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Development of a novel one-pot reaction system utilizing a bifunctional Zr-based metal–organic framework†

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A novel one-pot reaction system is developed by utilizing a bifunctional metal–organic framework photocatalyst (Zr-MOF-NH_2). Zr-MOF-NH_2 promotes sequential photocatalytic oxidation and Knoevenagel condensation reaction to produce benzylidenemalononitrile from benzyl alcohol and malononitrile under UV-light irradiation.

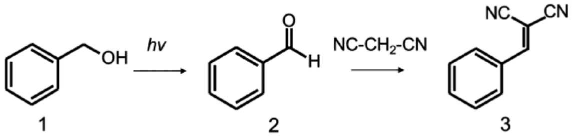
In recent years, much attention has been paid to one-pot reactions as an attractive synthetic concept for improving overall process efficiency and reducing production wastes.[1] Designing new catalysts with spatially isolated multiple active sites is required to progress multi-step reaction cascades. Various catalytic systems have been proposed for the realization of one-pot reactions, but many of these employ homogeneous catalysts, which generally suffer from product contamination and limited recyclability.[2] Therefore, development of heterogeneous catalysts that promote one-pot reactions is currently the focus of intensive research.[3]

Inorganic–organic hybrid materials have also attracted considerable attention since they not only combine the respective beneficial characteristics of inorganic and organic components, but also often exhibit unique properties that exceed the expectations for a simple mixture of the components.[4] The construction of hybrid materials offers an almost infinite number of chemical and structural possibilities, namely, the structural diversity of inorganic–organic hybrid materials allows for accurate material design. Among them, metal–organic frameworks (MOFs), also called porous coordination polymers (PCPs), have been of great interest because of their attractive properties including high specific surface areas, well-ordered porous structures and structural designability.[5] Taking advantage of these features, MOFs have been actively studied for many applications such as gas storage, gas separation, sensing and catalysis.[6] In addition, since the topology and surface functionality of MOFs can be readily tuned by modifying or varying the constituent metal–oxo clusters and bridging organic linkers, MOFs have emerged as an interesting platform to engineer molecular solids for multifunctional catalysts.[7] Although several reaction systems have been proposed so far based on the multifunctionality of organic linkers or coordinatively unsaturated metal sites in MOF catalysts, there is no report describing multifunctionality combined with photocatalytic and catalytic activities utilizing MOF materials.

Herein we report the development of a novel one-pot reaction system utilizing photocatalytic and basic properties of an amino-functionalised Zr-based MOF (UiO-66-NH_2) here denoted as Zr-MOF-NH_2. Zr-MOF-NH_2 promotes sequential photocatalytic oxidation and Knoevenagel condensation reaction: the conversion of benzyl alcohol into benzaldehyde through photocatalytic oxidation over Zr–oxo clusters and Knoevenagel condensation of benzaldehyde with malononitrile over –NH_2 groups, as shown in Scheme 1.

Zr-MOF-NH_2 was prepared according to the literature.[8] Briefly, a mixture of $ZrCl_4$, 2-aminobenzene-1,4-dicarboxylic acid (H_2BDC-NH_2), ion-exchanged water and DMF was reacted under solvothermal conditions at 393 K for 24 h under autogenous pressure.

XRD, N_2 adsorption, diffuse reflectance UV-Vis and FT-IR measurements were conducted to confirm the formation of Zr-MOF-NH_2. Zr-MOF-NH_2 exhibits a diffraction pattern



Scheme 1 One-pot sequential photocatalytic oxidation and Knoevenagel condensation reaction over Zr-MOF-NH_2.

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consistent with the previously reported pattern of the UiO-66 type structure (see Fig. S1 in ESI†). The specific surface area of Zr-MOF-NH_2 was determined to be 1071 m^2 g^{-1} using BET (Brunauer–Emmett–Teller) method based calculations on its N_2 adsorption isotherm (Fig. S2†). This value is similar to that of Zr-MOF which has also the same UiO-66 type structure (1141 m^2 g^{-1}). The diffuse reflectance UV-Vis spectrum also indicates the successful formation of Zr-MOF-NH_2 (Fig. S3†). In addition, the FT-IR spectrum of Zr-MOF-NH_2 shows bands at 3388 and 3512 cm^{-1} corresponding to the symmetric and asymmetric stretching of primary amines (see Fig. S4 in the ESI†), suggesting that the –NH_2 groups are free without coordination. These results clearly indicate the successful formation of Zr-MOF-NH_2.

In an investigation exploring the potential catalytic activity of Zr-MOF-NH_2, photocatalytic oxidation of benzyl alcohol was performed under UV-light irradiation (Fig. S5†). For comparison with the Zr-MOF-NH_2 catalyst, the reaction was also performed over Zr-MOF without –NH_2 groups and Al-MOF-NH_2 (MIL-53(Al)-NH_2)[9] which does not have photocatalytic activity. As shown in Fig. S5,† Zr-MOF-NH_2 and Zr-MOF catalyse the reaction to produce benzaldehyde as the product, whereas benzaldehyde is not generated over Al-MOF-NH_2. This result suggests that Zr–oxo clusters within Zr-MOF-NH_2 and Zr-MOF behave as photocatalysts under UV-light irradiation. Subsequently, the Knoevenagel condensation reaction of benzaldehyde with malononitrile was carried out at 363 K over Zr-MOF-NH_2, Zr-MOF and Al-MOF-NH_2, as shown in Fig. S6.† The reaction efficiently proceeds over Zr-MOF-NH_2 and Al-MOF-NH_2. It is well-known that the Knoevenagel condensation reaction proceeds through the formation of an imine intermediate on the catalysts containing organic amines, followed by the addition of an active methylene group.[10] Therefore, the reaction is promoted more efficiently over the catalysts with –NH_2 groups than over the catalysts without –NH_2 groups. It should be noted that Al-MOF-NH_2 exhibits higher catalytic activity for the reaction than Zr-MOF-NH_2, although both MOFs have –NH_2 groups within their structures. This result can be attributed to the large pore size of Al-MOF-NH_2 (0.85 nm)[11] compared to that of Zr-MOF-NH_2 (0.6 nm).[8] The large pore size enables facile diffusion of the substrates and products, resulting in the higher catalytic activity. Furthermore, the total basicities of Zr-MOF-NH_2 and Al-MOF-NH_2 were also determined to be 1.25 and 1.58 mmol g^{-1}, respectively, using an acid–base titration method. This basicity difference also accounts for the difference in the activity between Zr-MOF-NH_2 and Al-MOF-NH_2. In addition, interestingly, the reaction is also catalysed by Zr-MOF that does not contain –NH_2 groups. In general, Knoevenagel condensation reactions are promoted not only by base catalysts but also by Lewis acid catalysts.[12] It has been widely studied that coordinatively unsaturated metal sites in MOFs can act as Lewis acid catalysts. These facts suggest that coordinatively unsaturated metal sites in MOFs catalyse the Knoevenagel condensation reaction, generating benzylidenemalononitrile as the product. The results obtained from the above effort show that Zr-MOF-NH_2 possesses both photocatalytic activity and basicity that play key roles for respective photocatalytic oxidation and Knoevenagel condensation reactions.

The potential use of Zr-MOF-NH_2 as a bifunctional catalyst for the one-pot reaction was investigated next. For this purpose, Zr-MOF-NH_2 was employed to promote one-pot synthesis of benzylidenemalononitrile (**3**) from benzyl alcohol and malononitrile that takes place through sequential photocatalytic oxidation and Knoevenagel condensation reaction under UV-light irradiation at 363 K. Inspection of the time course of the process displayed in Fig. 1 shows that benzylidenemalononitrile is efficiently generated from benzyl alcohol (**1**) *via* a pathway involving initial formation of benzaldehyde (**2**), and that the yield of **3** reaches 91% after a 48 h reaction time. It is also shown that the reaction does not take place in the absence of a catalyst (entry 11 in Table 1). These observations clearly demonstrate that Zr-MOF-NH_2 serves as an effective bifunctional catalyst for this one-pot reaction. However, an excess amount of malononitrile (3 mmol) is used for the one-pot reaction compared with benzyl alcohol (0.1 mmol). Interestingly, UV-light irradiation decreases the reaction rate of the second step of the reaction (Knoevenagel condensation), as shown in Fig. S7.† Therefore, the excess amount of malononitrile is required for the efficient progress of the reaction. A detailed study into the reason why UV-light irradiation decreases the reaction rate is now underway.[13]

The stability of Zr-MOF-NH_2 was investigated by XRD measurements before and after the reaction, as shown in Fig. 2. The diffraction peaks corresponding to the UiO-66 structure is maintained even after the reaction, indicating that Zr-MOF-NH_2 possesses high durability toward the one-pot reaction cascades.

Moreover, a reusability test was carried out after the first run. Although the reaction rate is decreased, an 89% yield of the final product is achieved after reaction for 72 h. This result suggests that the catalyst can be reused as a heterogeneous catalyst with slight decrease in the activity.

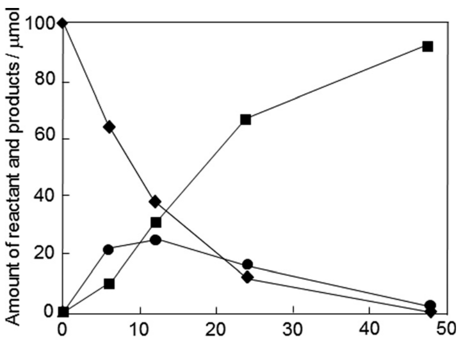
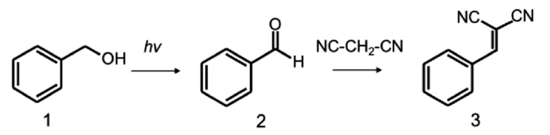


Fig. 1 Time course of the one-pot sequential photocatalytic oxidation and Knoevenagel condensation reaction over Zr-MOF-NH_2 under UV-light irradiation at 363 K: benzyl alcohol (◆), benzaldehyde (●), benzylidenemalononitrile (■).

Table 1 One-pot sequential photocatalytic oxidation and Knoevenagel condensation reaction using various catalysts[a]



Entry	Catalyst	Conv. (%)	Yield (%)	
			2	3
1	Zr-MOF-NH$_2$	100	2	91
2[b]	Zr-MOF-NH$_2$	100	89	1
3[c]	Zr-MOF-NH$_2$	0	0	0
4	Zr-MOF	96	62	28
5	ZrO$_2$	100	75	2
6	Zr-MOF + MCM-41-NH$_2$[d]	71	6	61
7	ZrO$_2$ + MCM-41-NH$_2$[e]	77	2	59
8	Al-MOF-NH$_2$	0	0	0
9	Zn-MOF-NH$_2$	37	28	7
10	Ti-MOF-NH$_2$	100	51	32
11	No catalyst	0	0	0

[a] Reaction conditions: benzyl alcohol (0.1 mmol), malononitrile (3 mmol), *p*-xylene (4 mL), catalyst (100 mg), 363 K, UV-light irradiation, 48 h. [b] The reaction was performed at 298 K. [c] The reaction was performed without UV-light irradiation. [d] A mixture of Zr-MOF (50 mg) and MCM-41-NH$_2$ (50 mg) was employed as the catalyst. [e] A mixture of ZrO$_2$ (50 mg) and MCM-41-NH$_2$ (50 mg) was employed as the catalyst.

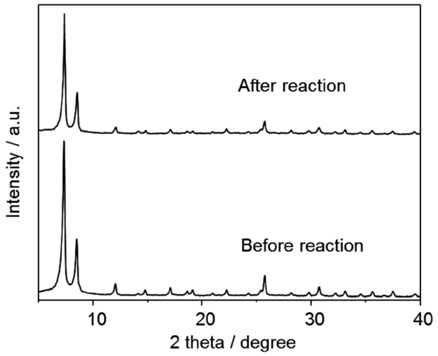


Fig. 2 XRD patterns of Zr-MOF-NH$_2$ before and after the one-pot reaction.

For comparison purposes, some control reactions and one-pot reactions catalysed by conventional solid and other MOF catalysts were performed (Table 1). When the reaction is performed under UV-light irradiation at 298 K (entry 2), the second step (Knoevenagel condensation of benzaldehyde with malononitrile) does not proceed efficiently whereas the first step of the reaction (photocatalytic oxidation of benzyl alcohol) proceeds to produce benzaldehyde. It was also found that the reaction between benzyl alcohol and malononitrile does not occur without UV-light irradiation (entry 3), because the first step in the pathway does not take place. From these results, the UV-light irradiation and heating up to 363 K were confirmed to be required to progress the one-pot reaction sequences. In addition, when Zr-MOF or ZrO$_2$ is employed (entry 4, 5), the second step does not take place efficiently. It is noteworthy that Zr-MOF-NH$_2$ exhibits higher activity than the mixture of Zr-MOF and amino-functionalised MCM-41 (MCM-41-NH$_2$)[14,15] or the mixture of ZrO$_2$ and MCM-41-NH$_2$, suggesting that the combination of a Zr–oxo cluster and a BDC-NH$_2$ unit existing close to each other would be favourable for the one-pot reaction. On the other hand, the reaction hardly occurs over Al-MOF-NH$_2$ that does not exhibit photocatalytic activity. These results clearly demonstrate that the existence of both photocatalytic activity and basicity, like those found in Zr-MOF-NH$_2$, is necessary for the promotion of the one-pot benzylidenemalononitrile forming process. Moreover, Zn-MOF-NH$_2$ (IRMOF-3) and Ti-MOF-NH$_2$ (MIL-125(Ti)-NH$_2$) were also prepared and employed for the reaction (entry 9, 10).[16] Since both Zn-MOF-NH$_2$ and Ti-MOF-NH$_2$ possess –NH$_2$ groups and are known to show photocatalytic activities under light irradiation,[17] it is expected that the one-pot reaction also proceeds efficiently as well as over Zr-MOF-NH$_2$. However, their catalytic activities are lower than that of Zr-MOF-NH$_2$. These facts are rationalized by the stability of the MOF catalysts under the reaction conditions. XRD measurements revealed that the structures of Zn-MOF-NH$_2$ and Ti-MOF-NH$_2$ are collapsed during the reaction, whereas the structure of Zr-MOF-NH$_2$ is maintained under the same conditions. Therefore, Zr-MOF-NH$_2$ exhibits higher activity toward one-pot sequential photocatalytic oxidation and Knoevenagel condensation reaction.

Finally, the Zr-MOF-NH$_2$ catalyst was applied to another one-pot reaction of benzyl alcohol and ethyl cyanoacetate to produce ethyl α-cyanocinnamate in order to investigate the substrate applicability. The reaction was carried out under the same conditions as the one-pot benzylidenemalononitrile forming process except that ethyl cyanoacetate was used in place of malononitrile. Ethyl α-cyanocinnamate as the final product is generated *via* benzaldehyde as the intermediate product over Zr-MOF-NH$_2$, and the yield reaches 89% after a reaction time of 96 h. This fact suggests that the developed system can be applied to various one-pot processes.

Conclusions

In summary, we have prepared and studied a bifunctional metal–organic framework photocatalyst consisting of a Zr–oxo cluster and 2-aminobenzene-1,4-dicarboxylic acid as an organic linker (Zr-MOF-NH$_2$). First, photocatalytic oxidation of benzyl alcohol and Knoevenagel condensation of benzaldehyde with malononitrile were explored as test reactions for the evaluation of the photocatalytic and basic properties of Zr-MOF-NH$_2$, respectively. Zr-MOF-NH$_2$ was found to catalyse both reactions, indicating that Zr-MOF-NH$_2$ possesses both photocatalytically active and basic sites. Subsequently, Zr-MOF-NH$_2$ was applied to the one-pot reaction to produce benzylidenemalononitrile through sequential photocatalytic oxidation and Knoevenagel condensation under UV-light irradiation. Benzylidenemalononitrile as the final product was efficiently generated *via* benzaldehyde as the intermediate product over Zr-MOF-NH$_2$. In this process, the Zr–oxo cluster catalyses the first step of the reaction (photocatalytic oxidation of benzyl alcohol), and subsequently the –NH_2 group catalyses the second step (Knoevenagel condensation of benzaldehyde with malononitrile), resulting in the progress of the one-pot reaction. To the best of our knowledge, this is the first example of one-pot reaction systems utilizing the photocatalytic and basic properties of MOF materials. The observations made in this investigation should offer new insight into the design and manipulation of specifically functioning MOF catalysts.

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