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Metal–Organic Layers Hierarchically Integrate Three Synergistic Active Sites for Tandem Catalysis

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Abstract: We report the design of a bifunctional metal-organic layer (MOL), Hf_{12} -Ru-Co, composed of $[Ru(DBB)(bpy)_2]^{2+}$ [DBB-Ru, DBB = 4,4'-di(4-benzoato)-2,2'-bipyridine; bpy =2,2'-bipyridine] connecting ligand as a photosensitizer and $Co(dmgH)_2(PPA)Cl$ (PPA-Co, dmgH = dimethylglyoxime;PPA = 4-pyridinepropionic acid) on the Hf_{12} secondary building unit (SBU) as a hydrogen-transfer catalyst. Hf₁₂-Ru-Co efficiently catalyzed acceptorless dehydrogenation of indolines and tetrahydroquinolines to afford indoles and quinolones. We extended this strategy to prepare Hf₁₂-Ru-Co-OTf MOL with a $[Ru(DBB)(bpy)_2]^{2+}$ photosensitizer and Hf_{12} SBU capped with triflate as strong Lewis acids and PPA-Co as a hydrogen transfer catalyst. With three synergistic active sites, Hf₁₂-Ru-Co-OTf competently catalyzed dehydrogenative tandem transformations of indolines with alkenes or aldehydes to afford 3alkylindoles and bisindolylmethanes with turnover numbers of up to 500 and 460, respectively, illustrating the potential use of MOLs in constructing novel multifunctional heterogeneous catalysts.

Introduction

Metal-organic layers (MOLs), a 2D monolayered version of 3D MOFs,^[1-21] have recently provided a tunable material platform for the design of heterogeneous catalysts featuring isolated, uniform, and well-defined active sites (Figure 1 a).^[22-31] Hierarchical integration of multiple catalytic centers into MOLs can facilitate synergistic or tandem catalysis to potentially afford atom-economic and stepefficient synthetic methodologies.[32,33] Although several MOLs with two different active centers have been constructed (Figure 1b)^[34–38] and some of them have shown enhanced catalytic performance over their homogenous counterparts,^[37,38] the design of MOLs containing three or more different catalytic centers remains a challenge.^[23,39]

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Figure 1. a),b) Schematic representation of MOLs with one (a) or two (b) catalytic centers. c) Rational design of a new trifunctional MOL with three different catalytic centers.

Nature synergistically integrates a number of enzymes to perform complicated biosynthetic transformations. For example, "ubiquitin-mediated protein degradation" relies on ternary enzyme systems to degrade unneeded or damaged proteins.^[40] Inspired by nature, chemists have devoted significant efforts to develop multicatalytic systems as mimics for natural multienzymatic complexes to perform complex transformations. Despite the considerable progress in binary catalysis,[41-44] ternary catalysis is less developed. The key challenge in ternary catalysis is the mutual quenching of catalytic centres. We posit that MOLs can integrate multiple isolated active centres in a site-isolate fashion to enhance catalytic performance. Herein we report the rational design of the first trifunctional MOL containing a photosensitizer, a Lewis acid, and a hydrogen transfer catalyst for dehydrogenative tandem transformations of indolines to 3-alkylindoles and bisindolylmethanes.

Catalytic acceptorless dehydrogenation (CAD) is an environmentally benign synthetic strategy that does not require chemical oxidants and generates dihydrogen as the only by-product.^[45,46] CAD of N-heterocycles provides facile

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access to important motifs for pharmaceuticals and bioactive molecules.[47,48] Recently, photo-induced catalytic acceptorless dehydrogenation reactions have received increased interest due to their ability to facilitate important transformations under mild conditions.^[49-54] In this work, we designed trifunctional Hf12-Ru-Co-OTf MOL consisting of $[Ru(DBB)(bpy)_2]^{2+}$ [DBB = 4,4'-di(4-benzoato)-2,2'-bipyridine; bpy = 2,2'-bipyridine] ligand as photosensitizer and Hf₁₂ SBU capped with triflate (OTf) as strong Lewis acid and Co(dmgH)₂(PPA)Cl (PPA-Co, dmgH = dimethylglyoxime; PPA = 4-pyridinepropionic acid) as hydrogen transfer catalyst. Hf12-Ru-Co-OTf catalyzed synergistic tandem transformations of indolines to 3-alkylindoles and bisindolylmethanes via acceptorless dehydrogenation and electrophilic substitution of N-heterocycles (Figure 1c). This multi-catalytic system allows the combination of multiple transformations in a one-pot manner, bypassing the traditional stop-andgo approach.[55]

Results and Discussion

We first prepared bifunctional Hf12-Ru-Co MOL containing [Ru(DBB)(bpy)₂]²⁺ photosensitizer and PPA-Co hydrogen transfer catalyst for acceptorless dehydrogenation of Nheterocycles (Figure 2). Free-standing Hf₁₂-Ru MOL of the formula $Hf_{12}(\mu_3-O)_8(\mu_3-OH)_8(\mu_2-OH)_6(DBB-Ru)_6(TFA)_6$ was prepared through a solvothermal reaction between HfCl₄ and RuCl₂(DBB)(bpy)₂ in N,N-dimethylformamide (DMF) at 80°C using trifluoroacetic acid (TFA) and water as modulators. $^{[56]}\ Hf_{12}\ SBUs$ in $Hf_{12}\mbox{-}Ru$ are laterally connected by [Ru(DBB)(bpy)₂]²⁺ ligands to form an infinite 2D network and vertically terminated by six trifluoroacetate (TFA) groups. Transmission electron microscopy (TEM, Figure S4a) and atomic force microscopy (AFM, Figure S4b) analyses supported the monolayer morphology of Hf12-Ru with a diameter of ≈ 100 nm and a thickness of ≈ 1.6 nm (Figure S4c). Hf₁₂-Ru subsequently reacted with Co(dmgH)₂-(PPA)Cl (Figure 2d) in DMF at room temperature to generate Hf_{12} -Ru-Co of the formula $Hf_{12}(\mu_3-O)_8(\mu_3-OH)_8(\mu_2-OH)_8(\mu_3-OH)$ OH)₆(DBB-Ru)₆(PPA-Co)₆ (Figure 2 a).

The monolayer structure of Hf₁₂-Ru-Co was confirmed by TEM (Figure 2e) and AFM (Figures 2g,h) imaging. The measured thickness of 3.6 nm is consistent with the modeled height of 3.5 nm for PPA-Co-capped Hf₁₂-SBU (Figure S15). High-resolution TEM (HRTEM) showed a 6-fold symmetry (Figure 2 f), consistent with the projection of Hf₁₂-Ru-Co structure along the vertical direction. Hf₁₂-Ru-Co retained the crystallinity of Hf₁₂-Ru as shown by their similar PXRD patterns, which matched well with that simulated from the proposed Hf₁₂ MOL structure (Figure 2c). In addition, the ¹H NMR spectrum of digested Hf₁₂-Ru-Co exhibited a [Ru-(DBB)(bpy)₂]²⁺ to PPA-Co ratio of \approx 1:1 (Figures 2 b and S8), consistent with the proposed molecular formula of Hf₁₂-Ru-Co. This result indicates complete replacement of TFA groups by PPA-Co groups on the Hf₁₂-SBUs.

In light of the prevalence of indole and quinoline derivatives in pharmaceuticals,^[57,58] we used acceptorless dehydrogenation of indolines and tetrahydroquinolines as



Figure 2. Synthesis and characterization of Hf₁₂-Ru-Co. a) Synthetic route to Hf₁₂-Ru-Co. b) ¹H NMR spectrum of digested Hf₁₂-Ru-Co. Peaks labeled with blue and yellow stars are assigned to [Ru(DBB)-(bpy)₂]²⁺ and PPA-Co, respectively c) PXRD patterns of Hf₁₂-Ru and Hf₁₂-Ru-Co (freshly prepared or after reaction) and the simulated pattern for the Hf₁₂ MOL. d) Single-crystal X-ray structure of PPA-Co with thermal ellipsoids set at 50% probability (CCDC number given in the Supporting Information). e)–h) TEM image (e), HRTEM image (f), AFM topography (g) and height profile (h) along the white line in (g), of Hf₁₂-Ru-Co.

model reactions to evaluate the synergistic catalytic performance of $[Ru(DBB)(bpy)_2]^{2+}$ photosensitizer and PPA-Co catalyst in Hf₁₂-Ru-Co. Upon blue LED irradiation, Hf₁₂-Ru-Co (0.4 mol% based on Co) competently catalyzed dehydrogenation of indolines and tetrahydroquinolines with turnover

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numbers of up to 250 (Table 1). Gas chromatography confirmed the generation of H_2 as the by-product. A range of indolines bearing various functional groups including -Me, -F, -Cl, -Br, and -OMe underwent acceptorless dehydrogenation smoothly to afford target indoles **2a–2h** in >96% isolated yields. No obvious electronic and steric effects were observed. Hf₁₂-Ru-Co also catalyzed more challenging acceptorless dehydrogenation of tetrahydroquinolines. Halogen-containing substrates afforded dehydrogenation products 4c and 4d in 95% and 94% isolated yields, respectively. In contrast, the relatively electron-deficient substrate 3e bearing the ester group gave a reduced yield of 42% for 4e, likely due to less favorable single electron oxidation by the photoexcited photosensitizer. Although 8- and 2-methyl tetrahydroquinolines reacted efficiently to produce 4b and 4f, respectively, the use of 4-methyl tetrahydroquinoline led to a mixture of products 4g and 4g' in 1:1 ratio. The formation of 4g' can be attributed to the cross-coupling between in situ generated intermediates of 1,4-dihydroquinoline and 3,4-dihydroquinoline followed by further acceptorless dehydrogenation.

The excellent dehydrogenation efficiency of H_{12} -Ru-Co shown in Table 1 indicates synergistic catalytic performance of $[Ru(DBB)(bpy)_2]^{2+}$ photosensitizer and PPA-Co catalyst. On this basis, we synthesized trifunctional H_{12} -Ru-Co-OTf MOL consisting of $[Ru(DBB)(bpy)_2]^{2+}$ photosensitizer, Hf-OTf Lewis acid, and PPA-Co hydrogen transfer catalyst. Hf_{12} -Ru-Co-OTf was synthesized from Hf_{12} -Ru in two steps. Treatment of Hf_{12} -Ru with trimethylsilyl triflate (TMS-OTf)

Table 1: Hf_{12} -Ru-Co catalyzed acceptorless dehydrogenation of *N*-heterocycles.^[a]



[a] Reactions at 0.1 mmol scale with 0.4 mol% Hf₁₂-Ru-Co (based on Co) at room temperature; yields of isolated products and TONs are shown in parentheses.

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in benzene at room temperature afforded Hf_{12} -Ru-OTf with a formula of $Hf_{12}(\mu_3-O)_8(\mu_3-OH)_8(\mu_2-OH)_6(DBB-Ru)_6(OTf)_6$. Next, Hf_{12} -Ru-OTf reacted with 3.0 equiv of Co(dmgH)₂-(PPA)Cl (relative to Hf_{12} -SBU) to give Hf_{12} -Ru-Co-OTf of the formula $Hf_{12}(\mu_3-O)_8(\mu_3-OH)_8(\mu_2-OH)_6(DBB-Ru)_6(PPA-Co)_3(OTf)_3$ (Figure 3a).

Both Hf_{12} -Ru-OTf and Hf_{12} -Ru-Co-OTf exhibited similar PXRD patterns to that of Hf_{12} -Ru (Figure 3d), suggesting their identical structure. ¹H and ¹⁹F NMR spectra of digested Hf_{12} -Ru-OTf showed only one set of signals assignable to $[Ru(DBB)(bpy)_2]^{2+}$ (Figure S9) and one peak corresponding to HOTf (Figure S10), respectively, indicating complete replacement of TFA groups by OTf⁻ on the Hf_{12} -SBUs. On the other hand, the ¹H NMR spectrum of digested Hf_{12} -Ru-Co-OTf showed two sets of signals assignable to [Ru(DBB)-



Figure 3. Synthesis and characterization of Hf₁₂-Ru-Co-OTf. a) Synthetic route to Hf₁₂-Ru-Co-OTf. b) ¹H NMR spectrum of digested Hf₁₂-Ru-Co-OTf. Peaks labeled with blue and yellow stars are assigned to [Ru(DBB)(bpy)₂]²⁺ and PPA-Co, respectively c) ¹⁹F NMR spectrum of digested Hf₁₂-Ru-Co-OTf. d) PXRD patterns of Hf₁₂-Ru, Hf₁₂-Ru-OTf, and Hf₁₂-Ru-Co-OTf (freshly prepared or after reaction) and the simulated pattern for the Hf₁₂ MOL. e) Fluorescence spectra of free NMA (black) and NMA bound to Hf₁₂-Ru-OTf (blue) and Hf₁₂-Ru-Co-OTf (red) in MeCN at 298 K. f) TEM image of Hf₁₂-Ru-Co-OTf.

 $(bpy)_2]^{2+}$ and PPA-Co in approximately 2:1 molar ratio (Figures 3b and S11), consistent with the proposed molecular formula of Hf₁₂-Ru-Co-OTf. Additionally, the ¹⁹F NMR spectrum of digested Hf₁₂-Ru-Co-OTf exhibited one signal corresponding to HOTf (Figures 3c and S12). The Lewis acidity of Hf₁₂-Ru-OTf and Hf₁₂-Ru-Co-OTf was probed by *N*-methylacridone (NMA) fluorescence method.^[59-60] Upon coordinating to Hf₁₂-Ru-OTf and Hf₁₂-Ru-Co-OTf, the λ_{max} values of NMA emissions shifted from 433 nm to 471 nm and 470 nm, respectively (Figure 3e). This result shows that both Hf₁₂-Ru-OTf and Hf₁₂-Ru-Co-OTf exhibit strong Lewis acidity that is comparable to Sc(OTf)₃.^[38] Hf₁₂-Ru-Co-OTf showed similar sizes and morphologies to Hf₁₂-Ru-Co by TEM and HRTEM analysis (Figures 3 f and S13).

As shown in Scheme S9, Hf_{12} -Ru-Co-OTf retained the high synergistic catalytic performance of Hf_{12} -Ru-Co for acceptorless dehydrogenation. Interestingly, the strong Lewis acid center in Hf_{12} -Ru-Co-OTf efficiently catalyzed electrophilic substitution of in situ generated indoles with alkenes or aldehydes to afford 3-alkyl indoles and bisindolylmethanes (BIMs), respectively, with turnover numbers of up to 500 and 460. In the presence of 0.2 mol % Hf_{12} -Ru-Co-OTf (based on Co), various indolines with -Cl, -Br, -Me, and -OMe substituents reacted with 2-butenone smoothly in a stepwise manner, leading to the corresponding 3-alkyl indoles 5a-5f in 85% to quantitative isolated yields (Table 2). The dehydrogenative tandem transformation of indoline with 4-penten-3one afforded the coupling product 5g in 94% yield. Importantly, Hf_{12} -Ru-Co-OTf catalyzed reactions of indolines with

Table 2: Hf_{12} -Ru-Co-OTf catalyzed dehydrogenative tandem transformations of indolines.^[a]



[a] Reactions at 0.1 mmol scale with 0.2 mol % Hf₁₂-Ru-Co-OTf (based on Co) at room temperature; yields of isolated products and TONs are shown in parentheses.

benzaldehydes to afford bisindolylmethane (BIM) derivatives **6a–6d** in 85–92% isolated yields (Table 2). Methyl- and fluoro-substituted benzaldehydes also worked well in this coupling reaction, suggesting the tolerance to substrates with different electronic properties. It is worth noting that the BIM scaffold exists prevalently in pharmaceuticals and nature products.^[61] BIM derivatives have found applications as inhibitors to cancer cell targets.^[62]

Hf₁₂-Ru-Co and Hf₁₂-Ru-Co-OTf were stable under catalytic conditions as illustrated by the maintenance of PXRD patterns in recovered MOLs (Figure 2c and Figure 3d). In addition, Hf₁₂-Ru-Co and Hf₁₂-Ru-Co-OTf were recovered and used in five runs of catalytic reactions with no significant decrease in product yields (Figures 4a and S16). Hf₁₂-Ru-Co and Hf₁₂-Ru-Co-OTf exhibited better synergistic catalytic performance over the homogeneous counterparts (Figure 4b, Schemes S11–S13). The isolation of three different catalytic sites in Hf₁₂-Ru-Co-OTf prevents their deleterious mutual deactivation, the foremost challenge in homogeneous ternary catalysis,^[55] resulting in excellent synergistic tandem catalytic performance.

We conducted several control experiments to probe the reaction mechanism. No reaction was observed in the absence of light (Figure 4c, top), suggesting the photocatalytic nature of this synergistic catalysis. Only a trace amount of dehydrogenation product 2a was obtained with Hf₁₂-Ru as catalyst



Figure 4. a) Yields of **2a** with recovered Hf_{12} -Ru-Co in five consecutive runs. b) Time-dependent yields of **2a** with different catalysts. c) Control experiments under different conditions. d) Proposed reaction mechanism.

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(Figure 4c, middle), indicating the crucial role of cobaloxime as a hydrogen transfer catalyst. Hf_{12} -Ru-Co catalyzed hydrogen transfer from indoline to 1,1-diphenylethene (Scheme S10), which supports the involvement of metal-hydride intermediate in the reaction. Without the strong Lewis acidic site, Hf_{12} -Ru-Co only catalyzed the acceptorless dehydrogenation of indoline but did not mediate subsequent electrophilic alkylation (Figure 4c, bottom). These control experiments support the critical role of [Ru(DBB)(bpy)₂]²⁺ photosensitizer, Hf-OTf Lewis acid, and PPA-Co hydrogen transfer catalyst in Hf_{12} -Ru-Co-OTf.

On the basis of these experimental results and literature precedents,^[47,48] we propose a plausible reaction mechanism in Figure 4d. Upon blue LED irradiation, the photoexcited $[Ru^{II}]^*$ delivers one electron to the $[Co^{III}]$ species to generate the [Co^{II}] compound and strongly oxidizing [Ru^{III}] complex. Single electron oxidation of indoline by [Ru^{III}] affords [Ru^{II}] and radical cation intermediate A. Deprotonation of A forms α -carbon radical **B**. The [Ru^{II}] photocatalyst is excited by blue LED to restart the photocatalytic cycle. Radical addition reaction of **B** to [Co^{II}] gives the [Co^{III}]–C bonded intermediate C. Subsequent β -H elimination of C yields indole 3 and the [Co^{III}]-H intermediate. Protonation of [Co^{III}]-H produces H₂ and regenerates [Co^{III}] hydrogen transfer catalyst to finish the Co-catalytic cycle. In the meantime, upon coordinating to the strongly Lewis acidic Hf₁₂-SBU, vinyl ketone becomes electron deficient and attacks indole 3 at the most electronrich β -position. The resulting intermediate **E** reacts with an incoming vinyl ketone to release product 5 and restart the Lewis acid catalytic cycle. The hierarchical integration of three different catalytic centers into the MOL not only prevents mutual deactivation but also facilitates electron and radical transfer to enhance the synergistic tandem catalytic activity.

Conclusion

In summary, we have prepared the new bifunctional Hf_{12} -Ru-Co MOL by linking cobaloxime-capped Hf12-SBUs with Ru-photosensitizer-based bridging ligands. Hf12-Ru-Co exhibited excellent synergistic catalytic performance in acceptorless dehydrogenation of indolines and tetrahydroquinolines. We further designed the new trifunctional Hf₁₂-Ru-Co-OTf MOL containing Ru-photosensitizer, Co-hydrogen transfer catalyst, and strong Lewis acid catalyst for dehydrogenative tandem catalysis. Hf₁₂-Ru-Co-OTf efficiently catalyzed dehydrogenative tandem transformations of indolines with vinyl ketones or aldehydes to afford a variety of 3alkylindoles and bisindolylmethanes (BIMs) with turnover numbers of up to 500 and 460, respectively. The integration of three isolated, uniform, and well-defined catalytic centers into the MOL enhances the multicatalytic performance by preventing mutual deactivation and increasing local concentrations. This work highlights the potential of MOLs as a 2D material platform for designing multi-catalytic systems for tandem catalysis.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: dehydrogenation · metal–organic layers · photocatalysis · tandem catalysis · trifunctional materials

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Research Articles

Tandem Catalysis

Y. Quan, G. Lan, W. Shi, Z. Xu, Y. Fan, E. You, X. Jiang, C. Wang, W. Lin* ______

Metal–Organic Layers Hierarchically Integrate Three Synergistic Active Sites for Tandem Catalysis



A tri-functional metal–organic layer with $[Ru(DBB) (bpy)_2]^{2+}$ photosensitizers and Hf_{12} secondary building units capped with triflate groups as strong Lewis acid sites and PPA-Co groups as hydrogen-transfer catalysts synergistically catalyzed dehydrogenative tandem transformations of indolines with alkenes or aldehydes to afford 3-alkylindoles and bisindolyl-methanes, respectively.

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