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A Bifunctional, Site-Isolated Metal–Organic Framework-Based Tandem Catalyst

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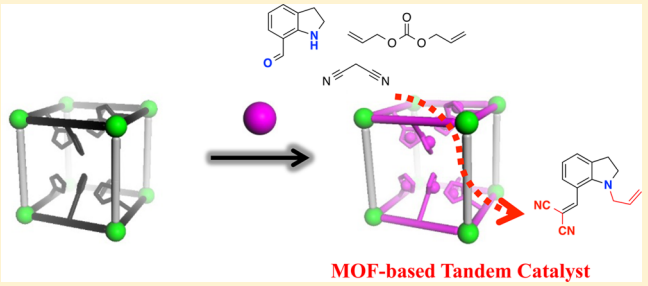
Supporting Information

ABSTRACT: Herein, we present the synthesis of a metal–organic framework-based tandem catalyst that contains two distinct catalytic domains. Zn(II)-based IRMOF-9-Irdcppy-NH_2 (IRMOF = isoreticular metal–organic framework) has both organocatalytic amine and organometallic Ir(I) groups that were incorporated by both pre- and postsynthetic functionalization methods. The isolated amine and Ir(I) sites of IRMOF-9-Irdcppy-NH_2 are shown to be independently catalytically active for performing a Knoevenagel condensation and allylic N-alkylation, respectively. More importantly, IRMOF-9-Irdcppy-NH_2 can act as a tandem catalyst for both of these organic transformations in a one-pot reaction, which cannot be achieved efficiently using the combined, homogeneous analogues.



INTRODUCTION

Metal–organic frameworks (MOFs) continue to be developed as promising materials for applications such as gas storage[1,2] and catalysis.[3] Taking the advantage of the functional tunability of MOFs, researchers have incorporated different types of catalytic groups into MOFs, including organocatalysts,[4,5] organometallics,[6−14] transition metals,[15−17] and radical species.[18] MOFs are attractive platforms for immobilizing catalysts compared to other materials (e.g., zeolites, activated carbons, and silica) because of their porosity,[19] thermal stability, high density of catalytic centers,[3] and ordered structures.[9] Despite the great number of reports on MOF-based catalysts, there are a limited number of MOF-based tandem catalysts. Tandem catalysts are single systems that are comprised of more than one active catalyst.[20] The use of tandem catalysts in organic synthesis allows the one-pot formation of products that cannot be achieved by a single catalyst. However, the required reaction conditions and catalyst compatibility are difficult to identify in homogeneous systems.

The often rigid, ordered structures of MOFs make many of them quite suitable for engineering multiple isolated catalytic sites. Although controlling the precise relative position of functional groups within the crystals of MOFs can be challenging,[21−23] a single MOF can be engendered with multiple functional groups via prefunctionalization[19] and postsynthetic modification (PSM) methods.[24] For example, the Kim group has presented the use of MIL-101(Al)-NH_2 as a bifunctional, site-isolated Lewis acid–Brønsted base heterogeneous catalyst.[25] MIL-101(Al)-NH_2 contained Lewis acidic Al(III) centers at the secondary building units (SBUs) and Brønsted basic amines on the 2-amino-1,4-dicarboxylate (NH_2-bdc^{2-}) organic struts within the framework. MIL-101(Al)-NH_2 was shown to be an effective catalyst for a tandem Meinwald rearrangement and Knoevenagel condensation. Similarly, Cr-MIL-101 and UiO-66 decorated with both Brønsted acids and bases have been reported to act as tandem catalysts.[26−29] These recent reports provide examples of using MOFs as platforms to design tandem catalysts; however, the catalytic groups used in these studies were limited to either organocatalysts or the SBUs. In addition, the use of SBU nodes as catalytic sites limits the choice of MOFs, as well as the ability to tune in the desired reactivity. It is also possible that reactivity at the SBU could lead to MOF degradation over time.

EXPERIMENTAL SECTION

The synthesis of all ligands and detailed characterization of MOFs can be found in the Supporting Information.

MOFs Synthesis. *Synthesis of IRMOF-9.* [1,1′-Biphenyl]-4,4′-dicarboxylic acid (H_2bpdc, 50 mg, 0.2 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (178 mg, 0.6 mmol) were added to *N*,*N*′-dimethylformamide (DMF, 15 mL) in a scintillation vial. The mixture was sonicated at 55 °C for ∼30 min. The vial was then transferred into a preheated isotherm oven at 120 °C for 24 h. After the sample had cooled to room temperature, clear block crystals of IRMOF-9 were obtained. The crystals were rinsed with DMF (3 × 10 mL), and DMF was then exchanged with $CHCl_3$ (3 × 15 mL). Fresh $CHCl_3$ was replaced every day for 3 days, and the crystals were stored in $CHCl_3$ prior to any further experiments.

Synthesis of IRMOF-9-dcppy. H_2dcppy (50 mg, 0.2 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (177 mg, 0.6 mmol) were dissolved in DMF (10 mL) with sonication in a scintillation vial. The vial was then transferred into a preheated isotherm oven at 120 °C for 24 h. After the sample had cooled to room temperature, clear block crystals of

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IRMOF-9-dcppy were obtained. The crystals were rinsed with DMF (3 × 10 mL), and DMF was then exchanged with $CHCl_3$ (3 × 15 mL). Fresh $CHCl_3$ was replaced every day for 3 days, and the crystals were stored in $CHCl_3$ prior to any further experiments.

Synthesis of IRMOF-9-dcppy-NH_2. 2,2′-diamino[1,1′-biphenyl]-4,4′-dicarboxylic acid (H_2bpdc-$(NH_2)_2$), (735 mg, 2.7 mmol), 6-(4-carboxyphenyl)nicotinic acid (H_2dcppy) (657 mg, 2.7 mmol), and $Zn(NO_3)_2{\cdot}6H_2O$ (3.41 g, 18 mmol) were dissolved in DMF (100 mL) with sonication. The solution was then divided into 10 equal fractions in 10 scintillation vials (10 mL in each vial) and transferred to a programmable oven. These vials were heated at a rate of 2.5 °C/min from 35 to 100 °C. The temperature was held at 100 °C for 18 h and then decreased to 35 °C at a rate of 2.5 °C/min. Clear blocks of amber crystals were obtained as IRMOF-9-dcppy-NH_2. The crystals were rinsed with DMF (3 × 10 mL), and DMF was then exchanged with $CHCl_3$ (3 × 15 mL). Fresh $CHCl_3$ was replaced every day for 3 days, and the crystals were stored in $CHCl_3$ prior to any further experiments.

Cyclometalation of IRMOF-9-dcppy-NH_2 To Produce IRMOF-9-Irdcppy-NH_2. $[Ir(COD)(OCH_3)]_2$ (COD = 1,5-cyclooctadiene, 106 mg, 0.16 mmol) was dissolved in $CHCl_3$ (4 mL) in a scintillation vial. IRMOF-9-dcppy-NH_2 (100 mg, ∼0.16 mmol of $dcppy^{2-}$) was added to the scintillation vial. The vial was then transferred to a preheated oven at 55 °C for 24 h. After the sample had cooled to room temperature, the crystals were rinsed with and soaked in $CHCl_3$ (3 × 15 mL). The rinsing procedure was repeated every day for 3 days.

Catalysis Experiments. *Control: Tandem Reaction without a Catalyst.* Indoline-7-carboxyaldehyde (44 mg, 0.30 mmol), diallyl carbonate (430 μL, 3.0 mmol), and malonitrile (198 mg, 3.0 mmol) were added to $CDCl_3$ (8 mL). The reaction mixture was heated at 55 °C for 24 h in an oven. Afterward, the mixture was cooled to room temperature and characterized by ^{1}H NMR, which showed no conversion (Table 1 and Figure S5 of the Supporting Information).

Table 1. Summary of Control and Catalytic Reactions

	catalytic reaction 1[a]	catalytic reaction 2[a]	tandem reaction[a]
no MOF	0	0	0
homogeneous catalysts[b]	n/a[c]	n/a[c]	35%
IRMOF-9[b]	0	n/a[c]	0
IRMOF-9-dcppy[b]	0	n/a[c]	0
IRMOF-9-dcppy-NH_2[b]	90%	0	0
IRMOF-9-Irdcppy-NH_2[b]	92%	90%	95 ± 4%

[a]Conversion determined ^{1}H NMR spectroscopy. [b]Reaction conditions are detailed in the Experimental Section. [c]Not applicable.

Control: Tandem Reaction with IRMOF-9. Indoline-7-carboxyaldehyde (44 mg, 0.30 mmol), diallyl carbonate (430 μL, 3.0 mmol), and malonitrile (198 mg, 3.0 mmol) were added to $CDCl_3$ (8 mL). IRMOF-9 (∼50 mg, stored in $CHCl_3$) was removed from $CHCl_3$ and evacuated under vacuum for ∼30 s to remove residual solvent. The $CDCl_3$ solution was then transferred to the vial containing IRMOF-9. The reaction mixture was heated at 55 °C for 24 h in an oven. Afterward, the mixture was cooled to room temperature and characterized by ^{1}H NMR, which showed no conversion (Table 1 and Figure S5 of the Supporting Information).

Control: Knoevenagel Condensation with IRMOF-9-dcppy. Indoline-7-carboxyaldehyde (44 mg, 0.30 mmol) and malonitrile (198 mg, 3.0 mmol) were added to $CDCl_3$ (8 mL). IRMOF-9-dcppy (∼50 mg, stored in $CHCl_3$) was removed from $CHCl_3$ and evacuated under vacuum for ∼30 s to remove residual solvent. The $CDCl_3$ solution was then transferred to the vial containing IRMOF-9-dcppy. The reaction mixture was heated at 55 °C for 24 h in an oven. Afterward, the mixture was cooled to room temperature and characterized by ^{1}H NMR, which showed no conversion (Table 1 and Figure S5 of the Supporting Information).

Catalysis with IRMOF-9-dcppy-NH_2. Indoline-7-carboxyaldehyde (44 mg, 0.30 mmol) and malonitrile (198 mg, 3.0 mmol) were added to $CDCl_3$ (8 mL). IRMOF-9-dcppy-NH_2 [∼100 mg, ∼0.13 mmol of bpdc-$(NH_2)_2^{2-}$ stored in $CHCl_3$] was removed from $CHCl_3$ and evacuated under vacuum for ∼30 s to remove residual solvent. The $CDCl_3$ solution was then transferred to the vial containing IRMOF-9-dcppy-NH_2. The reaction mixture was heated at 55 °C for 24 h in an oven. Afterward, the mixture was cooled to room temperature and characterized by ^{1}H NMR, which showed ∼90% conversion of indoline-7-carboxyaldehyde into 2-(indolin-7-ylmethylene)-malononitrile (**1**). Diallyl carbonate (430 μL, 3.0 mmol) was subsequently added to this mixture. The reaction mixture was then heated at 55 °C for 24 h in an oven. Afterward, the mixture was cooled to room temperature and characterized by ^{1}H NMR, which showed no conversion of **1** to 2-((1-allylindolin-7-yl)methylene)malononitrile (**2**) (Table 1 and Figure S5 of the Supporting Information).

Catalysis with IRMOF-9-Irdcppy-NH_2. Indoline-7-carboxyaldehyde (44 mg, 0.30 mmol) and malonitrile (198 mg, 3.0 mmol) were added to $CDCl_3$ (8 mL). IRMOF-9-Irdcppy-NH_2 [∼100 mg, ∼0.13 mmol of bpdc-$(NH_2)_2^{2-}$, ∼0.015 mmol of Ir, stored in $CHCl_3$] was removed from $CHCl_3$ and evacuated under vacuum for ∼30 s to remove residual solvent. The $CDCl_3$ solution was then transferred to the vial containing IRMOF-9-Irdcppy-NH_2. The reaction mixture was heated at 55 °C for 24 h in an oven. Afterward, the mixture was cooled to room temperature and characterized by ^{1}H NMR, which showed ∼92% conversion of indoline-7-carboxyaldehyde to **1** (Table 1). Diallyl carbonate (430 μL, 3.0 mmol) was subsequently added to this reaction mixture. The reaction mixture was then heated at 55 °C for 24 h in an oven. Afterward, the mixture was cooled to room temperature and characterized by ^{1}H NMR, which showed ∼90% conversion of **1** to **2** (Table 1).

Tandem Catalysis Using IRMOF-9-Irdcppy-NH_2. Indoline-7-carboxyaldehyde (44 mg, 0.30 mmol), diallyl carbonate (430 μL, 3.0 mmol), and malonitrile (198 mg, 3.0 mmol) were added to $CDCl_3$ (8 mL). IRMOF-9-Irdcppy-NH_2 [∼100 mg, ∼0.13 mmol of bpdc-$(NH_2)_2^{2-}$, ∼0.015 mmol of Ir, stored in $CHCl_3$] was removed from $CHCl_3$ and evacuated under vacuum for ∼30 s to remove residual solvent. The $CDCl_3$ solution was then transferred to the vial containing IRMOF-9-Idcppy-NH_2. The reaction mixture was heated at 55 °C for 36 h in an oven. Afterward, the mixture was cooled to room temperature and characterized by ^{1}H NMR, which showed ∼95% conversion of indoline-7-carboxyaldehyde to **2** (Table 1 and Figure S5 of the Supporting Information).

Tandem Catalysis Using a Homogeneous Catalyst. Indoline-7-carboxyaldehyde (44 mg, 0.30 mmol), diallyl carbonate (430 μL, 3.0 mmol), and malonitrile (198 mg, 3.0 mmol) were added to $CDCl_3$ (8 mL). Dimethyl 2,2′-diamino[1,1′-biphenyl]-4,4′-dicarboxylate (18 mg, 0.06 mmol) and $[Ir(COD)(OCH_3)]_2$ (4.5 mg, 0.007 mmol, 5 mol % Ir) were sequentially added to the $CDCl_3$ solution. The reaction mixture was incubated at 55 °C for ∼5 days. Afterward, the mixture was cooled to room temperature and characterized by ^{1}H NMR, which showed a ∼35% conversion of indoline-7-carboxyaldehyde to **2** (Table 1 and Figure S7 of the Supporting Information).

Control: Filtration. Indoline-7-carboxyaldehyde (44 mg, 0.30 mmol), diallyl carbonate (430 μL, 3.0 mmol), and malonitrile (198 mg, 3.0 mmol) were added to $CDCl_3$ (8 mL). IRMOF-9-Irdcppy-NH_2 [∼100 mg, ∼0.13 mmol of bpdc-$(NH_2)_2^{2-}$, ∼0.015 mmol of Ir, stored in $CHCl_3$] was removed from $CHCl_3$ and evacuated under vacuum for ∼30 s to remove residual solvent. The $CDCl_3$ solution was then transferred to the vial containing IRMOF-9-Idcppy-NH_2. The reaction mixture was heated at 55 °C in an oven. After ∼8 h, the MOF was removed from the reaction mixture via filtration. The mixture was characterized by ^{1}H NMR, which showed an ∼35% conversion of indoline-7-carboxyaldehyde to **2**. The reaction mixture was incubated at 55 °C for an additional 24 h in an oven. After ∼24 h, ^{1}H NMR characterization of the reaction mixture showed no further conversion of indoline-7-carboxyaldehyde to **2** (the overall conversion remained at ∼35%).

Recyclability of IRMOF-9-Irdcppy-NH_2 under Ambient Conditions. After the first tandem catalytic reaction was completed (see above), the MOF was rinsed with $CDCl_3$ (3 × 5 mL) and soaked in $CDCl_3$. This rinsing procedure was repeated every day for 3 days prior

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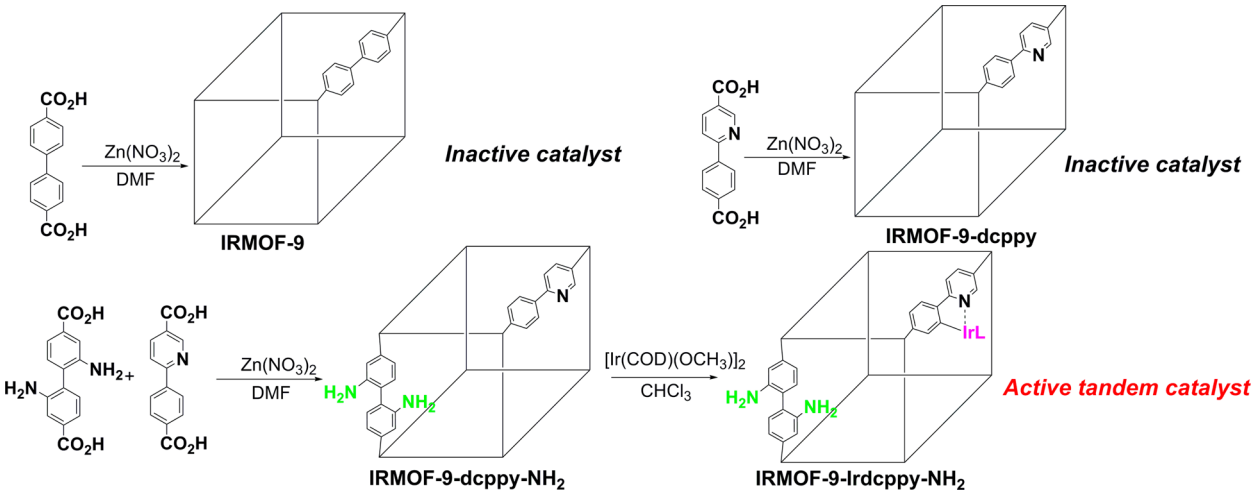
Scheme 1. Synthesis of IRMOF-9, IRMOF-9-dcppy, and IRMOF-9-Irdcppy-NH_2



to the next catalytic run. The second and third catalytic runs were conducted under identical conditions as described above.

Recyclability of IRMOF-9-Irdcppy-NH_2 under an Inert Atmosphere. The first run of the tandem catalysis was conducted under identical conditions as described above, but under an Ar atmosphere. After the first catalytic run was completed, the MOF was rinsed with $CDCl_3$ (3 × 5 mL) and soaked in $CDCl_3$ under an Ar atmosphere. This rinsing procedure was repeated every day for 3 days prior to the next catalytic reaction. The second and third catalytic runs were conducted under identical conditions as described above, but under an Ar atmosphere.

Stability of IRMOF-9-Irdcppy-NH_2 in the Presence of Malonitrile. Pristine IRMOF-9-Irdcppy-NH_2 (~100 mg) was combined with malonitrile (198 mg, 3.0 mmol) in $CHCl_3$ (8 mL). The solution was then incubated at 55 °C for 5 days in an oven. After the solution had cooled to room temperature, the MOF was rinsed with $CHCl_3$ (3 × 5 mL) and soaked in $CHCl_3$ prior to PXRD analysis.

RESULTS AND DISCUSSION

The tandem catalysis of the Knoevenagel condensation and allylic N-alkylation in a one-pot reaction would be predicted to be difficult because a nucleophilic amine could act as a substrate for alkylation via the Ir(I)phenylpyridine complex.[12] However, in a MOF, these catalytic sites can be isolated within the framework to prevent this unproductive reaction. We utilize a mixed-linker approach to integrate H_2bpdc-$(NH_2)_2$ and H_2dcppy to produce IRMOF-9-dcppy-NH_2 (Scheme 1). IRMOF-9-dcppy-NH_2 can be treated with $[Ir(COD)(OCH_3)]_2$ to obtain IRMOF-9-Irdcppy-NH_2 as previously reported (Scheme 1).[23]

Powder X-ray diffraction (PXRD) analysis reveals an interpenetrated structure for IRMOF-9-dcppy-NH_2, which resembles the parent IRMOF-9 lattice (Figure 1). Furthermore, the unit cell of IRMOF-9-dcppy-NH_2 is in agreement with IRMOF-9 (Table S1 of the Supporting Information). ^{1}H NMR digestion of IRMOF-9-dcppy-NH_2 confirms ~57 ± 3% incorporation of dcppy^{2-} and ~43 ± 3% incorporation of bpdc-$(NH_2)_2^{2-}$ (Figure S1 of the Supporting Information). After the treatment with $[Ir(COD)(OCH_3)]_2$, PXRD analysis of IRMOF-9-Irdcppy-NH_2 shows the intact framework (Figure 1 and Figure S2 of the Supporting Information). Inductively coupled plasma mass spectrometry (ICP-MS) unambiguously showed that the framework contained 2.84 ± 0.33 wt % Ir, which indicated that ~9% of the total dcppy^{2-} ligands were modified with Ir(I) (Figure S2 and Table S2 of the Supporting Information). Interestingly, the synthesis of IRMOF-9-NH_2 using only H_2bpdc-$(NH_2)_2$ and $Zn(NO_3)_2$ was not successful under identical solvothermal conditions.

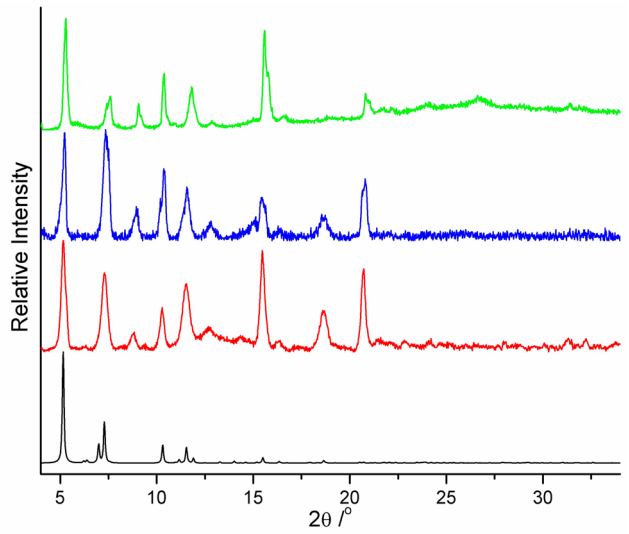


Figure 1. PXRD analysis of simulated IRMOF-9 (black), IRMOF-9-dcppy-NH_2 (red), and IRMOF-9-Irdcppy-NH_2 before (blue) and after (green) the first catalytic run under ambient conditions.

The porosity and thermal stability of parent IRMOF-9-dcppy-NH_2 and cyclometalated IRMOF-9-Irdcppy-NH_2 were also analyzed via a N_2 sorption experiment at 77 K and thermal gravimetric analysis (TGA) (Figures S3 and S4 of the Supporting Information). Brunauer–Emmett–Teller (BET) surface area measurements of IRMOF-9-dcppy-NH_2 and IRMOF-9-Irdcppy-NH_2 gave values of 1810 ± 57 and 1964 ± 34 m^2/g, respectively (Table S2 of the Supporting Information). These surface areas are similar to that of the parent IRMOF-9 (~1900 m^2/g).[30] TGA of these MOFs revealed high thermal stability up to ~400 °C, also comparable to that of IRMOF-9.[30]

With the desired MOF in hand, we chose to investigate the catalytic activity of IRMOF-9-Irdcppy-NH_2. Because of the different molar ratio of bpdc-$(NH_2)_2^{2-}$ to Ir(I) (~8:1) in IRMOF-9-Irdcppy-NH_2, the control and tandem reactions were conducted with the use of ~5 mol % Ir catalyst and a greater mole percentage of bpdc-$(NH_2)_2^{2-}$. The combination of

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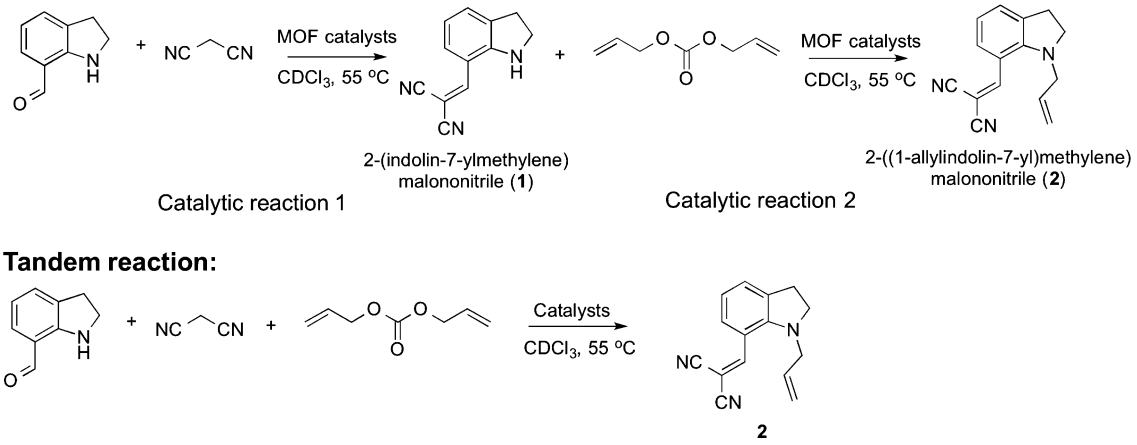
Scheme 2. Knoevenagel Condensation (reaction 1), Allylic N-Alkylation (reaction 2), and Tandem Catalytic Reactions



indoline-7-carboxyaldehyde and malonitrile with IRMOF-9-dcppy-NH_2 [~40 mol % bpdc-$(NH_2)_2^{2-}$] in $CDCl_3$ at 55 °C yielded the corresponding Knoevenagel condensation product **1** (Scheme 2, Table 1, and Figure S5 of the Supporting Information). As expected, no alkylated product **2** is obtained in the presence of diallyl carbonate even after ~1.5 day with IRMOF-9-dcppy-NH_2 as a catalyst (Scheme 2, reaction 2, Table 1, and Figure S5 of the Supporting Information). In addition, no condensation reaction occurs when IRMOF-9 or IRMOF-9-dccpy is used as a catalyst (Table 1 and Figure S5 of the Supporting Information), ruling out the possibility that the ZnO_4 SBUs or the phenylpyridine moieties of the $dcppy^{2-}$ ligand are active catalytic species. Finally, these results indicate that the secondary amine moiety of indoline-7-carboxyaldehyde is incapable of catalyzing the Knoevenagel condensation reaction. These reactions all indicate that the amine functionality in IRMOF-9-dcppy-NH_2 is responsible for the Knoevenagel condensation reaction.

After the catalytic activity of IRMOF-9-dcppy-NH_2 had been confirmed, metal-loaded IRMOF-9-Irdcppy-NH_2 [~40 mol % bpdc-$(NH_2)_2^{2-}$, ~5 mol % Ir] was used for the tandem reaction among indoline-7-carboxyaldehyde, malonitrile, and diallyl carbonate (Scheme 2, tandem reaction). The final product **2** of the tandem reaction was obtained in good yield at 55 °C after ~1.5 day [~95 ± 4% (Table 1 and Figures S5 and S6 of the Supporting Information)]. Earlier studies of MOF catalysts have given similar results, with ~99% conversion for the N-alkylation of amines achieved in ~30 h, and ~85% conversion for a tandem Meinwald rearrangement−Knoevenagel condensation in ~96 h was reported.[12,25] The heterogeneous nature of IRMOF-9-Irdcppy-NH_2 was confirmed by removal of IRMOF-9-Irdcppy-NH_2 (after ~8 h) from the reaction mixture, which resulted in no further progression of the catalytic reaction, providing evidence of the heterogeneous nature of this catalyst. ICP-MS analysis of IRMOF-9-Irdcppy-NH_2 before (2.84 wt % Ir) and after one catalytic run [2.26 wt % Ir (Table S2 of the Supporting Information)] indicated minimal loss of Ir.

The similar one-pot reaction using homogeneous catalysts was also investigated. Using dimethyl 2,2′-diamino[1,1′-biphenyl]-4,4′-dicarboxylate [the methyl ester form of H_2bpdc-$(NH_2)_2$] and $[Ir(COD)(OCH_3)]_2$[31,32] as catalysts, the desired product **2** was obtained in only 35% yield at 55 °C after ~5 days (Scheme 2 and Figures S7 and S8 of the Supporting Information). ^1H NMR characterization of the homogeneous catalytic reaction after 5 days reveals the disappearance of dimethyl 2,2′-diamino[1,1′-biphenyl]-4,4′-dicarboxylate species (Figure S6 of the Supporting Information). The disappearance and/or degradation of dimethyl 2,2′-diamino[1,1′-biphenyl]-4,4′-dicarboxylate is likely due to alkylation of the amine functionality (Figure S9 of the Supporting Information).

The recyclability of IRMOF-9-Irdcppy-NH_2 was also investigated. Between reaction runs, the MOF was isolated by filtration and then rinsed and soaked in $CDCl_3$. This procedure was repeated every day for 3 days prior to the next catalytic run to remove substrates or products that might produce pore blocking.[12] BET area measurement of IRMOF-9-Irdcppy-NH_2 after one catalytic run under ambient conditions revealed a surface area of 1711 ± 57 m^2/g (Figure S3 of the Supporting Information). In the second and third runs, no conversion of reactants to final product was found after ~1.5 days under identical reaction conditions. As previously observed, the decrease in catalytic activity may be due to the effects of air on the Ir centers.[12] Therefore, the tandem reaction (Scheme 2) with IRMOF-9-Irdcppy-NH_2 was explored under an Ar atmosphere. As expected, the first catalytic run gives ~95% conversion of the final product at 55 °C after ~1.5 days (Figure 2), with the second run giving ~24% conversion of the desired product, and the third run giving no conversion. The decreased catalytic activity is likely due to degradation of the MOF, as PXRD analysis showed a substantial loss of crystallinity after the second and third runs. The PXRD of IRMOF-9-Irdcppy-NH_2 changes substantially across the course of multiple catalytic runs, and after the third catalytic run, few reflections remain and a predominantly amorphous pattern is observed (Figure S10 of the Supporting Information). The decreased crystallinity of IRMOF-9-Irdcppy-NH_2 may be caused by the mildly acidic malonitrile substrate. To test this hypothesis, a pristine batch of IRMOF-9-Irdcppy-NH_2 was incubated in a $CDCl_3$ solution containing malonitrile at 55 °C for 3 days. PXRD analysis showed that after incubation, IRMOF-9-Irdcppy-NH_2 had undergone a transformation to a different phase (Figure S10 of the Supporting Information). The phase transformation of IRMOF-9-Irdcppy-NH_2 after incubation in malonitrile suggests that this substrate is not well-tolerated by this MOF architecture.

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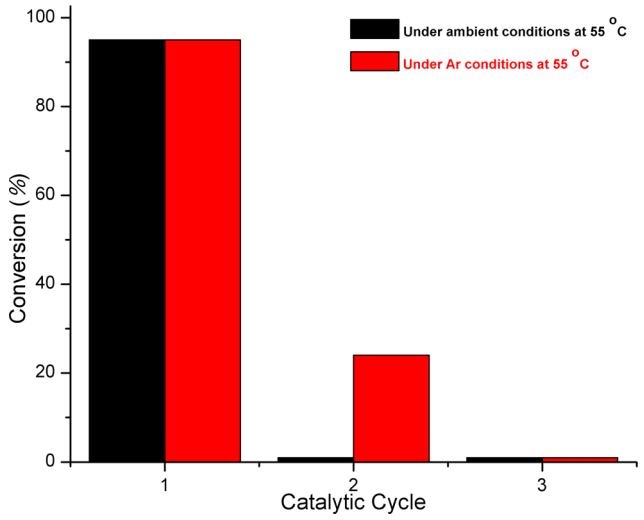

Figure 2. Recyclability of the IRMOF-9-Irdcppy-NH_2 catalyst under ambient and Ar conditions.

CONCLUSION

In conclusion, this study presents the synthesis of a site-isolated bifunctional MOF that is capable of acting as a tandem catalyst for both the Knoevenagel condensation and allylic N-alkylation reactions. The bifunctional MOF represents a rare MOF-based tandem catalyst that contains both organocatalytic and organometallic Ir(I) centers. Even though this bifunctional MOF is only highly active for one catalytic run, the MOF does achieve reactivity that was not effectively achieved by the component catalysts in a solution state. More importantly, the study demonstrates the potential use of MOFs to engender complex catalytic systems that are not limited to any single class of catalytic species. Future efforts will be focused on the development of more stable MOF-based tandem catalysts with control of the amount of catalytic species.

ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization of ligands and MOFs and catalysis experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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