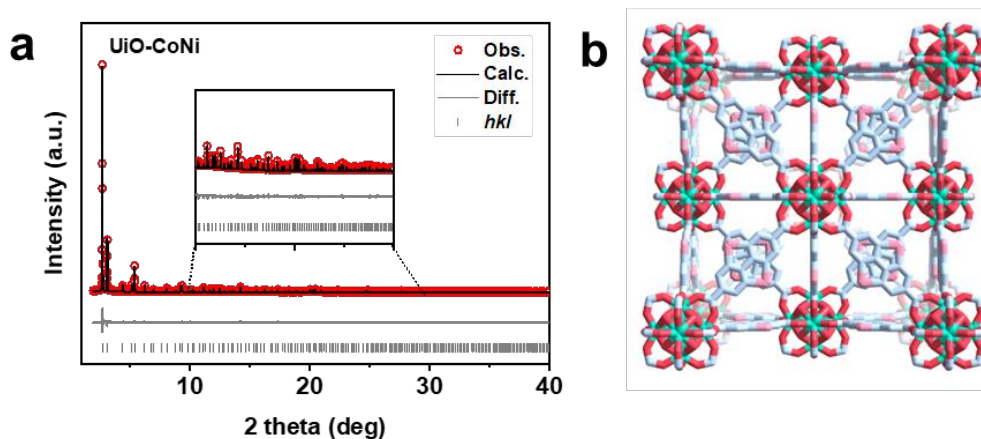


Fig. 4.19 (a) High-resolution synchrotron PXRD patterns collected on Beanline BL02B2 at SPring-8 ($\lambda = 0.729589 \text{ \AA}$) and the corresponding Rietveld refinement profiles of UiO-CoNi, and (b) the respective Rietveld refined crystal structure.

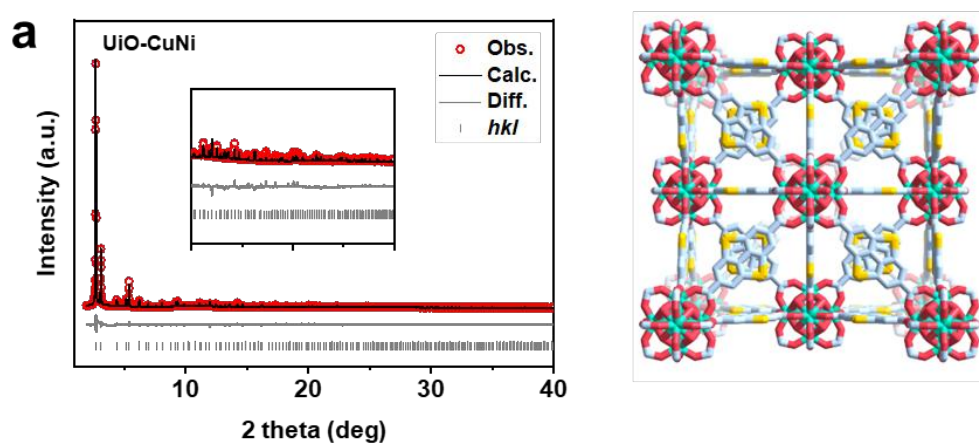


Fig. 4.20 (a) High-resolution synchrotron PXRD patterns collected on Beanline BL02B2 at SPring-8 ($\lambda = 0.729589 \text{ \AA}$) and the corresponding Rietveld refinement profiles of UiO-CuNi, and (b) the respective Rietveld refined crystal structure.

Table 4.4. Crystallographic data of the synchrotron PXRD measurements of UiO-FeCu, UiO-FeCo, and UiO-CoCu.

	UiO-FeCu	UiO-FeCo	UiO-CoCu
X-ray energy (keV)	16.99	16.99	16.99
Wavelength (Å)	0.729589	0.729589	0.729589
2θ-zero point (°)	-0.00019	-0.00019	-0.00019
Space group	$Fm\bar{3}m$	$Fm\bar{3}m$	$Fm\bar{3}m$
Crystal system	Cubic	Cubic	Cubic
a (Å)	26.81400	26.80590	26.83294
2θ range for refinement (°)	1.95-78	1.95-70	1.95-78
Number of parameters	47	42	41
Number of <i>hkl</i> s	2617	2015	2624
Refinement methods	Rietveld	Rietveld	Rietveld
R _{wp} /R _{exp} /R _p (%)	9.324/0.895/6.400	8.918/0.920/6.051	9.997/1.100/7.022
<i>Gof</i>	10.414	9.9694	9.092

R_{wp}: weighted profile; R_{exp}: expected; R_p: profile; *gof*: goodness-of-fit.

Table 4.5. Crystallographic data of the synchrotron PXRD measurements of UiO-CoNi, and UiO-CuNi.

	UiO-CoNi	UiO-CuNi
X-ray energy (keV)	16.99	16.99
Wavelength (Å)	0.729589	0.729589
2θ-zero point (°)	-0.00019	-0.00019
Space group	<i>Fm$\bar{3}$m</i>	<i>Fm$\bar{3}$m</i>
Crystal system	Cubic	Cubic
a (Å)	26.83208	26.83537
2θ range for refinement (°)	1.95-70	1.95-78
Number of parameters	40	42
Number of <i>hkl</i> s	2022	2624
Refinement methods	Rietveld	Rietveld
R _{wp} /R _{exp} /R _p (%)	9.896/1.011/6.844	9.570/0.966/6.388
<i>Gof</i>	9.788	9.7913

R_{wp}: weighted profile; R_{exp}: expected; R_p: profile; *gof*: goodness-of-fit.

Table 4.6. Atomic parameters of UiO-FeCu from Rietveld refinement.

Atom	x	y	z	SOF	Beq ($\text{\AA}^2$)	Wyckoff letter
Zr1	-0.09279	0	0	1	2	24e
O1	0.06916	0	0.13452	1	2	96j
O2	0.04721	0.04721	0.04721	1	2	32f
C1	0.1174	0	0.1174	1	10	48h
C2	0.15722	0	0.15722	1	10	48h
C3	0.20656	0	0.14399	1	10	96j
C4	0.24269	0	0.18012	1	10	96j
C5	0.22947	0	0.22947	1	10	48h
C6	0.18012	0	0.24269	1	10	96j
C7	0.14399	0	0.20656	1	10	96j
Fe/Cu	0.31717	0	0.17621	0.15	10	96j

Table 4.7. Atomic parameters of UiO-FeCo from Rietveld refinement.

Atom	x	y	z	SOF	Beq ($\text{\AA}^2$)	Wyckoff letter
Zr1	-0.09177	0	0	1	1	24e
O1	0.12711	0	0.0637	1	2	96j
O2	0.04773	0.04773	0.04773	1	2	32f
C1	0.1167	0	0.1167	1	10	48h
C2	0.15653	0	0.15653	1	10	48h
C3	0.2059	0	0.1433	1	10	96j
C4	0.24204	0	0.17944	1	10	96j
C5	0.22881	0	0.22881	1	10	48h
C6	0.17944	0	0.24204	1	10	96j
C7	0.1433	0	0.2059	1	10	96j
Fe/Co	0.31655	0	0.17554	0.13	10	96j

Table 4.8. Atomic parameters of UiO-CoCu from Rietveld refinement.

Atom	x	y	z	SOF	Beq ($\text{\AA}^2$)	Wyckoff letter
Zr1	-0.09253	0	0	1	2	24e
O1	0.11863	0	0.07607	1	2	96j
O2	0.14347	0.14347	0.14347	1	2	32f
C1	0.1168	0	0.1168	1	8	48h
C2	0.15659	0	0.15659	1	8	48h
C3	0.20591	0	0.14338	1	8	96j
C4	0.24201	0	0.17948	1	8	96j
C5	0.2288	0	0.2288	1	8	48h
C6	0.17948	0	0.24201	1	8	96j
C7	0.14338	0	0.20591	1	8	96j
Co/Cu	0.31644	0	0.17558	0.13	8	96j

Table 4.9. Atomic parameters of UiO-CoNi from Rietveld refinement.

Atom	x	y	z	SOF	Beq ($\text{\AA}^2$)	Wyckoff letter
Zr1	-0.09194	0	0	1	2	24e
O1	-0.13283	0	-0.08547	1	2	96j
O2	-0.0488	-0.0488	-0.0488	1	2	32f
C1	0.1167	0	0.1167	1	10	48h
C2	0.15649	0	0.15649	1	10	48h
C3	0.20581	0	0.14328	1	10	96j
C4	0.24192	0	0.17938	1	10	96j
C5	0.2287	0	0.2287	1	10	48h
C6	0.17938	0	0.24192	1	10	96j
C7	0.14328	0	0.20581	1	10	96j
Co/Ni	0.31635	0	0.17548	0.13	10	96j

Table 4.10. Atomic parameters of UiO-CuNi from Rietveld refinement.

Atom	x	y	z	SOF	Beq ($\text{\AA}^2$)	Wyckoff letter
Zr1	-0.09700	0	0	1	2	24e
O1	0.12307	0	0.06044	1	2	96j
O2	0.05093	0.05093	0.05093	1	2	32f
C1	0.11680	0	0.11680	1	10	48h
C2	0.15659	0	0.15659	1	10	48h
C3	0.20590	0	0.14337	1	10	96j
C4	0.24200	0	0.17947	1	10	96j
C5	0.22879	0	0.22879	1	10	48h
C6	0.17947	0	0.24200	1	10	96j
C7	0.14337	0	0.20590	1	10	96j
Cu/Ni	0.31643	0	0.17557	0.14	10	96j

Building on the previous investigation of UiO-Cu-x in **Chapter 3** and the quantitative analysis of EXAFS and Rietveld refinement of PXRD, we have established a clearer understanding of the crystal structure of UiO-M_AM_B at the molecular level. Through precise engineering of the bpydc and bpdc linker ratio in UiO-M_AM_B, we deduced that in each theoretical structural formula unit of UiO-67, the bpydc linker is shared between two units. Consequently, each formula unit accommodates one metal atom, making the appearance of neighboring metal motifs. The two metal motifs in the neighboring bpydc linker are located approximately 5.3 Å apart, a distance suitable for facilitating C-C coupling.

4.3.2 Photocatalytic CO₂RR Performance

To assess the photocatalytic CO₂RR performance of bimetallic atom UiO-M_AM_B, a series of experiments were conducted to be performed. In a general experiment, the catalyst is estimated in CO₂-saturated deionized water with TEOA as a sacrificial agent under a 300 W Xe light illumination. As shown in **Fig. 4.21**, we first evaluated the catalytic performance of UiO-67 and single-atom UiO-M_A. Both UiO-67 and UiO-M_A exclusively produced C₁ products. UiO-67 produced HCOOH as the dominant product, at rates of 70.4 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with negligible CO production. Similarly, UiO-Fe and UiO-Cu exhibited HCOOH production rates of 65.1 and 72.1 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively, while also producing CO. In contrast, the Co-based single-atom UiO-Co showed a reduced HCOOH production rate of 46.1 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$.

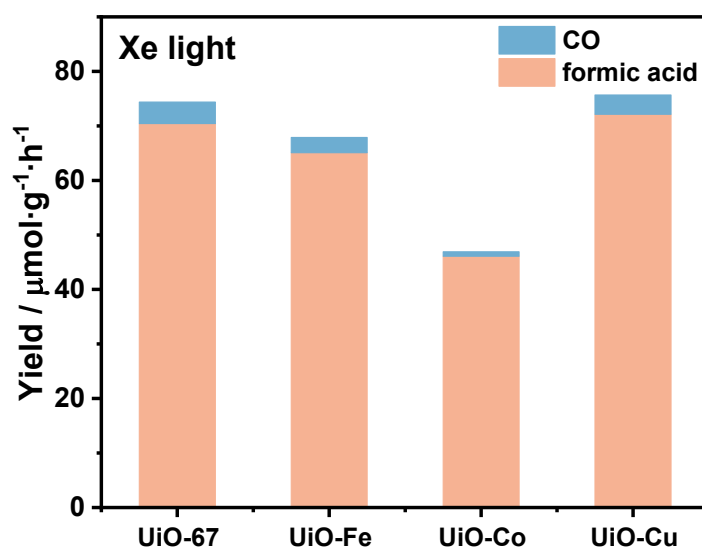


Fig. 4.21 CO₂RR performance of UiO-67, UiO-Fe, UiO-Co, and UiO-Cu under Xe light illumination using TEOA as the sacrificial agent.

The bimetallic UiO-M_AM_B series (DACs) exhibits distinct and tunable photocatalytic

CO₂RR behavior (**Fig. 4.22**). Adjusting the M_A/M_B pairs directly influences product selectivity. When M_B is Ni atoms, the UiO-M_ANi demonstrated the ability to convert CO₂ to HCOOH, while UiO-FeNi achieved the highest HCOOH product rate of 90.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. UiO-FeFe, UiO-FeCu, UiO-CoCu and UiO-CuCu exhibited the ability to convert CO₂ to C₂ products. Notably, UiO-CuCu exhibited the highest acetic acid selectivity, with a production rate of 47.0 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, and 97.8% selectivity. UiO-CoCu displayed the highest acetic acid production rate of 71.0 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, with 97% selectivity. Furthermore, UiO-FeFe and UiO-FeCu not only produced acetic acid but also further converted it to acetaldehyde. These intriguing catalytic findings highlight the effectiveness of tailoring bimetallic active sites within the UiO-67 framework to control the selectivity of photocatalytic CO₂ reduction products.

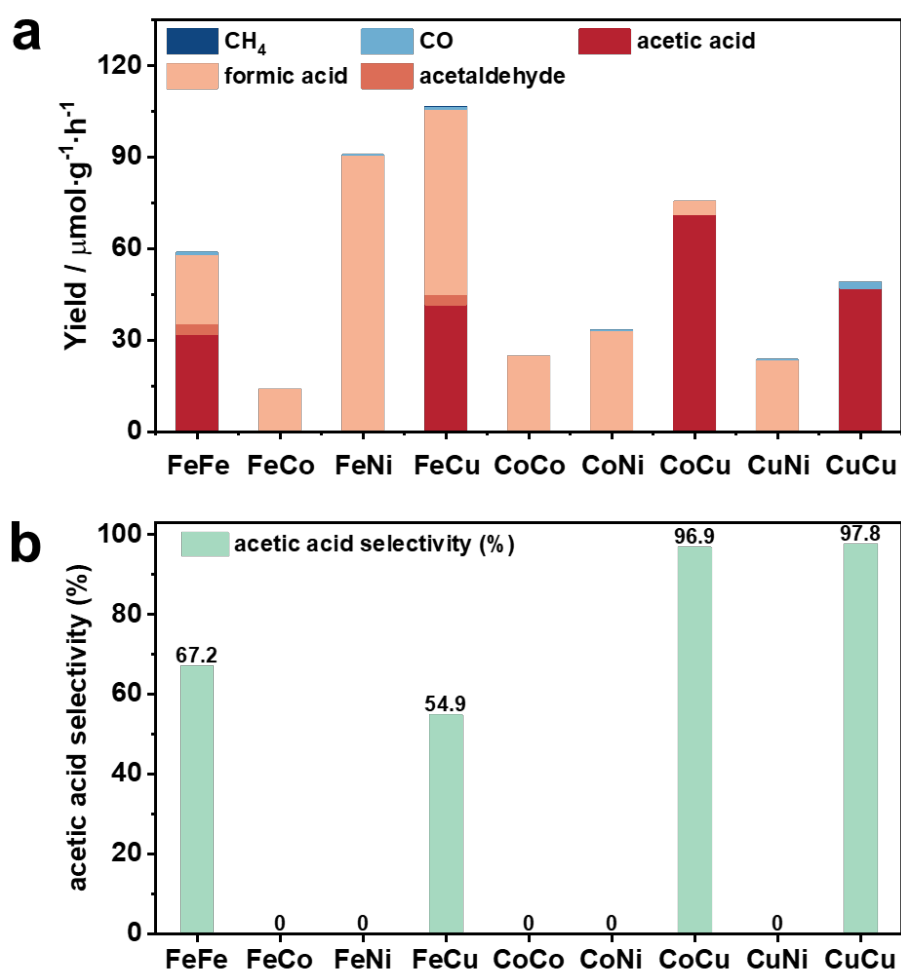


Fig. 4.22 (a) CO₂RR performance of UiO-M_AM_B (M_A = Fe, Co, Cu, M_B = Fe, Co, Ni, Cu) under Xe light illumination using TEOA as the sacrificial agent and **(b)** their acetic acid selectivity.

Table 4.11. TON value for the total product of catalysts.

Catalyst	TON _{total} *	TON _{acetic acid}
UiO-Fe	185.29	0
UiO-Co	128.04	0
UiO-Cu	206.59	0
UiO-FeFe	161.03	86.58
UiO-FeCo	38.11	0
UiO-FeNi	248.27	0
UiO-CoCo	68.29	0
UiO-CoNi	91.74	0
UiO-CoCu	206.60	194.19
UiO-CuNi	64.81	0
UiO-CuCu	134.33	128.48

* TON was calculated using 30 mg of catalyst with an average weight percentage of active sites after 5 hours of illumination.

Additionally, we investigated the impact of different photocatalytic conditions on the photocatalytic CO₂ reduction selectivity. When the light source was changed to a 440 nm wavelength (visible light range, LED lamp), the performance of the catalysts was shown in depicted in **Fig. 4.23**. UiO-67 and UiO-M_A showed no visible light response and produced nil detectable products. Notably, most UiO-M_AM_B catalysts exhibited visible light responsiveness. Especially for UiO-M_ANi, they shifted selectivity, generating C₂ products as the dominant product. This suggests that activation at high-energy wavelengths enhances CO₂ reduction and C–C bond formation, while lower-energy light suppresses byproduct formation, thereby favoring C₂₊ product selectivity.

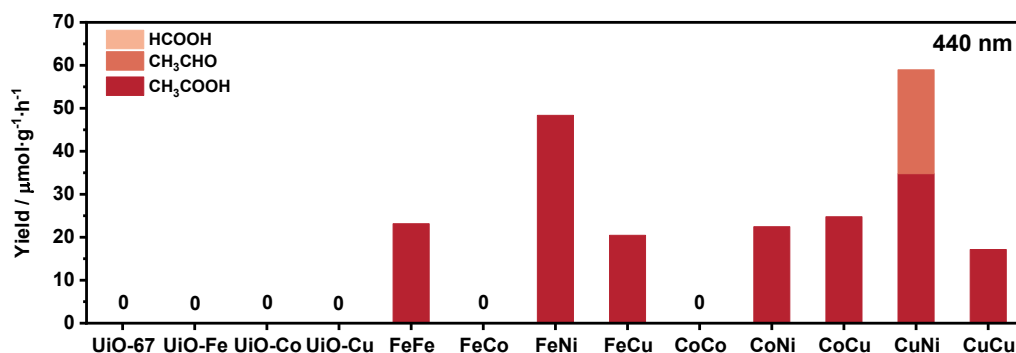


Fig. 4.23 Control CO₂RR performance of UiO-67 and UiO-M_AM_B (M_A = Fe, Co, Cu, M_B = Fe, Co, Ni, Cu) under 440 nm LED light illumination using TEOA as the sacrificial agent.

As shown in **Fig. 4.24**, a series of control experiments of catalytic conditions were also conducted to investigate the role of the catalyst. Using UiO-CoCu as the representative example, we observed nil activity in the condition of the absence of CO₂, light, sacrificial reagent (TEOA), and photocatalyst.

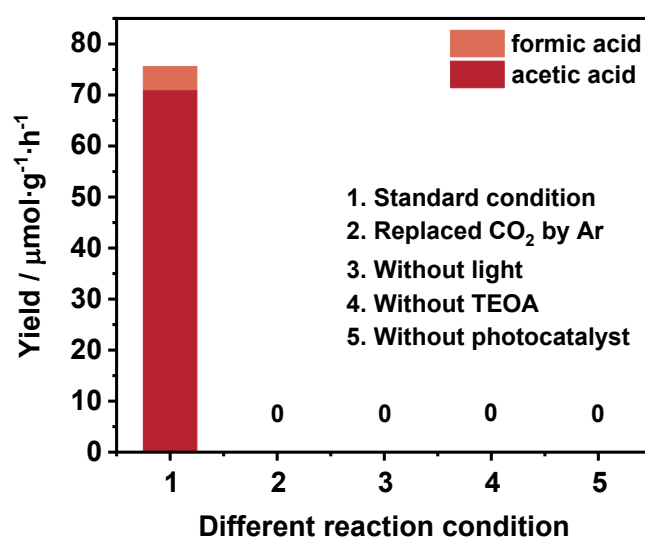


Fig. 4.24 Control experiments utilizing UiO-CoCu as the photocatalyst under different reaction conditions.

4.3.3 Photophysical Properties of UiO- $M_A M_B$

To comprehensively explore the electronic transfer process of bimetallic UiO- $M_A M_B$, we systematically compared the photophysical properties of pristine UiO-67, ‘single-atom’ UiO- M_A , and ‘dual-atom’ UiO- $M_A M_B$. UV-visible diffuse reflectance spectra revealed that metal incorporation broadens the photoresponsive range of both UiO- M_A and UiO- $M_A M_B$ catalysts. As shown in **Fig. 4.25**, a noticeable redshift into the visible region in both UiO- M_A and UiO- $M_A M_B$ was observed, attributed to metal $d-d$ transitions²³⁻²⁵. This expanded light absorption enhances the light-harvesting capability and catalytic efficiency of UiO- $M_A M_B$, consistent with its superior photocatalytic CO₂ reduction performance.

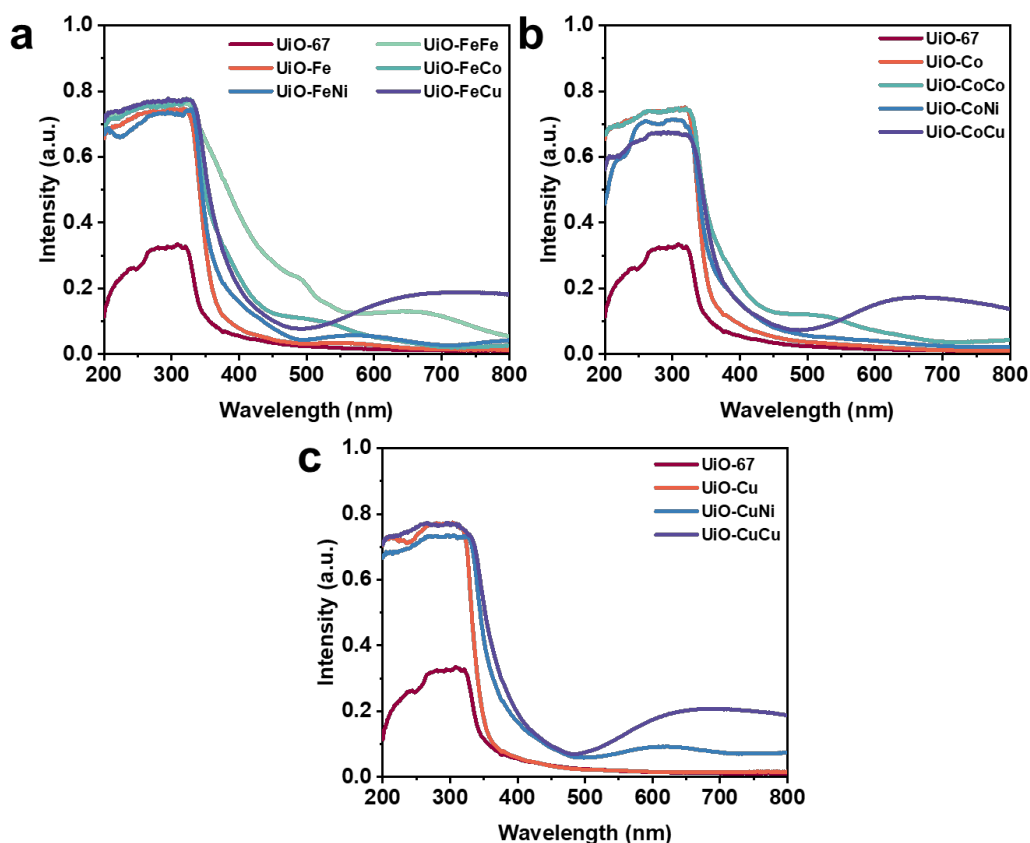


Fig. 4.25 UV-vis spectra of (a) UiO-Fe M_B series, (b) UiO-Co M_B series, (c) UiO-Co M_B series (M_B = Fe, Co, Ni, Cu).

As illustrated in **Fig. 4.26 – 4.29**, the bandgap energies of the as-prepared samples were calculated using Kubelka-Munk-transformed UV-vis data. The bandgap of UiO-MA catalysts ranges from 3.52 to 3.67 eV, showing a minimal impact of metal introduction on pristine UiO-67 (3.64 eV) (**Fig. 4.26**). Similarly, introducing M_B species slightly reduces the bandgap of most UiO- $M_A M_B$, except notably in UiO-FeFe (3.00 eV). These insignificant differences in the apparent bandgap energies suggest that the superior catalytic reactivity of UiO- $M_A M_B$ originates from the local structures rather than significant electronic band alterations.

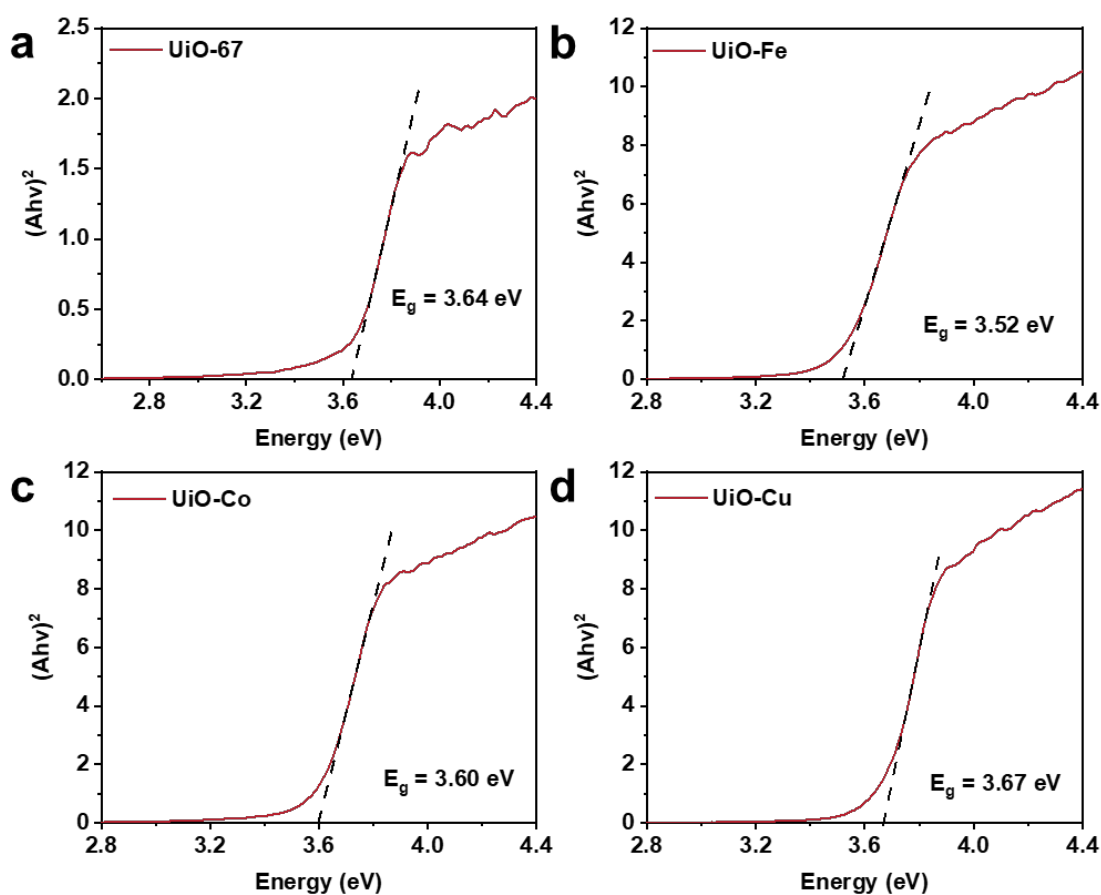


Fig. 4.26 Plots of $(ah\nu)^2$ vs. photon energy for (a) UiO-67, (b) UiO-Fe, (c) UiO-Co, and (d) UiO-Cu.

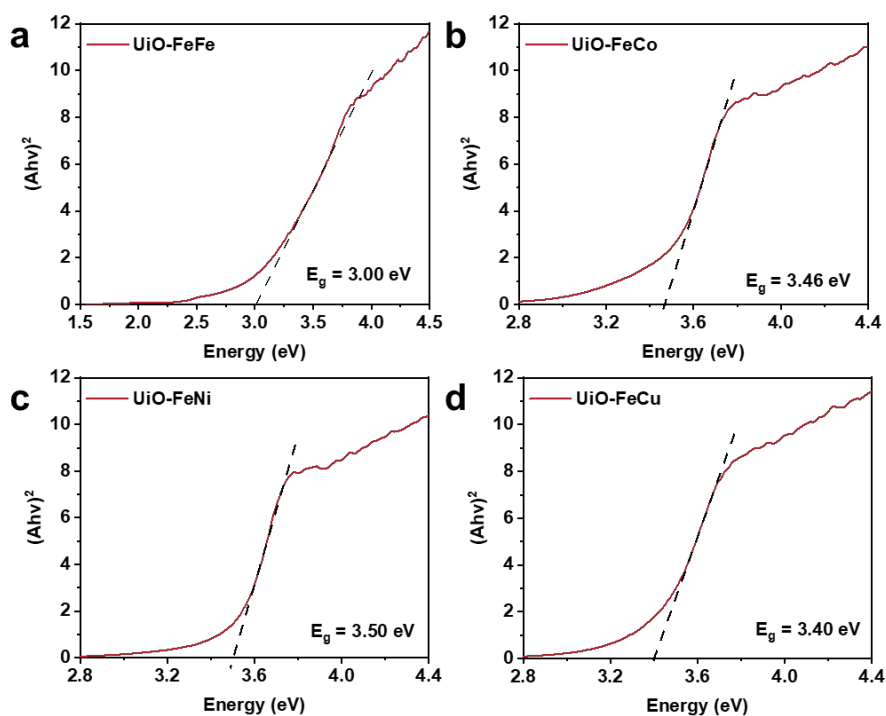


Fig. 4.27 Plots of $(ah\nu)^2$ vs. photon energy for (a) UiO-FeFe, (b) UiO-FeCo, (c) UiO-FeNi, and (d) UiO-FeCu.

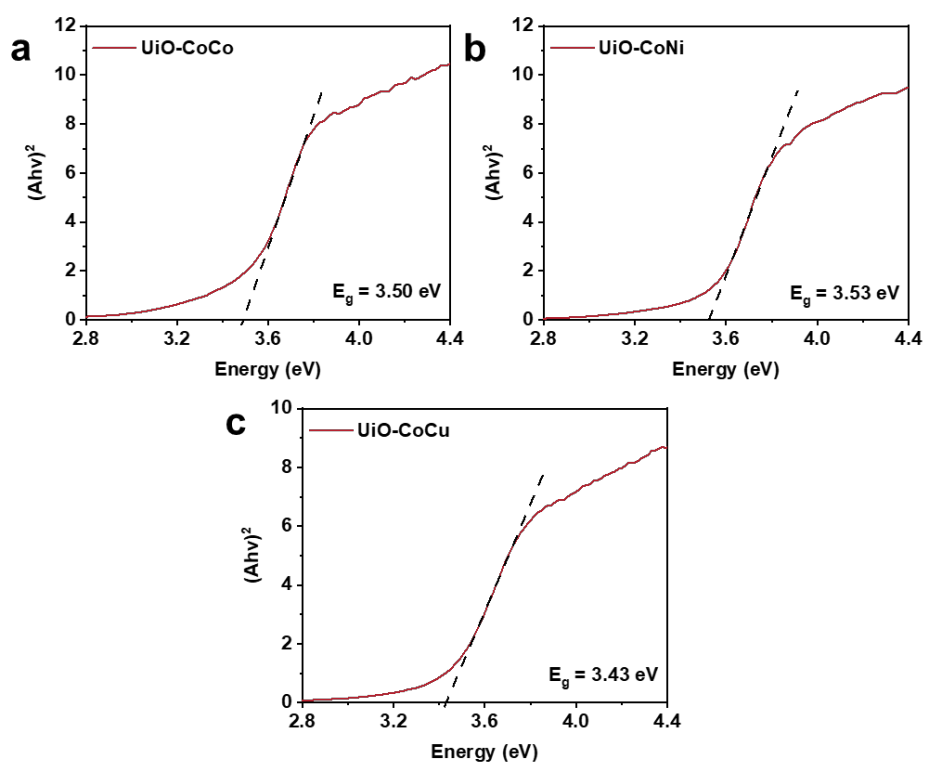


Fig. 4.28 Plots of $(ah\nu)^2$ vs. photon energy for (a) UiO-CoCo, (b) UiO-CoNi, and (c) UiO-CoCu.

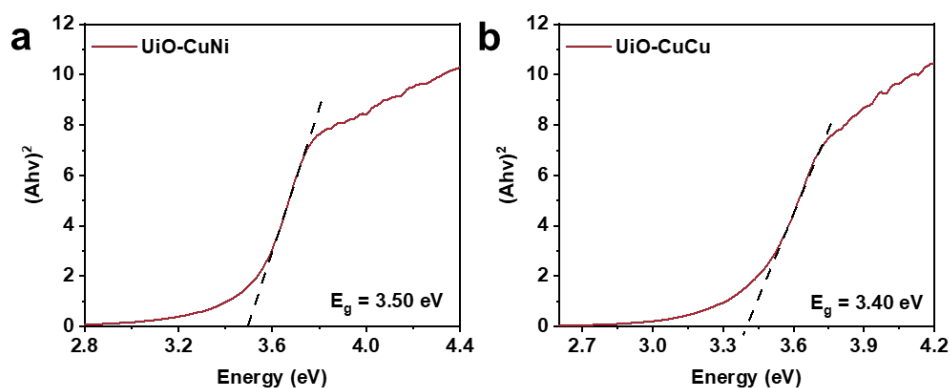


Fig. 4.29 Plots of $(\alpha h\nu)^2$ vs. photon energy for (a) UiO-CuNi, (b) UiO-CuCu.

The electronic band structure of as-prepared samples was further investigated through Mott-Schottky analysis to determine the CB positions, as shown in **Fig. 4.30 – 4.31**. The value of the VB was calculated using equation (9), and the band parameters are summarized in **Table 4.12**. The band structure of UiO-67 aligns with previous studies²⁶, whereas UiO-M_{AMB} possesses a band structure enabling photocatalytic conversion of CO₂ to C₂ products^{27, 28}.

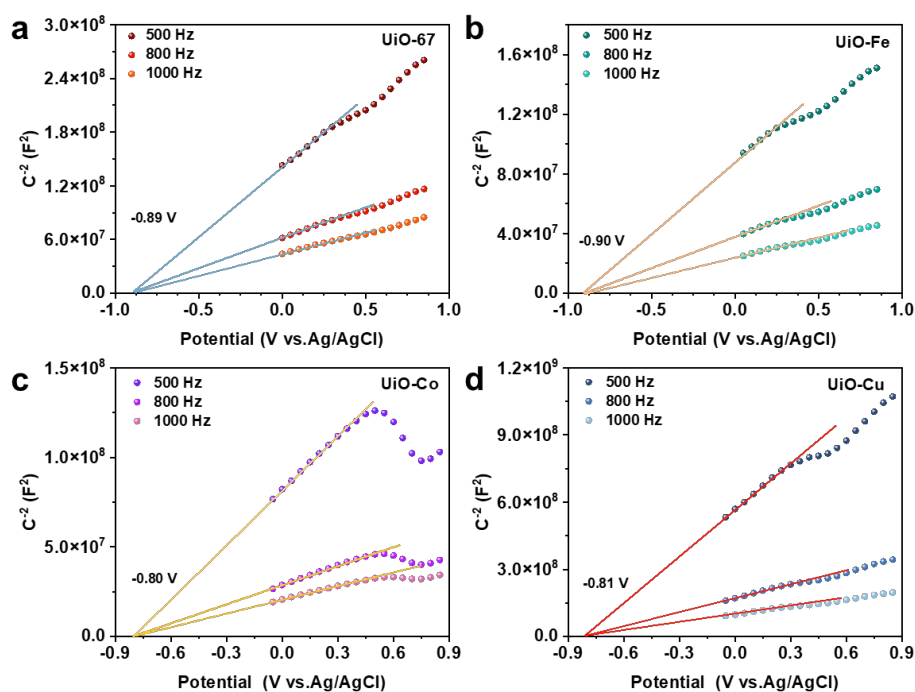


Fig. 4.30 Mott-Schottky plots of (a) UiO-67, (b) UiO-Fe, (c) UiO-Co, and (d) UiO-Cu, measured at 500, 800, and 1000 Hz in 0.1 M Na₂SO₄ electrolyte (pH = 7).

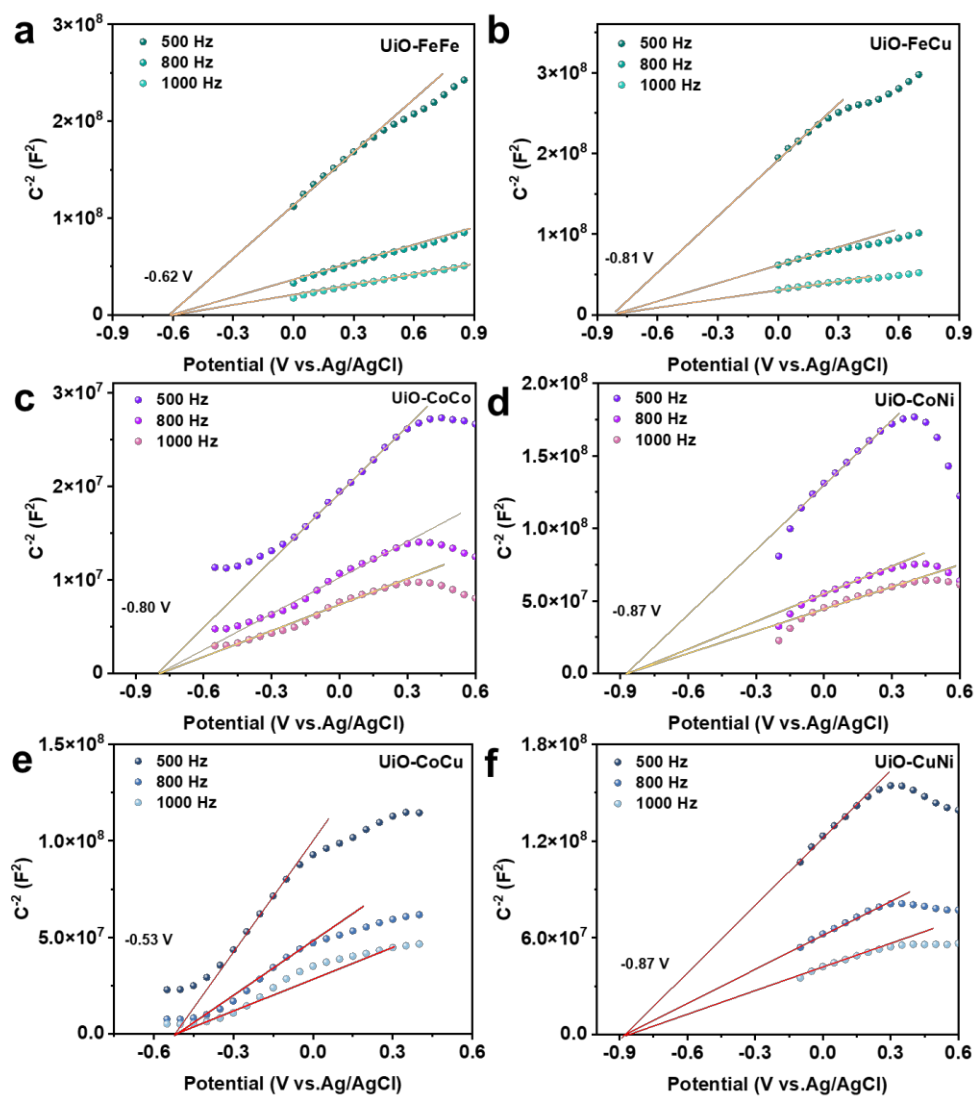


Fig. 4.31 Mott-Schottky plots of (a) UiO-FeFe, (b) UiO-FeCu, (c) UiO-CoCo, (d) UiO-CoNi, (e) UiO-CoCu, and (f) UiO-CuNi measured at 500, 800, and 1000 Hz in 0.1 M Na₂SO₄ electrolyte (pH = 7).

Table 4.12. Summary of estimated band gap, CB, and VB positions for the as-samples.

Sample	CB <i>vs.</i> RHE (eV)	VB <i>vs.</i> RHE (eV)	E _g (eV)
UiO-67	-0.48	3.16	3.64
UiO-Fe	-0.49	3.03	3.52
UiO-FeFe	-0.20	2.80	3.00
UiO-FeCu	-0.40	3.00	3.40
UiO-Co	-0.39	3.21	3.60
UiO-CoCo	-0.39	3.11	3.50
UiO-CoNi	-0.46	3.07	3.53
UiO-CoCu	-0.12	3.38	3.50
UiO-Cu	-0.40	3.27	3.67
UiO-CuNi	-0.46	3.04	3.50

Fig. 4.32 shows that UiO-67 exhibits the highest PL intensity, reflecting rapid electron-hole recombination. In contrast, both UiO-M_A and UiO-M_AM_B demonstrate significantly lower PL intensities, confirming that the introduction of metal effectively enhances charge transfer, thereby suppressing electron-hole pair recombination in UiO-67.

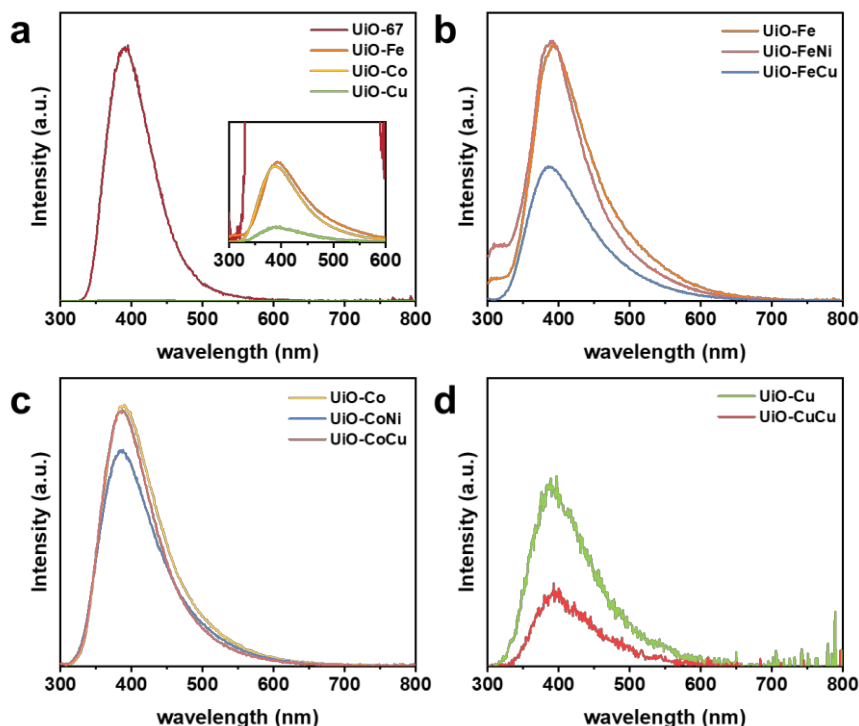


Fig. 4.32 PL spectra of (a) UiO-67, UiO-Fe, UiO-Co, and UiO-Cu, (b) UiO-FeNi, UiO-FeCu, (c) UiO-CoNi, UiO-CoCu, and (d) UiO-CuCu.

To further explore the charge carrier dynamics, we employed TRPL spectroscopy (**Fig. 4.33**). TRPL lifetime represented the effective lifetime of photogenerated electron-hole pairs²⁹. UiO-67 exhibited the longest lifetime of 1.92 ns, whereas all the metal-introduced UiO- M_A and UiO- $M_A M_B$ displayed much shorter lifetimes. This trend suggests enhanced charge separation and migration to catalytic sites, rather than detrimental recombination within the bulk structure³⁰. Notably, the UiO-FeCu and UiO-CoCu showed the shortest lifetimes, indicating the synergistic effect of Co/Cu and Fe/Cu bimetallic sites effectively enhances charge transfer. Further biexponential fitting analysis reveals two recombination pathways. The faster decay component (τ_1) corresponds to non-radiative recombination mediated by trap states³¹. In UiO-67, τ_1 reached the longest lifetime of 1.16 ns, which is attributed to LCCT processes. By contrast, in UiO- $M_A M_B$ like UiO-CoCu for example, the shorter lifetime of τ_1 (0.70 ns)

is consistent with LMCT dynamics. The slower decay component (τ_2) reflects intrinsic radiative recombination of free carriers³¹.

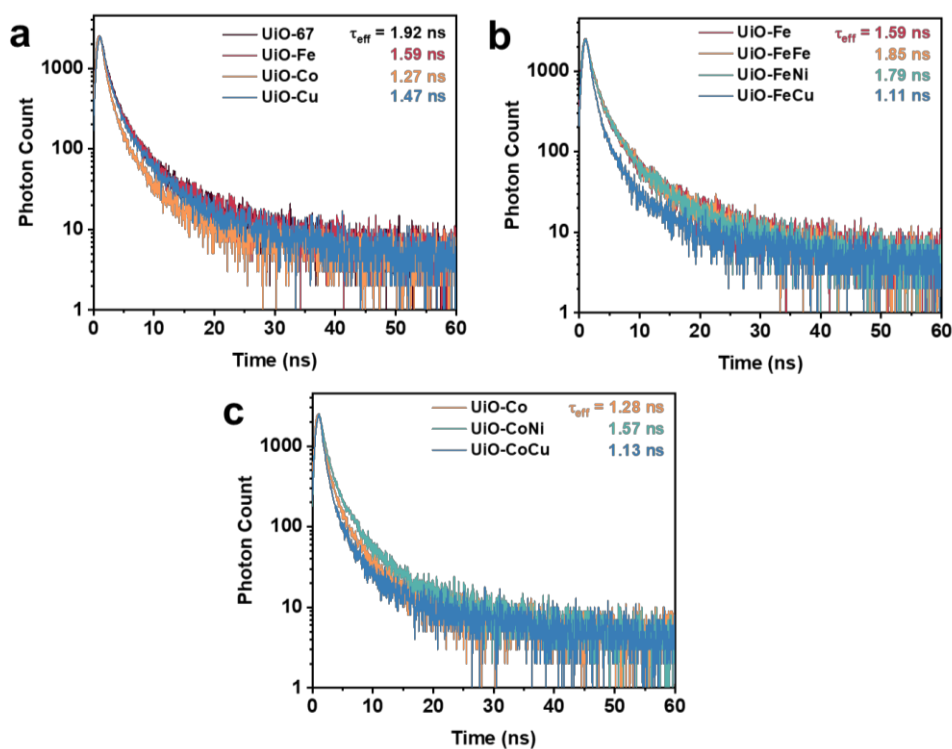


Fig. 4.33 TRPL spectra of (a) UiO-67, UiO-Fe, UiO-Co, and UiO-Cu; (b) UiO-FeFe, UiO-FeNi, UiO-FeCu; (c) UiO-CoNi and UiO-CoCu.

Table 4.13. Lifetime components in TRPL decay fitted by double exponential components.

Sample	τ_1 (ns)	A ₁ (%)	τ_2 (ns)	A ₂ (%)	τ_{eff} (ns)
UiO-67	1.158	79.98	4.993	20.02	1.926
UiO-Fe	0.836	73.45	3.700	26.55	1.597
UiO-Co	0.717	76.93	3.138	23.07	1.276
UiO-Cu	0.900	80.73	3.888	19.27	1.475
UiO-FeFe	0.679	87.99	3.396	12.01	1.006
UiO-FeCo	0.581	83.69	3.902	16.31	1.123
UiO-FeNi	0.923	71.69	3.977	28.31	1.788
UiO-FeCu	0.696	83.20	3.145	16.80	1.108
UiO-CoNi	0.888	77.83	3.944	22.17	1.566
UiO-CoCu	0.702	77.83	3.944	22.17	1.128

4.3.4 CO₂RR Mechanism of UiO-M_AM_B

To elucidate the crucial factor enabling UiO-M_AM_B to steer CO₂RR products from C₁ to C₂₊, we first employed *in-situ* DRIFTS to investigate potential intermediate species during the reaction. We selected UiO-Fe and UiO-FeCu as representative examples of SACs and DACs for investigating C₁ and C₂₊ product intermediates, respectively. As depicted in **Fig. 4.34**, the *in-situ* DRIFTS data for UiO-67 revealed distinct IR peaks at 1086 and 1342 cm⁻¹, characteristic of *CHO, and *COOH species, respectively, which are the typical intermediates for C₁ products^{32, 33}. In contrast, both UiO-Fe and UiO-FeCu exhibited these peaks alongside additional spectral features at 1674 and 1720 cm⁻¹, corresponding to carbonyl stretching vibrations (*CO_{stretching}), revealing *CO adsorption at metal sites^{34, 35}. Moreover, UiO-FeCu displayed the unique IR peak at

1457 cm^{-1} , attributed to $^*\text{OC-CO}$, 1265 and 1560 cm^{-1} , corresponding to $^*\text{HOC-CO}$ ^{36, 37}. These IR peaks are indicative of C_2 intermediates, providing compelling evidence that the neighboring $\text{M}_\text{A}\cdots\text{M}_\text{B}$ motifs in bimetallic catalysts play a pivotal role in facilitating C–C coupling, thus promoting the formation of C_{2+} products.

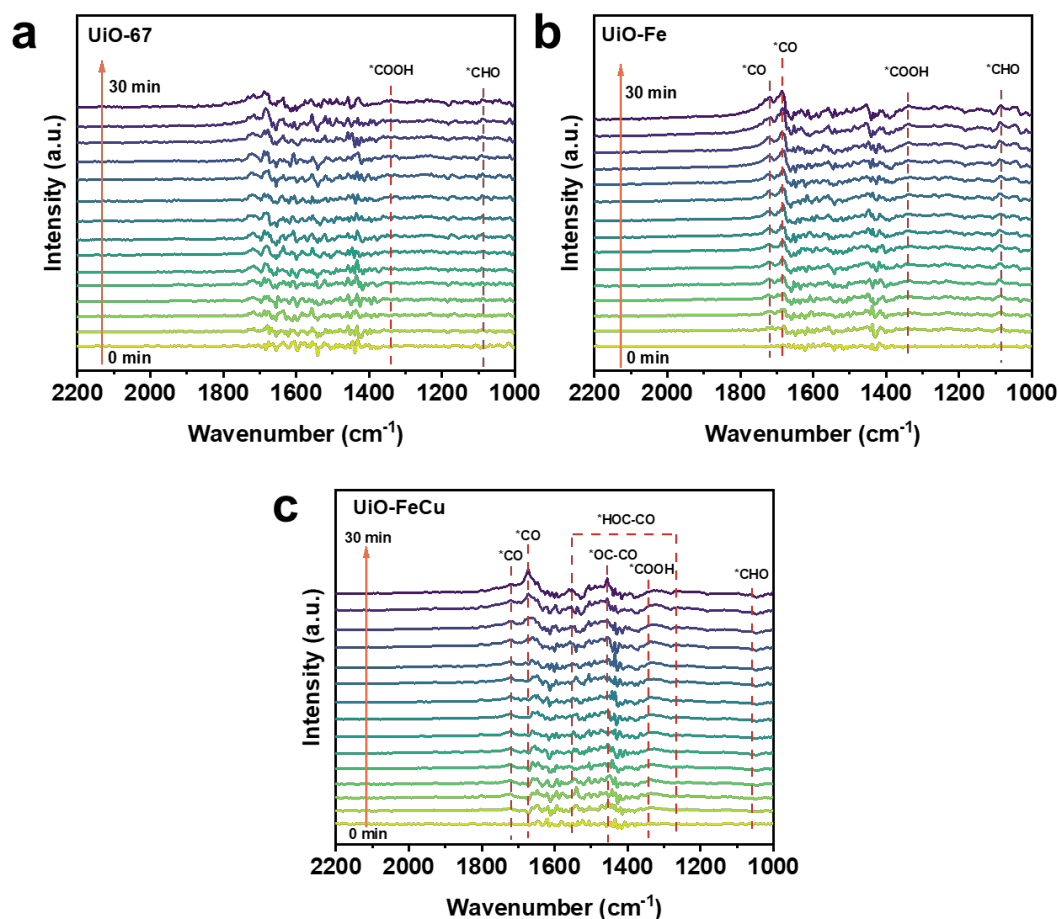


Fig. 4.34 *In-situ* DRIFTS spectra for CO_2RR over (a) UiO-67, (b) UiO-Fe, and (c) UiO-FeCu.

DFT calculations were employed to investigate selectivity control across various metal pairs in $\text{UiO-M}_\text{A}\text{M}_\text{B}$ catalysts. Accordingly, we first selected UiO-FeNi and UiO-CoCu as representative examples for investigating C_1 and C_{2+} product formation pathways based on the Gibbs free energy change. In UiO-FeNi, CO_2 adsorption was stronger at the Ni site (-0.94 eV) compared to the Fe site (-0.31 eV), indicating a preferential

adsorption at Ni sites (**Fig. 4.35a**). **Fig. 4.35b** presents its corresponding Gibbs free energy diagrams. Previous studies identify *OCHO and *OCOH as crucial intermediates for forming *HCOOH and *CO products, respectively, with *CO serving as the key coupling intermediate for subsequent C₂⁺ production. Although the free energy of *HCOOH and *CO are similar, the energy barrier for *CO₂-to-*OCOH conversion is more positive than that for the *CO₂-to-*OCHO conversion. This indicates that UiO-FeNi favors the CO₂ hydrogenation pathway towards *HCOOH generation over *CO generation, aligning with our experimental catalytic observations. In UiO-CoCu, CO₂ adsorption was stronger at the Co site (-0.64 eV) compared to the Cu site (-0.24 eV), indicating a preferential adsorption at Co sites (**Fig. 4.35a**). We then calculated the Gibbs free energy for the intermediate reactions involved in CO₂ reduction on UiO-CoCu as shown in **Fig. 4.35c**. When considering isolated single-atom sites (Co or Cu sites), the energy barriers for sustained CO₂ hydrogenation to form *CO intermediate production are high, indicating an unfavorable pathway for C₂ product generation. In contrast, considering the synergistic effect of neighboring motifs of the Co and Cu sites enables alternating CO₂ adsorption, forming M-*CO₂ intermediates with lower energy barriers. Subsequently, the Co and Cu sites alternately hydrogenated these species, forming *CO and *COH intermediates, facilitating C–C coupling and ultimately producing CH₃COOH.

with C₂₊ products formation. As a result, the upward shift of the *d*-band center serves as a reliable descriptor for catalytic performance. Additionally, the synergistic effect of the bimetallic atom sites significantly influences the *d*-band center of the catalyst. The moderate *d*-band center of **Cu** and **Fe** SA generally helps lower the energy barrier for C–C coupling, enhancing the selectivity for C₂₊ products. Conversely, **Ni** and **Co** SA cause a downward shift of the *d*-band center due to their intrinsic properties, which does not favor the stabilization of intermediates or C–C coupling.

Fig. 4.36b illustrates the CO₂ adsorption capacity at individual metal sites in UiO-MAMB. We found that the type of neighboring metal sites and their microenvironment modulate the CO₂ adsorption capacity, thereby controlling CO₂ adsorption and activation towards specific pathways at the dominant site. As established in **Fig. 4.35**, the PDS of the reaction occurs during the conversion of *CO₂ to either *OCHO (leading to HCOOH, C₁ product) or *OCOH (favoring C₂₊ products).

Fig. 4.36c correlates the Gibbs free energy difference between *OCHO and *HCOOH ($\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$), for the sites A and B with the *d*-band center energy. This difference provides insight into product selectivity. UiO-FeCu, and UiO-CuCu exhibit a strongly negative $\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$, favoring *OCOH generation at site A, resulting in C₂₊ products formation. UiO-CoCu and UiO-FeFe display a near-zero (slightly positive) $\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$ at site A, still favoring C₂₊ products formation. However, UiO-CoCo has a negative $\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$, but a downshifted *d*-band center, leading to C₁ product formation. Clearly, the CO₂RR selectivity of a catalyst is not only related to the $\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$, but also needs to be considered concerning the position of the *d*-band center (electronic configuration descriptor). When the *d*-band center is closer to the Fermi level, a **negative** $\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$ indicates greater thermodynamic stability for

*OCOH, promoting *CO formation and subsequent C–C coupling toward C₂₊ products. A **near-zero** $\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$ signifies competing formation of *OCHO and *OCOH intermediates, still enabling pathways toward C₂₊ products. However, the **high positive** $\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$ suggests the strong stabilization of *OCHO, driving selectivity toward C₁ products. Furthermore, Ni-based UiO-M_ANi exhibit much positive $\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$ values for both site A and B, strongly indicating preferentially stabilizes the *OCHO intermediate. Based on our CO₂ adsorption energy calculations, Ni sites are speculated to have a higher affinity for CO₂ adsorption compared to other metal sites, steering the reaction pathway towards C₁ product formation by modulating the electronic structure of the catalyst.

Fig. 4.36d presents the calculated adsorption energies of the *CO intermediate derived from *OCOH conversion at site A and site B in UiO-M_AM_B. These energies reflect the strength of *CO adsorption, which not only indicates the effective conversion of *OCOH-to-*CO, but also correlates with the C–C coupling efficiency. Among the catalysts yielding C₂₊ products (UiO-FeFe, UiO-FeCu, UiO-CoCu, and UiO-CuCu), UiO-CuCo and UiO-CuCu exhibit a more moderate *CO adsorption energy barrier, which may enhance selectivity by facilitating *CO mobility for subsequent C–C coupling.

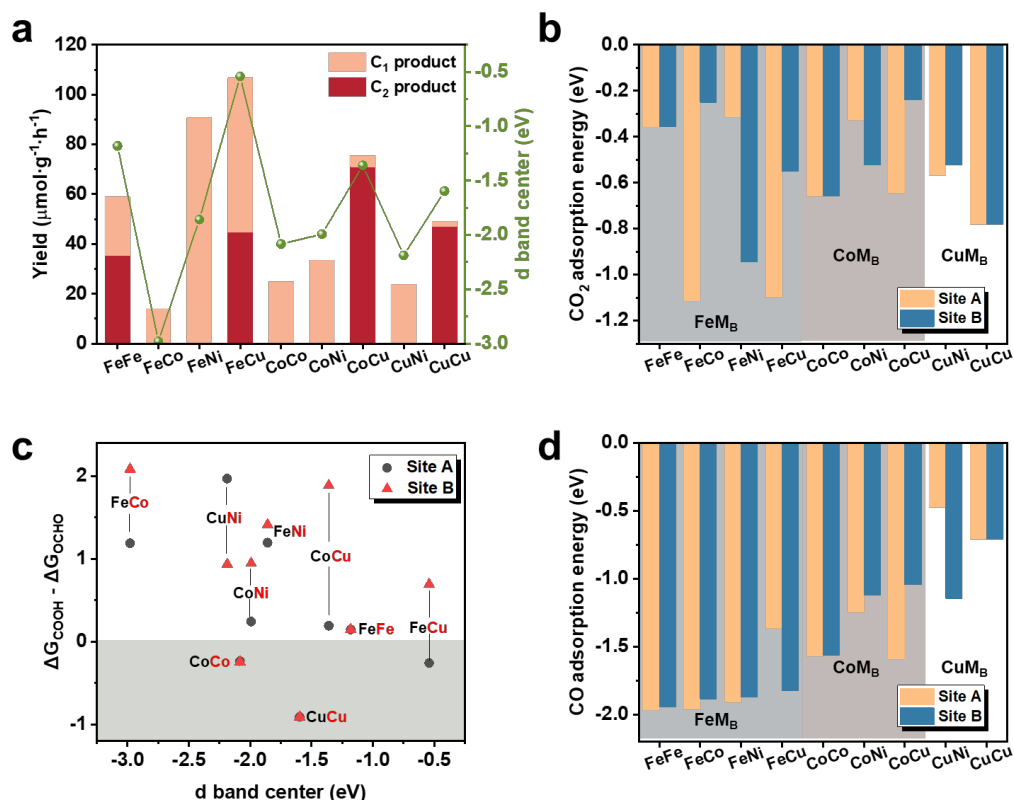


Fig. 4.36 (a) The relationship of the calculated d-band center energy of UiO-M_{AM}B and CO₂RR activity. (b) Calculated adsorption energies of the CO₂ molecule on site A and site B in UiO-M_{AM}B. (c) The relationship between the calculated d-band center energy of UiO-M_{AM}B and Gibbs free energy differential of *OCOH and *OCHO of site A and site B in UiO-M_{AM}B. (d) Calculated adsorption energies of the *CO intermediate on site A and site B in UiO-M_{AM}B.

4.4 Proposed Chemical Model

By integrating our *in-situ* DRIFTS analysis and DFT calculation, we accordingly propose the following CO₂RR pathway for UiO-M_{AM}B: Under the light illumination, the UiO-67/UiO-M_A (SACs) effectively absorbs CO₂, activating it to form *CO₂ intermediates. These intermediates undergo hydrogenation to produce *OCOH, which serves as a precursor for formic acid production. In contrast, UiO-M_{AM}B (DACs)

leverages the precisely positioned dual metal sites (distance of ~ 5.3 Å) and their synergistic effects to steer selectivity towards C_{2+} product formation. The synergy between site A and site B modulates the stabilization of $^*CO_2$ and controls the formation of $^*OCHO$ intermediates by adjusting the bimetallic site combination. For instance, the Fe and Cu sites in UiO-FeCu cooperatively stabilize $^*OCHO$, which subsequently converts to $^*CO$. This enables efficient C–C coupling through pathways involving $^*OC-^*CO_2$, $^*OC-^*COOH$, and $^*OC-^*CO$, resulting in the selective production of acetic acid.

UiO- $M_A M_B$ exhibits different photocatalytic CO_2RR selectivity in the presence of neighboring metal motifs, which is mainly due to the synergistic effect of the metal pairs. The **Cu and Fe motifs** serve as effective active site for adsorbing CO_2 and stabilizing intermediates. In contrast, **Ni and Co motifs** are **less favorable** for stabilizing C_2 intermediates. Strategic selection of metal pairs leverages this synergy to optimize the catalyst's electronic structure for targeted C_{2+} products formation. These results underscore the critical importance of bimetallic sites and their synergistic interactions in promoting efficient C–C coupling, leading to improved CO_2 conversion efficiency and enhanced selectivity for valuable C_{2+} chemicals.

4.5 Conclusion

In conclusion, we have successfully engineered bimetallic metal sites with precise spatial control, enabling fine-tuned regulation of the metal combination to synergistically steer the selectivity of photocatalytic CO_2RR . The successful integration within UiO- $M_A M_B$ was confirmed through meticulous characterization using cutting-edge techniques, including TEM, XAFS, and Rietveld refinement of PXRD, demonstrating the precise arrangement of neighboring metal motifs. Crucially, these

motifs, positioned approximately 5.3 Å apart on adjacent bpydc linkers, not only promote the C–C coupling pathway but also significantly reduce the energy barrier of the potential-determining step. Strategic selection of the metal combinations yielded synergistic effects, optimizing the electronic structure, coordination environment, and active sites accessibility. This approach identified FeFe, CoCu, and CuCu as an effective bimetallic pair in UiO-M_AM_B for the selective production of CH₃COOH.

Therein, we employed the ***d*-band center** as the reliable electronic structure descriptor and $\Delta G_{\text{COH}} - \Delta G_{\text{CHO}}$ as the C₂₊ product selectivity descriptor for evaluating the catalytic performance of site A and site B in UiO-M_AM_B (**Fig. 4.37**). The closer the *d*-band center is to the Fermi level, indicating in stronger the binding energies with CO₂ and its intermediates. A **negative** $\Delta G_{\text{COH}} - \Delta G_{\text{CHO}}$ or **near-zero** $\Delta G_{\text{COH}} - \Delta G_{\text{CHO}}$ indicates the favoring for *OCOH, promoting *CO formation and subsequent C–C coupling toward C₂₊ products. However, the **high positive** $\Delta G_{\text{COH}} - \Delta G_{\text{CHO}}$ suggests the strong stabilization of *OCHO, driving selectivity toward C₁ products. **Cu** and **Fe motifs** serve as effective active sites for C–C coupling for C₂₊ products, whereas **Ni** and **Co motifs** are less favorable for C₂₊ products formation.

These findings deepen our mechanistic understanding of CO₂ reduction and establish a foundation for future exploration of supported DACs with varied metal site pairs and support matrices. Collectively, it offers valuable insights for developing advanced photocatalysts, enabling precise control over product selectivity through the strategic design of metal site pairings and leveraging the unique photochemical properties of MOFs.

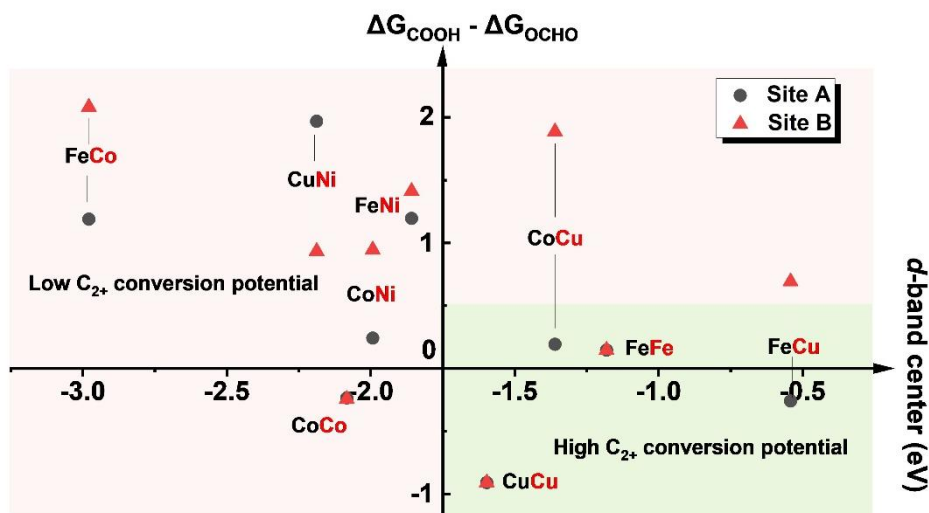


Fig. 4.37 Schematic representation of the proposed synergistic bimetallic active sites in UiO-MAM_B for CO₂RR conversion to C₂₊ products. It correlates the relationship between the d -band center energy (x-axis, electronic structure descriptor) and calculated Gibbs free energy difference between *OCOH and *OCHO intermediates at site A (black) and site B (red) (y-axis, selectivity descriptor). An upward shift of the d -band center toward the Fermi level indicates stronger binding of CO₂ and its intermediates. A negative or near-zero value of $\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$ indicates greater stability for *OCOH, promoting C–C coupling toward C₂₊ products rather than HCOOH.

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Chapter 5 Precise Modulation of 3d/4d Bimetallic Sites in Metal-Organic Framework for Photocatalytic CO₂ Reduction to Acetic Acid

5.1 Introduction

In **Chapter 4**, we investigated the characterization of 3d-3d transitional metal pairs and their synergistic effects on CO₂RR selectivity. In addition to 3d transition metals, 4d transition metals are also promising candidates for CO₂RR conversion to high-value chemicals¹⁻⁴. The key advantage of 4d metals over 3d metals is their distinct electronic structure. Due to the broader diffusivity of their *d*-orbitals, 4d transition metals provide stronger overlap with ligand orbitals, facilitating the formation of stable complexes, particularly in higher oxidation states. This richer coordination chemistry of 4d transition metals, coupled with superior orbital energy matching CO₂ frontier orbitals, as well as enhanced stability of key intermediates, allows for highly efficient C–C coupling pathways, which is a critical step for producing valuable multi-carbon products from CO₂RR.

Herein, we utilized UiO-67 as a structural matrix to host precisely positioned 3d/4d-TM bimetallic active sites with rationally engineered interatomic distances. These tailored 3d/4d-TM pairs were designed with the aim of exploring the selective conversion of CO₂ to C₂ products and identifying the key factors for enhancing the performance in the CO₂RR towards C₂₊ products. The precise location of the metal sites and their atomic-level parameters were revealed and identified by Rietveld refinement of high-resolution diffraction data, XAFS and resonant XRD (RXRD). Finally, the functional role of these metal active sites for steering selectivity during photocatalytic CO₂RR was elucidated through *in-situ* FTIR spectroscopy and DFT calculations.

5.2 Experimental Procedures

All of the reagents were purchased from Dieckmann Company (Acros, Macklin, Alfa Aesar, and others) without further purification.

5.2.1 Synthesis of Metal-Bipyridine Complexes (Metal-bpy), UiO- M_A , UiO-67 and UiO-67-bpy

The metal-bpy, UiO- M_A , UiO-67 and UiO-67-bpy were synthesized according to the procedure detailed in **Chapter 4.2**.

5.2.2 Synthesis of UiO- $M_A M_B$ (Secondary Metal Incorporation)

Dual-metal catalysts (UiO- $M_A M_B$, 3d-4d metal pairs) were prepared by anchoring secondary metals onto UiO- M_A :

UiO- M_A (1 mmol) and a secondary metal salt (1 mmol; rhodium(III) chloride trihydrate, ruthenium(III) chloride hydrate, or palladium(II) chloride) were dispersed in 15 mL methanol. The suspension was stirred vigorously at 55 °C for 24 h. The product was isolated by centrifugation, washed with methanol three times, and vacuum-dried overnight.

5.2.3 Synthesis of UiO- $M_A M_{B(high)}$ (High N-ligands ration)

UiO- $M_A M_{B(high)}$ was prepared analogously to UiO- M_A and UiO- $M_A M_B$ but with different ratios of ligands and metal salts:

ZrCl₄ (120 mg), H₂bpdc (94 mg), H₂bpydc (16 mg), M-bpy complex (Fe-bpy: 32 mg; Co-bpy: 21 mg), and benzoic acid (1.88 g) were dispersed in DMF/ethanol (16:4 v/v). Subsequent procedures (ultrasonication, heating, washing, drying) followed identical conditions to UiO- M_A synthesis. Its theoretical molecular formula is Zr₆O₄(OH)₄(bpydc)_{1.5}(bpdc)_{4.5}M_{A0.75}.

UiO-M_A(high) (1 mmol) and a secondary metal salt (1.5 mmol; rhodium(III) chloride trihydrate, ruthenium(III) chloride hydrate, or palladium(II) chloride) were dispersed in 15 mL methanol. Subsequent procedures (ultrasonication, heating, washing, drying) followed identical conditions to UiO-M_AM_B synthesis. Its theoretical molecular formula is Zr₆O₄(OH)₄(bpydc)_{1.5}(bpdcc)_{4.5}M_A_{0.75}M_B_{0.75}.

5.2.4 Attempted Synthesis of Pd-bpy

Synthesis of an analogous Pd(II)-bpy complex was attempted using palladium(II) chloride as metal precursor, following identical reaction conditions (1.1 mmol metal salt, 1 mmol H₂bpydc, 50 mL methanol, 60 °C, 24 h). However, X-ray fluorescence (XRF) elemental analysis of all resulting solids consistently revealed Palladium content below 0.1 wt%. This indicates unsuccessful quantitative complexation of palladium(II) with the H₂bpydc ligand under these conditions.

5.3 Results and Discussion

5.3.1 Characterization and Atomic Structure of UiO-M_AM_B

The synthesis method of UiO-M_AM_B (3d/4d) follows the same sequential approach described in **Chapter 4** UiO-M_AM_B (3d/3d) for and is not repeated here. As illustrated in **Fig. 5.1**, metal B (M_B, site B) was substituted with 4d transition metal (Ru, Rh and Pd), which are more favorable for C-C coupling and intermediates stabilization compared to 3d transition metal. Similarly, we attempted to incorporate Pd atoms into the bipyridine linker, which was also unsuccessful. The design idea of this work goes through a stepwise strategy to introduce a 3d and 4d transition metal at precise locations within the UiO-67 matrix. To ensure an approximate 1:1 stoichiometric ratio between metal A and metal B (M_A : M_B), the ratio of M_A-bpy complex to bpydc linker in the

UiO-67 was strictly maintained at 1:1 during synthesis.

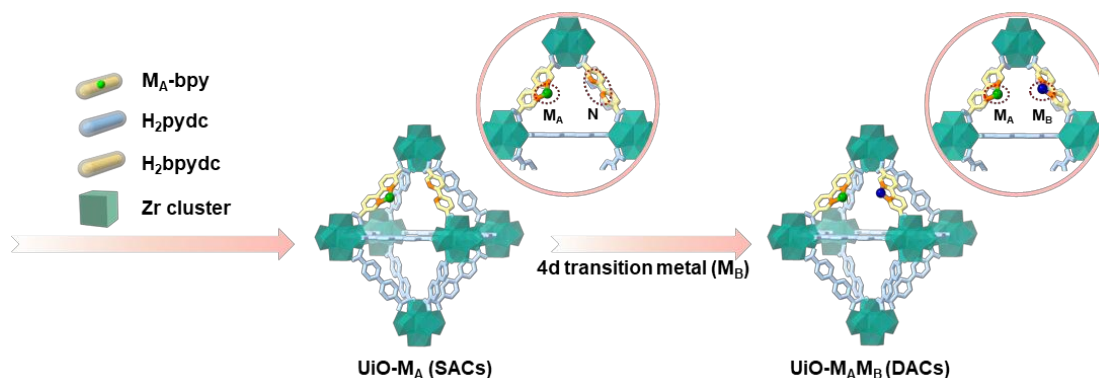


Fig. 5.1 Schematic representation of the synthetic process for UiO-M_AM_B (M_A = Fe, Co, and Cu, M_B = Ru, Rh, and Pd).

The morphology of UiO-M_AM_B was characterized by SEM and HAADF-STEM as illustrated in **Fig. 5.2 – 5.7**. All metalated samples maintained with well-defined octahedral structure characteristic of UiO-67, as shown in **Fig. 5.2**. Notably, no metal aggregation was observed on the crystalline surface, confirming that the introduction of metals preserved the integrity of the UiO-M_AM_B crystallization process. Among the observed samples, UiO-CoPd exhibited the smallest average particle size of approximately 100 nm, whereas UiO-FePd, UiO-CuPd, and UiO-FeRh displayed the larger particle size with approximately 300 nm. This size disparity may be attributed to the influence of Co-bpy on the hydrothermal crystal growth process. Element mapping derived from TEM images confirmed that the metals are present as uniformly dispersed ions rather than agglomerates. This uniform dispersion suggests successful incorporation of the metal ions into the framework, a critical factor for ensuring consistent material properties. To investigate the arrangement and interactions of metal atoms within the UiO-67 framework, the iDPC technique was employed for atomic-level observation. Using UiO-FePd as a representative example, iDPC imaging along the [110] direction (**Fig. 5.6 – 5.7**) revealed no significant distortion or contrast differences in the Zr₆O₄ secondary building units compared to UiO-67. Benzene rings

in pristine UiO-67 showed parallel alignment to [110] with a clear linear arrangement. In the case of UiO-FePd, they appeared blurred and broadened. This alteration is likely due to the twisting of the metal-bpy linkers, which adopt a more relaxed energy state within the framework. Additionally, bright atomic dots observed near the benzene rings strongly indicate that Fe and Pd atoms are anchored to the bpydc linkers, rather than attached to the Zr_6O_4 units. Simulated structural models were provided for distinguishing the structural differences between UiO-67 and UiO-FePd. Collectively, these results demonstrate a successful synthesis strategy of UiO-M_{AMB} with atomic-scale metal definition and dispersion in an ideal position.

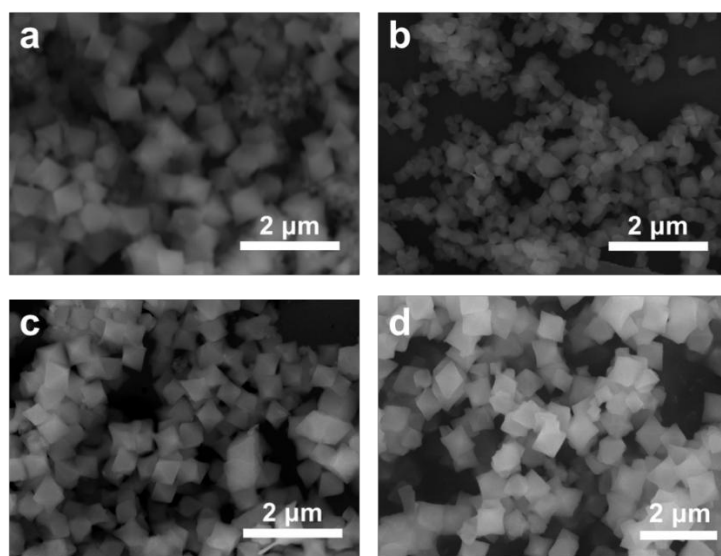


Fig. 5.2 SEM images of (a) UiO-FePd, (b) UiO-CoPd, (c) UiO-CuPd, and (d) UiO-FeRh.

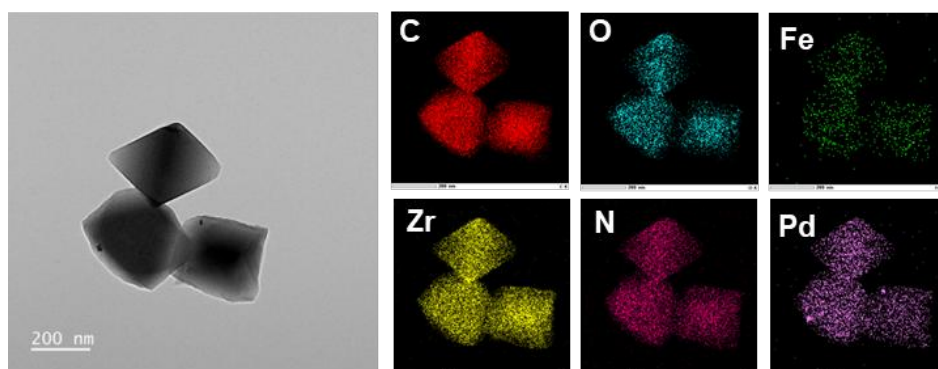


Fig. 5.3 TEM image and element mapping of UiO-FePd.

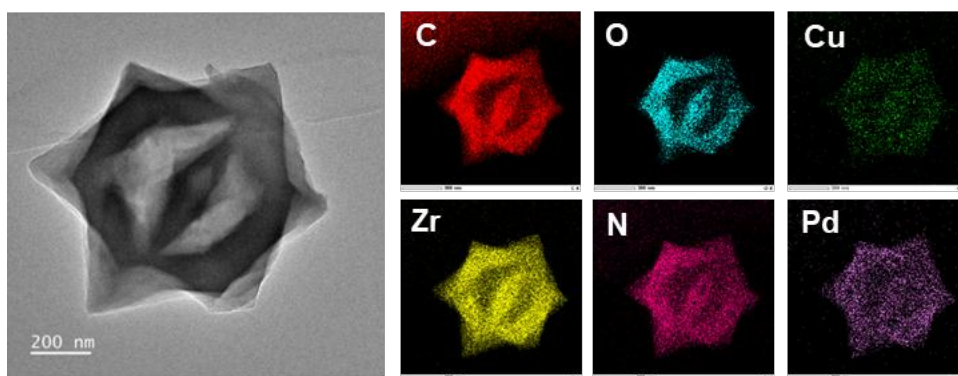


Fig. 5.4 TEM image and element mapping of UiO-CuPd.

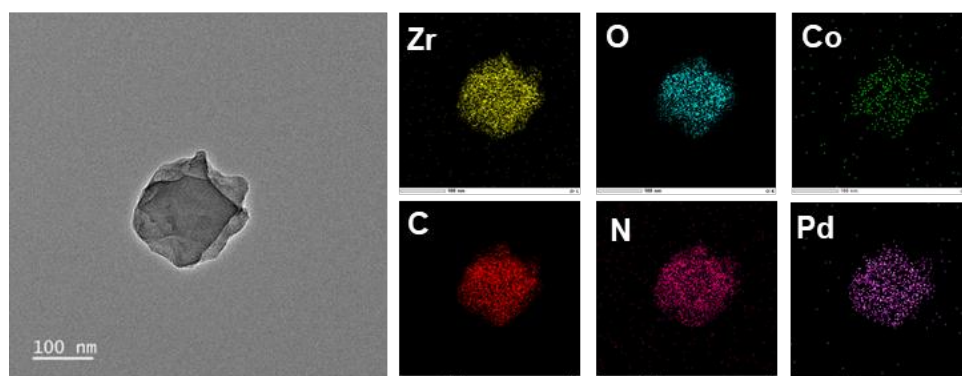


Fig. 5.5 TEM image and element mapping of UiO-CoPd.

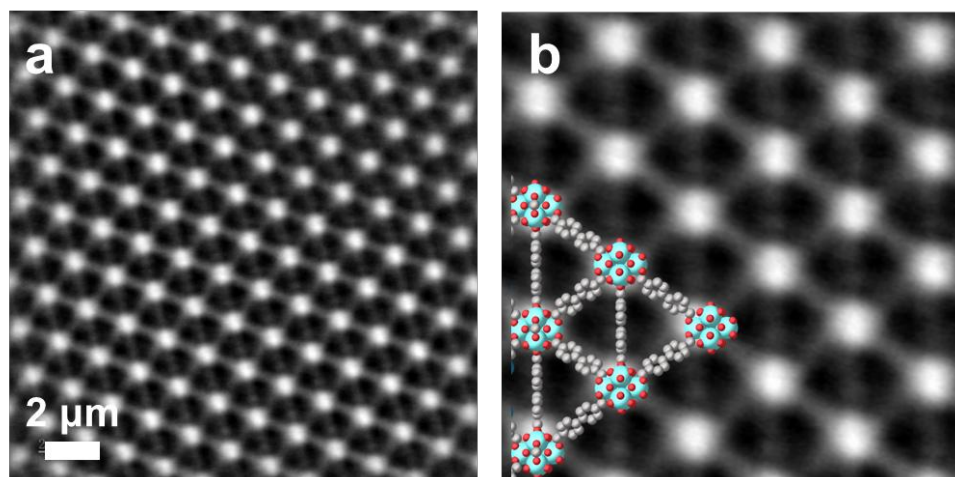


Fig. 5.6 (a) iDPC-STEM image and (b) the structural model with magnified iDPC-STEM image of UiO-67 viewing along $[110]$ crystal direction.

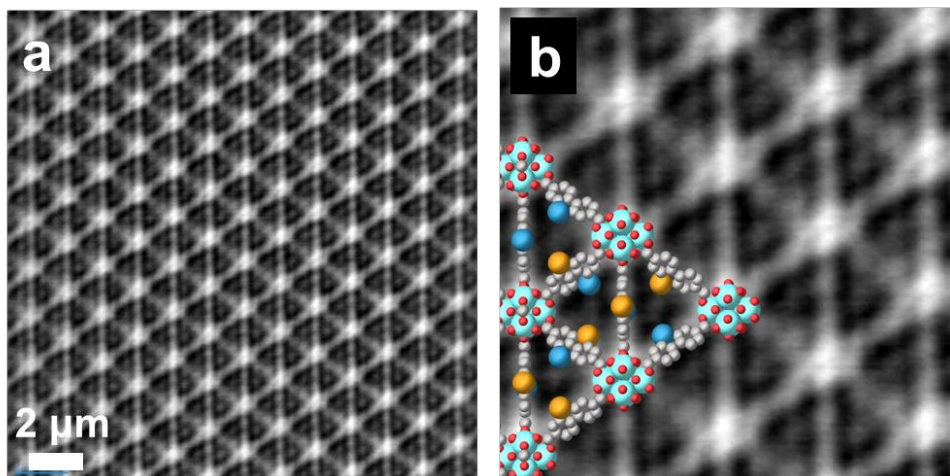


Fig. 5.7 (a) iDPC-STEM image and (b) the structural model with magnified iDPC-STEM image of UiO-FePd viewing along [110] crystal direction.

XPS was employed to analyze the chemical composition and surface chemical state of as-prepared samples, as shown in **Fig. 5.8**. XPS survey spectra for UiO-FePd and UiO-CuPd revealed distinct peaks corresponding to Zr 3*d*, O 1*s*, C 1*s* and N 1*s*. However, peaks characteristic of the metals was not observed, owing to their exceedingly low concentrations. Despite this, indirect evidence of metal incorporation was observed through changes in the N 1*s* peak. For UiO-CuPd, which serves as a representative example of UiO-M_AM_B materials, the characteristic peaks of Zr 3*d*, O 1*s*, and C 1*s* exhibited no significant shifts, thereby confirming that the structural integrity of the UiO-67 matrix was maintained. However, the N 1*s* characteristic peaks in UiO-CuPd were broader and showed a slight increase in intensity around 400 eV, which was also displayed in the N 1*s* patterns of UiO-Cu and UiO-FePd (**Fig. 5.9d** and **Fig. 5.10**). This phenomenon is attributed to electron transfer towards the metal sites anchored within the domain⁵⁻⁶. This observed electron transfer further substantiates the successful incorporation of metal ions into the bpydc linkers of the UiO-67 matrix.

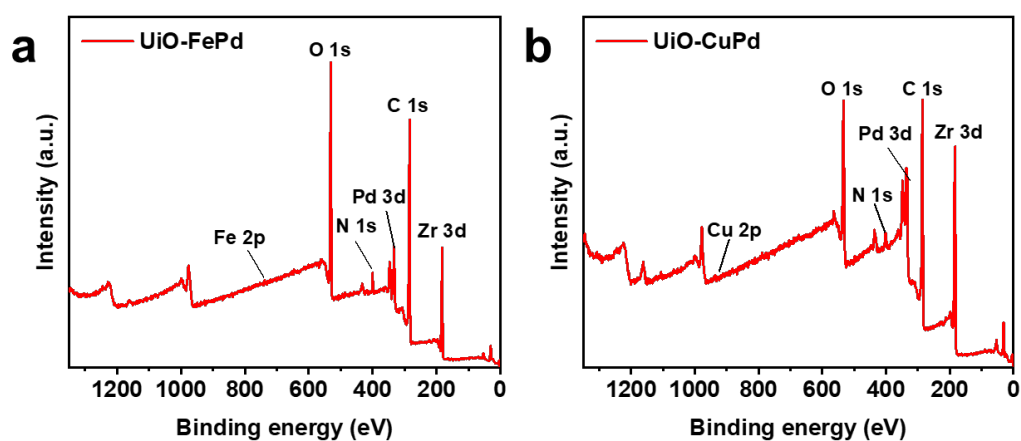


Fig. 5.8 XPS survey spectrum of (a) UiO-FePd, and (b) UiO-CuPd.

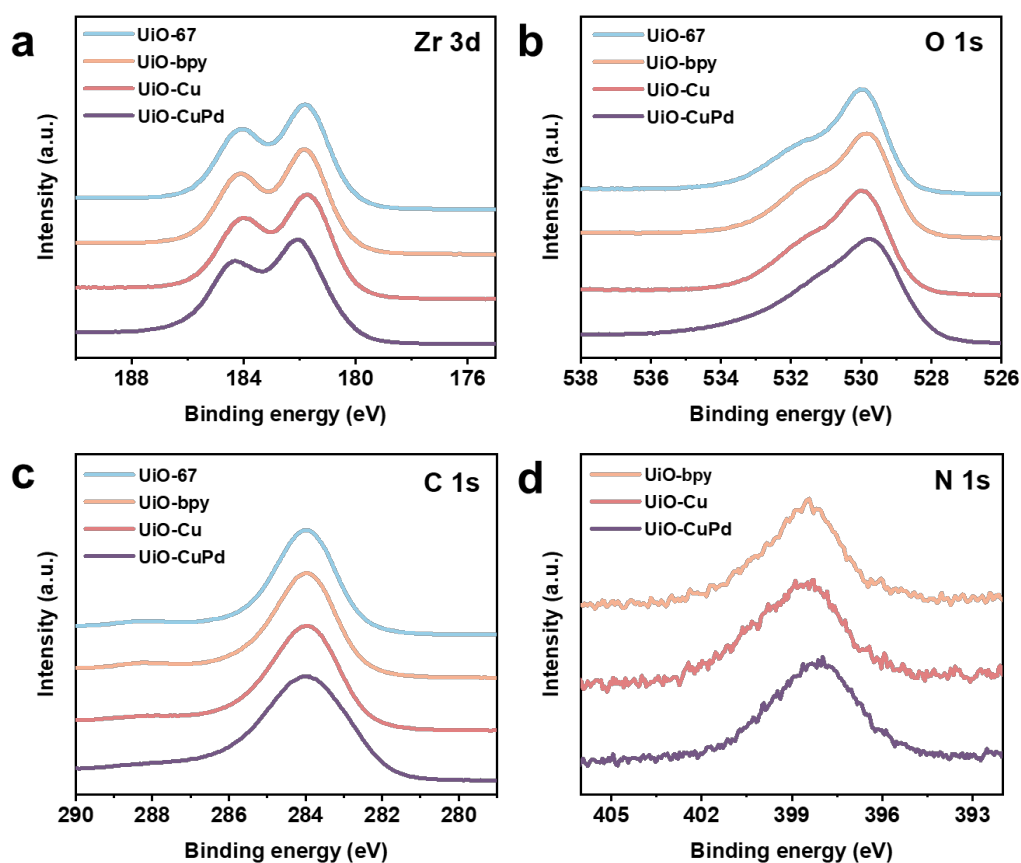


Fig. 5.9 XPS (a) Zr 3d, (b) O 1s, (c) C 1s, and (d) N 1s spectra of UiO-67, UiO-bpy, UiO-Cu, and UiO-CuPd.

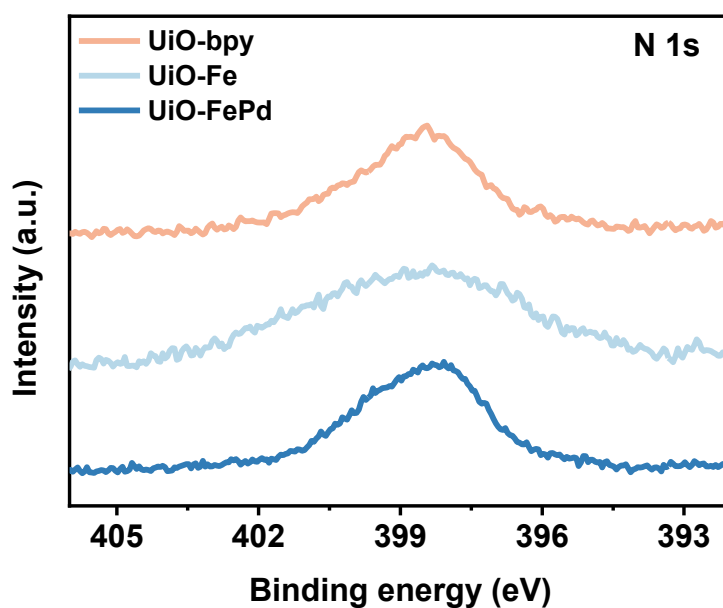


Fig. 5.10 XPS N 1s spectra of UiO-bpy, UiO-Fe, and UiO-FePd.

The PXRD analysis, illustrated in **Fig. 5.11**, provided additional confirmation of the structural integrity and exceptional crystallinity across all synthesized samples. A comprehensive analysis of the crystallographic parameters will follow in the dedicated section on synchrotron XRD and their refinements. Furthermore, XRF quantification data, as outlined in **Table 5.1**, indicated that metal A/B ratios fluctuated between 30% and 70%, which was acceptable for the predetermined design goals.

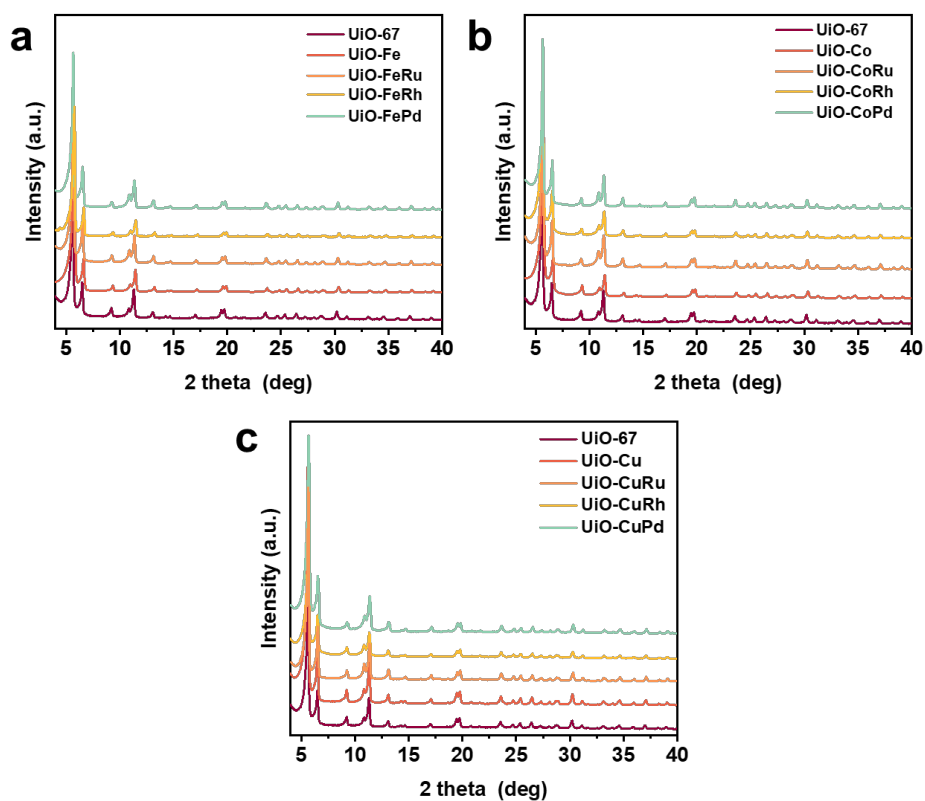


Fig. 5.11 XRD patterns for (a) UiO-FeM_B series, (b) UiO-CoM_B series and (c) UiO-CuM_B (M_B = Ru, Rh and Pd) series.

Table 5.1. Element contents of as-prepared samples from XRF analysis.

Sample (UiO-M _A M _B)	element		
	Zr (weight%)	M _A (weight%)	M _B (weight%)
UiO-FeRu	42.92	0.79	1.30
UiO-FeRh	46.97	0.93	2.46
UiO-FePd	43.74	2.43	4.42
UiO-CoPd	39.67	1.36	4.34
UiO-CoRh	24.85	1.10	2.48
UiO-CuRu	29.06	0.51	2.42
UiO-CuRh	32.74	1.10	2.67
UiO-CuPd	28.67	1.26	4.23

To investigate the chemical coordination environment of metal centers in UiO-M_AM_B, EXAFS spectra were employed, with WT analysis initially utilized to clearly distinguish different atoms within the atomic shell. The WT, which enhances correlation between k- and R-space data as shown in **Fig. 5.12 – 5.16**, was calculated using the software package developed by Funke and Chukalina with a Morlet wavelet configured at $\kappa = 10$ and $\sigma = 1$. For 3d transition metals (M_A) in all samples, the highest WT intensities were observed at a lobe centered at approximately $k \approx 6 \text{ \AA}^{-1}$ and $R \approx 1.6 \text{ \AA}$, corresponding to nitrogen atoms surrounding the metal centers. In contrast, for 4d transition metals (M_B), in addition to the Metal–N pathway similar to that of 3d metals, another lobe was observed at $k \approx 8.5\text{--}10.5 \text{ \AA}^{-1}$ and $R \approx 1.9\text{--}2.2 \text{ \AA}$, which is attributed to Metal–Cl interactions resulting from the use of metal chloride precursor compounds in the synthesis process. Notably, the absence of a significant peak corresponding to Metal–Metal backscattering in all samples indicates that metal species exist as dispersed atomic species within the UiO-67 framework, thereby ruling out the formation of metallic clusters or alloys. To further elucidate the metal coordination environment, quantitative fitting of the EXAFS data was performed, with results summarized in **Table 5.2**. UiO-FePd was used as the representative display model of different 3d/4d combinations. The Pd K-edge was best fitted with a Pd–N(O) pathway at a R of 2.01 $\text{\AA}$ and a CN of 1.9, indicating that Pd atoms are primarily bound to two nitrogen sites from the bpydc linkers, while another pathway revealed a Pd–Cl pathway at 2.27 $\text{\AA}$ with a coordination number of 2.0. Ru and Rh centers showed analogous coordination geometries with Pd center in UiO-M_AM_B. For the Fe K-edge, a single pathway was identified with Fe–N(O) pathway ($R = 2.00 \text{ \AA}$ and $\text{CN} = 5.8$), where the elevated coordination number, given the similar electron densities of nitrogen and oxygen, may suggest interactions with water or hydroxyl groups during synthesis. This

characteristic is also observed in other 3d transition metal centers in UiO- $M_A M_B$. These atomic structural resolution results provide compelling evidence that the metals incorporated into the UiO-67 framework are isolated single atoms in bpydc linker.

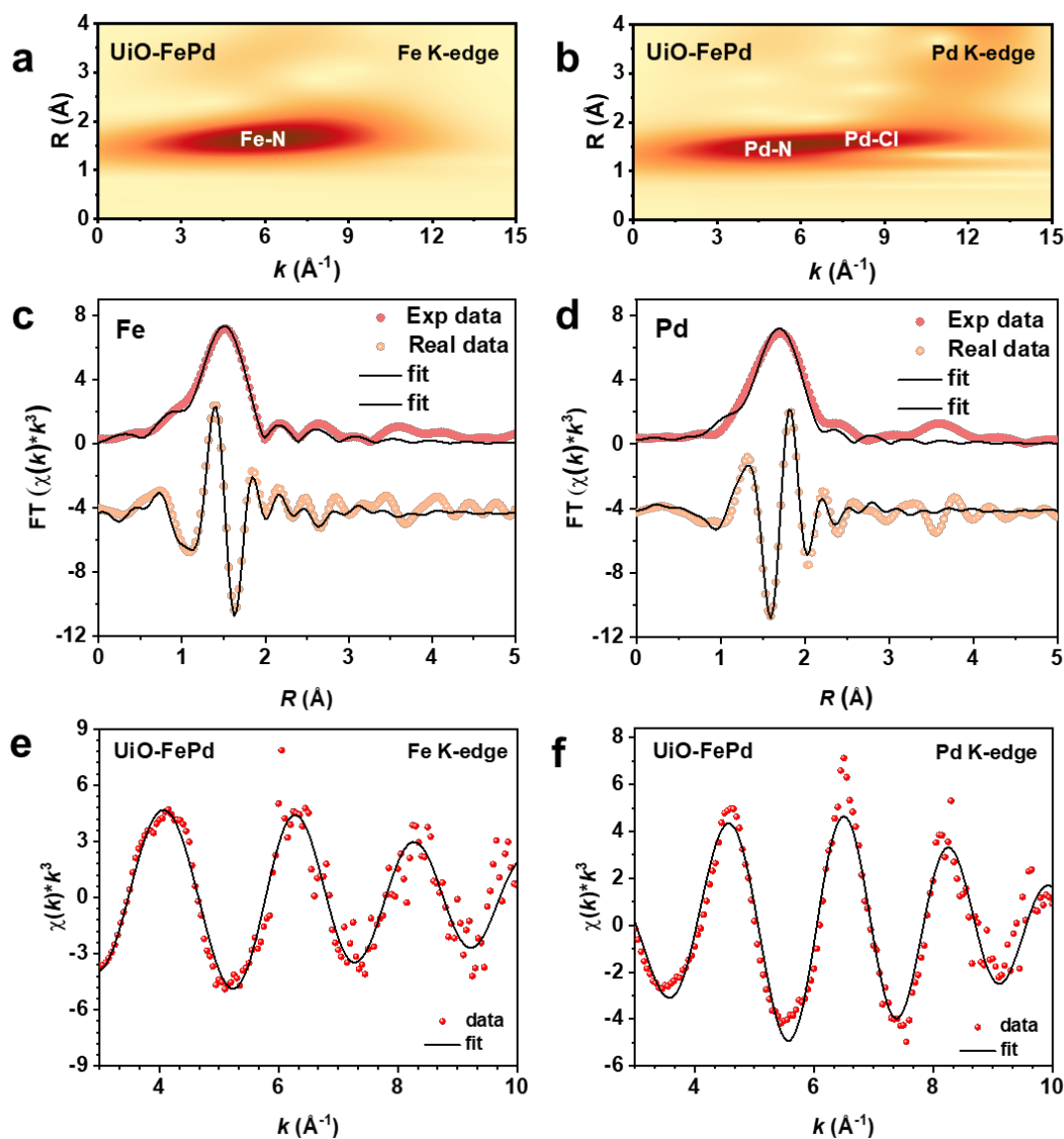


Fig. 5.12 (a, b) Wavelet transform plots of k^3 weighted EXAFS signal, using Morlet wavelet with $\kappa = 10$, $\sigma = 1$, (c, d) EXAFS in R-space representations ($|\chi(R)|$ and $\text{Re}[\chi(R)]$ parts) and (e, f) in k-space of the Fe and Pd K-edge of UiO-FePd.

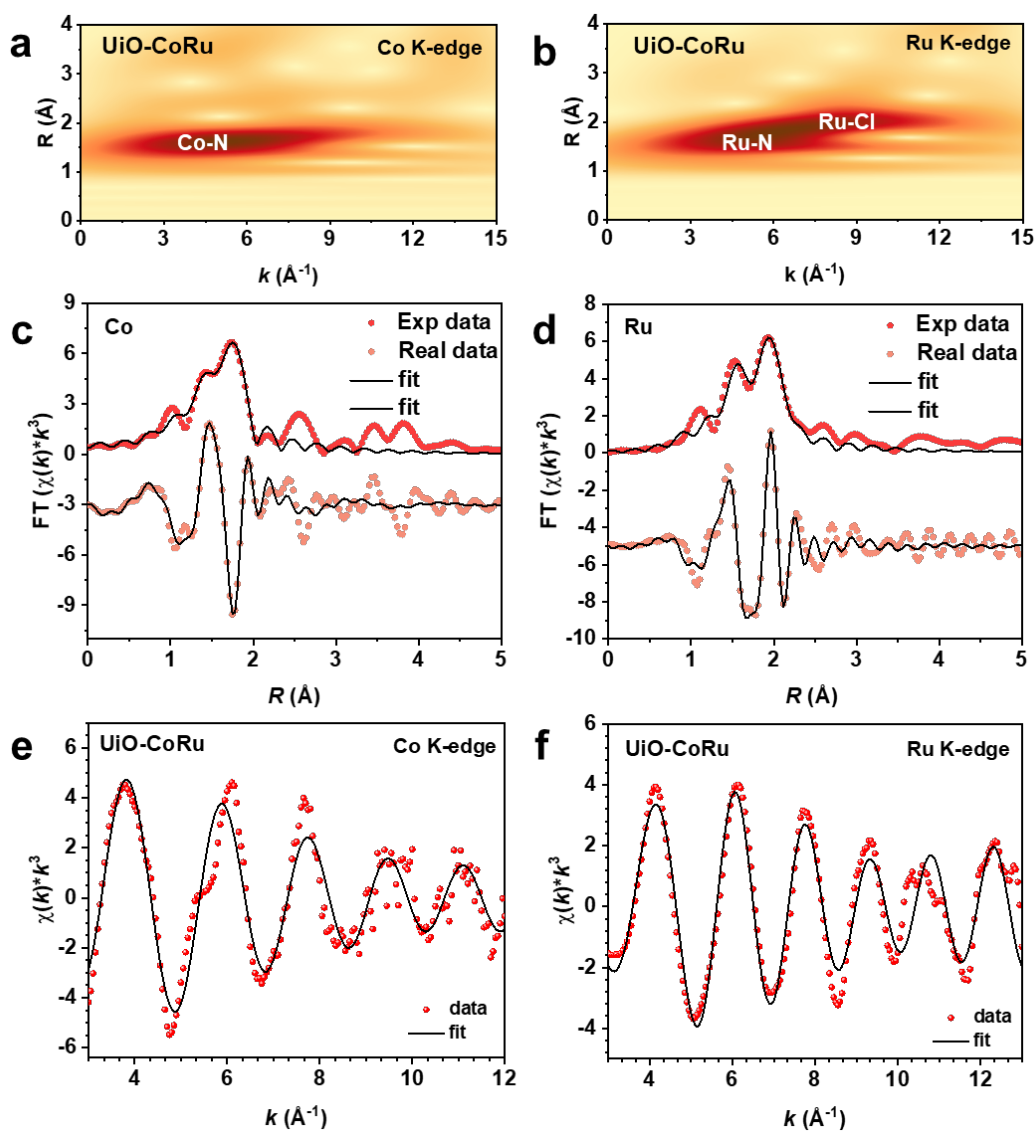


Fig. 5.13 (a, b) Wavelet transform plots of k^3 weighted EXAFS signal, using Morlet wavelet with $\kappa = 10$, $\sigma = 1$, (c, d) EXAFS in R-space representations ($|\chi(R)|$ and $\text{Re}[\chi(R)]$ parts) and (e, f) in k-space of the Co and Ru K-edge of UiO-CoRu.

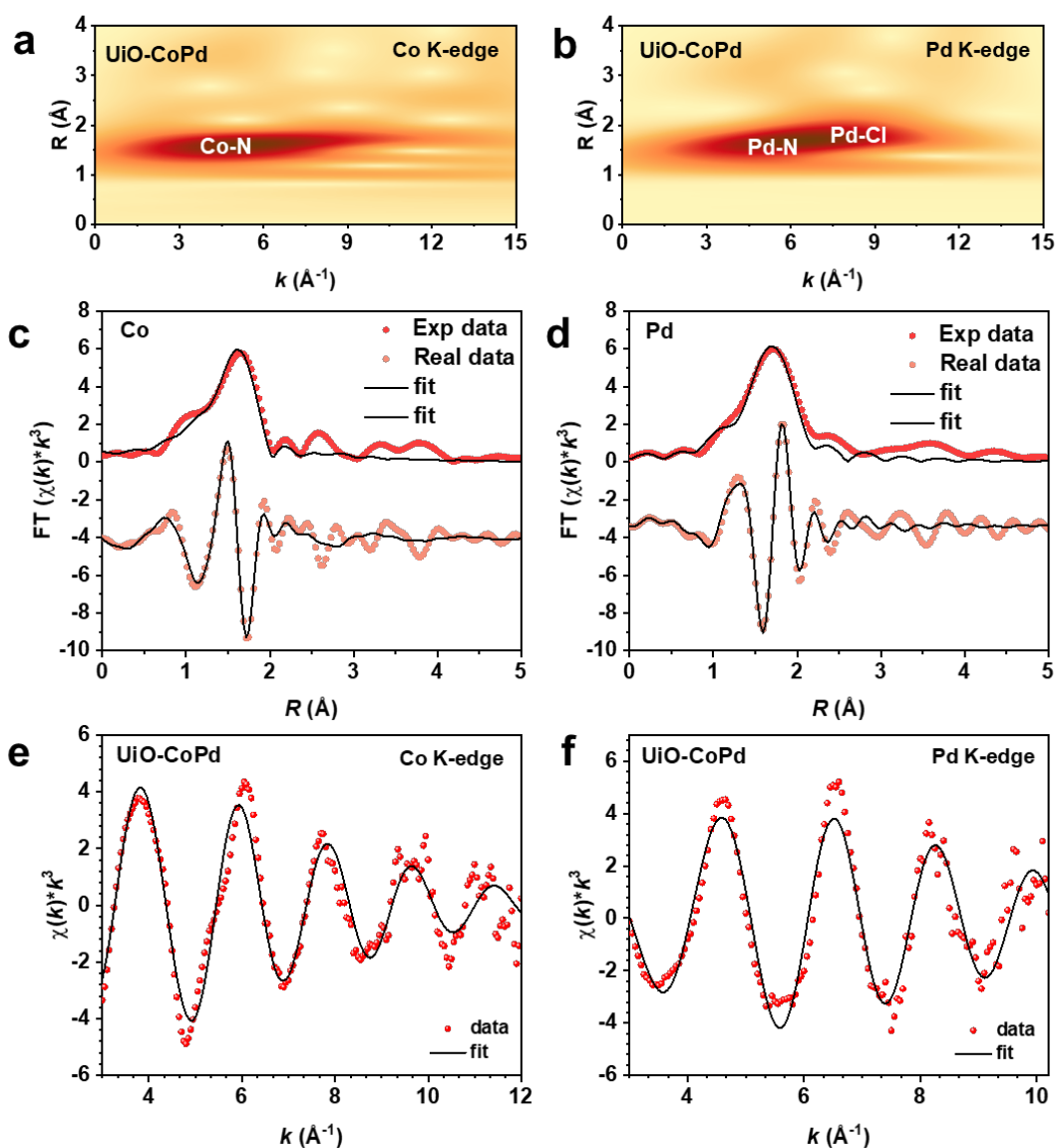


Fig. 5.14 (a, b) Wavelet transform plots of k^3 weighted EXAFS signal, using Morlet wavelet with $\kappa = 10$, $\sigma = 1$, (c, d) EXAFS in R-space representations ($|\chi(R)|$ and $\text{Re}[\chi(R)]$ parts) and (e, f) in k-space of the Co and Pd K-edge of UiO-CoPd.

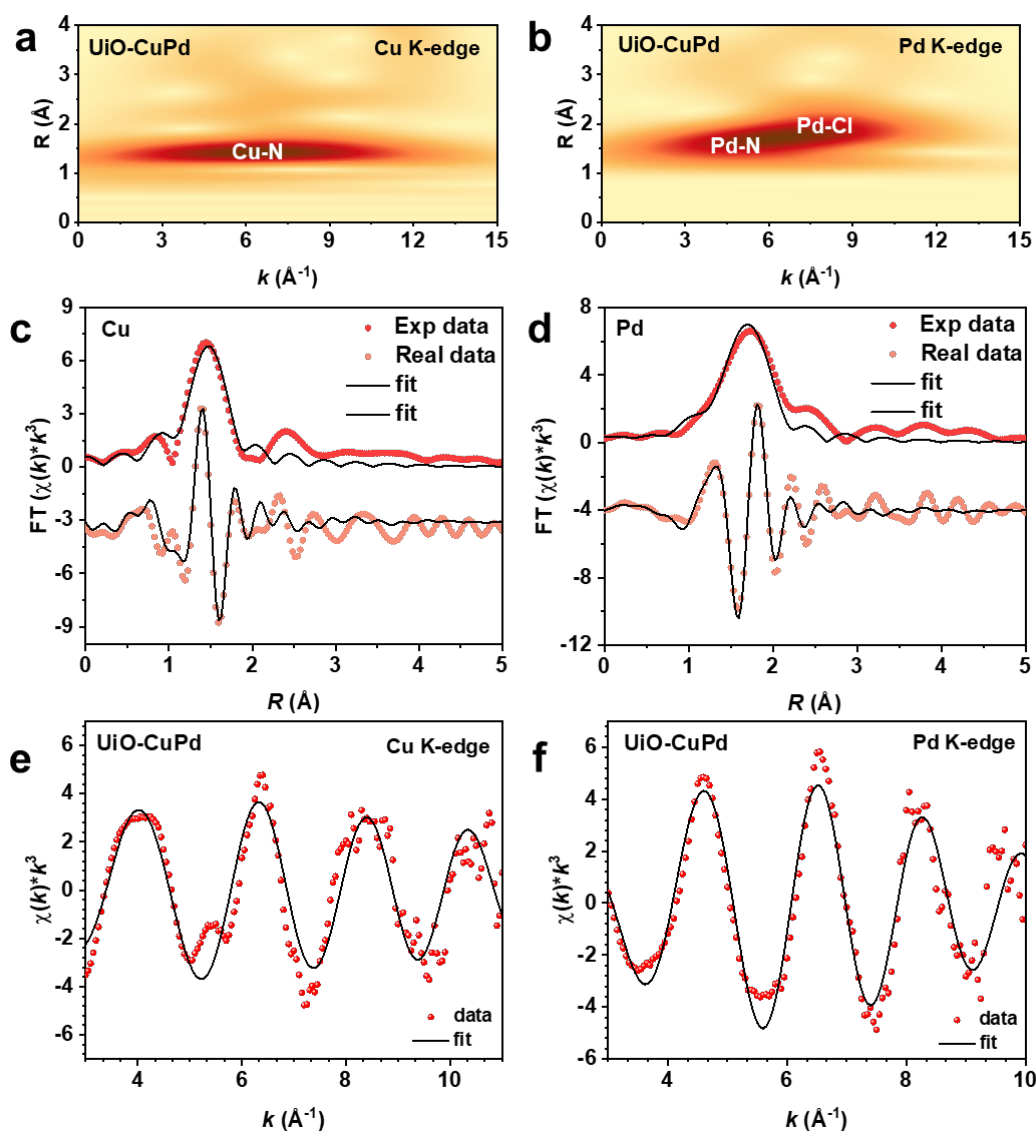


Fig. 5.15 (a, b) Wavelet transform plots of k^3 weighted EXAFS signal, using Morlet wavelet with $\kappa = 10$, $\sigma = 1$, (c, d) EXAFS in R-space representations ($|\chi(R)|$ and $\text{Re}[\chi(R)]$ parts) and (e, f) in k-space of the Cu and Pd K-edge of UiO-CuPd.

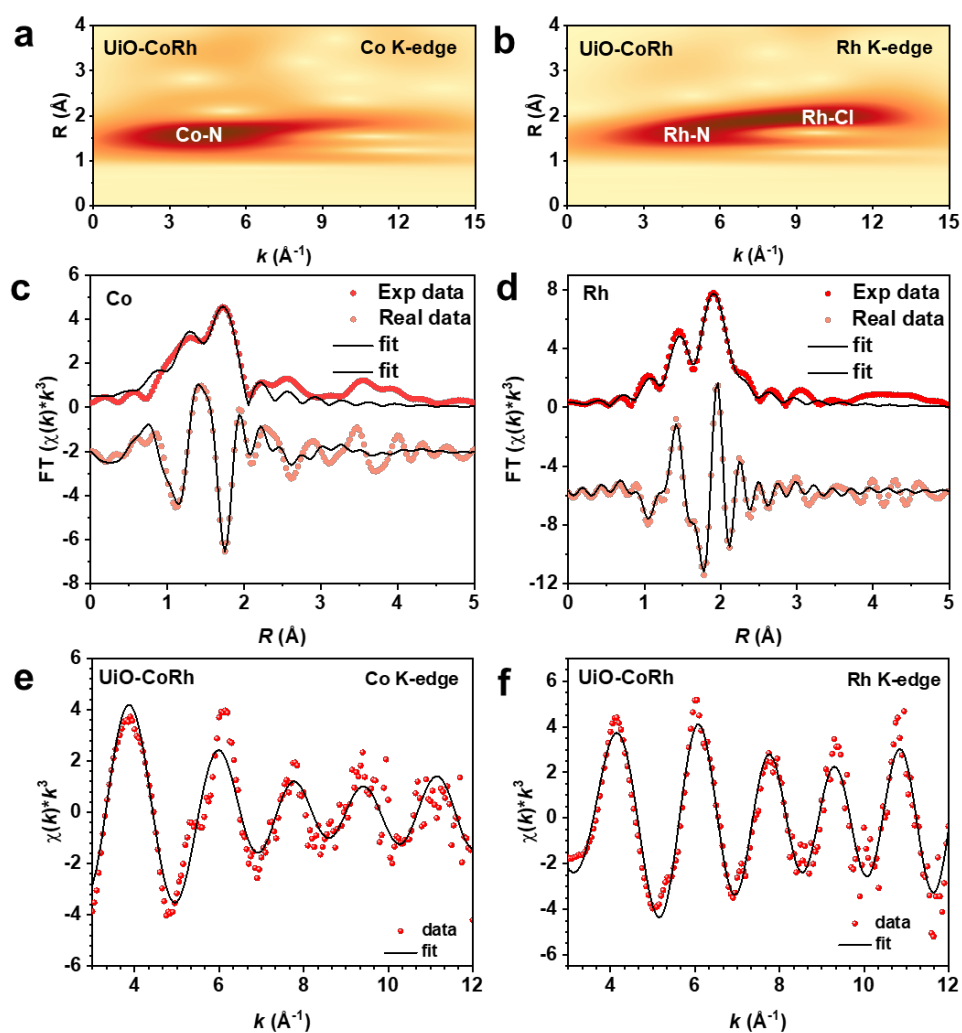


Fig. 5.16 (a, b) Wavelet transform plots of k^3 weighted EXAFS signal, using Morlet wavelet with $\kappa = 10$, $\sigma = 1$, (c, d) EXAFS in R-space representations ($|\chi(R)|$ and $\text{Re}[\chi(R)]$ parts) and (e, f) in k-space of the Co and Rh K-edge of UiO-CoRh.

Table 5.2. Curve fitting parameters for metal K-edge EXAFS for UiO-M_AM_B.

Sample	Path	<i>N</i>	<i>R</i> / Å	σ^2 / Å ²	ΔE_0	R-factor	k range
UiO-FePd	Fe–N(O)	5.8(4)	2.00(1)	0.006(1)	-8.0(9)	0.006	3-10.0
	Pd–N(O)	1.9(3)	2.01(3)	0.002(1)	1.7(5)	0.019	3-10.5
	Pd–Cl	2.0(2)	2.27(1)	0.003(1)			
UiO-CoRu	Co–N(O)	2.1(4)	1.98(2)	0.002(1)	-4.9(12)	0.009	3.0-13.9
	Co–N(O)	3.5(3)	2.11(2)	0.003(2)			
	Ru–N(O)	2.0(3)	2.10(1)	0.003(1)	-8.2(6)	0.020	3-14
	Ru–Cl	2.0(1)	2.37(1)	0.003(1)			
UiO-CoPd	Co–N(O)	5.8(5)	2.09(1)	0.008(2)	-6.1(11)	0.009	3-12
	Pd–N(O)	1.9(4)	2.01(5)	0.004(2)	0.3(4)	0.011	3-10.2
	Pd–Cl	2.0(2)	2.26(2)	0.007(4)			
UiO-CuPd	Cu–N(O)	4.0(3)	1.94(2)	0.003(1)	-8.0(8)	0.020	3-11
	Pd–N(O)	2.0(4)	2.02(3)	0.005(3)	2.9(7)	0.019	3-10
	Pd–Cl	1.9(2)	2.27(1)	0.003(1)			
UiO-CoRh	Co–N(O)	2.1(4)	1.91(2)	0.003(2)	-7.5(19)	0.016	3-12
	Co–N(O)	4.1(4)	2.07(2)	0.004(1)			
	Rh–N(O)	2.1(3)	2.04(1)	0.002(1)	2.2(3)	0.012	3-13
	Rh–Cl	2.6(1)	2.35(1)	0.003(1)			

S_0^2 was fixed as 0.9. ΔE_0 is refined as a global fit parameter.

Data range: $1.0 \leq R \leq 2.5$ -3.0 Å.

σ^2 is the Debye-Waller factor (a measure of thermal/lattice vibrations of atoms).

The atomic crystal structures of the samples were further elucidated using high-resolution synchrotron PXRD. The high-resolution PXRD data were collected on Beamline BL02B2 at SPring-8 (Japan) and TPS19A at NSRRC (Taiwan). The PXRD patterns, presented in **Fig. 5.17 – 5.20**, reveal that all synthesized samples possess a cubic lattice (space group of $Fm\bar{3}m$) with a lattice parameter remaining relatively constant at *ca.* 26.8 Å. Incorporation of metal species resulted in insignificant fluctuations ($\sim 0.01\%$), indicating minimal structural distortion. Moreover, the Bragg peaks display high symmetry, as exemplified in **Fig. 5.17** and corroborated by the quantitative analysis in **Table 5.3**, indicating that a homogeneous modification process occurs during metalation procedures.

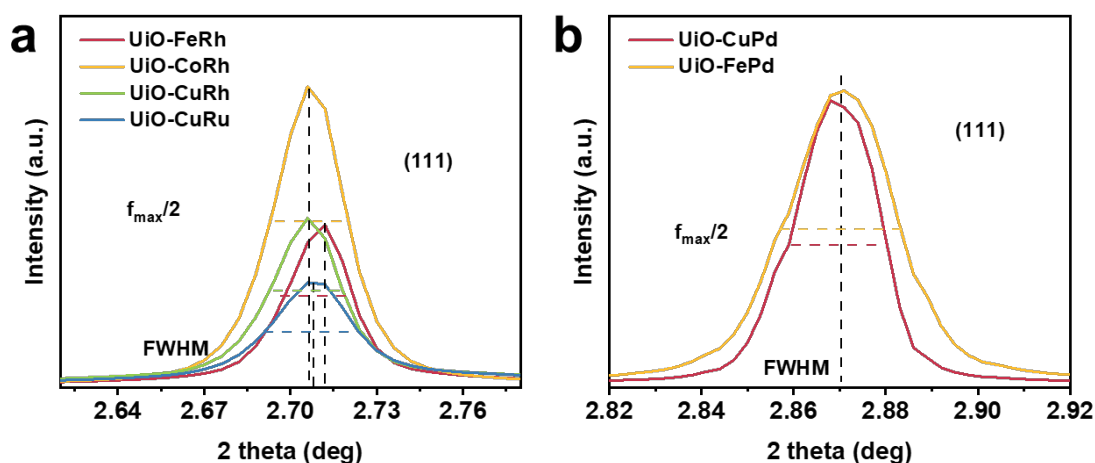


Fig. 5.17 Comparison of the Bragg peak (111) over **(a)** UiO-FeRh, UiO-CoRh, UiO-CuRh and UiO-CuRu, which the synchrotron PXRD data were collected on Beamline BL02B2 at SPring-8; **(b)** for UiO-CuPd and UiO-FePd, which the synchrotron PXRD data were collected on Beamline TPS19A at NSRRC.

Table 5.3. Quantitative peak parameters of samples from synchrotron PXRD.

	UiO-FeRh	UiO-CoRh	UiO-CuRh	UiO-CuRu
Peak asymmetry parameter	0.0003	0.0001	0.0001	0.0001
LVol-Integral breadths	116.6	239.0	109.1	93.8
LVol-FWHM	162.6	333.2	152.2	130.9
Microstrain (ϵ_0)*	0.00004	0.00004	0.00004	0.01298
Strain (Gaussian)	0.00010	0.00010	0.00010	0.00010
Strain (Lorentzian)	0.00010	0.00010	0.00010	0.05191

LVol - Volume weighted mean column heights.

ϵ_0 - dislocations, vacancies, and other defects, calculated from FWHMs.

Table 5.4 Quantitative peak parameters of samples from synchrotron PXRD.

	UiO-FePd	UiO-CuPd
Peak asymmetry parameter	0.0001	0.0001
LVol-Integral breadths	198.4	288.8
LVol-FWHM	217.0	298.27
Microstrain (ϵ_0)*	0.01235	0.00043
Strain (Gaussian)	0.00010	0.00167
Strain (Lorentzian)	0.04940	0.00010

LVol - Volume weighted mean column heights.

ϵ_0 - dislocations, vacancies, and other defects, calculated from FWHMs.

Rietveld refinement of PXRD data was carried out to elucidate the crystal structures of the samples, as shown in **Fig. 5.18 – 5.23**. In general, the reliability of Rietveld refinement was assessed using the R_{wp} value and the difference between experimental data and refinement profiles. Low R_{wp} value and minimal difference, as reported in **Table 5.5 – 5.6**, indicate high quality of the refinement results. The SOF of metal sites was constrained based on the element analysis from XRF spectroscopy. Refined atomic

parameters for the samples were summarized in **Table 5.7 – 5.12**. Notably, the metal sites are bonded to the N moieties of the bpydc linkers, consistent with prior investigations. Furthermore, the observation of highly symmetrical peaks in the PXRD patterns confirms that metal sites and bpydc linkers are homogeneously distributed and statistically unbiased within the UiO-67 framework.

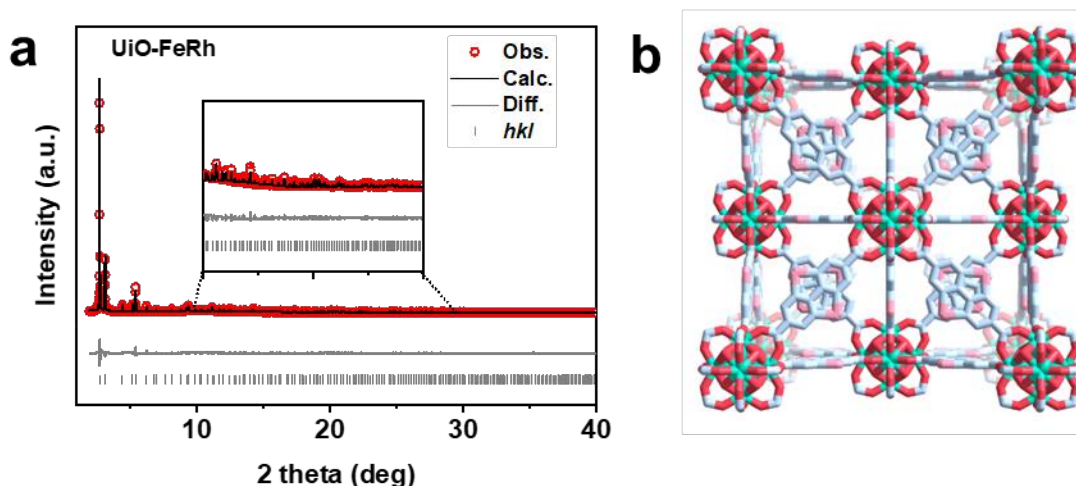


Fig. 5.18 (a) High-resolution synchrotron PXRD pattern collected on Beanline BL02B2 at SPring-8 ($\lambda = 0.729589 \text{ \AA}$) and the corresponding Rietveld refinement profile of UiO-FeRh, and **(b)** the respective Rietveld refined crystal structure.

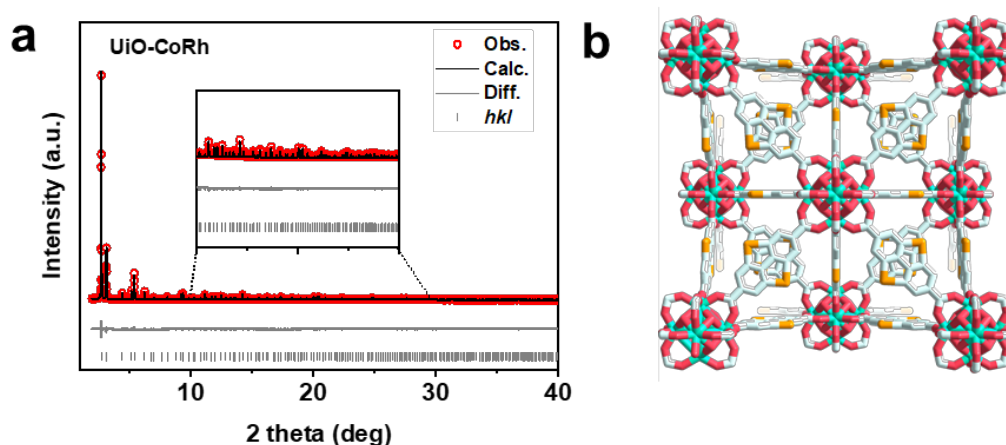


Fig. 5.19 (a) High-resolution synchrotron PXRD patterns collected on Beanline BL02B2 at SPring-8 ($\lambda = 0.729589 \text{ \AA}$) and the corresponding Rietveld refinement

profiles of UiO-CoRh, and **(b)** the respective Rietveld refined crystal structure.

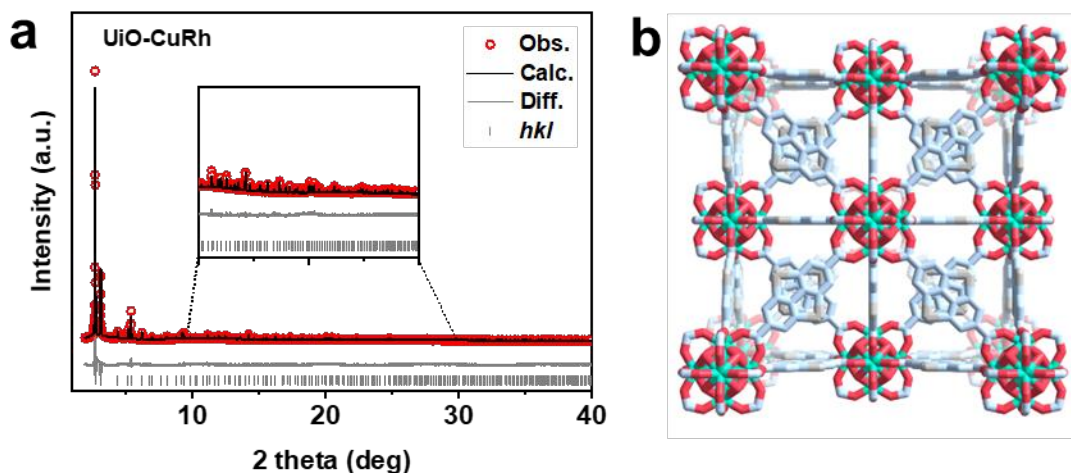


Fig. 5.20 (a) High-resolution synchrotron PXRD patterns collected on Beanline BL02B2 at SPring-8 ($\lambda = 0.729589 \text{ \AA}$) and the corresponding Rietveld refinement profiles of UiO-CuRh, and **(b)** the respective Rietveld refined crystal structure.

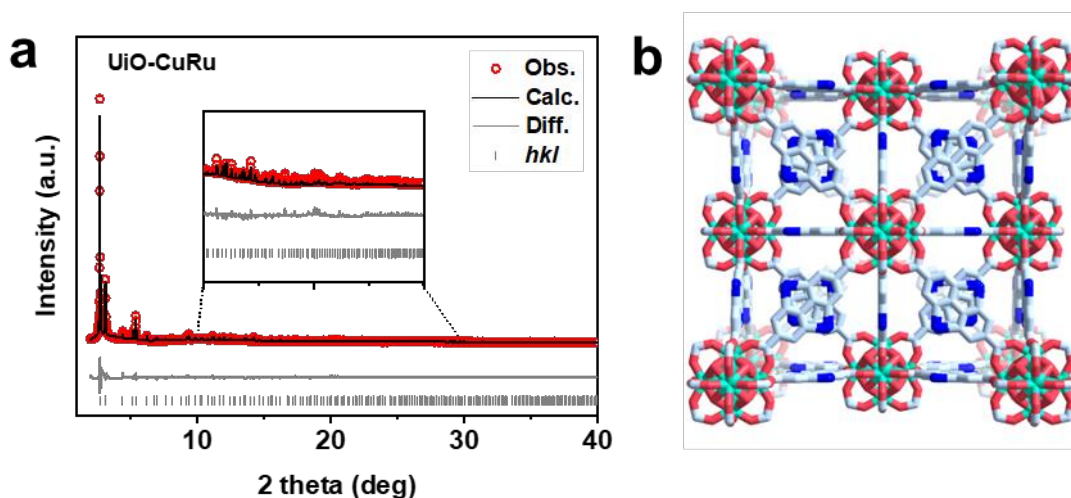


Fig. 5.21 (a) High-resolution synchrotron PXRD patterns collected on Beanline BL02B2 at SPring-8 ($\lambda = 0.729589 \text{ \AA}$) and the corresponding Rietveld refinement profiles of UiO-CuRu, and **(b)** the respective Rietveld-refined crystal structure.

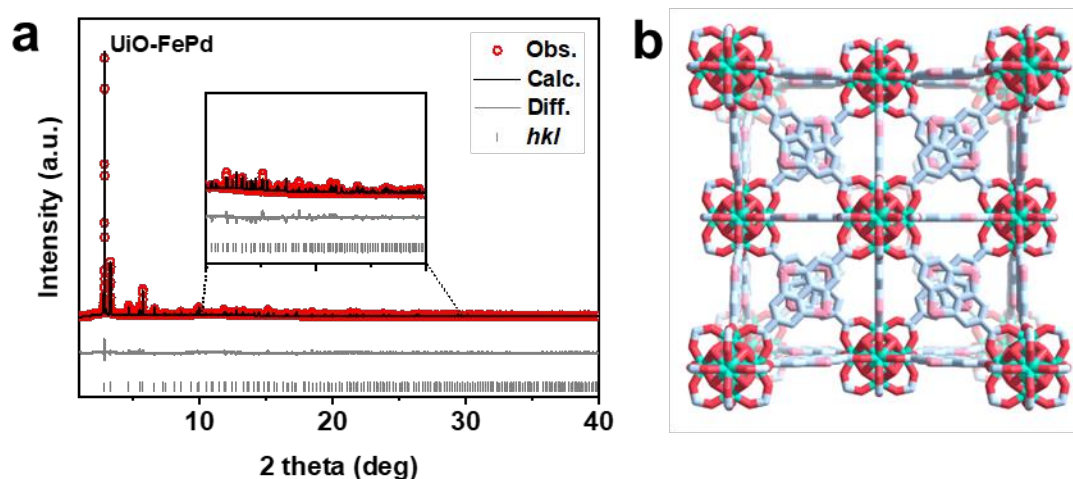


Fig. 5.22 (a) High-resolution synchrotron PXRD patterns collected on Beanline TPS19A at NSRRC ($\lambda = 0.77489 \text{ \AA}$) and the corresponding Rietveld refinement profiles of UiO-FePd, and (b) the respective Rietveld refined crystal structure.

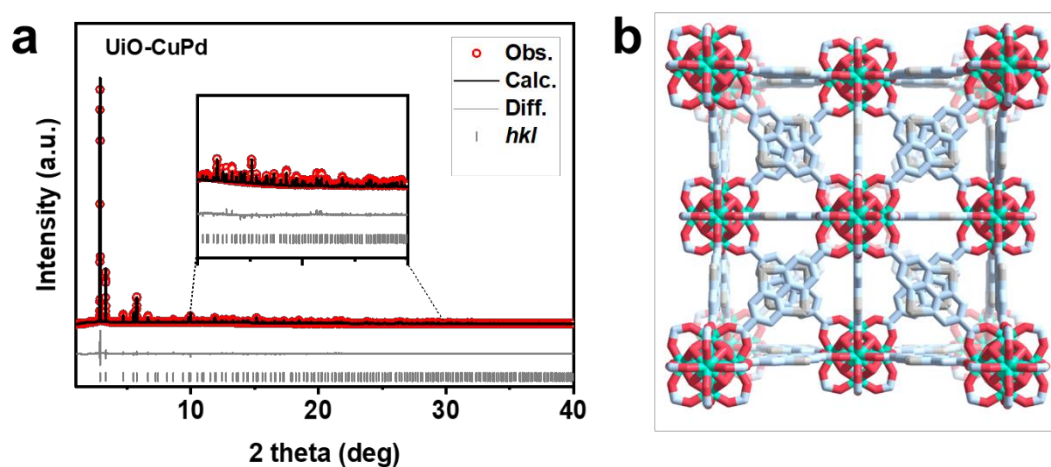


Fig. 5.23 (a) High-resolution synchrotron PXRD patterns collected on Beanline TPS19A at NSRRC ($\lambda = 0.77489 \text{ \AA}$) and the corresponding Rietveld refinement profiles of UiO-CuPd, and (b) the respective Rietveld refined crystal structure.

Table 5.5. Crystallographic parameters derived from the synchrotron PXRD measurements of UiO-FeRh, UiO-CoRh, and UiO-CuRh.

	UiO-FeRh	UiO-CoRh	UiO-CuRh
X-ray energy (keV)	16.99	16.99	16.99
Wavelength (Å)	0.729589	0.729589	0.729589
2 θ -zero point (°)	-0.00019	-0.00019	-0.00019
Space group	$Fm\bar{3}m$	$Fm\bar{3}m$	$Fm\bar{3}m$
Crystal system	Cubic	Cubic	Cubic
a (Å)	26.80101	26.81158	26.83537
2 θ range for refinement (°)	1.95-70	1.95-78	1.95-78
Number of parameters	37	39	42
Number of <i>hkl</i> s	2015	2617	2624
Refinement methods	Rietveld	Rietveld	Rietveld
R _{wp} /R _{exp} /R _p (%)	8.962/0.987/6.9212	9.694/0.988/6.935	9.775/0.962/6.330
<i>Gof</i>	9.078	9.807	10.162

R_{wp}: weighted profile; R_{exp}: expected; R_p: profile; *gof*: goodness-of-fit.

Table 5.6. Crystallographic parameters derived from the synchrotron PXRD measurements of UiO-FeRh, UiO-CoRh, and UiO-CuRh.

	UiO-CuRu	UiO-FePd	UiO-CuPd
X-ray energy (keV)	16.99	16.00	16.00
Wavelength (Å)	0.729589	0.77489	0.77489
2θ-zero point (°)	-0.00019	0.000008	0.000008
Space group	$Fm\bar{3}m$	$Fm\bar{3}m$	$Fm\bar{3}m$
Crystal system	Cubic	Cubic	Cubic
a (Å)	26.82778	26.77882	26.79100
2θ range for refinement (°)	1.95-78	0.935-90	0.935-90
Number of parameters	43	42	42
Number of <i>hkl</i> s	2624	3.64	3064
Refinement methods	Rietveld	Rietveld	Rietveld
R _{wp} /R _{exp} /R _p (%)	9.980/0.994/6.643	9.959/2.221/6.540	9.074/2.330/6.094
<i>Gof</i>	10.041	4.485	3.894

Table 5.7. Atomic parameters of UiO-FeRh from Rietveld refinement.

Atom	x	y	z	SOF	Beq ($\text{\AA}^2$)	Wyckoff letter
Zr1	-0.09043	0	0	1	1	24e
O1	0.12535	0	0.05537	1	1.5	96j
O2	0.06234	0.06234	0.06234	1	1.5	32f
C1	0.1167	0	0.1167	1	10	48h
C2	0.15654	0	0.15654	1	10	48h
C3	0.20591	0	0.14331	1	10	96j
C4	0.24206	0	0.17945	1	10	96j
C5	0.22883	0	0.22883	1	10	48h
C6	0.17945	0	0.24206	1	10	96j
C7	0.14331	0	0.20591	1	10	96j
Fe/Rh	0.31658	0	0.17555	0.13	10	96j

Table 5.8. Atomic parameters of UiO-CoRh from Rietveld refinement.

Atom	x	y	z	SOF	Beq ($\text{\AA}^2$)	Wyckoff letter
Zr1	-0.09175	0	0	1	1	24e
O1	0.128	0	0.06442	1	1.5	96j
O2	0.05045	0.05045	0.05045	1	1.5	32f
C1	0.1167	0	0.1167	1	10	48h
C2	0.15652	0	0.15652	1	10	48h
C3	0.20588	0	0.1433	1	10	96j
C4	0.24201	0	0.17943	1	10	96j
C5	0.22879	0	0.22879	1	10	48h
C6	0.17943	0	0.24201	1	10	96j
C7	0.1433	0	0.20588	1	10	96j
Co/Rh	0.3165	0	0.17553	0.13	10	96j

Table 5.9. Atomic parameters of UiO-CuRh from Rietveld refinement.

Atom	x	y	z	SOF	Beq ($\text{\AA}^2$)	Wyckoff letter
Zr1	-0.09180	0	0	1	1	24e
O1	0.12150	0	0.05812	1	1.5	96j
O2	0.05808	0.05808	0.05808	1	1.5	32f
C1	0.11680	0	0.11680	1	10	48h
C2	0.15660	0	0.15660	1	10	48h
C3	0.20628	0	0.14328	1	10	96j
C4	0.24265	0	0.17965	1	10	96j
C5	0.22934	0	0.22934	1	10	48h
C6	0.17965	0	0.24265	1	10	96j
C7	0.14328	0	0.20628	1	10	96j
Cu/Rh	0.31709	0	0.17575	0.13	10	96j

Table 5.10. Atomic parameters of UiO-CuRu from Rietveld refinement.

Atom	x	y	z	SOF	Beq ($\text{\AA}^2$)	Wyckoff letter
Zr1	0.08547	0	0	1	2	24e
O1	-0.12419	0	-0.04206	1	2	96j
O2	0.07409	0.07409	0.07409	1	2	32f
C1	0.11670	0	0.11670	1	10	48h
C2	0.15650	0	0.15650	1	10	48h
C3	0.20583	0	0.14328	1	10	96j
C4	0.24194	0	0.17939	1	10	96j
C5	0.22872	0	0.22872	1	10	48h
C6	0.17939	0	0.24194	1	10	96j
C7	0.14328	0	0.20583	1	10	96j
Cu/Ru	0.31638	0	0.17549	0.13	10	96j

Table 5.11. Atomic parameters of UiO-FePd from Rietveld refinement.

Atom	x	y	z	SOF	Beq ($\text{\AA}^2$)	Wyckoff letter
Zr1	-0.09213	0	0	1	1	24e
O1	0.12715	0	0.06064	1	1.5	96j
O2	0.05669	0.05669	0.05669	1	1.5	32f
C1	0.11670	0	0.11670	1	10	48h
C2	0.15657	0	0.15657	1	10	48h
C3	0.20599	0	0.14333	1	10	96j
C4	0.24216	0	0.17951	1	10	96j
C5	0.22892	0	0.22892	1	10	48h
C6	0.17951	0	0.24216	1	10	96j
C7	0.14333	0	0.20599	1	10	96j
Fe/Pd	0.31675	0	0.17560	0.15	10	96j

Table 5.12. Atomic parameters of UiO-CuPd from Rietveld refinement.

Atom	x	y	z	SOF	Beq (Å ²)	Wyckoff letter
Zr1	-0.09202	0	0	1	1	24e
O1	0.12772	0	0.06434	1	1.5	96j
O2	0.05293	0.05293	0.05293	1	1.5	32f
C1	0.11670	0	0.11670	1	10	48h
C2	0.15655	0	0.15655	1	10	48h
C3	0.20595	0	0.14332	1	10	96j
C4	0.24211	0	0.17948	1	10	96j
C5	0.22887	0	0.22887	1	10	48h
C6	0.17948	0	0.24211	1	10	96j
C7	0.14332	0	0.20595	1	10	96j
Cu/Pd	0.31666	0	0.17557	0.15	10	96j

Our structural analyses from **Chapters 3** and **4** reveal that the metal positions in UiO- $M_A M_B$ are anchored to N atoms of the bpydc linkers. Simulations indicate a distance of approximately 5.3 Å between two metal motifs ($M \cdots M$) on neighboring bpydc linkers. However, these characterization techniques have limited insight into the exact and respective positions of M_A and M_B within the MOF framework. For instance, in UiO-FePd, while the PXRD data refined structural model has confirmed the statistical regularity of bimetallic atom positions, it however cannot determine whether M_A and M_B anchor to neighboring linkers as proposed in the ideal crystal structure model, or if alternative distributions like $Fe \cdots Fe$ or $Pd \cdots Pd$ dominate.

PXRD is effective for establishing the overall crystallinity and statistical positioning of

atoms within MOFs. However, in the case of bimetallic UiO- $M_A M_B$, it fails to resolve the specific arrangement of M_A (e.g., Fe) and M_B (e.g., Pd) across neighboring bpydc linkers. This ambiguity necessitates advanced methods to probe the local coordination environment and confirm the distribution of bimetallic sites.

To overcome this limitation, we employed RXRD, targeting structural features associated with the specific metal sites. Synchrotron PXRD measurements were performed below the Pd and Rh K-edges for UiO-CuPd, UiO-FePd, UiO-CoRh, and UiO-FeRh to highlight specific atomic information. RXRD data for UiO-CuPd and UiO-FePd were collected on Beamline TPS19A (NSRRC), while data for UiO-CoRh and UiO-FeRh were obtained on Beamline BL02B2 (SPring-8). Using UiO-CuPd as a model system, the theoretical K-edge of Pd is 24,350 eV. We systematically collected PXRD data starting at 24,310 eV (40 eV below the K-edge), increasing the incident X-ray energy in 5 eV increments. This approach enabled focused interrogation of Pd-based building units and detected subtle structural changes within the UiO-67 framework. As shown in **Fig. 5.24**, distinct diffraction peaks emerged at *ca.* 4.7° as X-ray energy closed and approached the Pd K-edge. This peak signifies a symmetry reduction in UiO-CuPd and UiO-FePd as the wavelength neared the Pd K-edge. Notably, these localized structural distortions cannot be explained by simple peak shifts expected for the $Fm\bar{3}m$ space group. As shown in **Fig. 5.25**, subsequent modeling confirmed that the diffraction peaks corresponding to $Fm\bar{3}m$ remain unchanged as the incident X-ray energy increases. In contrast, the emergent peak at ~4.7° aligns with the simulated XRD pattern of the $Fm\bar{3}$ space group, which lacks diagonal “m” symmetry ($\{1\ 1\ 0\}$ plane). Within this reduced-symmetry space plane, we identified the cause of symmetry breaking, fulfilling our structural objectives. The enhanced atomic diffraction of Pd near its K-edge disrupts the symmetry of UiO-67, suggesting a fixed, non-random distribution of Pd atoms at

the bpydc linker sites. Similar findings were observed in RXRD experiments targeting Rh metals in UiO-CoRh, and UiO-FeRh (**Fig. 5.24 – 5.28**). Distinct diffraction peaks at *ca.* 4.7°, 8.9°, and 9.7°, indexed as (331), (733), and (840)/(480), emerged as X-ray energy neared and approached the Rh K-edge, also attributing to $Fm\bar{3}$ space group. Collectively, these RXRD and PXRD analyses unveil a dual-metal coordination environment within the UiO-M_AM_B framework. As illustrated in **Fig. 5.29**, the two metal motifs on neighboring bpydc linkers predominantly exist as Fe(Cu)•••Pd(Rh) (M_A•••M_B) pairs configurations. These results further indicate that bimetallic sites M_A and M_B in UiO-M_AM_B are not randomly distributed but are anchored in a specific M_A•••M_B configuration on neighboring bpydc linkers.

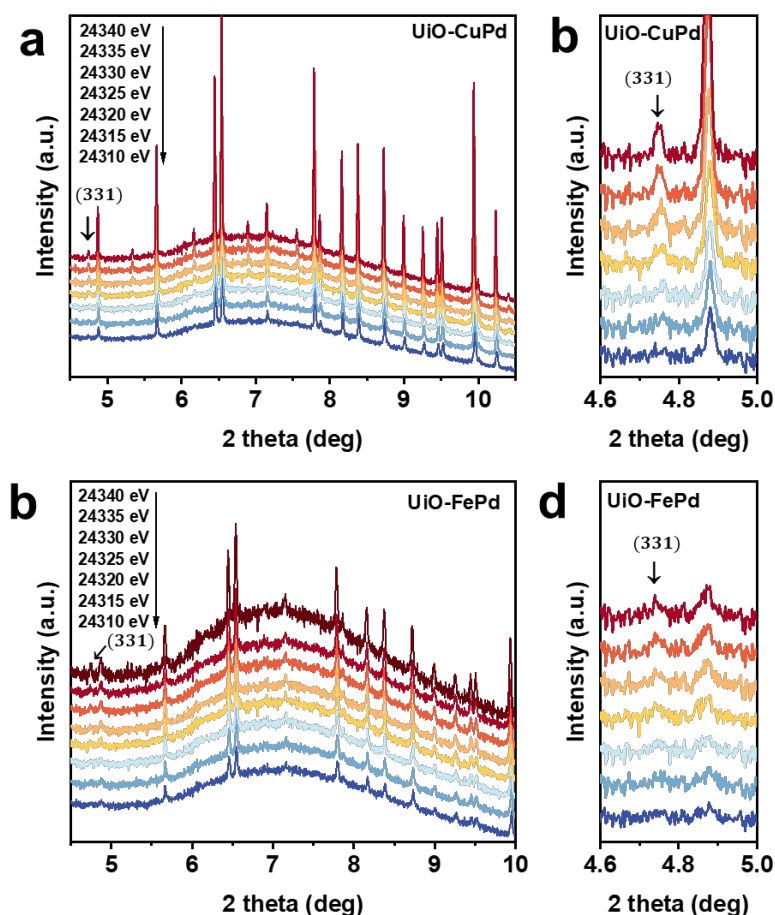


Fig. 5.24 Experimental RXRD pattern at Pd pre-K-edge resonant energies (24,310-

24,340 eV) for (a) UiO-CuPd and (c) UiO-FePd, with magnified regions in (b) and (d), respectively.

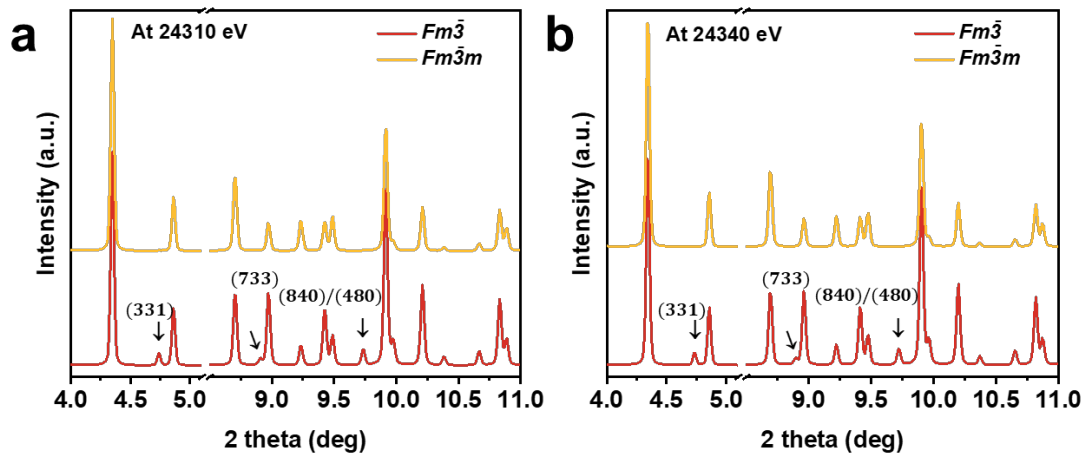


Fig. 5.25 Simulated PXRD patterns of UiO-67 for the space group of $Fm\bar{3}m$ and $Fm\bar{3}$ at (a) 24310 eV and (b) 24340 eV, near Pd K-edge.

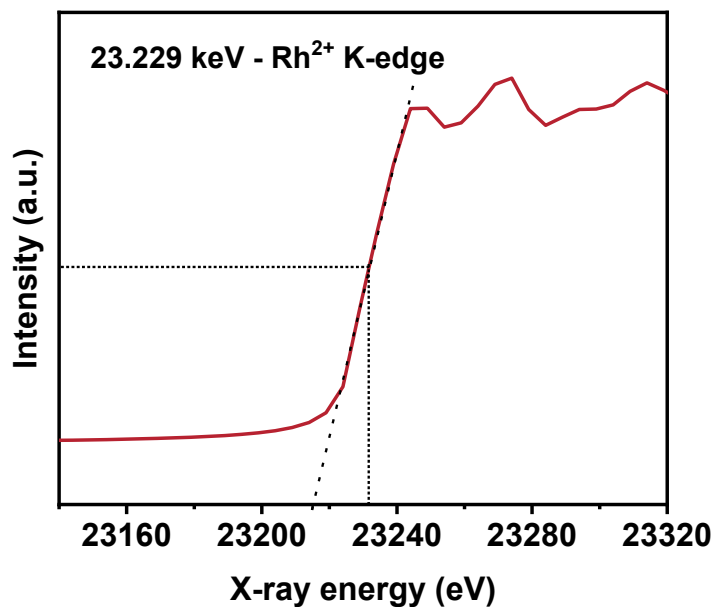


Fig. 5.26 Experimental fluorescence spectra over the Rh K-edge of UiO-CoRh.

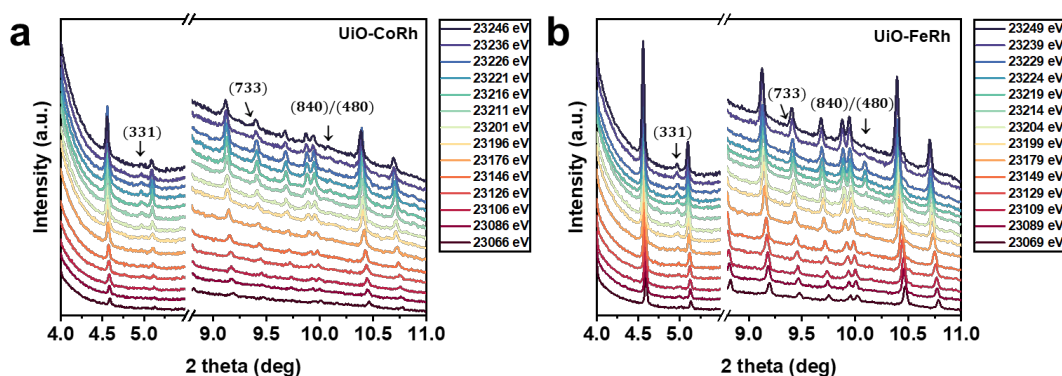


Fig. 5.27 Experimental RXRD pattern at Rh pre-K-edge resonant energies (23,066-23,069 eV) for (a) UiO-CoRh and (b) UiO-FeRh.

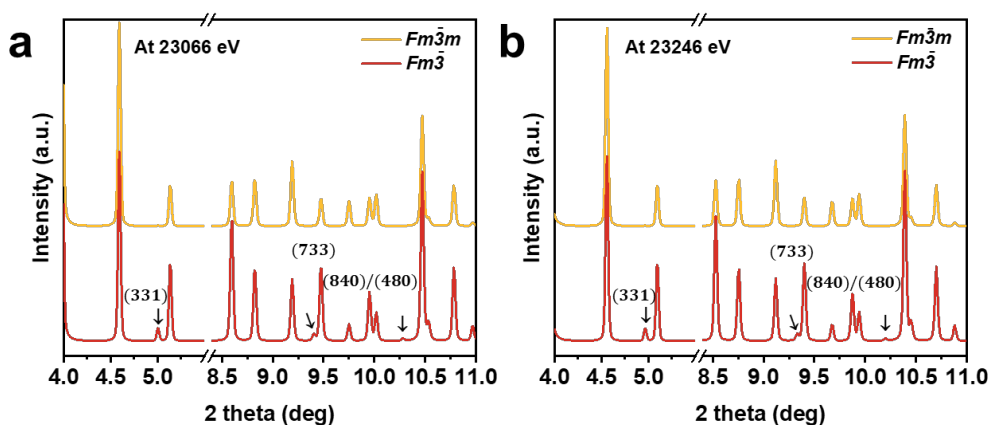


Fig. 5.28 Simulated PXRD patterns of UiO-67 for the space group of $Fm\bar{3}m$ and $Fm\bar{3}$ at (a) 23066 eV and (b) 23246 eV, near Rh K-edge.

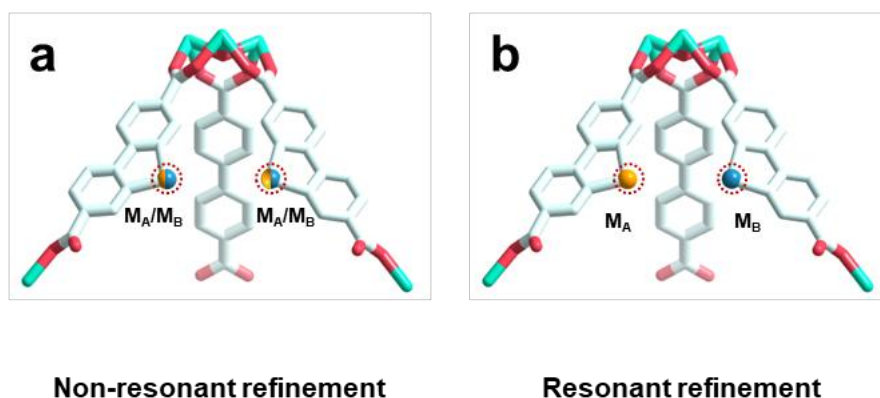


Fig. 5.29 Schematic illustration of structural refinement methodologies for determining metal site: (a) Non-resonant XRD (PXRD); (b) RXRD in UiO- $M_A M_B$ viewed along the $\{110\}$ plane.

5.3.2 Photocatalytic CO₂RR Performance

The photocatalytic CO₂RR performance of UiO-M_AM_B was evaluated under simulated solar irradiation (300 W Xe lamp) in CO₂-saturated aqueous system containing TEOA as the sacrificial agent (**Fig. 5.30**). Compared to the performance of UiO-67, UiO-M_A and UiO-M_AM_B (3d/3d) catalysts outlined in **Chapter 4**, all UiO-M_AM_B variants demonstrated the ability to produce C₂⁺ products with varying selectivity. This suggests that 4d transition metals (Ru, Rh, and Pd) are particularly effective for photocatalytic CO₂RR targeting C₂⁺ products. Notably, UiO-M_APd exhibited the highest CH₃COOH production rate while UiO-M_ARh displayed the lowest acetic acid production and selectivity. UiO-CoPd achieved a significant acetic acid production rate of 61.94 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with an exceptional selectivity of 99%. Furthermore, UiO-CuPd not only produced acetic acid but also further converted it into acetaldehyde.

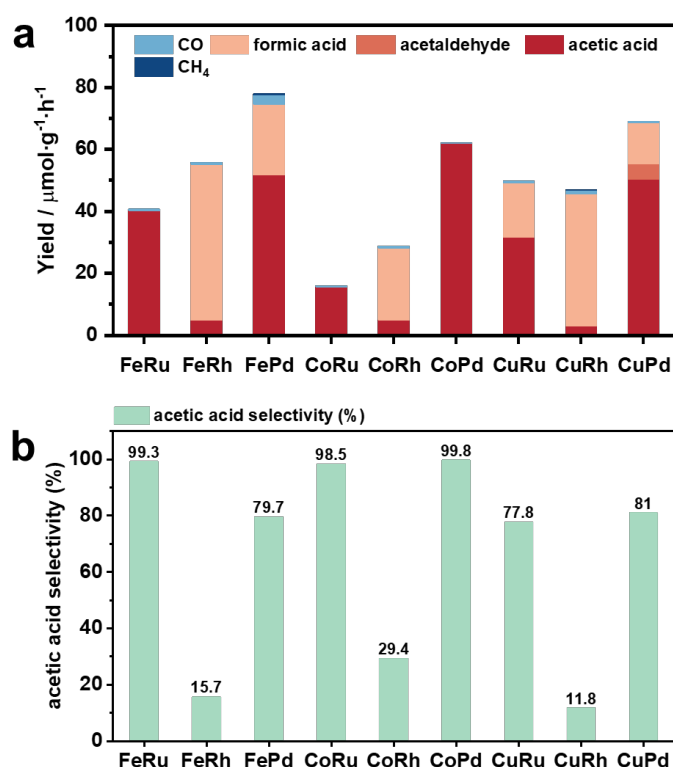


Fig. 5.30 (a) CO₂RR performance of UiO-FeM_B, UiO-CoM_B, and UiO-CuM_B (M_B =

Ru, Rh, and Pd) under Xe light illumination using TEOA as the sacrificial agent and **(b)** their acetic acid selectivity.

Table 5.13. TON value for the total product of catalysts.

Catalyst	TON _{total} *	TON _{acetic acid}
UiO-FeRu	111.64	110.09
UiO-FeRh	152.99	13.07
UiO-FePd	213.59	141.53
UiO-CoRu	43.79	42.47
UiO- CoRh	78.53	13.53
UiO-CoPd	169.32	168.74
UiO-CuRu	135.73	86.33
UiO-CuRh	127.95	8.04
UiO-CuPd	189.50	138.26

* TON was calculated using 30 mg of catalyst with an average atomic percentage of active sites (0.045 atomic%) in 5 hours of illumination.

Additional experiments explored how different photocatalytic conditions affect CO₂ reduction selectivity, using UiO-M_APd as the representative catalysts (**Fig. 5.31**). Control experiments replaced the Xe lamp with light at specific wavelengths. At 370 nm illumination, all UiO-M_APd produced a range of products, including formic acid, acetic acid, and acetaldehyde, but with low selectivity for acetic acid. At 440 nm illumination, all UiO-M_APd catalysts showed enhanced selectivity for acetic acid. Notably, UiO-FePd achieved a production rate of 48.9 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with 99% selectivity. These findings highlight the influence of wavelength on product selectivity and the superior performance of Pd-based UiO-M_AM_B catalysts.

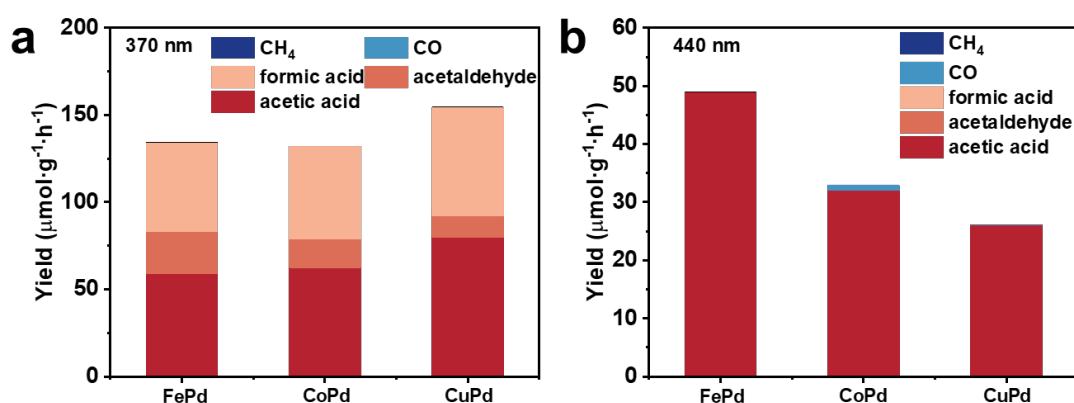


Fig. 5.31 Control CO₂RR performance of UiO-FePd, UiO-CoPd and UiO-CuPd under (a) 370 nm and (b) 440 nm LED light illumination using TEOA as the sacrificial agent.

Using UiO-FePd as a representative catalyst, further reaction conditions were investigated to assess their impact on photocatalytic CO₂RR performance. **Fig. 5.32a** illustrates the effect of wavelength on photocatalytic performance. Note that the performance under Xe light (simulated solar light) cannot be directly compared to that under monochromatic wavelengths. As the wavelength increased, the total molar carbon product yield of UiO-FePd also increased, peaking at 390 nm with a maximum total molar carbon product yield of 157 μmol·g⁻¹·h⁻¹. At this wavelength, acetic acid production was the highest, reaching 72.39 μmol·g⁻¹·h⁻¹ but selectivity decreased to 80%. Beyond 390 nm, the yield of acetic acid production decreased to 48.95 μmol·g⁻¹·h⁻¹ at 440 nm, while selectivity improved to 99%. This suggests that higher-energy wavelengths (shorter wavelengths) enhance CO₂ reduction and C-C bond formation, whereas lower-energy light (longer wavelengths) suppresses byproduct formation, favoring C₂+ product selectivity. Control experiments were conducted to evaluate the necessity of each reaction component. UiO-FePd showed no activity in the absence of catalyst, light, sacrificial agent, or CO₂, confirming the essential role of each in the

photocatalytic process (**Fig. 5.32b**). Interestingly, increasing the pressure in the reaction system did not significantly enhance the reaction rate or selectivity, as shown in **Fig. 5.32b – c** and **Fig. 5.33**, suggesting that the reaction is strongly governed by equilibrium.

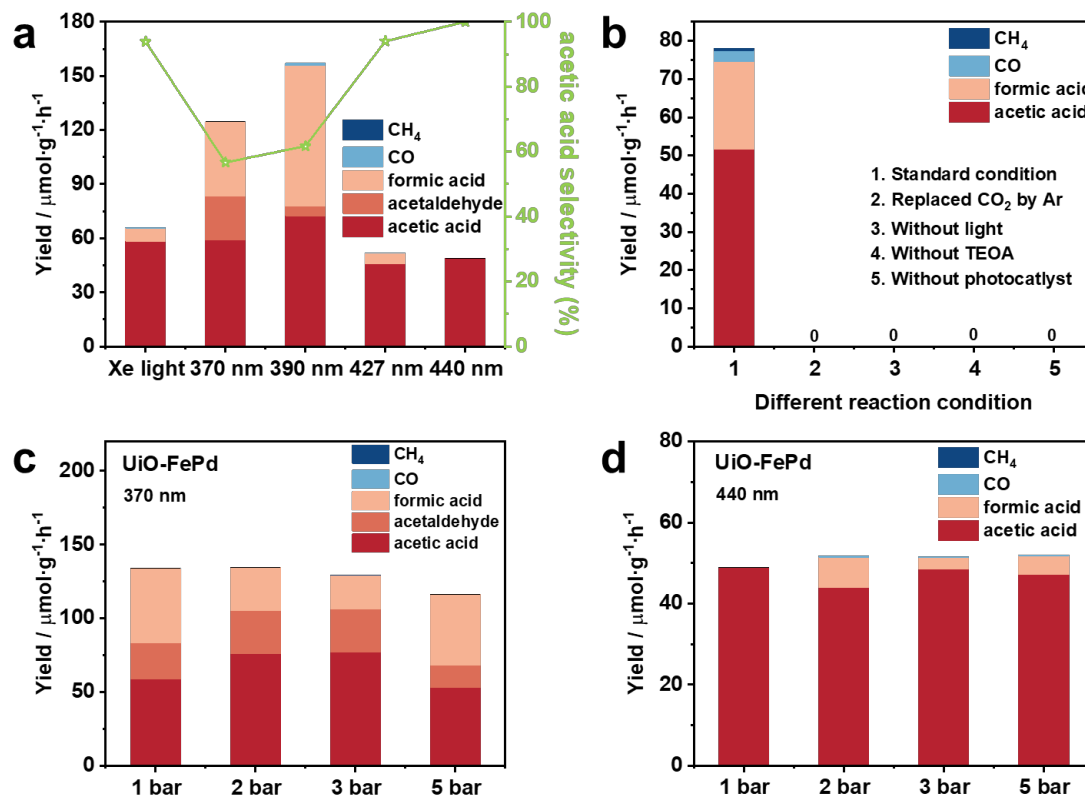


Fig. 5.32 Control experiments utilizing UiO-FePd as photocatalyst with (a) different light source, (b) different reaction conditions, under (c) 370 nm and (d) 440 nm LED light source at different pressure conditions.

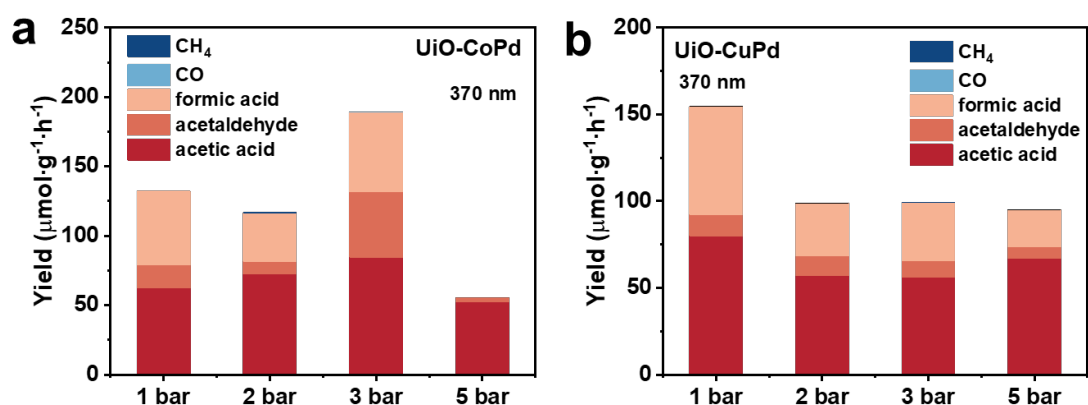


Fig. 5.33 Control experiment utilizing (a) UiO-CoPd and (b) UiO-CuPd as photocatalysts under 370 nm LED light source at different pressure conditions.

The stability of UiO-FePd was assessed over five consecutive photocatalytic cycles, as shown in **Fig. 5.34a**. The production yield of acetic acid decreased significantly, retaining only 10% of its initial value after five cycles. PXRD analysis revealed complete structural degradation of the UiO-FePd framework, indicating poor stability under prolonged reaction conditions (**Fig. 5.34b**).

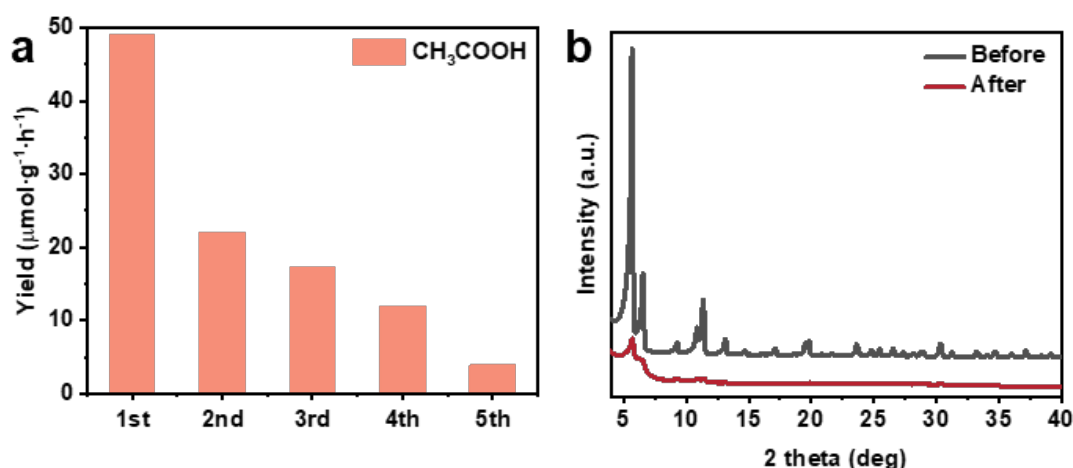


Fig. 5.34 (a) Photocatalytic stability and **(b)** XRD patterns of UiO-FePd before and after five recycling reactions.

Tris(bipyridine)ruthenium(II) chloride ($[\text{Ru}(\text{bpy})_3]^{2+}$, Rubpy), known for its ability to absorb ultraviolet and visible light, is commonly utilized as a photosensitizer in photocatalytic reaction⁷⁻⁸. Herein, we conducted a control experiment by substituting the role of Ru sites with Rubpy in UiO-FeRu. As shown in **Fig. 5.35a**, the catalytic performance of UiO-Fe combined with Rubpy (UiO-Fe+Rubpy) was inferior to that of the single-atom catalyst UiO-Fe and the bimetallic-atom catalyst UiO-FeRu. Critically, the UiO-Fe+Rubpy was observed nil activity of acetic acid production, demonstrating that the precise design of the bimetallic structure is critical for product selectivity. Additionally, we explored the effect of metal site concentrations on the photocatalytic CO_2RR . As shown in **Fig. 5.35b**, the catalytic performance of UiO-Fe and UiO-Co decreased with increasing metal site concentration. This suggests that an excess of

metal sites is detrimental to the catalytic reaction, likely due to steric hindrance within the UiO-67 framework.

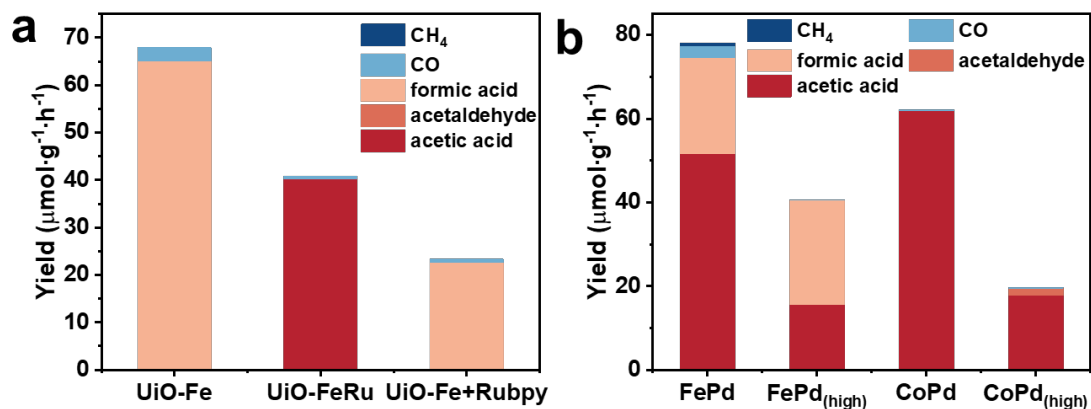


Fig. 5.35 Control CO₂RR performance of (a) UiO-Fe, UiO-FeRu, UiO-Fe+Rubpy, and (b) UiO-FePd, UiO-FePd_(high), UiO-CoPd, and UiO-CoPd_(high) under Xe light irradiation.

5.3.3 Photophysical Properties of UiO-M_AM_B

To elucidate the electronic transfer process of bimetallic UiO-M_AM_B, we investigated their photophysical properties using UV-visible diffuse reflectance spectroscopy as shown in **Fig. 5.36**. The results highlight significant enhancements in light absorption due to metal incorporation. Given that the Ru atom is a strong candidate for light absorption, all UiO-M_ARu samples exhibited the highest visible light absorption. Similarly, UiO-M_ARh and UiO-M_APd showed enhanced absorption bands in the 400–600 nm range, attributable to metal *d-d* transitions⁹. The broadened absorption and increased intensity across the visible wavelength range correlate strongly with improved photocatalytic activity, consistent with observed catalytic performance. The impact of metal site concentration was further explored. As shown in **Fig. 5.36d**, increasing the M_A concentration in UiO-M_A catalysts slightly enhanced their visible light photoresponse. However, when the M_B concentration was increased in UiO-

$M_{A(\text{high})}$ catalysts, the differences in absorption between high- and low-concentration UiO-FeRh and UiO-FePd were minimal (**Fig. 5.36e**). This suggests that the introduction of Rh and Pd, which inherently absorb visible light strongly, dominates the photoresponse, reducing the impact of concentration variations.

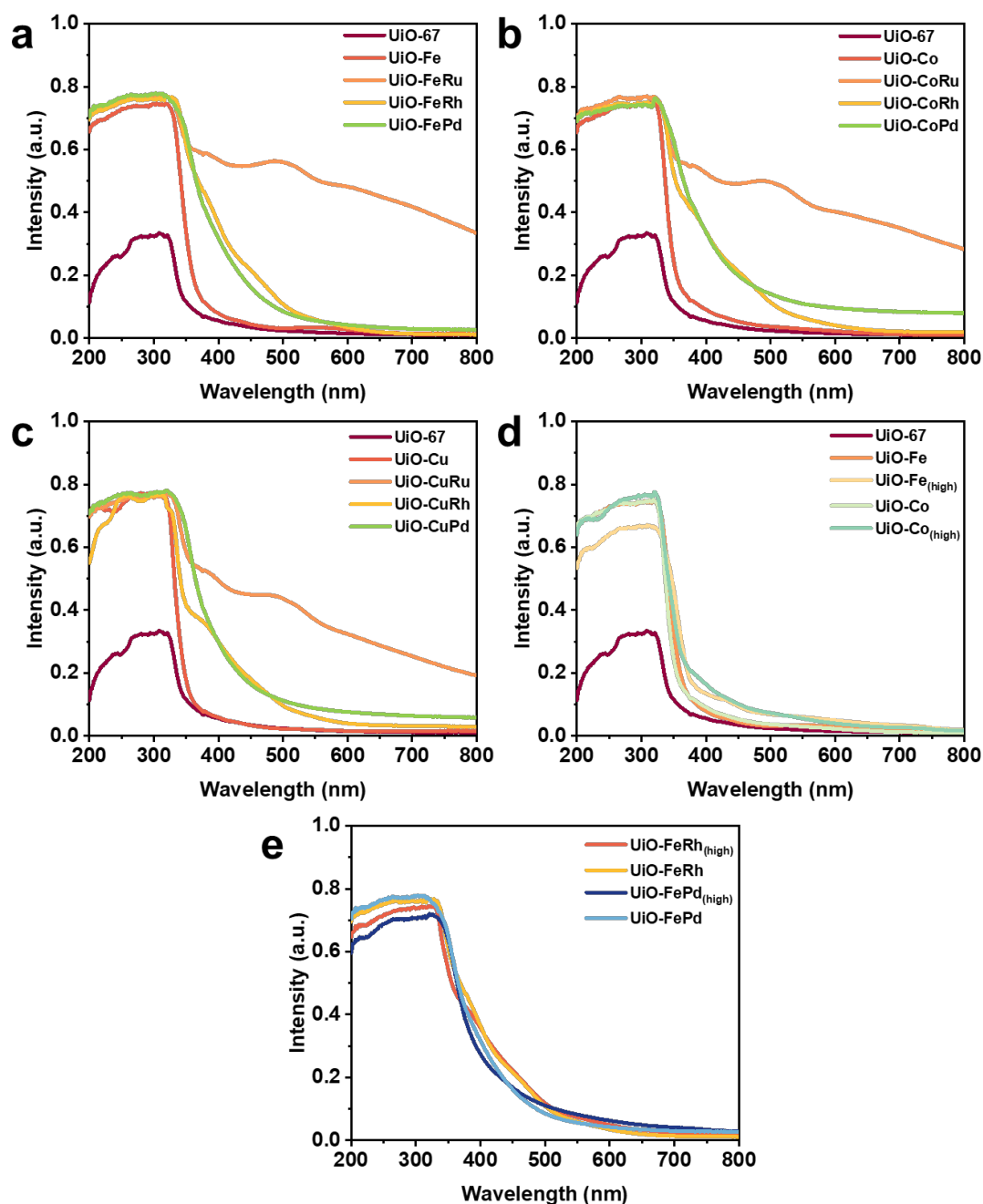


Fig. 5.36 UV-vis spectra of (a) UiO-FeM_B series, (b) UiO-CoM_B series, (c) UiO-CoM_B

series ($M_B = \text{Ru}$, Ru and Pd), **(d)** UiO-Fe , $\text{UiO-Fe}_{(\text{high})}$, UiO-Co and $\text{UiO-Co}_{(\text{high})}$, and **(e)** $\text{UiO-FeRh}_{(\text{high})}$, UiO-FeRh , $\text{UiO-FePd}_{(\text{high})}$, and UiO-FePd .

To investigate the electronic structure of the synthesized materials, bandgap energies were calculated using Kubelka-Munk-transformed UV-visible diffuse reflectance spectroscopy data¹⁰. As illustrated in **Fig. 5.38 – 5.39**, the bandgap energies of $\text{UiO-M}_A\text{M}_B$, ranging from 3.21 to 3.54 eV, are obviously lower than those of UiO-67 and UiO-M_A (*ca.* 3.60 eV, **Fig. 5.37**). This reduction in bandgap is attributed to the introduction of metal species, which enhances the electronic properties and supports improved photocatalytic performance.

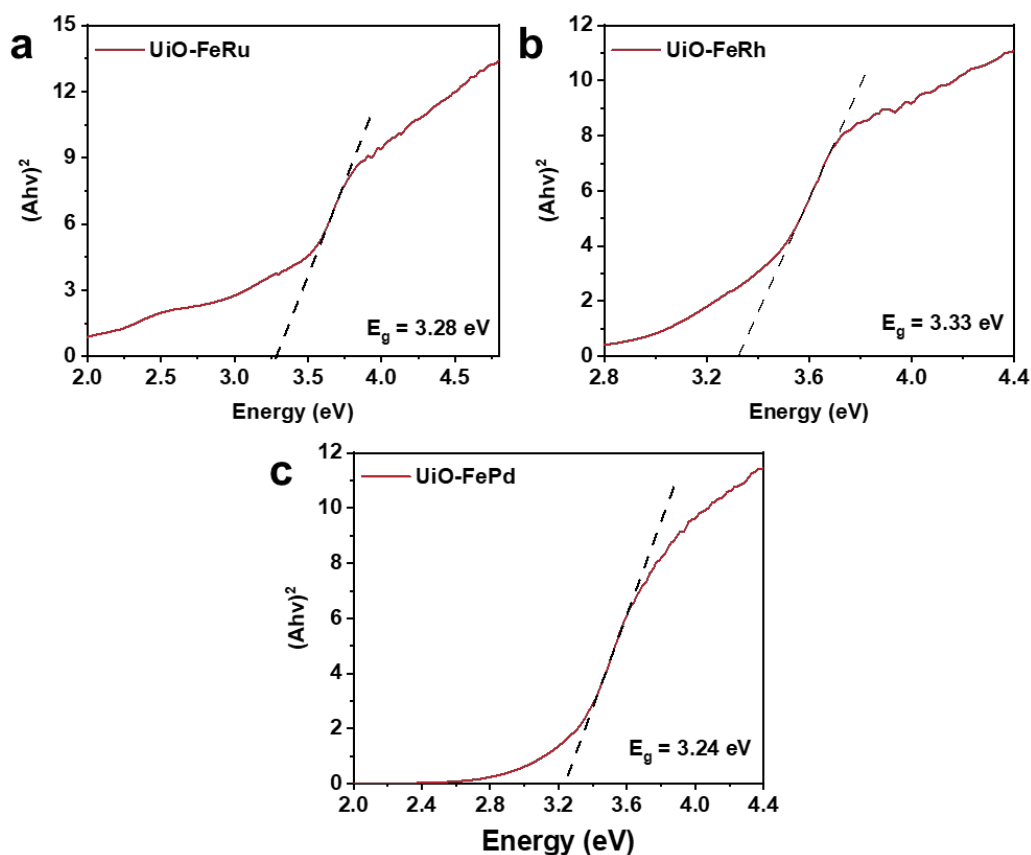


Fig. 5.37 Plots of $(\alpha h\nu)^2$ vs. photon energy for **(a)** UiO-FeRu , **(b)** UiO-FeRh and **(c)** UiO-FePd .

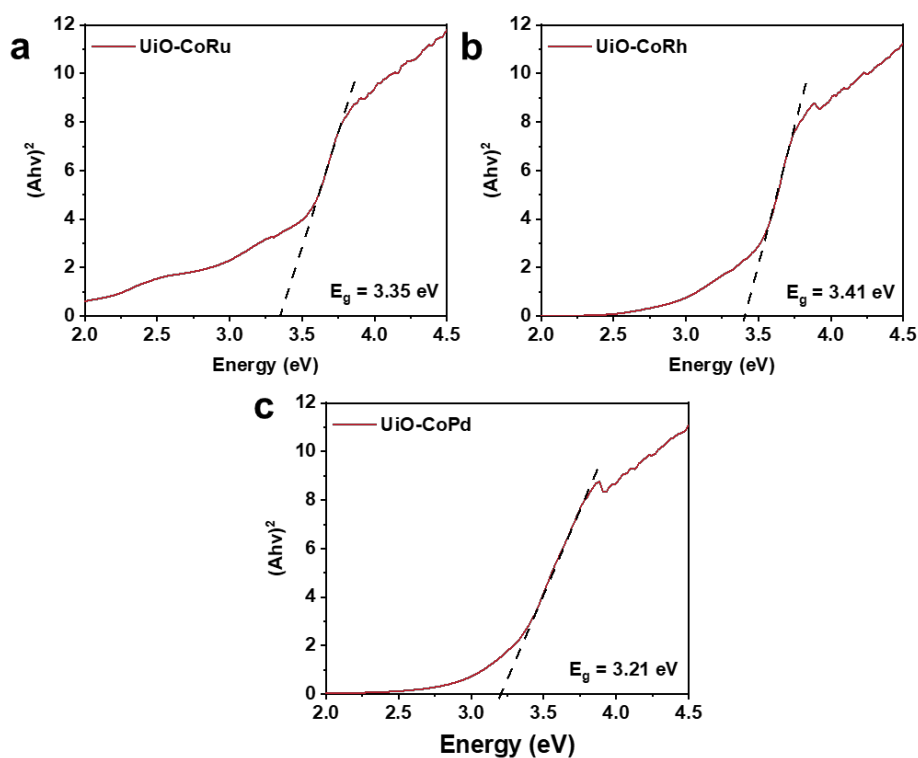


Fig. 5.38 Plots of $(\alpha h\nu)^2$ vs. photon energy for (a) UiO-CoRu, (b) UiO-CoRh and (c) UiO-CoPd.

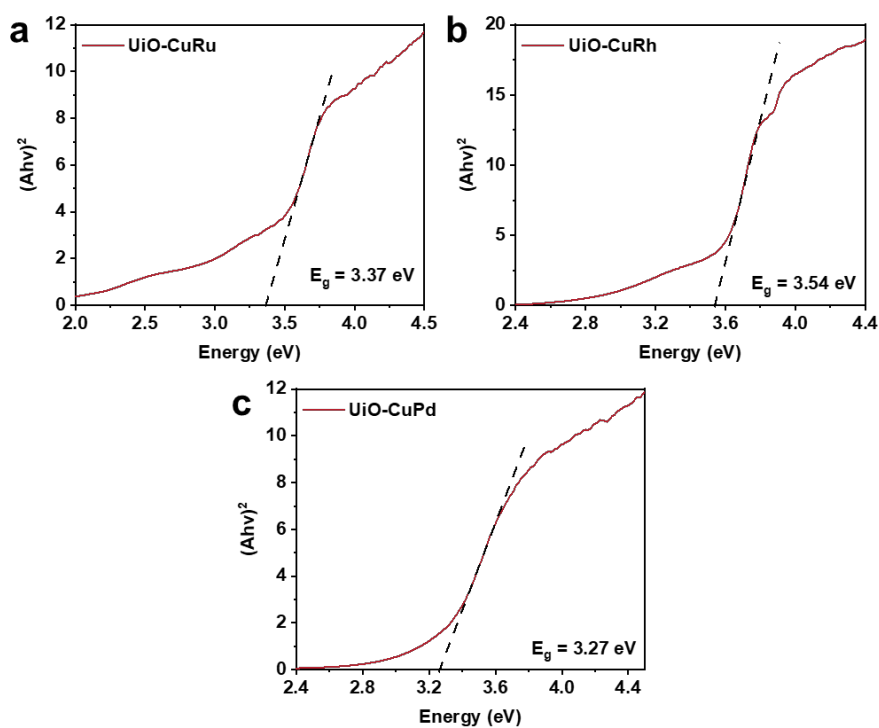


Fig. 5.39 Plots of $(\alpha h\nu)^2$ vs. photon energy for (a) UiO-CuRu, (b) UiO-CuRh and (c) UiO-CuPd.

Mott-Schottky analysis was performed to determine the CB positions, as shown in **Fig. 5.40**. The VB energies were computationally derived and were summarized in **Table 5.14**. The calculated band structure of the MOF aligns well with the energetic requirements for the formation of acetic acid in photocatalytic CO₂RR, confirming the suitability for this catalytic process¹¹⁻¹².

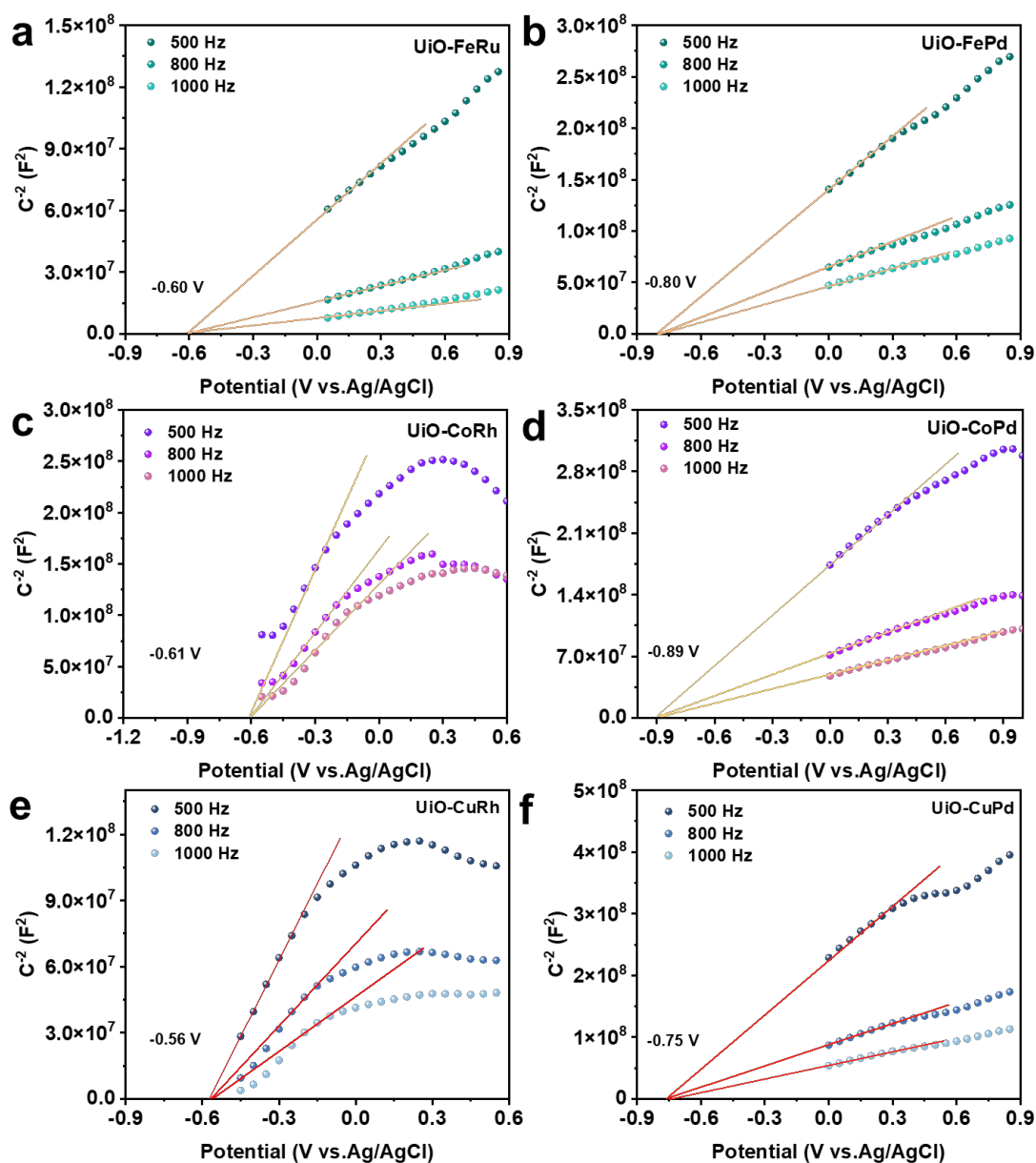


Fig. 5.40 Mott-Schottky plots of (a) UiO-FeRu, (b) UiO-FePd, (c) UiO-CoRh, (d) UiO-

CoPd, (e) UiO-CoRh and (f) UiO-CuPd measured at 500, 800, and 1000 Hz in 0.1 M Na₂SO₄ electrolyte (pH = 7).

Table 5.14. Summary of estimated band gap, CB, and VB positions for as-prepared samples.

Sample	CB vs. RHE (eV)	VB vs. RHE (eV)	E _g (eV)
UiO-FeRu	-0.19	3.09	3.28
UiO-FePd	-0.39	2.85	3.24
UiO-CoRh	-0.20	3.21	3.41
UiO-CoPd	-0.48	2.73	3.21
UiO-CuRh	-0.15	3.39	3.54
UiO-CuPd	-0.34	2.93	3.27

Fig. 5.41 shows the transient photocurrent responses of as-prepared samples under 370 nm LED light illumination with on-off cycling. For instance, **Fig. 5.41a** demonstrated that UiO-FePd exhibited the highest photocurrent density compared to UiO-67 and UiO-Fe. This indicates that UiO-FePd excels in generating and transferring electron-hole pairs, enhancing its photocatalytic efficiency.

PL spectroscopy was employed to investigate the recombination dynamics of the photo-induced electron-hole pairs of catalysts. As shown in **Fig. 5.42a**, incorporating a second 4d transition metal (M_B) into UiO-M_A slightly affected its PL intensity. However, both UiO-M_A and UiO-M_AM_B exhibited significantly lower PL intensities compared to UiO-67. This suggests that the metal active sites facilitate charge separation, thereby suppressing electron-hole pair recombination in UiO-67.

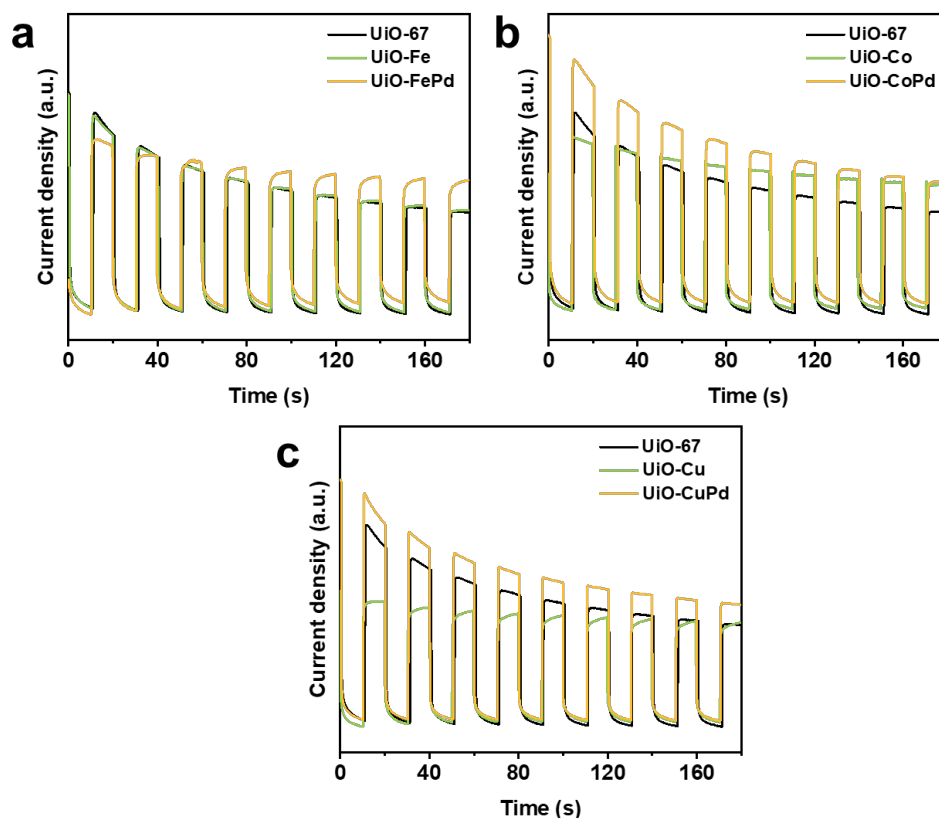


Fig. 5.41 Transient photocurrent response spectra of (a) UiO-67, UiO-Fe and UiO-FePd, (b) UiO-67, UiO-Co and UiO-CoPd, and (c) UiO-67, UiO-Cu and UiO-CuPd.

TRPL spectroscopy was utilized to examine the carrier dynamics of the catalyst, as shown in **Fig. 5.42**. The effective lifetime, derived from the TRPL spectra by fitting with a biexponential function (**Table 5.15**), represents the average survival time of photogenerated electron-hole pairs¹³. Compared with UiO-67 results from **Chapter 4** (**Table 4.13**), UiO-M_ARu and UiO-M_ARh emerged an obvious reduction in lifetime, while UiO-M_APd showed only a slight decrease. Detailed analysis of the decay components (τ_1 and τ_2) revealed that UiO-M_APd has a longer fast decay component (τ_1), associated with non-radiative recombination via trap states, and a longer slow decay component (τ_2), indicative of intrinsic radiative recombination of free carriers¹⁴. Moreover, the fraction of τ_1 in UiO-M_APd is substantially lower than in UiO-67 and other UiO-M_AM_B catalysts. This observation, combined with catalytic performance and

PL data, suggests that the prolonged stay time of carriers at the Pd site may be responsible.

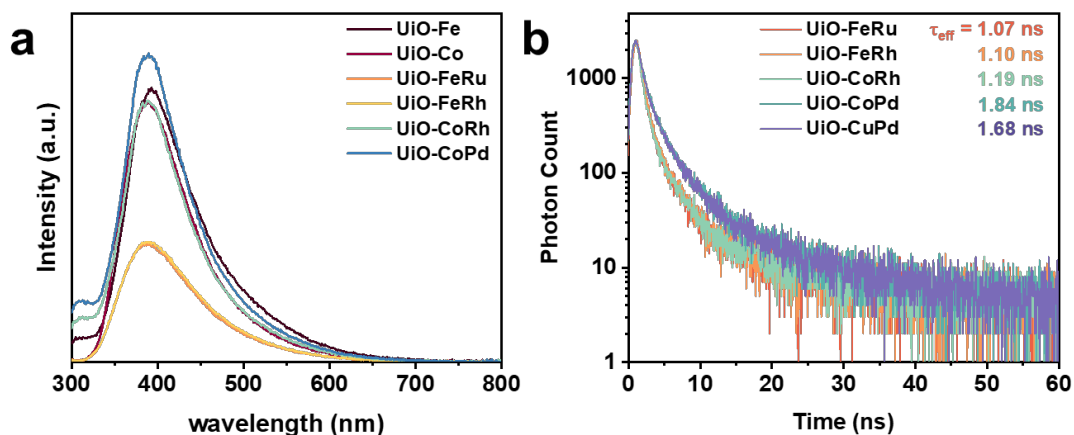


Fig. 5.42 (a) PL spectra of UiO-Fe, UiO-Co, UiO-FeRu, UiO-FeRh, UiO-CoRh, and UiO-CoPd; (b) TRPL spectra of UiO-FeRu, UiO-FeRh, UiO-CoRh, UiO-CoPd and UiO-CuPd.

Table 5.15. Lifetime components in TRPL decay fitted by double exponential components.

Sample	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{eff}
UiO-FeRu	0.708	85.67	3.244	14.33	1.070
UiO-FeRh	0.703	84.64	3.311	15.36	1.104
UiO-FePd	0.918	78.69	5.751	21.31	1.948
UiO-CoRh	0.700	82.15	3.428	17.85	1.187
UiO-CoPd	0.995	72.68	4.100	27.32	1.844
UiO-CuPd	0.859	72.03	3.813	27.97	1.685

5.3.4 CO₂RR Mechanism of UiO-*MAM_B*

As shown in **Fig. 5.43**, *in-situ* DRIFTS was employed to probe the key intermediates generated during the photocatalytic CO₂RR, using UiO-FePd as a representative UiO-

$M_A M_B$. Compared to UiO-67 and UiO-Fe (**Fig. 4.34**), three additional IR peaks emerged in UiO-FePd, including $*OC-CO$ at 1484 cm^{-1} , and $*HOC-CO$ at 1240 and 1515 cm^{-1} ¹⁵⁻¹⁶. These spectral features conclusively demonstrate that the neighboring $M_A \cdots M_B$ motifs in bimetallic catalysts play a pivotal role in facilitating C–C coupling, thereby promoting the formation of C_{2+} products.

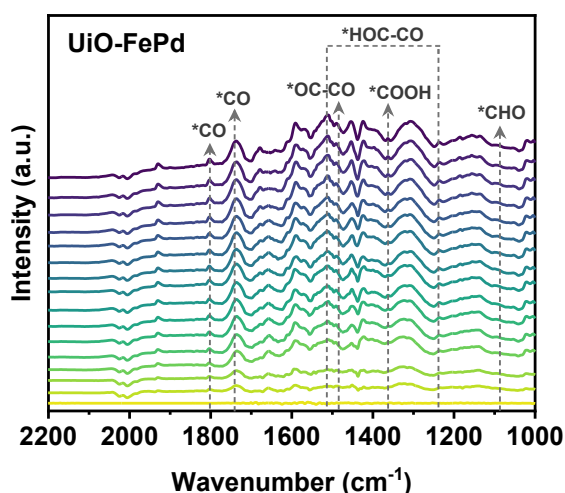


Fig. 5.43 *In-situ* DRIFTS spectra for CO_2RR over UiO-FePd.

To investigate C_2 products formation from the CO_2RR , we selected UiO-FeRu catalyst as a representative for DFT calculations. First, we evaluated the CO_2 adsorption energy at different metal sites within UiO-FeRu (**Fig. 5.44**). The CO_2 adsorption energy was significantly stronger at Ru sites than at Fe sites, confirming preferential CO_2 adsorption on Ru sites. We then calculated the Gibbs free energy for the intermediate reactions involved in CO_2 reduction on UiO-FeRu. When considering isolated single-atom sites (Fe or Ru sites), the energy barriers for sustained CO_2 hydrogenation to form $*CO$ intermediate production are high, indicating an unfavorable pathway for C_2 product generation. In contrast, considering the synergistic effect of neighboring motifs of the Ru and Fe sites enables alternating CO_2 adsorption, forming $M-*CO_2$ intermediates with lower energy barriers. Subsequently, the Ru and Fe sites alternately

hydrogenated these species, forming $^*\text{CO}$ and $^*\text{COH}$ intermediates, facilitating C-C coupling and ultimately producing CH_3COOH .

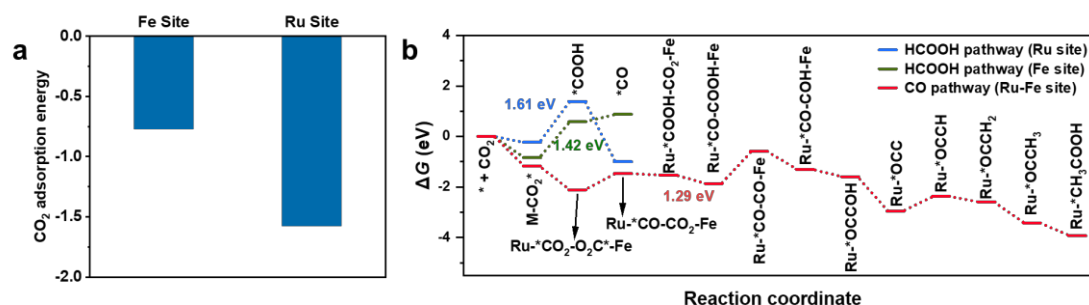


Fig. 5.44 (a) CO_2 adsorption energy on Fe or Ru site, (b) calculated Gibbs free energy profiles for the CO_2RR steps over UiO-FeRu .

To elucidate how the bimetallic pairs in $\text{UiO-M}_\text{A}\text{M}_\text{B}$ impart CO_2RR selectivity, we calculated the d -band center model, as shown in **Fig. 5.45a**. In this model, the closer the d -band center is to the Fermi level, the greater the number of empty anti-bonding states formed, resulting in stronger binding energies with CO_2 and its intermediates. Specifically, Fe- and Cu-based pairs in $\text{UiO-M}_\text{A}\text{M}_\text{B}$ exhibit a pronounced upshift of the d -band center toward the Fermi level compared with Co-based catalysts. This shift correlates with improved catalytic performance, emphasizing the critical role of Fe and Cu motifs in promoting C–C coupling. Furthermore, **Ru**- and **Pd**-based pairs consistently show superior performance in $\text{UiO-M}_\text{A}\text{M}_\text{B}$ catalysts, attributed to their high electronegativity and nearly fully occupied d -band configuration (similar with $\text{Fe}^{3+}/\text{Cu}^{2+}$), which collectively optimizes the electronic structure of the catalysts. In contrast, **Rh** motifs induce a downward shift of the d -band center due to its intrinsic properties, impeding intermediate stabilization and C–C coupling, resulting in low C_{2+} selectivity.

Fig. 5.45b illustrates site-specific CO_2 adsorption capacity in $\text{UiO-M}_\text{A}\text{M}_\text{B}$. The identity

of neighboring metal sites and their microenvironments modulates CO₂ adsorption, directing activation toward specific pathways at dominant sites. Building on **Chapter 4**, $\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$ for the sites A and B were calculated and correlated with the catalysts' d-band center energy to evaluate the SA performance in steering C₂⁺ pathways. As shown in **Fig. 5.45c**, negative and near-zero value of $\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$ for most M_A or some M_B sites favor *OCOH stabilization, enhancing selectivity. Conversely, Rh sites in UiO-FeRh/UiO-CuRh significantly alter the electronic structure, impeding *OCOH stabilization at both M_A and M_B sites and disfavoring C–C coupling. **Fig. 5.45d** presents the calculated adsorption energies of the *CO intermediate derived from *OCOH conversion at site A and site B in UiO-M_AM_B. All samples exhibit moderate *CO adsorption energies, facilitating efficient *OCOH-to-*CO conversion and optimal *CO mobility for subsequent C–C coupling.

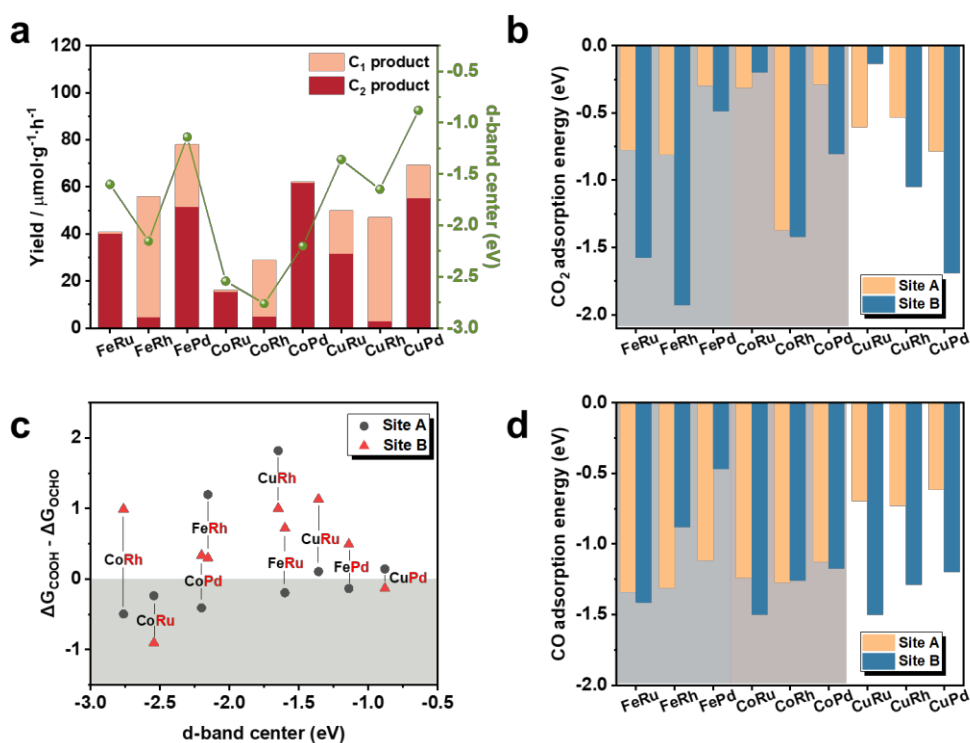


Fig. 5.45 (a) The relationship of the calculated *d*-band center energy of UiO-M_AM_B and CO₂RR activity. (b) Calculated adsorption energies of the CO₂ molecule on site A and

site B in UiO-M_AM_B. (c) The relationship between the calculated d-band center energy of UiO-M_AM_B and Gibbs free energy differential of *OCOH and *OCHO of site A and site B in UiO-M_AM_B. (d) Calculated adsorption energies of the *CO intermediate on site A and site B in UiO-M_AM_B.

5.4 Proposed Chemical Model

We propose a general design rule that bimetallic sites can synergistically steer the catalyst's electronic structure to optimize targeted C₂₊ products formation in CO₂RR. By strategically selecting metal pairs, we can leverage this synergy to optimize the *d*-band center positions and reduce the energy barrier for key intermediate formation. SAs of **Cu, Fe, Ru and Pd** are effective active sites for CO₂ adsorption and intermediates stabilization, while SAs of **Ni, Co and Rh** are less favorable for stabilizing C₂ intermediates. However, the specific coordination environment can significantly influence the catalytic properties of these metal sites. To predict catalyst performance, we propose key descriptors such as ***d*-band center position, CO₂/*CO adsorption energy, and ΔG differences for PDS**. These descriptors allow us to preliminarily and comprehensively assess the synergistic effects of the metal pairs. This approach positions metal-pair engineering as a key strategy for synergistically controlling CO₂RR outcomes, providing a clear blueprint for designing next-generation catalysts.

5.5 Conclusion

In conclusion, we have demonstrated the structural engineering of bimetallic catalysts with rationally controlled site positions to steer the selectivity of photocatalytic CO₂RR. Utilizing UiO-67 as a supported matrix, we precisely positioned bimetallic active sites with defined interatomic distances. Advanced characterization techniques, including STEM, XAFS, Rietveld refinement of PXRD, and RXRD, enabled the atomic-level

determination of the coordination environments of bimetallic sites. Crucially, a functional bimetallic motif ($M_A \cdots M_B$) with an intermetallic distance of *ca.* 5.3 Å on adjacent bpydc linkers was revealed. This specific configuration enables the selective conversion of CO₂ to C₂ products. Strategic selection of the metal pairs generated synergistic effects that optimized the electronic structure, coordination environment, and active sites accessibility, thereby modulating the selectivity toward CH₃COOH. Specifically, SAs of **Cu**, **Fe**, **Ru** and **Pd** were identified as the effective active sites for CO₂ adsorption and intermediates stabilization, while SAs of **Co** and **Rh** are less favorable for stabilizing C₂ intermediates.

Through systematic tuning of metal combinations, we identified that the key factors governing efficiency and selectivity towards C₂₊ products are: (1) optimizing CO₂ adsorption capacity, (2) stability of key intermediates, and (3) the energy barrier of the PDS. Therefore, we proposed key descriptors including ***d*-band center position**, **CO₂/*CO adsorption energy**, and **ΔG differences for PDS** to evaluate the catalytic performance of synergistic effects of the metal pairs in converting CO₂-to-C₂₊ products (**Fig. 5.46**). The closer the d-band center is to the Fermi level, indicating in stronger the binding energies with CO₂ and its intermediates, which is beneficial for C₂₊ intermediates formation and stabilization. A **negative ΔG_{COH}-ΔG_{CHO}** or **near-zero ΔG_{COH}-ΔG_{CHO}** indicates the favoring for *OCHO, promoting *CO formation and subsequent C–C coupling toward C₂₊ products. However, the **high positive ΔG_{COH}-ΔG_{CHO}** suggests the strong stabilization of *OCHO, driving selectivity toward C₁ products. These critical factors can be effectively modulated through the strategic selection of metal pairs, providing valuable mechanistic insights for the rational design of catalysts targeting specific high-value carbon products in CO₂RR.

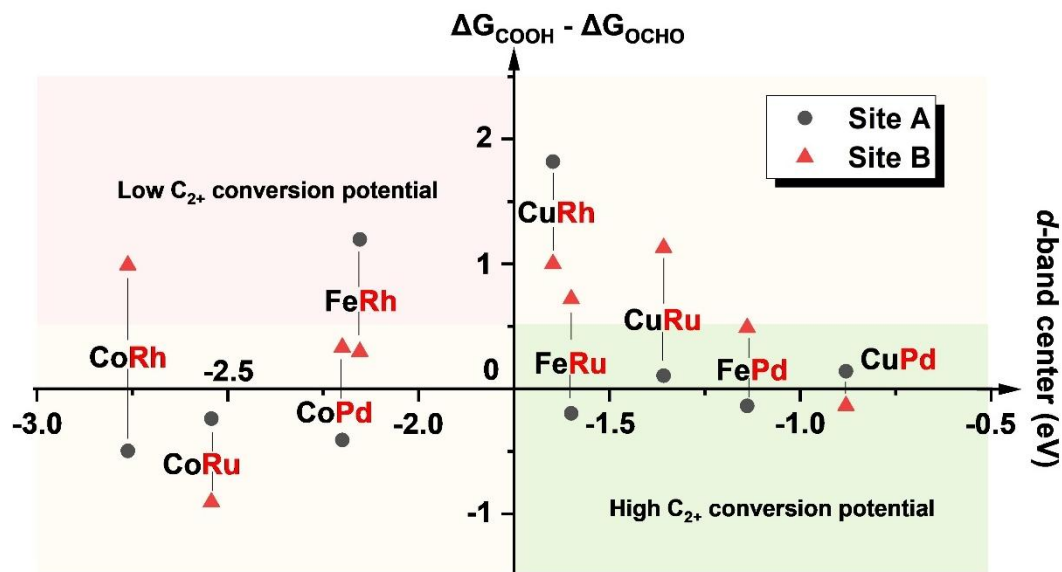


Fig. 5.46 Schematic representation of the proposed synergistic bimetallic active sites in UiO- $\text{M}_{\text{A}}\text{M}_{\text{B}}$ for CO_2RR conversion to C_{2+} products. It correlates the relationship between the d -band center energy (x-axis, electronic structure descriptor) and calculated Gibbs free energy difference between $^*\text{OCOH}$ and $^*\text{OCHO}$ intermediates at site A (black) and site B (red) (y-axis, selectivity descriptor). An upward shift of the d -band center toward the Fermi level indicates stronger binding of CO_2 and its intermediates. A negative or near-zero value of $\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$ indicates greater stability for $^*\text{OCOH}$, promoting C–C coupling toward C_{2+} products rather than HCOOH .

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Chapter 6 Conclusion and Future Directions

6.1 Conclusion

In this thesis, we have successfully designed and synthesized a series of dual catalytic active sites within MOF using UiO-67 as a supporting matrix. The targeted geometric structure of the catalyst was precisely engineered to control the distribution, nuclearity, and composition of metal pairs, thereby steering the chemoselective CO₂RR conversion toward C₂ products. Advanced characterization techniques, including STEM, XAFS, Rietveld refinement of PXRD, and RXRD, were leveraged to determine the atomic-level location and coordination environment of the bimetallic active sites. The structure-activity relationship and synergistic effects of metal pairs in DACs were explored using *in-situ* DRIFTS and DFT calculations.

In **Chapter 3**, we successfully engineered a series of supported atomic copper sites in DACs with well-controlled site distribution to selectively drive photocatalytic CO₂RR toward either C₁ or C₂₊ products. The pivotal role of **dual atomic copper site** in dictating product selectivity has been investigated through a combination of characterization techniques and DFT calculations. At low Cu content, isolated Cu sites presented as SAs preferentially stabilize *COOH intermediates, favoring C₁ product formation. At higher Cu loadings, neighboring Cu···Cu dual atom motifs facilitate C–C coupling via the *OCCOH intermediate, significantly reducing the activation energy and achieving high selectivity for acetic acid.

In **Chapter 4**, we have engineered 3d/3d bimetallic metal sites in DACs with precise spatial control by a stepwise synthesis strategy, building on the investigation of **Chapter 3**. This approach allowed fine-tuned regulation of the metal combination, synergistically steering the selectivity of photocatalytic CO₂RR. Structural analysis

confirmed bimetallic motifs ($M_A\cdots M_B$) positioned approximately 5.3 Å apart on adjacent bpydc linkers. This control over metal combinations demonstrated a synergistic effect, which optimized the electronic structure, coordination environment, and active sites accessibility, thereby modulating the selectivity toward acetic acid. Furthermore, Optimal pairs (**FeFe**, **CoCu**, and **CuCu**) were identified as effective bimetallic pairs in UiO- $M_A M_B$ for the selective production of acetic acid. We employed the ***d*-band center** as the reliable electronic structure descriptor and $\Delta G_{\text{COOH}} - \Delta G_{\text{CHO}}$ as the C_{2+} product selectivity descriptor to evaluate the catalytic performance of site A and site B in UiO- $M_A M_B$. Consequently, **Cu** and **Fe** SA were identified as effective active sites for C–C coupling for C_{2+} products, whereas **Ni** and **Co** SA were less favorable for C_{2+} products formation.

In **Chapter 5**, we further investigated how dual-atom combinations influence the synergistic effect of the selectivity of CO_2RR . A series of 3d/4d transition metal pairs have been synthesized within UiO-67 and analyzed. Leveraging the unique electronic configurations of 3d and 4d metals, along with advanced characterization techniques, we precisely identified the **locations of specific metal sites** as functional bimetallic motifs ($M_A\cdots M_B$), rather than random distributions ($M_A\cdots M_A$, and $M_B\cdots M_B$). This specific configuration enables the selective conversion of CO_2 to C_2 products. Notably, FeRu, CoRu, and CoPd metal pairs exhibited superior selectivity by stabilizing CO_2 and key intermediates, as well as promoting C–C coupling within UiO- $M_A M_B$, leading to the selective production of acetic acid. We identified key factors governing efficiency and selectivity towards C_{2+} products, including optimizing CO_2 adsorption capacity, stabilizing key intermediates, and minimizing the energy barrier of the PDS. Consequently, we proposed key descriptors including ***d*-band center position**, **$\text{CO}_2/^*\text{CO}$ adsorption energy**, and **ΔG differences for PDS** to evaluate catalytic

performance and synergistic effects of the metal pairs in converting CO₂-to-C₂₊ products. A d-band center is closer to the Fermi level, was found to be beneficial for formation and stabilization of C₂₊ intermediates. A **negative** or **near-zero** $\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$ indicates the favoring of *OCOH formation, subsequently promoting *CO formation and C–C coupling toward C₂₊ products. Conversely, the **high positive** $\Delta G_{\text{OCOH}} - \Delta G_{\text{OCHO}}$ suggests the strong stabilization of *OCHO, driving selectivity toward C₁ products. These critical factors can be effectively modulated through the strategic selection of metal pairs, providing valuable mechanistic insights for the rational design of catalysts targeting specific high-value carbon products in CO₂RR.

In summary, this work has developed a stepwise strategy for rational design of DACs by tailoring metal atomic sites supported MOFs for systematic investigation of the structure-selectivity relationship in photocatalytic CO₂RR towards C₂₊ products. Initially, the influence of metal concentration on selectivity was investigated, providing insights into the effects of site density. Subsequently, bimetallic catalysts with precisely defined site positions were engineered. Advanced characterization techniques elucidated the coordination environments and electronic structures of these sites, revealing their synergistic effects on catalytic performance.

6.2 Future Directions

Although this thesis has analyzed several key factors at bimetallic sites that influence the selectivity of photocatalytic CO₂RR to C₂₊ products, several fundamental questions remain unresolved. Building on our findings, we propose the following research directions to enable precise atomic-level modulation of metal active sites, further elucidating how coordination environment and spatial structure dictate CO₂ reduction selectivity and establishing an effective catalytic landscape in high chemoselectivity

towards specific C₂₊ products.

6.2.1 Investigation of the Spatial Structure-Selectivity Relationship

Utilizing the inherent tunability of MOFs, future studies should systematically vary the coordination species and number (e.g., M-N₄, M-N₃, M-N₂) at metal active sites. Investigating how spatial constraints, arising from different coordination numbers, impact CO₂ adsorption, activation, and ultimately, product selectivity, thereby refining the structure-selectivity relationship theory.

6.2.2 Exploring the Role of the MOF Matrix

Expanding current preparation methods to synthesize bimetallic site catalysts within diverse MOF crystals will enable tailored control over key parameters. These include intermetallic distances, metal coordination environments, structural configurations, and the electron transport capabilities of the host MOF matrix. Such studies will provide deeper insights into their effects on catalytic performance and selectivity.

6.2.3 Integrating Machine Learning for Predictive Design

Developing predictive models correlating dual-atom catalyst structure with photocatalytic CO₂RR reactivity is a promising avenue. Through a supervised machine learning algorithm, simultaneous interrogation of reactivity descriptors, high-throughput catalytic experimentation, and structure-reactivity/selectivity correlations, would generate sound operational models pertaining to the catalytic landscapes that characterise several competing reaction pathways. The design of the ‘second-generation’ dual-atom catalysts with improved chemoselectivity and reaction efficiency will be envisioned.