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A Focused Review on Bio-inspired Multi-site Water Oxidation Catalysis by Ruthenium Complexes

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Abstract. The creation of efficient water oxidation catalysts (WOCs) is a key area of advancement in sustainable energy researches, particularly for enabling large-scale hydrogen production through water electrolysis. Recent advances in molecular catalyst design have highlighted the prominence of multi-site ruthenium-based systems, with Ru(bda) (bda = 2,2'-bipyridine-6,6'-dicarboxylate) complexes emerging as a benchmark due to their mechanistic versatility and tunable reactivity. Substantial progress has been achieved through strategic modifications of Ru(bda) catalysts, including dimerization, macrocyclization, and integration into covalent organic frameworks (COFs). Dimeric Ru(bda) systems, for instance, exhibit exceptional turnover frequencies (TOFs) by leveraging intramolecular radical coupling to circumvent the concentration limitations typical of bimolecular O-O bond formation pathways. Meanwhile, macrocyclic Ru(bda) derivatives, inspired by the natural oxygen-evolving complex (OEC), demonstrate enhanced proton-coupled electron transfer (PCET) kinetics, with TOFs reaching 7.9 s^{-1}, attributed to the preorganization of water molecules within their confined cavities. Further innovations include embedding Ru(bda) units into COFs or immobilizing them on carbon nanotubes (CNTs). These hybrid architectures combine the precision of molecular catalysis with the stability of heterogeneous systems, enabling efficient water oxidation via the I2M mechanism. Notably, Ru(bda)-CNT assemblies achieve record-breaking performance with TOFs exceeding 3200 s^{-1}. This review underscores the transformative potential of multi-site Ru(bda) catalysts and outlines a roadmap for rational catalyst design. However, challenges such as long-term stability under oxidative conditions and the scalability of noble-metal-based systems remain to be addressed. Future research directions may focus on elucidating structure-activity relationships and exploring earth-abundant alternatives to further advance practical applications in renewable energy technologies.

Keywords: Ruthenium Complexes, Water Oxidation Catalysts, Multi-site Catalysis, Covalent Organic Frameworks, Proton-Coupled Electron Transfer.

1. Introduction

The continuous progression and development of modern human society demand significant energy, i.e., the world's energy demand is expected to double by 2050 from 23.23 trillion kWh to 60 trillion kWh [1]. Conventionally, energy is derived from fossil fuels (coal, petroleum, and natural gas), and significant consumption of fossil fuels in human history has resulted in serious environmental impacts such as global warming and climate change, jeopardizing the sustainable development of human society. Hence, the global community urges a paradigm shift in the energy landscape, iconized by the 2015 United Nations Climate Change Conference (COP 21) in Paris, which reached a landmark agreement to combat climate change and to accelerate and intensify the actions and investments needed for a sustainable low carbon future [2].

A crucial strategy for minimizing the carbon footprint associated with energy is the replacement of fossil fuels with sustainable sources (such as wind, hydro and solar energy). However, due to the intermittent nature of these renewables, influenced by seasonal and geographical constraints, the application scope of renewables is rather limited [3]. Consequently, the development of appropriate energy carriers is essential. Hydrogen (H_2), produced via electrolysis powered by green electricity from renewables, presents a promising solution. With a high energy density of 33.3 kWh/kg, H_2 can be directly used as the fuel in various applications, including fuel cell and heating [4]. Importantly, H_2 combustion produces only water (i.e., zero carbon emission), making it a potentially transformative clean energy carrier.

Green H_2 production via water electrolysis includes two key reactions: the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). The OER is particularly challenging because it is both thermodynamically demanding, requiring a potential of $E = 1.23 - 0.059 \times \mathrm{pH}$ V versus the normal hydrogen electrode (NHE), and kinetically sluggish due to the involvement of four electrons and four protons ($2H_2O \rightarrow 4H^+ + 4e^- + O_2$) [5]. These factors significantly hinder the overall efficiency of water splitting and its practical applications. In nature, the OER occurs efficiently during photosynthesis in plants, driven directly by the tyrosine/tyrosine radical pair, which operates at a redox potential of only 1.2 eV [6]. This natural system achieves turnover frequencies (TOFs) of $100 - 400\ s^{-1}$, vastly outperforming industrial catalysts such as RuO_2 and IrO_2 (Ibid). The catalytic center of photosynthesis features a multinuclear metal cluster (Mn_4CaO_5), which serves as a model for designing artificial catalysts. Efforts to replicate its structure and function have focused on developing dual-site and multi-site catalysts, with a particular emphasis on understanding their catalytic mechanisms at the molecular level. To progress the field, this paper reviews the recent advances in the design and mechanistic understanding of the multi-site water oxidation catalyst, highlighting key strategies and outlining the challenges for future development. Homogeneous ruthenium-based water oxidation catalysts (Ru-WOCs) have demonstrated superior performance in enhancing reaction rates, making them a key focus of research. This review therefore concentrates on Ru-based catalysts.

2. Water oxidation mechanisms

This review will focus on elucidating the role of multi-site strategies from the perspective of catalytic mechanisms. Water oxidation mechanisms can be broadly categorized into two: water nucleophilic attack (WNA) and interaction of two metal-oxo entities (I2M) [7]. In the WNA mechanism, water molecules act as nucleophiles, attacking high-valent metal-oxo intermediates (e.g., M=O) to form O-O bonds. This process begins with the metal center generating high-valent metal-oxo intermediates through multiple proton and electron transfer steps, which involves water binding and water activation. Subsequently, a water molecule nucleophilically attacks the M=O species to form O-O bonds, followed by peroxide activation and oxygen release to complete the catalytic cycle (left side, Figure 1). In contrast, the I2M mechanism (right side, Figure 1) involves the coupling of two metal-oxo intermediates with radical character to form O-O bonds. This is followed by the disproportionation of the bridged metal peroxo species and the release of oxygen, completing the catalytic cycle.

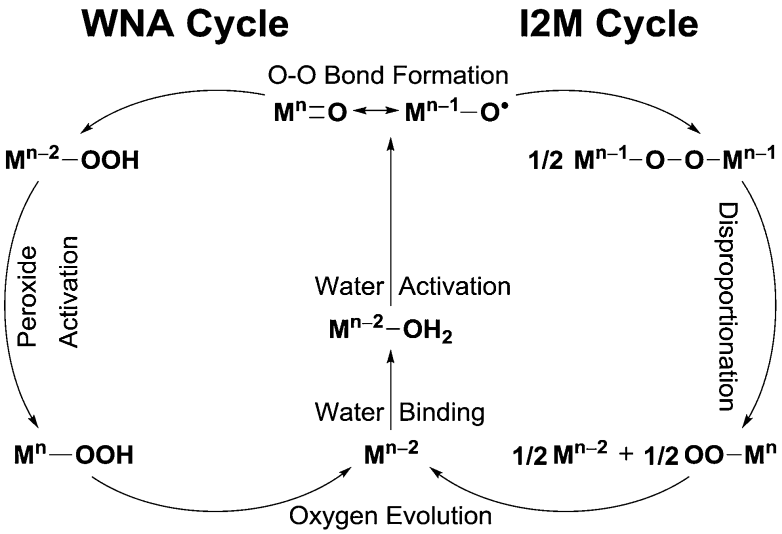

Figure 1. The WNA and I2M mechanisms of catalytic water oxidation

In terms of reaction kinetics, the WNA involves a nucleophilic attack by water molecules on a single metal-oxo intermediate, whereas the I2M mechanism involves radical coupling between two metal-oxo intermediates. Since the O-O bond formation is generally considered the rate-determining step (RDS) in most water oxidation reactions, their reaction rates differ significantly as shown in the following equations.

$$Rate_{WNA} = k\,[cat];\ TOF_{WNA} = k \tag{1}$$

$$Rate_{I2M} = k[cat]^2;\ TOF_{WNA} = k\left[cat\right] \tag{2}$$

The TOF of I2M exhibits catalyst concentration ([cat]) dependence, leading to faster kinetics at high [cat] compared to WNA. However, when homogeneous catalysts are immobilized on an electrode, diffusion limitations can hinder O-O bond formation, particularly for the I2M mechanism. Under such conditions, catalysts following the WNA mechanism are more advantageous. Consequently, the rational design of catalysts that operate via either WNA or I2M mechanisms is essential for advancing water oxidation catalysis.

3. Ru(bda) water oxidation catalyst

Ru(bda) is recognized as one of the most effective water oxidation catalysts. The monomeric Ru(bda) forms O−O bonds through a dual-site I2M mechanism. As shown in Figure 2, kinetic studies using 2 provide a clearcut insight into the mechanism of the O–O bond formation and reveal a radical coupling of $Ru^V{=}O$ species as a key process, where two $Ru^V{=}O$ intermediates couple to form a peroxo dimer, followed by rapid oxygen release. Isoquinolines were introduced as the axial ligand in 1 based on the idea that the barrier for the radical coupling of the Ru-O species could become lower due to non-covalent attractive interactions between isoquinolines. The catalyst's exceptional activity stems from its unique design, combining a bipyridine-dicarboxylate ligand motif with isoquinoline axial ligands. the bda ligand provides a stable equatorial coordination environment with negative charges, thereby enriching the electron density of the Ru center and facilitating water activation at lower potentials. The isoquinoline ligands facilitate O−O bond formation through non-covalent π-π stacking interactions, lowering the energy barrier for radical coupling of Ru^V-O species. Catalyst 1 displayed a remarkable turnover frequency (TOF) of 303 s^{-1}, which outperforms many previously reported water oxidation catalysts, including mono- and dinuclear ruthenium, iridium, manganese, cobalt, and iron complexes, which typically exhibit TOFs below 5 s^{-1} [8].

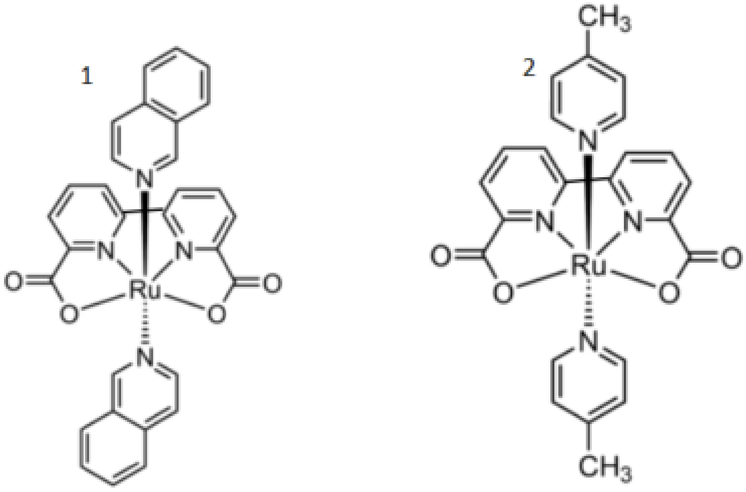

Figure 2. The molecular structure of the complex 1 and 2

4. Ru(bda) dimer

However, the reactivity of the above catalysts was found to significantly depend on the catalyst concentration due to the inherent bimolecular coupling of Ru^V=O active species during the O−O bond formation. This limitation poses a challenge for their practical application, whether in solution or on the electrode surface of a water-splitting device. It was proposed that by appropriately bridging two Ru(bda) units, the concentration constraint might be overcome by promoting easy intramolecular radical coupling of the oxidative intermediate Ru^V=O. A series of dimeric catalysts were synthesized based on Ru(bda), demonstrating markedly improved catalytic activity compared to their monomeric counterparts in a homogeneous solution.

The development of bridged dinuclear ruthenium complexes, such as dimer 1, dimer 2, and dimer 3, has significantly advanced water oxidation catalysis, as shown in Figure 3. These catalysts, derived from the Ru(bda) monomer, feature flexible bridging spacers that facilitate intramolecular radical coupling, thereby overcoming the concentration dependence typical of bimolecular O−O bond formation. Dimer 1, linked by three methylene linkers, achieved a turnover number (TON) of 20,780 (10,390 per Ru center) , significantly outperforming its monomeric precursor (TON = 1,550) [8]. Dimer 2, with four methylene linkers, showed slightly lower TON of 16,690 but maintained high efficiency The most active catalyst, dimer 3, incorporated a rigid -CH_2PhCH_2- spacer and achieved a remarkable TON of 42,840 (21,420 per Ru center) under optimized conditions, with an initial TOF of 40 s^{-1} [8]. This exceptional performance highlights the critical role of spacer flexibility in enhancing catalytic activity. The dinuclear design not only improves efficiency at low catalyst concentrations but also mimics the cooperative interactions seen in natural systems like the oxygen-evolving complex (OEC) of photosystem II [9-11].

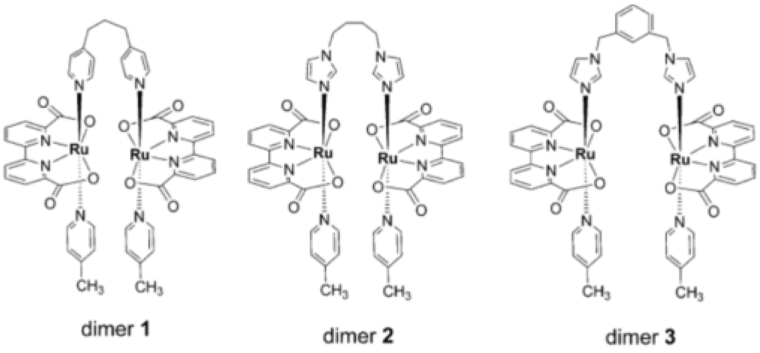

Figure 3. The structures of dimer 1, dimer 2, dimer 3

5. Ru(bda) macrocycle

Inspired by nature’s strategy of enhancing enzyme catalysis through complex supramolecular matrices in the second coordination sphere where weak non-covalent interactions lower activation barriers or facilitate substrate transport, supramolecular catalysts are designed to improve the OER by fine-tuning the second coordination sphere of the active center. This is accomplished by providing specific substrate binding sites or creating defined cavities that mimic enzymatic pockets.

In contrast to the Ru(bda) monomer that achieve high TOFs over 300 s^{-1} via the I2M mechanism, catalysts following the WNA mechanism are less active. So here is a strategy to achieve OEC-PSII-like catalytic activity via the WNA pathway by embedding Ru(bda) into a supramolecular architecture. The catalyst, a metallosupramolecular macrocycle $[Ru(bda)bpb]_3$ in Figure 4, positions three Ru(bda) subunits close together through axial coordination of 1,4-bis(pyrid-3-yl) benzene (bpb) linkers. Computational studies suggest that this arrangement preorganizes up to ten water molecules within the cavity, facilitating proton transfer during water oxidation via the hydrogen-bonded network. This design conceptually mimics the second coordination sphere of natural OEC-PSII, highlighting the importance of multinuclear catalysts for efficient oxygen evolution.

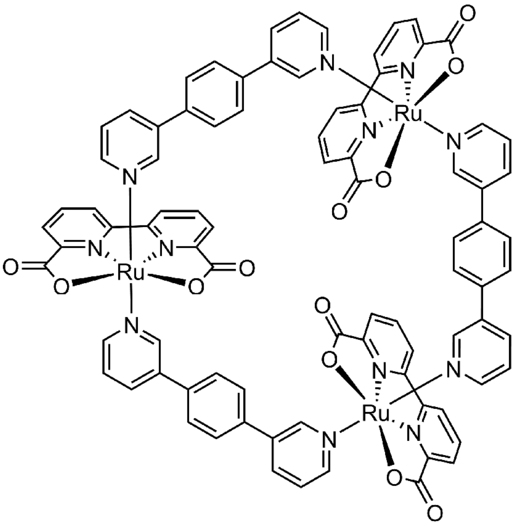

Figure 4. The structure of Macrocycle $[Ru(bda)bpb]_3$

The incorporation of Ru(bda) into macrocycles has proven effective for creating highly active multi-site water oxidation catalysts. Precise control over cavity size and geometry is crucial for facilitating substrate water binding and PCET processes, which drive water activation and O-O bond formation. There are a series of macrocyclic catalysts (MC1–MC4) as shown in Figure 5, and researchers have investigated the impact of cavity size on catalytic activity. Molecular dynamics simulations reveal that medium-sized catalysts, such as MC3, accommodate an extensive hydrogen-bonded water network, enhancing interactions between substrate water molecules and coordinated aqua/hydroxide ligands. This results in elongated RuO–H and shortened Ru–OH bonds, improving catalytic efficiency. Experimental results show a clear size dependence, with MC3 exhibiting the highest activity (TOF = 7.9 s^{-1}), while the smallest macrocycle, MC1, shows the lowest (TOF = 0.3 s^{-1}) [12]. The O-O bond formation proceeds via the WNA mechanism, and catalytic activity correlates with the hydrogen/deuterium (H/D) kinetic isotope effect (KIE). MC3 displays a KIE of 2.8, indicating a strong proton-coupled rate-determining step, while MC1 shows a negligible KIE of 1.2 [12-17].

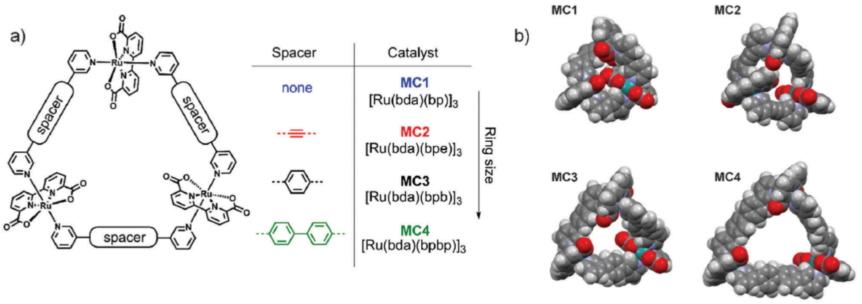

Figure 5. (a) Molecular structures and (b) space-filling models of catalysts MC1-4

To address the issue of poor water solubility of $[Ru(bda)bpb]_3$, which requires 50% (v/v) acetonitrile for catalysis, water-soluble derivatives were developed. By introducing triethylene glycol chains (MC2’) (Figure 6) or protonable tertiary amines (MC3’) into the bridging ligands, water solubility was significantly improved. MC2’ reduced the acetonitrile requirement by half, while MC3’ achieved full solubility in pure water under acidic conditions [18-24]. This enhanced solubility not only facilitated catalytic performance but also enabled stability verification via ^{1}H NMR under harsh conditions (pH=1, up to 355 K), avoiding acetonitrile-induced line broadening. These modifications provide crucial support for achieving eco-friendly, organic solvent-free water oxidation, laying the foundation for the development of more sustainable catalytic systems [12].

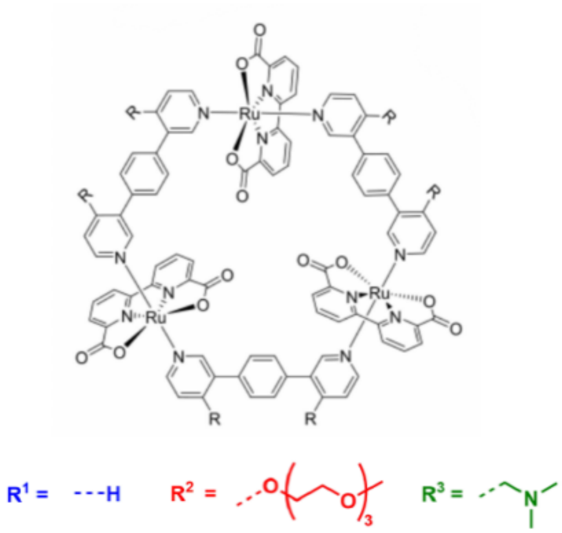

Figure 6. The Trinuclear Macrocycles MC1’ (R=R1), MC2’(R=R2) and MC3’(R=R3)

The catalytic efficiency of Ru(bda) macrocycles also depends on their nuclearity. The tetranuclear complex OEG-MC4 (Figure 7), with a TOF of 42±3 s^{-1}, outperforms trimeric oligoethylene glycol-MC3 (OEG-MC3, TOF = 26 s^{-1}) and dimeric OEG-MC2 (TOF = 12±2 s^{-1}) [25], demonstrating the positive correlation between macrocycle size and catalytic activity. The incorporation of OEG chains enhances solubility and catalytic performance, with OEG-MC4 showing exceptional activity even at very low concentrations (6 nM). Further analysis suggests that synergistic interactions between multiple Ru centers in OEG-MC4 enhance catalytic turnover. The multiple Ru centers in OEG-MC4 cooperate to accelerate O-O bond formation via the I2M mechanism, while flexible linkers stabilize reactive intermediates, boosting catalytic efficiency, making it a promising candidate for sustainable energy applications.

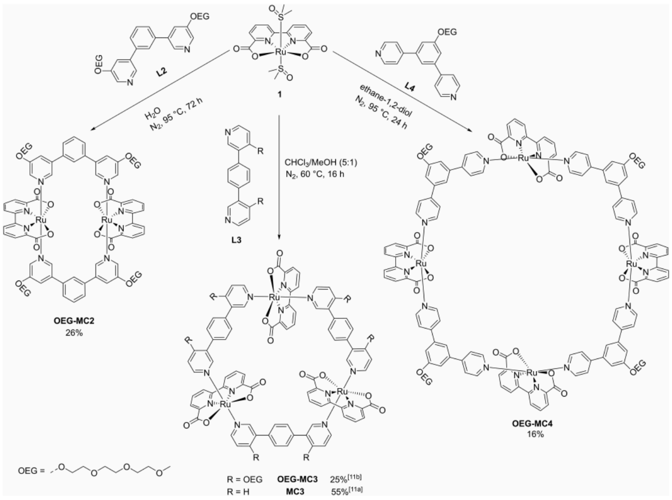

Figure 7. Synthesis of the new dimeric and tetrameric ruthenium macrocycles OEG-MC2 and OEG-MC4 as well as previously reported trimeric macrocycle OEG-MC3

The advancements in the development of efficient water oxidation catalysts (WOCs) have highlighted the potential of trinuclear Ru(bda) macrocyclic complexes for heterogeneous catalysis.

A notable study demonstrated the successful immobilization of a trinuclear Ru(bda) macrocycle (MC3) on multi-walled carbon nanotubes (MWCNTs) through non-covalent π–π interactions, enabling its application in electrochemical water oxidation (Figure 8). The immobilized catalyst exhibited exceptional performance, achieving a current density of 186 mA cm^{-2} at 1.45 V versus NHE, with an onset overpotential of 330 mV [26]. Remarkably, the catalyst demonstrated high stability, sustaining 1.8 million turnovers without degradation, as confirmed by X-ray absorption spectroscopy and electrochemical analyses.

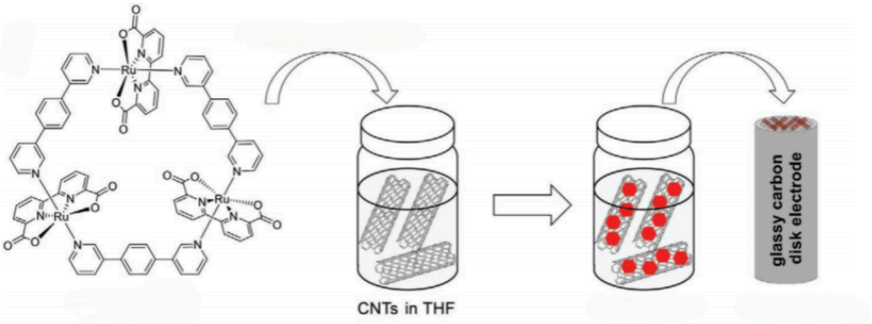

Figure 8. Ru(bda) macrocycles on carbon nanotubes achieve high-performance, stable water oxidation with low overpotentia

The study revealed that the catalytic activity of MC3’@CNT (MC3’ anchored on CNTs) could be further enhanced through an electrochemical activation process involving repetitive cyclic voltammetry scans. This activation led to the formation of a more active species, likely due to the coordination of additional water molecules to the Ru centers, as supported by semiempirical calculations. Foot-of-the-wave analysis indicated a WNA mechanism with a maximum turnover frequency (TOFmax) of 3,200 s^{-1}, one of the highest reported for Ru-based WOCs [26]. The high Faraday efficiency of 99% further confirmed the catalyst's efficiency in producing oxygen without significant side reactions. These findings underscore the potential of supramolecular Ru(bda) macrocycles for heterogeneous water oxidation, particularly when immobilized on conductive supports like CNTs. The study provides valuable insights into the design of efficient and stable WOCs for integration into water-splitting devices, paving the way for practical applications in renewable energy technologies. Future research could explore the immobilization of similar catalysts on other conductive surfaces or the development of hybrid materials to further enhance catalytic performance and stability.

6. Ru(bda) covalent organic framework

The synthesis of a highly crystalline covalent organic framework (COF) was pursued to enhance catalyst stability for chemical and photochemical water oxidation applications. The interpenetrated structure of this framework effectively preserved catalytic performance across multiple reaction cycles.

Integration of Ru(bda) catalysts into 3D imine polymers (Figure 9) yielded either amorphous Ru(bda)-polymer or crystalline Ru(bda)-COF, depending on the solvent conditions during synthesis. The amorphous variant displayed restricted catalytic activity, attributed to the disordered arrangement of Ru active sites, which favored the slower WNA pathway. In contrast, the crystalline CO’s well-defined framework promoted cooperative interactions among multiple active sites, enabling efficient water oxidation through the I2M mechanism.

The structural robustness of the material was further enhanced by a 5-fold interpenetrated dia-network, which contributed to exceptional stability. This design allowed the heterogeneous catalyst to be recycled repeatedly without significant degradation in activity. The modular nature of this approach suggests potential applicability for immobilizing other molecular catalysts, offering a promising strategy to combine molecular-level precision with enhanced durability and processability.

This study highlights the importance of crystalline frameworks in optimizing catalyst performance and stability, providing insights for the development of advanced catalytic systems for sustainable energy applications.

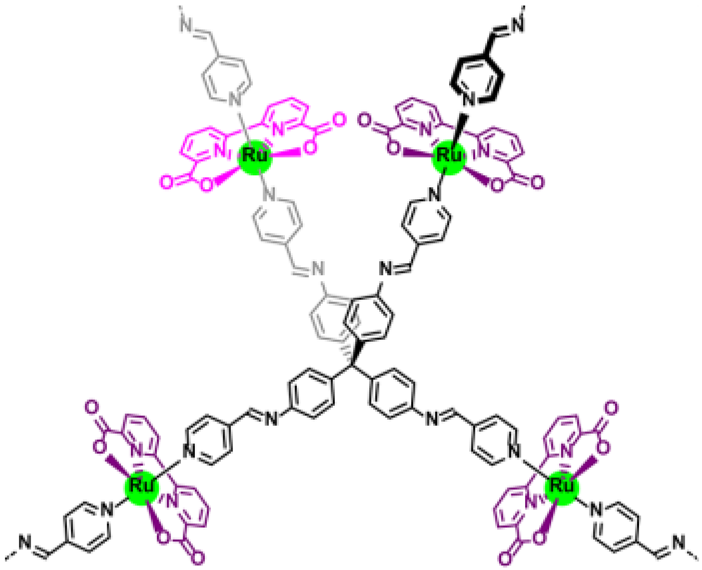

Figure 9. Long-range ordering of the Ru centers (green) on the interface of the interpenetrated dia-c5 net

7. Conclusion

Recent advances in Ru(bda)-based water oxidation catalysts demonstrate that precise structural control through dimerization, macrocyclization, and framework immobilization can simultaneously enhance activity, stability, and mechanistic efficiency. The field has evolved from studying discrete molecular catalysts to developing hierarchical architectures (COFs, CNT hybrids) that combine the benefits of homogeneous and heterogeneous systems. Key breakthroughs include achieving TOFs exceeding 3000 s^{-1} through optimized I2M pathways in crystalline frameworks, while maintaining stability via interpenetrated networks. However, challenges remain in bridging lab-scale performance with industrial requirements, particularly regarding long-term stability under high current densities and economic viability. Future research should focus on establishing universal design principles for earth-abundant alternatives, developing standardized device integration protocols, and employing computational tools to navigate the complex multi-site catalysts. These developments position molecular water oxidation catalysis as a maturing field transitioning from fundamental understanding to practical implementation in renewable energy systems.

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