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# Metal-Organic Layers Catalyze Photoreactions without Pore Size and Diffusion Limitations

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**Abstract:** Metal-organic-frameworks (MOFs) have emerged as promising single-site solid catalysts for organic reactions. However, MOF catalysts suffer from pore size limitation and slow diffusion, which become more detrimental for photoreactions. Metal-organic layers (MOLs) have unique ultrathin 2-D monolayer structures and overcome pore size and diffusion limitations. Here we report the synthesis of photoactive Zr-RuBPY MOL based on Zr-oxo clusters and [Ru(bpy)<sub>3</sub>]<sup>2+</sup>-containing linkers and its application in photocatalytic intramolecular and cross [2+2] cyclizations of enones as well as Meerwein addition reactions between aryl diazonium salts, styrenes, and nitriles. In contrast, the corresponding MOF catalyst failed in these photoreactions, due to either pore size limitation or restricted diffusion of reactive intermediates.

By harvesting sunlight to drive thermodynamically uphill reactions, photosynthesis has provided food and energy for the human kind. Chemists have sought to use light as an inexpensive, renewable, and environmentally friendly means to drive photochemical reactions for over a century.<sup>[1]</sup> Photocatalysis is now used in organic synthesis with high atom efficiency and product selectivity  $\ensuremath{^{[2]}}$  via shifting apparent thermodynamic equilibria of chemical reactions and allowing difficult reactions to be carried out under mild conditions.<sup>[3]</sup> Photocatalysts are often required in visible-light-driven organic reactions as the majority of organic substrates do not appreciably absorb in the visible spectrum.<sup>[4]</sup> As an example of the mostly studied photocatalysts,<sup>[2]</sup> [Ru(bpy)<sub>3</sub>]<sup>2+</sup> exhibits high absorption extinction coefficient, good solubility, adequate chemical stability, and long excited-state lifetime, enabling its application in a variety of photocatalytic organic cycloaddition,<sup>[5]</sup> reactions, such as [2+2] tin-free dehalogenation,<sup>[6]</sup> thio-ene reactions,<sup>[7]</sup> olefin epoxidation,<sup>[8]</sup> bimetallic photocatalysis,<sup>[9-10]</sup> and asymmetric photocatalysis.<sup>[11-</sup> <sup>12]</sup> However, Ru(bpy)<sub>3</sub><sup>2+</sup> and other homogeneous precious metalbased photocatalysts are difficult to separate from their reaction mixtures for reuse, spurring our interest in heterogenizing molecular photocatalysts to enhance their catalytic efficiencies and to facilitate their recycle and reuse.

Metal-organic frameworks (MOFs) are a novel class of porous crystalline materials based on metal cluster nodes interconnected with multidentate organic linkers.<sup>[13-15]</sup> MOFs have provided a tunable platform to design single-site solid catalysts for a number of organic transformations, but their use in heterogenizing molecular photocatalysts is much less explored.<sup>[16-23]</sup> In many photoreactions, photocatalysts enter excited states upon light irradiation and then react with organic substrates through single-

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electron transfer (SET) processes. The resultant radical intermediates must react with their partners within their typically short lifetimes to afford desired products. However, diffusion through nanometer-sized MOF channels is highly restricted,<sup>[24-27]</sup> which reduces the collision probability between reactive intermediates and their partners in photoreactions, presenting a significant hurdle for designing efficient MOF-based photocatalysts (Scheme 1a).



Scheme 1. Restricted vs. free diffusion of reactive species in MOFs (a) vs. MOLs (b) during photocatalysis. (c) Schematic showing the synthesis of Zr-RuBPY MOL.

Herein we report the use of 2-D metal-organic layers (MOLs) to overcome size and diffusion limitations in MOF photocatalysis. With one-dimension reduced to a monolayer thickness of 1-2 nm, MOLs inherit the heterogeneous, crystalline, single-site solid-state nature but not pore size limitation and diffusion restriction of 3-D MOF catalysts.<sup>[28]</sup> While the Zr-RuBPY MOL containing Ru(bpy)<sub>3</sub><sup>2+</sup> moieties exhibits high photocatalytic activities for [2+2] cycloadditions of bis(enones) and Meerwein additions between aryl diazonium salts, styrenes and nitriles under visible light irradiation, the UiO-67 MOF control containing Ru(bpy)<sub>3</sub><sup>2+</sup> was ineffective in these reactions. The MOLs overcome substrate size limitation and facilitate the diffusion of reactive intermediates (Scheme 1b), leading to enhanced activities than the MOF counterpart.

The Zr-BPY MOL was prepared by heating a mixture of ZrCl<sub>4</sub>, 4',6'-bis(4-benzoic acid)-(2,2'-bipyridine)-5-carboxylic acid (H<sub>3</sub>BPY), formic acid, and water in DMF at 120 °C for 24 h. Similar to previously reported MOLs, Zr-BPY showed a wrinkled nanosheet morphology by transmission electron microscopy (TEM) and kgd topology by powder X-ray diffraction (PXRD) (Figures 1a, 1b, and S2).<sup>[28-30]</sup> Zr-BPY was treated with Ru(bpy)<sub>2</sub>Cl<sub>2</sub> in ethanol at 80 °C for 24 h to afford the Zr-RuBPY

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MOL with characteristic absorption at 460 nm for the Ru(bpy)<sub>3</sub><sup>2+</sup> species (Figure S1). ICP-MS analysis of the digested Zr-RuBPY gave a Ru:Zr ratio of 1:4.2, corresponding the metalation of 71% BPY sites. Zr-RuBPY thus has an empirical formula of Zr<sub>6</sub>( $\mu_3$ -O)<sub>4</sub>( $\mu_3$ -OH)<sub>4</sub>(HCO<sub>2</sub>)<sub>6</sub>(BPY)<sub>2</sub>[Ru(bpy)<sub>2</sub>Cl<sub>2</sub>]<sub>1.42</sub>. TEM and PXRD indicated that the MOL morphology and topology were retained after post-synthetic metalation (Figures 1a, 1c, 1d). Atomic force spectroscopy (AFM) images indicated monolayer nature for the nanosheets with an average thickness of ~1.2 nm, which corresponds well to the can der Waals size of Zr<sub>6</sub> clusters (Figure 1e, 1f). We investigated photocatalytic activities of Zr-RuBPY in several prototypical photoreactions.



**Figure 1.** Characterization of Zr-RuBPY. (a) PXRD patterns of Zr-BPY and Zr-RuBPY. TEM images of (b) Zr-BPY and (c) Zr-RuBPY. (d) High-resolution TEM image of Zr-RuBPY and its fast Fourier transform (inset). (e) Tapping-mode AFM tomographic image of Zr-RuBPY. (f) Height profile along the green line of Zr-RuBPY.

We first used Zr-RuBPY as a photocatalyst in intramolecular [2+2] cycloadditions of bis(enones).<sup>[5]</sup> Bis(enone) **1a** was irradiated with 410 nm LED for 3 h in the presence of Zr-RuBPY, LiBF<sub>4</sub>, and diisopropylethylamine (DIPEA) to afford the *meso* diastereomer of the cyclobutane bicyclic dione **2a** in 82% yield and good selectivity (Table S1, SI). The catalytic performance of Zr-RuBPY was comparable to that of homogeneous Ru(bpy)<sub>3</sub><sup>2+</sup>. In contrast, the UiO-67 MOF with doped Ru(bpy)<sub>3</sub><sup>2+</sup>, UiO-Ru(bpy)<sub>3</sub> (Figures S5-10),<sup>[22]</sup> failed to promote [2+2] cycloaddition of **1a** in

8 h (Table S1, SI), likely due to the small MOF pores precluding the formation of sterically demanding transition state. No product was observed when Zr-BPY was used, indicating the photocatalytic role of  $Ru(bpy)_3^{2+}$  species (entry 4, Table S1, SI). Furthermore, the [2+2] cycloaddition did not proceed in the dark (entry 5, Table S1, SI), demonstrating the involvement of light-driven processes.

We further investigated the substrate scope for Zr-RuBPY catalyzed cycloaddition reactions (Table 1). In all bis(enones) studied (**1a-1e**), Zr-RuBPY afforded [2+2] cycloaddition products in 73-92% yields. In these examples, UiO-Ru(bpy)<sub>3</sub> gave <10% desired products. Electron-rich bis(enones) required longer reaction times than electron-deficient bis(enones). Zr-RuBPY also catalyzed [2+2] cycloaddition of a large substrate, *t*-butyl phenyl bis(enone) (entry 7, Table 1), albeit in a longer reaction time (12 h).

To test the heterogeneity of Zr-RuBPY, we determined the leaching of Ru and Zr into the supernatant after photocatalytic cycloaddition of **1a** for 3 h. ICP-MS analysis showed negligible leaching of Ru and Zr into the supernatant (2.3% and 0.3% for Ru and Zr, respectively). Zr-RuBPY was also readily recovered via centrifugation and used in three consecutive runs of photocatalytic cycloaddition of **1a** without loss of activity or diastereoselectivity (Table S2). Furthermore, PXRD studies showed that the MOL diffraction peaks were retained after photocatalysis (Figure S14).

Table 1. [2+2] intramolecular cycloadditions of bis(enones) with Zr-RuBPY and UiO-Ru(bpy)\_3 as photocatalysts.  $^{[a]}$ 

	Ru photocatalyst, LiBF <sub>4</sub> , DIPEA	
u Ukra-e	hv, MeCN, rt	

(R = H, a; R = Cl, b; R = Br, c; R = *t*Bu, d; R = OMe, e)

Entry	R	Catalyst	Time	Yield <sup>[b]</sup>	dr <sup>[c]</sup>
1		Zr-RuBPY	3h	82%	>10:1
2	Н	UiO- Ru(bpy)₃	8h	n.r.	
3		Zr-RuBPY	3h	86%	>10:1
4	CI	UiO- Ru(bpy)₃	3h	9%	
5		Zr-RuBPY	3h	92%	>10:1
6	Br	UiO- Ru(bpy)₃	3h	n.r.	
7		Zr-RuBPY	12h	79%	10:1
8	<i>t</i> Bu	UiO- Ru(bpy)₃	12h	<10%	
9		Zr-RuBPY	6h	73%	8:1
10	OMe	UiO- Ru(bpy)₃	6h	<10%	

<sup>[</sup>a] Reaction conditions: 1 mol% Zr-RuBPY or UiO-Ru(bpy)<sub>3</sub>, 2 eq. DIPEA, 2 eq. LiBF<sub>4</sub>, 6 mW/cm<sup>2</sup> 410 nm LED, MeCN (0.1M). [b] Isolated yields. [c] Diastereomer ratios determined by NMR.

We next examined the use of MOL and MOF photocatalysts in reductive cyclization of bis(enones) to afford monocyclic dione

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products with formic acid in place of LiBF<sub>4</sub>.<sup>[31]</sup> The switch of reaction pathways is believed to arise from different reactivities of neutral radical vs radical anion intermediates.<sup>[31]</sup> When photocatalytic reductive cyclization of bis(enones) 1a-1e were carried out in the presence of Zr-RuBPY or UiO-Ru(bpy)<sub>3</sub>, products 3a-3e were obtained in similarly high yields: 75-93% for Zr-RuBPY and 68-85% for UiO-Ru(bpy)<sub>3</sub> (Table 2). In all cases, racemic mixtures of (R,R)- and (S,S)-cyclopentyl diones were obtained without the formation of the meso diastereomer. Similar to [2+2] cycloaddition reactions, electron-deficient enones reacted faster than electron-rich enones and the large enone substrate with t-butyl groups needed a longer reaction time.

The two types of intramolecular photoreactions worked similarly for Zr-RuBPY but showed drastically different reactivities for UiO-Ru(bpy)<sub>3</sub>. We used molecular mechanics (UFF, Figure S11-12, SI) to model the products 2a and 3a from the two photocyclization reactions. Product 2a from the [2+2] cycloaddition reaction favors a conformation with the two phenyl groups extending like wings, leading to a triangular configuration with approximate dimensions of ~12.16 x 8.82 Å. In comparison, product 3a from the reductive cyclization reaction adopts a compact conformation of 10.17 × 5.48 Å in dimensions with the two phenyl rings paralleled to each other in a face-to-face manner. UiO-Ru(bpy)3 has a Ru loading of 16% relative to the dicarboxylate linkers according to NMR analysis (Figure S8, SI), corresponding to an approximate 1:1 ratio between the Ru(bpy)<sub>3</sub><sup>2+</sup> moiety and the octahedral pore. Most octahedral pores in UiO-Ru(bpy)<sub>3</sub> are thus occupied by Ru(bpy)<sub>3</sub><sup>2+</sup>, leaving tetrahedral pores to accommodate bis(enone) substrates. The tetrahedral pore of UiO-67 was reported to be 11.5~12 Å,[32-34] in between the sizes of 2a and 3a. As a result, reductive cyclization but not [2+2] cycloaddition can occur in tetrahedral pores of UiO-Ru(bpy)<sub>3</sub>. Moreover, as both intramolecular photoreactions have similar initiation mechanism by Ru(bpy)<sub>3</sub><sup>2+</sup>, diffusion cannot be a limiting factor. The different reactivities are a result of pore size limitation of MOF photocatalysts which does not apply to MOLs.

> Ru photocatalyst HCOOH, DIPEA

Table 2. Reductive cyclizations of bis(enones).[a]

	UiO-				
10	Ru(bpy)₃	6h	68%	>10:1	

[a] Reaction conditions: 2.5 mol% Zr-RuBPY or UiO-Ru(bpy)<sub>3</sub>, 10 eq. DIPEA, 5 eq. HCOOH, 6 mW/cm<sup>2</sup> 410 nm LED. [b] Isolated yields. [c] Diastereomer ratios determined by NMR.

We also studied intermolecular [2+2] cross cycloadditions of acyclic enones<sup>[35]</sup> with Zr-RuBPY and UiO-Ru(bpy)<sub>3</sub> as photocatalysts. Zr-RuBPY catalyzed cross cycloadditions between various enones and Michael acceptors to afford cyclobutyl diones in 55-81% yields (Table 3). Under identical condition, UiO-Ru(bpy)3 afforded cyclobutyl diones in much lower yields (5-26%). The cross-coupled products bear only one phenyl group and are thus significantly smaller than the intramolecular [2+2] cycloaddition products in Table 1. As a result, the transition states and intermediates for the cross cycloaddition reactions can be accommodated in the pores of UiO-Ru(bpy)<sub>3</sub> (Figure S13). We attribute the drastically different catalytic efficiencies between Zr-RuBPY and UiO-Ru(bpy)3 to restricted diffusion of reactive intermediates in MOF channels. Intermolecular [2+2] cross cycloadditions are believed to occur via SET from [Ru(bpy)3]+ to an enone to form the enolate anion which undergoes addition to the Michael acceptor to form the cyclobutyl dione product.<sup>[5, 35]</sup> In heterogeneous systems, this reaction mechanism is also supported by quenching of Ru(bpy)32+\* by DIPEA to form [Ru(bpy)<sub>3</sub>]<sup>+</sup> (Figures S15 and S16). Unlike unimolecular [2+2] cycloadditions and reductive cyclization reactions of bis(enones), the highly reactive enolate anions in cross cycloadditions must travel some distances to find Michael acceptors to lead to desired products (Scheme S1c, SI). In MOF channels, enolate anions can decompose before finding Michael acceptors due to restricted diffusion. The diffusion length of transient radicals was estimated to be ~1 nm in MOF channels (SI, Part 9), thus limiting the photocatalytic efficiency of MOF catalysts. In contrast, as a 2D material, Zr-RuBPY allows free diffusion of reaction substrates and intermediates in multicomponent photoreactions, leading to much higher photocatalytic efficiency than its MOF counterpart.

Table 3. Crossed [2+2] cycloadditions of acyclic enones.[a]

(1	<b>1a-e</b> R = H, <b>a</b> ; R	= Cl, <b>b</b> ; R = Br,	<b>c</b> ; R = <i>t</i> Bu,	<b>к</b> d; R = ОМе	За-е е, е)	R R <sub>1</sub>	4	5	ΠV,	Meon, It		<sup>1111</sup> 6	
Entry 1	R	Catalyst Zr-RuBPY	Time 6h	Yield <sup>[b]</sup> 80%	dr <sup>[c]</sup> >10:1	Entry	Enone (R <sub>1</sub> = )	Michael Acceptor (R <sub>2</sub> = )	Cyclo- adduct	Catalyst	Time	Yield <sup>[b]</sup>	dr <sup>[c]</sup>
2	Н	UiO-	Ch	0.00/	. 10.1	1		. ,		Zr-RuBPY	12h	75%	6:1
2		Zr-RuBPY	3h	82%	>10:1	2	H( <b>4a</b> )	Me ( <b>5a</b> )	6a	UiO- Ru(bpy)₃	12h	12%	6:1
1	CI	UiO- Bu(bpy))	2h	920/	>10.1	3				Zr-RuBPY	12h	78%	10:1
5		Zr-RuBPY	3h	88%	>10:1	4	H( <b>4a</b> )	Et ( <b>5b</b> )	6b	UiO- Ru(bpy)₃	12h	18%	8:1
C	Br	UiO-	2h	0.20/	. 10.1	5				Zr-RuBPY	12h	72%	>10:1
7		Zr-RuBPY	3h 12h	93%	>10:1	6	H( <b>4a</b> )	SEt ( <b>5c</b> )	6c	UiO- Ru(bpy)₃	12h	25%	>10:1
0	<i>t</i> Bu	UiO-	4.01-	05%	10.1	7				Zr-RuBPY	24h	55%	6:1
8 9	OMe	Zr-RuBPY	12h 6h	85% 75%	>10:1	8	0Me ( <b>4b</b> )	Me ( <b>5a</b> )	6d	UiO- Ru(bpy)₃	24h	<5%	

, in	Ĵ.	Ru photocatalyst, LiBF <sub>4</sub> , DIPEA	
R <sub>1</sub> 4 +	5 R2	hv, MeCN, rt	R1 6

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9				Zr-RuBPY	6h	81%	>10:1 Acknowledgements
10	Cl( <b>4c</b> )	Me ( <b>5a</b> )	6e	UiO- Ru(bpy)₃	6h	26%	>10:1

[a] Reaction conditions: 2.5 eq. Michael acceptor, 1 mol% Zr-RuBPYor UiO-Ru(bpy)<sub>3</sub>, 2 eq. DIPEA, 4 eq. LiBF<sub>4</sub>, 6 mW/cm<sup>2</sup> 410 nm LED, MeCN (0.1M). [b] Isolated yields. [c] Diastereomer ratios determined by NMR.

The superior photocatalytic activity of Zr-RuBPY over UiO-Ru(bpy)<sub>3</sub> was also demonstrated in Meerwein addition reactions (Table 4).[36] Zr-RuBPY efficiently catalyzed three-component Meerwein addition reactions between aryl diazonium salts, styrenes, and nitriles under LED irradiation to afford desired products in 55-83% yields. In contrast, UiO-Ru(bpy)<sub>3</sub> produced desired products in much lower 0-21% yields. The difference in photocatalytic activities of Zr-RuBPY over UiO-Ru(bpy)<sub>3</sub> is likely due to the ease of intermediate and substrate diffusion in 2-D MOLs but not 3-D MOFs.

Table 4. Meerwein addition reactions.[a]



Entry	Diazonium	Styrene	Nitrile	Adduct	Catalyst	Yield <sup>[b]</sup>	-['-]
	Sall $(R_1 = )$	$(R_2 = )$				R	[13]
1					Zr-RuBPY	83%	1
2	2-NO <sub>2</sub> (7a)	H ( <b>8a</b> )	MeCN	9a	UiO- Ru(bpy)₃	<10%	[14]
3					Zr-RuBPY	55%	[15]
4	4-OMe ( <b>7b</b> )	H ( <b>8a</b> )	MeCN	9b	UiO- Ru(bpy)₃	n.r.	[16]
5					Zr-RuBPY	76%	- 1
6	H ( <b>7c</b> )	H ( <b>8a</b> )	MeCN	9c	UiO- Ru(bpy)₃	<5%	[17]
7		00011			Zr-RuBPY	76%	[18]
8	2-NO <sub>2</sub> (7a)	( <b>8b</b> )	MeCN	9d	UiO- Ru(bpy)₃	21%	[19]
9				32	Zr-RuBPY	62%	-
10	2-NO <sub>2</sub> (7a)	H ( <b>8a</b> )	CICH <sub>2</sub> CN	9e	UiO- Ru(bpy)₃	15%	[20]

[a] Reaction conditions: 1 eq. diazonium salt, 2 eq. styrene, 0.5% Zr-RuBPY or UiO-(bpy)<sub>3</sub>, 1 eq. H<sub>2</sub>O, 6 mW/cm<sup>2</sup> 410 nm LED, MeCN or CICH<sub>2</sub>CN (0.25M), room temperature. [b] Isolated yields.

In summary, we synthesized photoactive Zr-RuBPY MOL via post-synthetic incorporation of Ru(bpy)<sub>3</sub><sup>2+</sup> into the backbone of Zr-BPY MOL. Zr-RuBPY was shown to be an efficient heterogeneous photocatalyst for intra/intermolecular [2+2] cycloaddition and Meerwein addition reactions under visible-light irradiation. In contrast, the corresponding MOF catalyst failed in these photoreactions, due to either pore size limitation or restricted diffusion of reactive intermediates. Our work highlights the potential of MOLs in catalyzing a variety of multicomponent photoreactions.

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Keywords: metal-organic layer • metal-organic framework, photocatalysis • photosensitizer • diffusion

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## COMMUNICATION

#### MOLs in photocatalysis:

As an ultrathin 2D material, metalorganic layers (MOLs) accommodate large reactants and facilitate free diffusion of reactive species involved in photochemical processes. MOLs showed excellent activities for several photoreactions in which MOFs failed to work due to pore size and diffusion limitations.

