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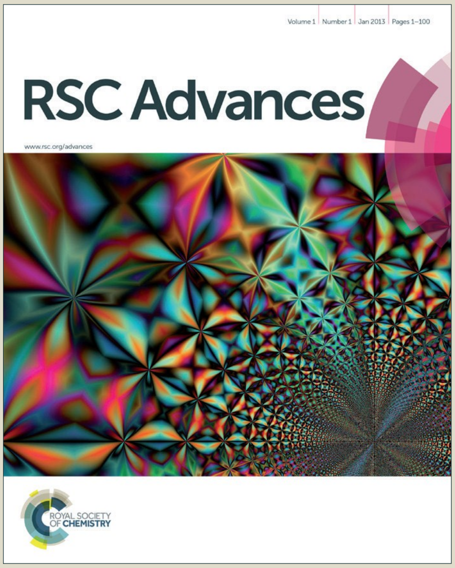

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A diiodo-BODIPY postmodified metal-organic framework for efficient heterogeneous organo-photocatalysis†

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Organic photosensitizer diiodo-BODIPY has been covalently conjugated to a Zr(IV)-based metal-organic framework with UiO topology *via* postsynthetic modification, which serves as a highly active and recyclable heterogeneous photocatalyst for aerobic cross dehydrogenative coupling and oxidation/[3+2] cycloaddition reactions under visible light irradiation.

In the past several years, visible light mediated photoredox catalysis has received a considerable attention, on account of the green and sustainable method for a variety of organic transformations under milder reaction conditions.[1,2] Moreover, it can generate some sophisticated molecules that are not easily accessible by conventional thermal reactions. Typically, the photoredox catalysts include noble metal Ru, Ir and Pt complexes,[1,3] as well as some of organic dyes,[4] such as eosin Y and Rose Bengal. As most of the reactions were performed homogenously, therefore, it is difficult to recycle the catalysts for reuse. Clearly, a straightforward solution for this challenge is the immobilization of photo-catalysts into insoluble solid-state materials, resulting in a heterogenous catalyst. In this regard, several types of materials, such as silicas,[5] polymers,[6] and metal-organic frameworks (MOFs),[7] have been employed to achieve this purpose. For example, Zhao's group has successfully incorporated $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) into organosilica for three photocatalytic transformations.[5a] Cooper and coworkers prepared Rose Bengal conjugated microporous polymers for aza-Henry reactions.[6c] Yu and Cohen reported a Zr-based MOF UiO-67 decorating with $[Ru(bpy)_3]^{2+}$ for aerobic oxidation of arylboronic acids under visible light irradiation.[7b]

Among these materials, MOFs as platforms for immobilizing catalysts are very attractive because of their highly tunable nature.[8] Especially, the postsynthetic modification (PSM) strategy allows various functional groups to be readily tagged into MOFs.[9] However, there are limited examples of MOFs with attached photosensitizers for photocatalytic organic transformations.[7,10] Thus, it is urgent to develop an effective and versatile method for introducing photocatalysts into MOFs, with a purpose of achieving highly active heterogeneous photo-catalysis. Thanks to their modular nature, it is readily easy to prepare MOFs with tagged reactive groups, such as amine and azide. This could provide many possibilities for incorporation of a photosensitizer into MOFs through various reactions, particularly for an organic photosensitizer. However, there are few examples in this regard.

UiO series of MOFs comprised of Zr_6-cluster secondary building units and dicarboxylate linkers represent a very rare kind of highly stable and porous MOF materials.[11] In this work, we chose the amine-tagged UiO-68 (Zr-MOF UiO-68-NH_2) because of its large cavities.[11] Then, an already established organic photocatalyst diiodo-BODIPY[12] was covalently conjugated to the above Zr-MOF (Fig. 1). Herein, we reported the example to validate the power of PSM for immobilizing photosensitizers within MOFs, which results in a highly active and recyclable heterogeneous photocatalyst for various organic transformations under visible light.

Fig. 1 Schematic representation of preparation for UiO-68-BP. Inset: the photographs of UiO-68-NH_2 (left) and UiO-68-BP (right) under ambient light.

The amine-tagged Zr-MOF UiO-68-NH_2 can be prepared in a large scale by our modified literature method.[13] A *N,N'*-

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dimethylformamide (DMF) solution of aminotriphenyldicarboxylic acid (amino-TPDC) and ZrCl$_4$ in the presence of HAc and water was heated to 100 °C for 2 days, giving the desired MOFs (for detail see ESI). As expected, powder X-ray diffraction (XRD) of as-synthesized products is similar to the simulated pattern from its single-crystal structure,[14] confirming the phase purity and UiO structural framework. Scanning electron microscopy (SEM) image reveals their hexagonal plate-like morphologies with diameter at ~100 nm and thickness at ~30 nm (Fig. 2a). Photocatalyst diiodo-BODIPY was covalently incorporated into UiO-68-NH$_2$ by the mild reaction between acyl chloride activated carboxylic group of organic species and amino group of bridging ligand, affording a deeply red solid UiO-68-BP (Fig. 1 and ESI for detail). Moreover, the post-modified UiO-68-BP still retained the original hexagonal plate-like morphologies and powder XRD pattern of its parent MOF (Fig. 2b and 2d).

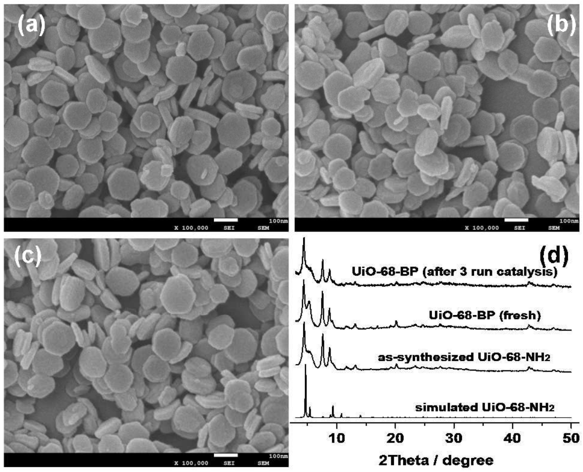
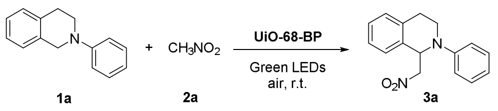


Fig. 2 Typical SEM images for UiO-68-NH$_2$ (a), UiO-68-BP (fresh, b) and UiO-68-BP after catalysis (c); (d) Powder XRD patterns for UiO-68-NH$_2$ and UiO-68-BP. Scale bar: 100 nm.

To verify that the immobilized diiodo-BODIPY in MOFs can still work as an effective photoredox catalyst, the aerobic cross dehydrogenative coupling (CDC) reaction of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a**) with nitromethane (**2a**) in presence of air was performed as a model (Table 1). To our delight, the mixture of **1a** and **2a** containing catalytic amount UiO-68-BP under the irradiation of green LEDs (λ_{max} = 520-530 nm) at room temperature for several hours, the formation of the desired cross-coupling product **3a** was observed in a satisfied yield (Table 1, entry 1-4). No significant improvement could be detected with increase of catalyst amount (Table 1, entry 5). Other samples with lower loading amount of diiodo-BODIPY exhibited lower catalytic activities (Table 1, entry 6-7). Control experiments demonstrated that each component of the reaction is critical to the reaction efficiency (Table 1, entry 8-12).

With this initial success, we subsequently screened the reaction scope (Table 2 and S1 in ESI). Various substituted 1,2,3,4-tetrahydroisoquinoline derivatives can undergo the CDC reaction with nitromethane efficiently, giving the products in good to excellent yields (Table 2, **3a-3g**). Moreover, the utilization of other nucleophiles, including nitroethane, nitropropane and dialkyl malonates, was also able to yield the desired products smoothly (Table 2, **3h-3l** and Table S1 in ESI).

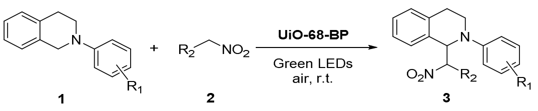
Table 1 Screening of the reaction conditions[a]

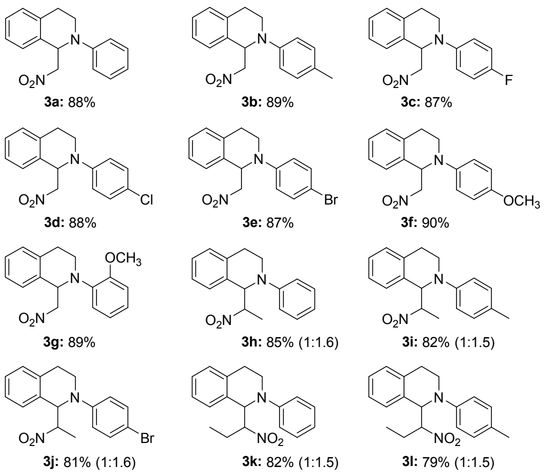


Entry	Conditions	Time (h)	Yield[b](%)
1	UiO-68-BP (1 mg)	2	72
2	UiO-68-BP (1 mg)	3	79
3	UiO-68-BP (2 mg)	2	76
4	UiO-68-BP (2 mg)	3	88
5	UiO-68-BP (5 mg)	3	89
6[c]	UiO-68-BP' (2 mg)	3	61
7[c]	UiO-68-BP" (2 mg)	3	77
8[d]	UiO-68-NH$_2$ (5mg)	3	trace
9	No catalyst	3	trace
10[e]	No light	-	n.r.
11[f]	No O$_2$	3	n.r.

[a] Reaction conditions: **1a** (0.1 mmol) and **2a** (1.0 mL), green LEDs (λ = 520-530 nm, 3W). The reaction was conducted in an air atmosphere at room temperature. [b] Yields were determined by ^{1}H NMR spectroscopy. n.r. = no reaction. [c] UiO-68-BP' and UiO-68-BP" refer to ~2% and ~7% of organic linkers in MOF was functionalized by diiodo-BODIPY, respectively. [d] The reaction was performed in the presence of UiO-68-NH$_2$. [e] The reaction mixture was stirred for 6 hours in the dark. [f] Degassed by nitrogen before irradiation.

Table 2 Aerobic CDC reactions of tetrahydroisoquinolines **1** with nitroalkan-es **2** catalyzed by UiO-68-BP[a]





[a] Reaction conditions: **1** (0.1 mmol), **2** (1 mL) and **UiO-68-BP** (2 mg) under air at room temperature, and the irradiation time was 3 h. Yields were determined by ^{1}H NMR. Ratios of the two diastereoisomers are given in parentheses.

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Meanwhile, the recyclability of UiO-68-BP as a heterogeneous catalyst was also investigated, which can be readily recovered from the reaction system by simple centrifugation. It was reused three photocatalysis recycles without obvious loss of catalytic activity (88%, 78% and 72%, respectively). The little decrease of yield should be attributed some minor decompositions of the organic photosensitizer diiodo-BODIPY caused by the long irradiation. However, SEM and powder XRD investigations of the recycled photocatalyst revealed that it still maintain the crystalline structure and framework as well as morphologies (Fig. 2c and 2d), mainly due to the highly stable UiO frameworks.

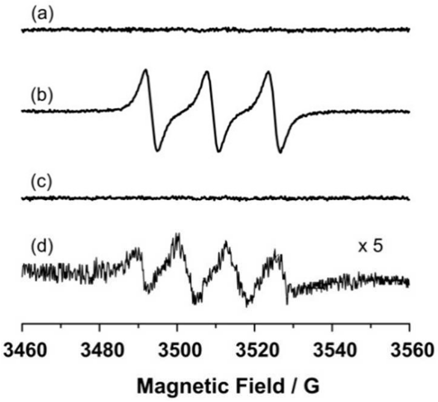
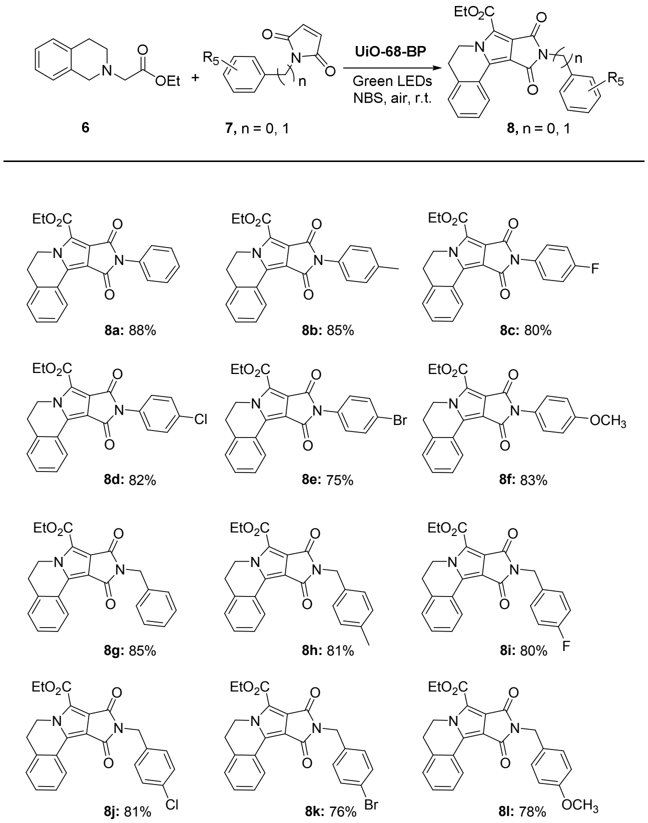


Fig. 3 ESR measurements of a solution in CH_3CN of UiO-68-BP without **1a** in the presence of DMPO (a) and TEMP (b) under the irradiation of green LEDs; a solution in CH_3CN of **UiO-68-BP** with **1a** in the presence of TEMP (c) and DMPO (d) under the irradiation of green LEDs.

As previously reported, BODIPYs attached heavy atoms serves as a good photosensitizer for producing singlet oxygen ($^1O_2$), because of the enhanced intersystem crossing capacity.[15] However, it was recently proposed that the superoxide radical anion ($O_2^{-\bullet}$) act as the active species in photo-promoted aerobic CDC reactions.[2e,2f,4e] Thus, electron spin resonance (ESR) measurements were performed to make it clear, in which 2,2,6,6-tetramethyl-1-piperidine (TEMP) and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) were employed to capture $^1O_2$ and $O_2^{-\bullet}$, respectively. As shown in Fig. 3, an expected characteristic signal of $^1O_2$ was observed upon irradiation of the CH_3CN mixture of UiO-68-BP and TEMP in air by green LEDs. However, the $^1O_2$ signal could not be detected when **1a** was added into the mixture. In contrast, there was no signal when DMPO was added into the CH_3CN mixture of UiO-68-BP, however, a characteristic signal of $O_2^{-\bullet}$ trapped by DMPO was clearly observed upon addition of **1a**. These above results indicate that although diiodo-BODIPY is a reported efficient sensitizer in the production of $^1O_2$,[15] however, this process is highly suppressed by the effective single electron transfer (SET) between **1a** and excited diiodo-BODIPY (**PS***) in the present case, along with the generation of the radical cation **1a**$^{\bullet+}$ and the radical anion **PS**$^{-\bullet}$. Subsequently, the generated radical anion **PS**$^{-\bullet}$ reacts with molecular oxygen to produce the superoxide radical anion $O_2^{-\bullet}$, which is a crucial intermediate in the reaction. Based on the above analysis, a similar and plausible mechanism was proposed in Scheme S3 (in ESI).[2e,2f,4e] Thus, these results confirmed that there still was the efficient SET process between the immobilized photocatalyst and substrate molecules.

Table 3 Oxidation-[3+2] cycloaddition-aromatization tandem reaction of **6** with **7** catalyzed by **UiO-68-BP**[a]



[a] Reaction conditions: a 1 mL CH_3CN solution of **6** (0.12 mmol), **7** (0.10 mmol) and **UiO-68-BP** (2 mg) was irradiated for 2 hours under air at room temperature; then, NBS (0.12 mmol) was added into the reaction mixture, which was stirred for further 10 min. Yields were determined by ^1H NMR.

In order to further explore the applications of such immobilized photocatalyst in MOFs, a series of oxidation-[3+2] cycloaddition-aromatization tandem reaction of **6** with **7** catalyzed by UiO-68-BP was performed. As shown in Table 3, most of the final pyrrolo[2,1-*a*]isoquinoline products were obtained in satisfactory yields. Moreover, other organic transformations mediated by oxygen, inculding aerobic amine coupling and aerobic oxidation of arylboronic acid and thioanisole, were also sucessfully and efficiently conducted in the presence of UiO-68-BP, indicating its a wide range of applications in organic photocatalysis (in ESI).

Conclusions

In summary, we have reported an organic photosensitizer diiodo-BODIPY postmodified metal-organic framework, which

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was used as a highly active and recyclable heterogeneous photocatalyst for aerobic cross dehydrogenative coupling and oxidation-[3+2] cycloaddition-aromatization tandem reactions as well as other oxidative reactions under visible light irradiation. The example demonstrated in this work has validated that the postsynthetic modification (PSM) strategy of MOFs can serve as a versatile and powerful method for incorporation of photosensitizers into MOFs. Moreover, it is expected that more heterogeneous photocatalysts based on MOFs with excellent photoredox properties will be constructed for promoting a wider scope of organic transformations by using visible light.

Acknowledgements

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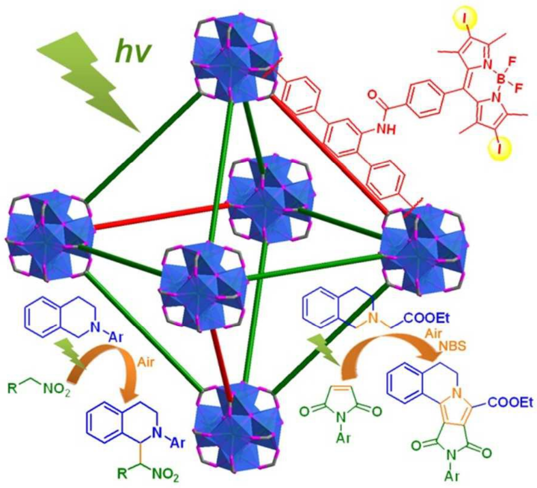

A diiodo-BODIPY postmodified MOF acts as a highly active and recyclable heterogeneous photocatalyst for aerobic CDC and oxidation/[3+2] cycloaddition reactions under visible light irradiation.