Robust Metal−Organic Framework Containing Benzoselenadiazole for Highly Efficient Aerobic Cross-dehydrogenative Coupling Reactions under Visible Light

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Supporting Information

ABSTRACT: A zirconium(IV)-based UiO-topological metal−organic framework (UiO-68Se) containing benzoselenadiazole was synthesized by an approach of the mixed dicarboxylate struts, which show highly efficient and recyclable photocatalytic activity for aerobic cross-dehydrogenative coupling reactions between tertiary amines and various carbon nucleophiles under visible-light irradiation.

The cross-dehydrogenative coupling (CDC) reactions from two different C−H bonds under oxidative conditions provide a simple and atom-economic method for the construction of C−C bonds,[1] because it could avoid the tedious pre- and defunctionalization of substrates. The past 10 years have witnessed huge progress in this field.[1,2] In particular, the recent development of visible-light-driven CDC reactions in the presence of photoredox catalysts via single-electron transfer (SET) has gained significant interest because of the mild and environmentally benign characteristics.[3] Various metal[4] and metal-free[5] photocatalysts have been employed to efficiently promote the cross-coupling reactions. However, most of these reactions were conducted homogeneously. There are only a few heterogeneous photocatalysts for CDC reactions.[6]

Metal−organic frameworks (MOFs)[7] are built by the coordination self-assembly of metal ions or clusters and multidentate organic linkers, which have exhibited highly promising applications in a wide variety of areas.[8] In contrast to pure inorganic materials such as metal oxide based heterogeneous photocatalysts,[6c,d] the hybrid and modular nature of MOFs allows a quite higher level of tailorability through ligand design,[9] postsynthetic modification,[10] and postsynthetic exchange,[11] thus resulting in the superior properties of MOFs. Indeed, many photoactive MOFs have recently been prepared for the degradation of organic pollutants, water splitting, and CO_2 reduction toward solar energy utilization.[12] On the other hand, less effort has been devoted to visible-light-induced sophisticated organic transformations.[13] Lin's group first incorporated noble-metal complexes, such as ruthenium(II), into UiO-67 MOFs for efficient aza-Henry reactions, oxidation of sulfides, and oxidative coupling of amines.[13a] The polypyridylruthenium complex was also introduced into UiO-67 MOFs via postsynthetic methods toward the aerobic oxidation of arylboronic acids.[13b] Duan et al. have utilized zinc-based MOFs consisting of triphenylamine for asymmetric α-alkylation of aldehydes with good enantioselectivity.[13c] Very recently, MOFs based on porphyrins and metalloporphyrins were developed as photoredox catalysts.[13d,e]

Although large progress has been made in MOF-based photocatalysts for organic reactions, there are still some challenges to be tackled, such as the complicated synthesis of porphyrins and the possible leaching of toxic elements caused by the decomposition of noble-metal complexes. Herein, we reported a straightforward construction of benzoselenadiazole containing the MOF UiO-68Se by an approach of mixed dicarboxylate struts (H_2**1** and H_2**2**; Figure 1), which has the robust parent UiO-68 $Zr_6O_4(OH)_4(TPDC)_6$ framework (TPDC = terphenyl-4,4″-dicarboxylic acid)[14] and exhibits a highly efficient and recyclable photocatalytic activity for aerobic CDC reactions of tertiary amines and various carbon nucleophiles under visible light.

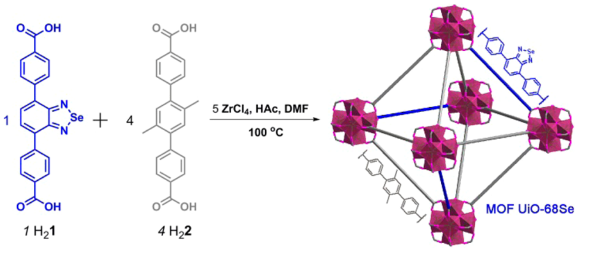

Figure 1. Schematic representation of the preparation for the MOF UiO-68Se.

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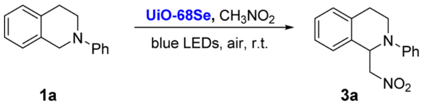
The new simple ligand H_2**1**, a benzoselenadiazole-functionalized TPDC, was conveniently synthesized in high yield, as described in Scheme S1 in the Supporting Information (SI). Dimethyl-substituted TPDC H_2**2** (Scheme S2 in the SI), owing to much better solubility, was synthesized to replace the original TPDC for preparation of the UiO-68 framework. Because of the same length of the two ligands, we utilized the mix-and-match synthetic strategy[13a,15] to construct a benzoselenadiazole-doped UiO-68 MOF (UiO-68Se). Specifically, UiO-68Se was synthesized by heating the mixture of $ZrCl_4$ and a combination of ligands H_2**1** and H_2**2** in *N*,*N*′-dimethylformamide using HAc as an additive at 100 °C for 2 days (for details, see the SI). Powder X-ray diffraction (XRD) confirmed its highly crystalline nature and the fact that it is isostructural with the parent UiO-68 framework (Figure S2 in the SI). Nitrogen sorption measurement at 77 K revealed a typical type I reversible isotherm with Brunauer−Emmett−Teller surface area of up to ~3500 $m^2\ g^{-1}$ (Figure S9 in the SI), indicating its high porosity.

Because of the presence of large open channels that will facilitate the diffusion of substrates and products, UiO-68Se was used as the heterogeneous photocatalyst for an aerobic CDC model reaction of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a**) with nitromethane. As shown in Table 1, for a mixture of **1a** and nitromethane containing a catalytic amount of UiO-68Se under irradiation of blue LEDs at ambient conditions for several hours, we observed formation of the desired cross-coupling product **3a** in good-to-excellent yield (entries 1−4). As expected, increasing the amount of catalyst and irradiation time gives high conversation and yield (entry 4). The inactivity of the parent MOF UiO-68M in this reaction confirmed that the benzoselenadiazole-functionalized TPDC ligand in UiO-68Se acts as a photocatalytically active center for this process (entry 5). Other control experiments demonstrated that each component of the reaction, including light, oxygen, and the MOF photocatalyst, is essential for the progress of the aerobic CDC reaction (entries 6−8).

Table 1. Screening of the Reaction Conditions[a]



entry	conditions	*T* (h)	conv (%)[b]	yield (%)[b]
1	UiO-68Se, 2 mg	2	76	68
2	UiO-68Se, 2 mg	4	89	84
3	UiO-68Se, 4 mg	2	86	82
4	UiO-68Se, 4 mg	4	100	90
5[c]	UiO-68M, 4 mg	4	trace	trace
6[d]	no catalyst	4	trace	trace
7[e]	no light		0	n.r.
8[f]	no oxygen	4	0	n.r.

[a] Reaction conditions: **1a** (0.1 mmol) and CH_3NO_2 (1.0 mL), blue LEDs (λ_{max} = 450 nm, 3 W). The reaction with stirring was conducted in an air atmosphere at room temperature. [b] Yield and conversion determined by ^1H NMR using methyl 3,5-dinitrobenzoate as an internal standard. n.r. = no reaction. [c] The reaction in the presence of UiO-68M was irradiated for 4 h. [d] The reaction without any catalyst was irradiated for 4 h. [e] The reaction in the presence of UiO-68Se was stirred in the dark for 6 h. [f] The reaction mixture was strictly degassed by nitrogen for 6 h and then irradiated under a nitrogen atmosphere for 4 h.

The heterogeneity of the MOF UiO-68Se was confirmed by removal of the catalyst after 1 h (yield: 32%), which resulted in almost no further production of **3a** after another 4 h of irradiation. This indicates that UiO-68Se acts as a purely heterogeneous catalyst with no leaching of catalytically active species into solution. The reusability of the UiO-68Se catalyst was also investigated. The same batch of UiO-68Se for the reaction of **1a** and nitromethane was performed over five successive catalytic cycles (Figure S10 in the SI). The results indicate that no obvious loss of activity of the catalyst occurs even after five cycles (yield: 78%). Besides, powder XRD measurements of the recycled photocatalyst revealed maintenance of its crystalline structure and framework (Figure 2), confirming the high stability of robust UiO frameworks.

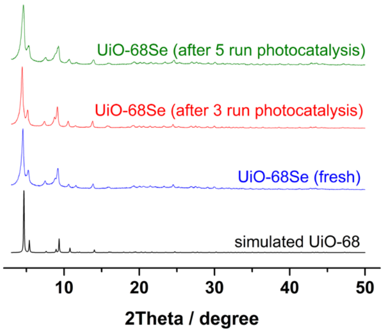


Figure 2. Powder XRD patterns for UiO-68Se.

It has been demonstrated that oxygen played an important role in the photoinduced aerobic CDC reactions.[4,5] To understand the MOF UiO-68Se photocatalysed process clearly, electron spin resonance (ESR) measurements were conducted in which 2,2,6,6-tetramethylpiperidine (TEMP) and 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) were used to capture singlet oxygen $^1O_2$ and superoxide radical anion $O_2^{\bullet-}$, respectively. As shown in Figure 3, upon irradiation of the CH_3CN mixture of UiO-68Se and TEMP in air, a typically characteristic signal of $^1O_2$ was clearly observed. However, the signal disappeared upon the addition of **1a** to the mixture. By contrast, a clear characteristic signal of $O_2^{\bullet-}$ was detected when DMPO was used as the radical scavenger. These findings indicate that $O_2^{\bullet-}$ is the active intermediate species in the reaction rather than $^1O_2$.

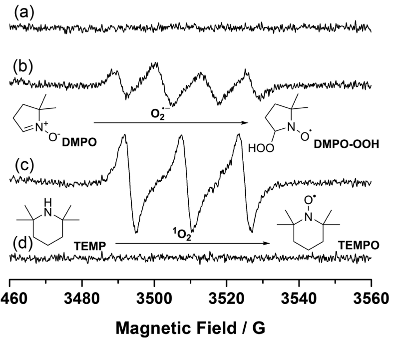


Figure 3. ESR spectra of a solution in CH_3CN of UiO-68Se without **1a** (a) and with **1a** (b) in the presence of DMPO under irradiation of blue LEDs for 30 s and a solution in CH_3CN of UiO-68Se without **1a** (c) and with **1a** (d) in the presence of TEMP under irradiation of blue LEDs for 30 s.

We proposed a plausible reaction mechanism based on the above results (Scheme S3 in the SI). Upon excitation of UiO-68Se (PS), SET from **1a** to PS* occurs with generation of the radical cation $\mathbf{1a}^{\bullet+}$ and the radical anion $\mathrm{PS}^{\bullet-}$, which transfer an electron to O_2 with the formation of $O_2^{\bullet-}$ and the simultaneous regeneration of the ground-state PS. Meanwhile, $O_2^{\bullet-}$ abstracts a proton from $\mathbf{1a}^{\bullet+}$, generating a hydroperoxide free radical and intermediate $\mathbf{1a}^{\bullet}$. The latter lose one electron to afford the imine cation, followed by nucleophile addition to give the product **3a**. With a well understanding of the reaction mechanism, we further extended the scope of this aerobic CDC reaction photocatalyzed by the MOF UiO-68Se shown in Table S1 (SI). It can be observed that various substituted tetrahydroisoquinoline derivatives can undergo aerobic CDC reactions with different nitroalkanes catalyzed by UiO-68Se under visible light, giving the coupling products in good-to-excellent yields. Moreover, the MOF-photocatalyzed CDC reaction can also be expanded to the direct construction of C−C bonds between *N*-aryltetrahydroisoquinolines with dialkyl malonates and ketones, with satisfactory yields (Table S2 in the SI).

In summary, we designed and synthesized a simple benzoselenadiazole-functionalized TPDC ligand. Subsequently, a noble-metal-free Zr-MOF with a UiO-68 framework was constructed by the straightforward reaction of $ZrCl_4$ with the mixed dicarboxylate struts. The robust MOF can act as a highly efficient and heterogeneous photoredox catalyst for aerobic CDC reactions between tertiary amines with various carbon nucleophiles under visible light. It is envisioned that the MOF can act as an ideal platform, allowing for the incorporation of more photoredox catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02626.

Experimental details, thermogravimetric analysis and nitrogen sorption of UiO-68Se, and other details (PDF)

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Notes

The authors declare no competing financial interest.

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