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J. Am. Chem. Soc., Just Accepted Manuscript • Publication Date (Web): 12 Jan 2020

Downloaded from pubs.acs.org on January 13, 2020

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Metal-Organic Layers for Synergistic Lewis Acid and Photoredox Catalysis

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Supporting Information Placeholder

ABSTRACT: We report the design of a new multifunctional metal-organic layer (MOL), Hf₁₂-Ir-OTf, comprising triflate (OTf)capped Hf₁₂ secondary building units (SBUs) and photosensitizing $Ir(DBB)[dF(CF_3)ppy]_2^+$ [DBB-Ir-F, DBB = 4,4'-di(4-benzoato)-2,2'-bipyridine; $dF(CF_3)ppy = 2-(2,4-difluorophenyl)-5-$ (trifluoromethyl)pyridine] bridging ligands. Hf12-Ir-OTf effectively catalyzed dehydrogenative cross-couplings of heteroarenes with ethers, amines, and unactivated alkanes with turnover numbers of 930, 790, and 950, respectively. Hf12-Ir-OTf also competently catalyzed late-stage functionalization of bioactive and drug molecules such as caffeine, Fasudil, and Metyrapone. The superior catalytic performance of Hf12-Ir-OTf over a mixture of photoredox catalyst and stoichiometric amounts of Brønsted acids or sub-stoichiometric amounts (20 mol%) of Lewis acids is attributed to the close proximity (1.2 nm) between photoredox and Lewis acid catalysts in Hf12-Ir-OTf, which not only facilitates the reaction between the carbon radical and the activated heteroarene but also accelerates the electron transfer from the nitrogen radical intermediate to the Ir(IV) species in the catalytic cycle.

Metal-organic frameworks (MOFs) have provided a tunable porous material platform for the design of heterogeneous catalysts with crystalline structures and uniform, isolated, and well-defined active sites.¹⁻¹⁰ In particular, MOFs with coordinatively unsaturated metal sites in their secondary building units (SBUs) have long been recognized and utilized as solid Lewis acid catalysts.¹¹⁻¹⁶ However, modest Lewis acidity of and unfavorable substrate access to SBUs have limited the applications of MOFs as solid Lewis acid catalysts. As Lewis acidity of MOFs has recently been drastically enhanced by introducing perfluorinated ligands and via SBU modifications,¹⁵⁻¹⁶ access to highly Lewis acidic SBUs remains a key hurdle to widespread applications of MOF-based Lewis acid catalysts.

Metal-organic layers (MOLs), a free-standing monolayered version of MOFs, have been recently developed as a new type of 2D molecular materials.¹⁷⁻¹⁸ MOLs are highly dispersible and have completely accessible active sites in addition to inheriting the advantages of MOFs including structural regularity, compositional diversity, and stability.¹⁹⁻²² We surmised that MOLs could provide an excellent 2D material platform to engineer highly effective heterogeneous catalysts with freely accessible Lewis acidic and other catalytic sites.²³⁻²⁵ Herein we report the design of a multifunctional MOL, Hf₁₂-Ir-OTf, consisting of triflate (OTf)-capped Hf₁₂ SBUs as a strong Lewis acid and Ir(DBB)[dF(CF₃)ppy]₂⁺ [DBB-Ir-F, DBB = 4,4'-di(4-benzoato)-2,2'-bipyridine; dF(CF₃)ppy = 2-(2,4difluorophenyl)-5-(trifluoromethyl)pyridine] ligands as a photoredox catalyst²⁶⁻³⁴ for synergistic catalytic dehydrogenative crosscouplings between a) MOFs with internal Lewis acid sites



Figure 1. (a) Schematic showing incompletely accessible internal Lewis acid sites in MOFs (labeled by black arrows) exemplified by coordinatively unsaturated metals on the SBUs of MOF-808 (left) and defect UiO-MOFs with missing linkers (right). (b) Schematic showing freely accessible external Lewis acid sites in the SBUs of Hf₁₂ MOLs (labeled by black arrows). (c) The proximity of Lewis acidic metal sites and photosensitizers in a MOL promotes synergistic Lewis acid and photoredox catalysis.

heteroarenes and ethers, protected amines, or unactivated alkanes. As a result of the proximity (\sim 1.2 nm) between the two catalytic

centers, 0.1 mol% Hf₁₂-Ir-OTf catalyzed dehydrogenative crosscoupling reactions to afford functionalized heteroarenes with turnover numbers of up to 950, outperforming homogeneously catalyzed reactions with the employment of stoichiometric amounts of Brønsted acids or sub-stoichiometric amounts of Lewis acids.³⁵

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Hf₁₂-Ir-OTf was synthesized in two steps. Free-standing Hf₁₂-Ir-TFA was first prepared through a solvothermal reaction between HfCl₄ and H₂(DBB-Ir-F) in N,N-dimethylformamide (DMF) at 80 °C using trifluoroacetic acid (H-TFA) and water as modulators. In Hf₁₂-Ir-TFA, Hf₁₂-SBUs are laterally bridged by DBB-Ir-F ligands and vertically terminated by trifluoroacetate (TFA) capping agents to generate an infinite 2D network with the formula of Hf₁₂(μ_3 -O)₈(μ_3 -OH)₈(μ_2 -OH)₆(DBB-Ir-F)₆(TFA)₆ (Figure S5, SI). The DBB-Ir-F to TFA ratio of 1:1 was confirmed by ¹⁹F NMR analysis of digested Hf₁₂-Ir-TFA (Figure S7, SI). Transmission electron microscopy (TEM, Figures 2e and S8, SI) and atomic force microscopy (AFM, Figure 2f) imaging verified the monolayer morphology of Hf₁₂-Ir-TFA with a diameter of ~300 nm and a thickness of ~1.7 nm (Figure 2g).



Figure 2. Preparation and characterization of Hf₁₂-Ir-OTf. (a) Replacement of TFA by OTF on Hf₁₂-SBU. (b) ¹⁹F NMR spectrum of the reaction supernatant and assignment of ¹⁹F peaks. (c) PXRD patterns of Hf₁₂-Ir-TFA and Hf₁₂-Ir-OTf (freshly prepared or after catalytic reaction) in comparison to the simulated pattern for the Hf₁₂ MOL. (d) ¹⁹F NMR spectrum of digested Hf₁₂-Ir-OTf. The molar ratio of DBB-Ir-F to HOTf is calculated as ~1:1. (e-g) TEM image (e), AFM topography (f), and height profile (g) of Hf₁₂-Ir-TFA. (h) TEM image of Hf₁₂-Ir-OTf shows its monolayer morphology.

The TFA groups in Hf₁₂-Ir-TFA were completely replaced with OTf groups via a metathesis reaction with trimethylsilyl triflate (TMS-OTf) to afford Hf₁₂-Ir-OTf of the formula Hf₁₂(μ ₃-O)₈(μ ₃-OH)₈(μ ₂-OH)₆(DBB-Ir-F)₆(OTf)₆ (Figures 2a and S9, SI). ¹⁹F

NMR analysis of the reaction supernatant revealed the formation of trimethylsilyl trifluoroacetate (TMS-TFA) and H-TFA (Figure 2b and S10-15, SI). ¹⁹F NMR analysis of digested Hf₁₂-Ir-OTf showed the presence of DBB-Ir-F bridging ligand and triflic acid (HOTf) in a 1:1 molar ratio but the absence of H-TFA (Figures 2d and S18, SI). ¹⁹F NMR analysis further showed that Hf₁₂-Ir-OTf was free of HOTf after washing with benzene twice (Figure S16, SI).

TEM and AFM imaging showed that Hf_{12} -Ir-OTf retained the monolayer structure of Hf_{12} -Ir-TFA (Figures 2h and S19, SI). Hf_{12} -Ir-OTf exhibited a similar PXRD pattern to that simulated from the structural model of the Hf_{12} MOL (Figure 2c). ¹H NMR analysis of digested Hf_{12} -Ir-OTf showed only one group of signals assignable to DBB-Ir-F (Figure S17, SI). UV-Vis and luminescence spectra indicated that Hf_{12} -Ir-OTf possessed the same characteristic absorption, excitation, and emission peaks as Me₂DBB-Ir-F and Hf_{12} -Ir-TFA (Figure S20, SI).

We determined Lewis acidity of Hf₁₂-Ir-OTf, Hf₁₂-Ir-TFA, and Sc(OTf)₃ using the reported N-methylacridone (NMA) fluorescence method.¹⁵⁻¹⁶ Upon excitation at 413.0 nm, NMA shows an emission maximum (λ_{max}) at 433.0 nm (Figure 3a, black). The λ_{max} of NMA red-shifts upon binding to a Lewis acid and the extent of the red-shift correlates to the Lewis acidity. After binding to Hf₁₂-Ir-OTf and Hf₁₂-Ir-TFA, the λ_{max} of NMA shifted to 472.8 and 467.7 nm (Figure 3a, blue and red), respectively. As a control, homogeneous Sc(OTf)₃ displayed a NMA emission λ_{max} at 472.6 nm (Figure 3a, green). These results indicate that Hf₁₂-Ir-OTf possesses a similar Lewis acidity to Sc(OTf)₃ and much higher Lewis acidity than Hf₁₂-Ir-TFA.

The identical photophysical property of Hf12-Ir-OTf to Me2DBB-Ir-F suggests its photosensitizing ability. With the shortest distance of 1.2 nm between the Lewis acid and photoredox sites in Hf₁₂-Ir-OTf (Figure S21, SI), we were intrigued if the proximity of the two active sites could promote synergistic catalysis. We used Minisci-type cross-couplings of heteroarenes as model reactions to evaluate the synergistic catalytic performance of Lewis acid and photoredox sites in Hf12-Ir-OTf.35 Functionalization of heteroarenes is of great significance owing to their prevalence in pharmaceutical compounds and bioactive molecules.³⁶⁻³⁷ Upon blue LED irradiation at room temperature, 0.1 mol% Hf12-Ir-OTf efficiently catalyzed dehydrogenative cross-couplings of heteroarenes with ethers,38 amines,39 and unactivated alkanes40-41 with turnover numbers of up to 930, 790, and 950, respectively. Cyclic and acyclic ethers underwent coupling reactions with isoquinoline smoothly to afford target products 1c-4c in 85-93% isolated yields and with excellent regioselectivity. The addition of ethers at the C1 position of isoquinoline is likely due to the polar effects of Lewis acid-bound isoquinoline.⁴² 2-Substituted quinoline afforded the C4-alkylated product while 4-substituted quinoline resulted in the functionalization at the C2 position (5c & 11c in Table 1). Pyridine and phenanthridine also underwent coupling reactions with cyclic ethers to afford 6c and 7c in high isolated yields.

In the presence of 0.1 mol% Hf₁₂-Ir-OTf, alkylamide and carbamate coupled with isoquinoline to give **9c** and **10c** in 79% and 74% isolated yields, respectively. No coupling product was observed when an electron-rich trialkylamine was used as the amine partner, due probably to the overoxidation of trialkylamine to the iminium cation which cannot react with Lewis acid-activated electron deficient heteroarenes. Quinoline and benzothiazole also coupled with carbamate to afford the corresponding products **11c** and **12c** in good isolated yields.

Table 1. Hf₁₂-Ir-OTf catalyzed dehydrogenative cross-coupling reactions.^a

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^aReactions at 0.1 mmol scale with 0.1 mol% Hf-Ir-OTf in dichloromethane at room temperature.

Hf12-Ir-OTf catalyzed dehydrocoupling of isoquinoline with unactivated cyclopentane, cyclohexane, and cycloheptane to afford target products 13c-15c in 92%, 95%, and 76% isolated yields, respectively. Such alkylated heteroarenes are difficult to prepare by conventional methods. Quinoline and pyrimidine derivatives also coupled with cyclohexane to afford 16c and 17c in 71% and 46% isolated yields, respectively. It is noteworthy that some of the products such as 3c and 9c are key scaffolds in drug molecules.⁴³ More importantly, Hf12-Ir-OTf competently catalyzed late-stage functionalization of bioactive and drug molecules. We successfully functionalized caffeine (the most consumed neurostimulant), Fasudil (a potent Rho-kinase inhibitor and vasodilator), and Metyrapone (a diagnostic agent for adrenal insufficiency) with tetrahydrofuran in the presence of 0.1 mol% Hf12-Ir-OTf to afford 18c-20c in high to moderate isolated yields. Freely accessible Lewis acidic and other catalytic sites in MOLs can thus be leveraged for synergistic catalysis and drug discovery.³⁶

The low loading (0.1 mol%) of Hf₁₂-Ir-OTf in these coupling reactions led to very high turnover numbers of 460 to 950 calculated on the basis of both the photosensitizer and the Lewis acid. This catalytic performance is vastly superior to homogeneously catalyzed reactions which require stoichiometric amounts of Brønsted acids or sub-stoichiometric amounts (20 mol%) Lewis acids.³⁵ We attribute the excellent catalytic performance of Hf₁₂-Ir-OTf to the proximity between DBB-Ir-F photosensitizers and Lewis acidic Hf sites on the SBUs. As shown in Figure 3b (black), Hf₁₂-Ir-TFA catalyzed reactions under identical conditions afforded the coupling product **1c** in only 8% yield. Although possessing similar Lewis acidity as Hf₁₂-Ir-OTf, Sc(OTf)₃ in combination with Hf₁₂-Ir-TFA produced **1c** in 23% yield only (Figure 3b, red). These results and additional control experiments (Table S1, SI) support the synergistic catalytic performance of the photoredox and Lewis acidic sites in Hf₁₂-Ir-OTf as a result of their proximity, highlighting the advantage of hierarchically installing cooperative catalytic sites in MOLs for synergistic catalysis.



Figure 3. (a) Fluorescence spectra of free NMA (black), NMA binding to Hf₁₂-Ir-OTf (blue), Hf₁₂-Ir-TFA (red), and Sc(OTf)₃ (green) in MeCN at 298 K. (b) Time-dependent yields of **1c** with different catalysts. (c) Control experiments under different conditions. (d) Proposed reaction mechanism.

 Hf_{12} -Ir-OTf was stable under photocatalytic conditions as evidenced by the retention of the PXRD pattern for the recovered Hf_{12} -Ir-OTf (Figure 2c) and the leaching of <1% Hf and <2% Ir into the supernatant by inductively coupled plasma mass spectrometry (ICP-MS). In addition, Hf_{12} -Ir-OTf was recovered and used in five runs of dehydrogenative cross-coupling between isoquinoline and tetrahydrofuran without significant decrease in catalytic activity (Figure S22, SI).

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We conducted several experiments to probe the reaction mechanism (Figure 3c). The dehydrogenative cross-coupling between isoquinoline and THF did not proceed in the absence of light or the photosensitizer, indicating the photocatalytic nature of this synergistic catalysis. The addition of a radical capture agent (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) completely inhibited the dehydrogenative cross-coupling reaction, supporting the involvement of a radical pathway in the reaction mechanism. Finally, the addition of 1,1-diphenylethene as a radical capture agent afforded 2-(2,2-diphenylvinyl)tetrahydrofuran **1d** and 1,1-diphenyl-'butoxyethene **1e** in 12% and 35% yields, respectively, but completely shut down the formation of **1c**. This result indicates the presence of both 'butoxy radical and α -tetrahydrofuran radical in the reaction.

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On the basis of these experimental results and literature precedents,³⁵ we propose a plausible reaction mechanism in Figure 3d. Single electron reduction of 'BuOOBz by the photoexited DBB-Ir-F ligand in Hf12-Ir-OTf generates the Ir(IV) species and electrophilic 'butoxy radical A, which undergoes hydrogen atom transfer (HAT) with sp^3 C-H to give the nucleophilic sp^3 carbon radical **B**. In the meantime, upon coordinating to the strongly Lewis acidic SBU, the heteroarene C becomes electron-deficient and susceptible to attack by the nucleophilic sp^3 carbon radical **B** generated by the photoredox center that is only 1.2 nm away. The radical addition process produces the electron-rich nitrogen radical intermediate **D**, which is oxidized by the Ir(IV) species to afford the secondary amine cation E and regenerate the Ir(III) species. The Ir(III) photocatalyst is excited by blue LED to restart the catalytic cycle on the left. Deprotonation of the amine cation E afforded Lewis acidbound functionalized heteroarene F. An incoming heteroarene substrate releases the functionalized heteroarene P and restarts the catalytic cycle on the right. In this mechanistic scenario, the close proximity of photoredox and Lewis acidic centers in Hf12-Ir-OTf not only facilitates the reaction between carbon radical B and activated heteroarene C, but also accelerates the electron transfer from the nitrogen radical intermediate **D** to the Ir(IV) species.

In summary, we have prepared multifunctional MOLs by directly incorporating photoredox catalysts as bridging ligands and activating trifluoroacetate-capped Hf12 SBUs with trimethylsilyl triflate to afford strongly Lewis acidic Hf sites. The resultant Hf12-Ir-OTf MOL effectively catalyzed dehydrogenative cross-couplings of heteroarenes with ethers, amines, and unactivated alkanes with turnover numbers of 930, 790, and 950, respectively. Hf12-Ir-OTf also competently catalyzed late-stage functionalization of bioactive and drug molecules such as caffeine, Fasudil, and Metyrapone. We attribute the excellent catalytic performance of Hf₁₂-Ir-OTf to the close proximity (1.2 nm) between photoredox and Lewis acid catalysts which not only facilitates the reaction between the carbon radical and the activated heteroarene but also accelerates the electron transfer from the nitrogen radical intermediate to the Ir(IV) species in the catalytic cycle. MOLs thus provide an excellent platform to design novel 2D materials with synergistic catalysts for the sustainable synthesis of complex organic molecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Synthesis and characterization of Hf₁₂-Ir-TFA and Hf₁₂-Ir-OTf, synergistically catalytic reactions, and mechanism study (PDF)

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

We thank Xiaomin Jiang, Xuanyu Feng, and Yang Song for experimental help. We acknowledge the National Science Foundation and the University of Chicago for founding support and the MRSEC Shared User Facilities at the University of Chicago (NSF DMR-1420709) for instrument access. XAS analysis was performed at Beamline 10-BM, supported by the Materials Research Collaborative Access Team (MRCAT). Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. DOE Office of Science by ANL, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

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