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An azobenzene-containing metal–organic framework as an efficient heterogeneous catalyst for direct amidation of benzoic acids: synthesis of bioactive compounds†

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An azobenzene-containing zirconium metal–organic framework was demonstrated to be an effective heterogeneous catalyst for the direct amidation of benzoic acids in tetrahydrofuran at 70 °C. This finding was applied to the synthesis of several important, representative bioactive compounds.

Reactions involving the formation of amide bonds have attracted much interest due to the pervasiveness of the latter in biologically active compounds, industrially-relevant polymers, and pharmaceutical products.^{1–3} Methodologies based on reactions of amines with alcohols, aldehydes, nitriles, and aryl halides/CO have been reported, often with poor atom economy and toxic/corrosive by-products.^{1,4,5} However, the direct condensation of a carboxylic acid with an amine remains the most desirable pathway as the only side product is water. Due to the high activation barrier of this route, protocols have been developed to employ homogeneous biocatalysts, Lewis acid catalysts based on boron reagents, or metal complexes to successfully form amides from carboxylic acids.^{4–6} The success of these homogeneous catalysts has led to a push to develop heterogeneous catalytic systems, including metal-based catalysts,⁷ Lewis acidic zeolites,⁸ solid-supported boronic acids,⁹ and immobilized enzymes.¹⁰ However, significant drawbacks remain as a result of the harsh conditions employed during the reaction, unavoidable by-products, complex synthesis of catalysts, or limitations of heterogeneous systems with respect to the substrate scope.^{4–10}

Therefore, the direct amidation of carboxylic acids, especially with less active substrates such as benzoic acids, catalyzed by more efficient heterogeneous catalysts remains an underdeveloped field.

Metal–organic frameworks (MOFs) are a class of crystalline, porous materials whose architectures can be designed and characterized at the atomic level.¹¹ MOFs are constructed by linking inorganic secondary building units (SBUs) and organic linkers, in which both components can be tailored to suit a particular application.¹¹ As a result of the modular approach to MOF synthesis, these materials have emerged as a class of promising heterogeneous catalysts for organic transformations.¹² It is worth noting that low stability towards moisture as well as various harsh chemical environments are often limitations of MOFs in catalysis.^{11,12} However, MOFs based on Zr₆O₄(OH)₄(CO₂)₁₂ clusters are advantageous for such applications as the resulting structures are typically moisture- and chemically-stable and integrate Lewis acidic zirconium sites within the backbone of the architecture.^{13,14}

By taking advantage of the chemically stable SBUs as well as by modifying the linker, we were able to change the stability as well as the reactivity of MOFs toward cross-coupling reactions.¹⁵ Herein, we report the synthesis and characterization of a zirconium-based MOF, termed Zr-AzoBDC (where AzoBDC = azobenzene-4,4'-dicarboxylate), and its application as a heterogeneous catalyst for direct amidation reactions. The design strategy was based on the hypothesis that a zirconium-based MOF with an azobenzene backbone would provide large enough pore space for the substrates to react, show better affinity towards reagents, and potentially promote direct coupling through a cooperative effect between the Lewis acidic SBUs and azofunctionalities.¹⁴ Indeed, Zr-AzoBDC demonstrated superior catalytic activity for amide formation under significantly milder conditions when compared to other zirconium-based MOFs, common Lewis and Brønsted acids, and other catalytically-active MOFs.

Zr-AzoBDC was solvothermally synthesized using slight modifications to previous reports.¹⁶ Specifically, H₂-AzoBDC and zirconium oxychloride octahydrate were reacted in *N,N*-dimethylformamide (DMF) with the addition of acetic acid as a

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† Electronic supplementary information (ESI) available: Synthesis and characterization of Zr-AzoBDC, additional catalytic data, and recycling studies. See DOI: 10.1039/c5cc05985b

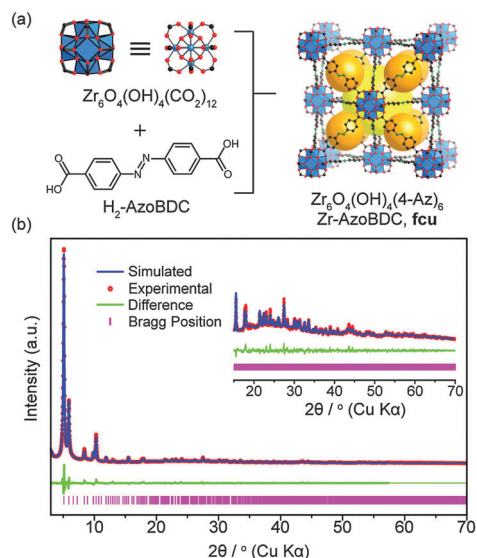


Fig. 1 (a) Building units used to generate Zr-AzoBDC with an **fcu** net. Zr-AzoBDC (right) results from $Zr_6O_4(OH)_4(CO_2)_{12}$ secondary building units (left) joined by azobenzene-4,4'-dicarboxylic acid (H_2 -AzoBDC) linkers (left). Orange and yellow spheres represent the tetrahedral and octahedral pore cavities, respectively. Atom colors: Zr, blue polyhedra; C, black; N, green; O, red. H atoms are omitted for clarity. (b) PXRD analysis showing the experimental pattern (red circles), simulated pattern (blue), and the difference plot (green). The Bragg positions are shown in pink. Inset: Satisfactory agreement extends to diffraction at higher angles.

modulator (Fig. 1a).¹⁶ The resulting solution was heated at 85 °C for three days, yielding an orange microcrystalline solid, which was subsequently activated and characterized (see ESI†). Scanning electron microscopy analysis revealed homogeneity with respect to the shape of the microcrystalline particles, which provides support to the hypothesis that a singular phase was synthesized (see Fig. S1, ESI†).

To elucidate the structural features of Zr-AzoBDC, powder X-ray diffraction (PXRD) analysis on an activated sample, in conjunction with structural modelling, was carried out (see ESI†). Specifically, from the unit cell parameters of the indexed PXRD pattern, a structural model was generated by linking the primarily observed cuboctahedral-shaped, 12-connected (12-c) $Zr_6O_4(OH)_4(CO_2)_{12}$ SBU with the linear AzoBDC linkers into a 12,2-c **fcu** net (see ESI†). A full profile pattern refinement was performed against the experimental PXRD pattern leading to refined unit cell parameters ($Fm\bar{3}$, $a = 29.3994 \text{ \AA}$) and satisfactory residual values ($R_p = 8.48\%$, $R_{wp} = 11.24\%$) (Fig. 1b, see Tables S1 and S2, ESI†). The three-dimensional structure of Zr-AzoBDC is described as face-centered cubic composed of both tetrahedral and octahedral cavities with internal pore diameters of *ca.* 14.8 Å and 16.8 Å, respectively, which are in turn connected by *ca.* 9.2 Å triangular windows. It is noted that these diameters are in line with those measured for the isorecticular (having the same topology) MOFs, UiO-66, -67, and -68 as well as MOF-806.¹³ The potential solvent accessible void, as calculated by PLATON,¹⁷ is 74%. This was supported by N_2 isotherm measurements at 77 K, in which Zr-AzoBDC exhibited significant uptake in the low-pressure region, resulting

in calculated Brunauer–Emmett–Teller and Langmuir surface areas of 3200 and 3500 $m^2 g^{-1}$, respectively (see Fig. S4, ESI†).

After structural characterization, the catalytic activity of Zr-AzoBDC for amidation reactions was investigated using a model coupling reaction of benzylamine (Bn-NH₂) with benzoic acid. Specifically, optimization of the catalytic activity with respect to solvent, temperature, and catalyst loading was undertaken (see Table S3, ESI†). During this process, molecular sieves were added to the reaction with the realized expectation that lower reaction temperatures would be obtained. Optimal results were obtained in tetrahydrofuran (THF) at 70 °C, with 10 mol% Zr-AzoBDC catalyst loading, when 82% gas chromatography (GC) yield was remarkably achieved (see Table S3, entry 1, ESI†). In particular, the role of solvent was found to play an important role in the reaction efficiency. Notably, in 1,4-dioxane, acetonitrile, and toluene, the model coupling reaction was inefficient with <20% yield (see Table S3, entries 2–4, ESI†). It was observed that by decreasing the Zr-AzoBDC catalyst loading, the reaction efficiency dropped significantly (see Table S3, entries 1, 5 and 6, ESI†). Catalytic reactions taken place at 60 °C afforded only 50% yield while reactions at increased temperatures (80 °C) produced similar results as the optimal reaction conditions (see Table S3, entries 1, 7 and 8, ESI†). Additionally, the formation of an ammonium carboxylate salt, which retarded the nucleophilic attack by the amine nitrogen atom, was likely to result in poor yields when benzoic acid was used in excess (see Table S3, entries 1 and 10, ESI†). As expected, reactions without the use of a molecular sieve offered <2% and 42% at 70 °C and 110 °C, respectively (see Table S3, entries 11 and 12, ESI†). Previous reports for the amidation of benzoic acid suffered from either harsh conditions, low reaction yields, or stoichiometric amounts of waste by-product derived from coupling reagents.^{18–21} Moreover, the lowest temperature reported for the amidation of benzoic acid, using metal- or borane-based heterogeneous catalysts, is 110 °C.^{7,9} Clearly, Zr-AzoBDC is considerably an improvement upon all of these drawbacks. As expected, only trace amounts of the desired products were observed when reactions were carried out without an added catalyst (see Table S3, entry 9, ESI†).

The suitability of Zr-AzoBDC as an effective heterogeneous catalyst was evaluated by comparative studies on the catalytic activity of two isorecticular Zr-MOFs, UiO-66 and UiO-67, which are built from the same Zr SBU and have the same underlying topology as Zr-AzoBDC.^{13,16} As is shown in Table 1, UiO-66 exhibited no appreciable catalytic activity (entry 2). This observation is attributed to the triangular pore windows (*ca.* 6 Å) and octahedral pore cavity (*ca.* 11 Å) being too small to accommodate the substrates within the UiO-66 structure.^{13,14} This points to the likelihood that catalytic amide formation does not occur solely on the surface of Zr-AzoBDC, but rather within the pores. When using UiO-67 as a catalyst, the yield noticeably increases (41% yield), as the adverse pore size effect is minimized (entry 3). However, the activity of UiO-67 remains much lower than that of Zr-AzoBDC. Interestingly, Zr-AzoBDC also exhibited significantly higher activity than previously used amidation catalysts, $ZrCl_4$ and $ZrOCl_2$ (entries 4 and 5).¹⁸ Other acid catalysts and catalytically active MOFs were also evaluated as shown in Table 1 (entries 6–15).²²

Table 1 Comparative study of catalysts^a

$\text{Ph-COOH} + \text{Bn-NH}_2 \xrightarrow[\text{4\AA MS, THF, 70 }^\circ\text{C, 24 h}]{\text{Catalyst (10 mol \%), 1.5 equiv.}} \text{Ph-CO-NH-Bn}$			
Entry	Type	Catalyst	GC yield (%)
1	Zr-MOFs	Zr-AzoBDC	82 (76)
2		UiO-66	Trace
3		UiO-67	41 (33)
4	Zr salts	ZrCl ₄	31
5		ZrOCl ₂	28
6	Other acids	H ₂ -AzoBDC	6
7		Triflic acid	4
8		TFA	7
9		<i>p</i> TSA	12
10		ZSM-5	8
11		HY zeolite	<2
12	Other MOFs	Co-ZIF-67	<2
13		Ni ₂ (BDC) ₂ (DABCO)	<2
14		Zn-ZIF-8	<2
15		Cu ₂ (BDC) ₂ (DABCO)	<2

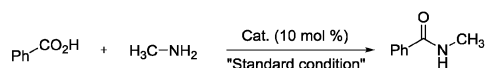
^a Volume of the solvent, 2 mL; 0.2 mmol scale. Bn-NH₂, benzylamine; MS, molecular sieve; TFA, trifluoroacetic acid; *p*TSA, *p*-toluenesulfonic acid; ZIF, zeolitic imidazolate framework; BDC, benzene-1,4-dicarboxylate; DABCO, 1,4-diazabicyclo[2.2.2]octane. Numbers in parentheses indicate isolated yields.

In order to highlight the role of the azo functionality in promoting the catalytic activity of Zr-AzoBDC, an amidation control reaction was performed, in which the resulting product is sufficiently small in molecular size (Scheme 1).

As is shown, the varying pore sizes of UiO-66 and UiO-67 did not significantly affect the reactivity. Thus, the high yield obtained with Zr-AzoBDC confirms the positive impact of the azo group on the catalyst activity. This finding was further supported by reactions using the AzoBDC linker and ZrOCl₂ metal cluster.

Control experiments, using the model amidation reaction with the corresponding optimized conditions, were subsequently performed to ensure that the catalytic activity did not originate from any leaching of Zr⁴⁺ ions from Zr-AzoBDC into the reaction mixture. As expected, there was no conversion detected in the catalyst-free reaction mixture after Zr-AzoBDC was removed (see ESI[†]). In addition, inductively coupled plasma mass spectrometry revealed the concentration of Zr⁴⁺ to be <10 ppm in the filtrate (see ESI[†]). Encouraged by these results, recycling studies were undertaken. At the end of each reaction period (24 h), Zr-AzoBDC was recovered from the reaction mixture, washed with the solvent, and re-used. This process was performed 5 times (see Fig. S13, ESI[†]). PXRD analysis of Zr-AzoBDC revealed that the crystallinity of this material was retained (see Fig. S14 and S15, ESI[†]). Clearly, the exceptional catalytic activity of Zr-AzoBDC was maintained without significant degradation.

To assess the substrate scope of the Zr-AzoBDC heterogeneous catalyst, we applied the optimized conditions to a variety



Catalyst	UiO-66	UiO-67	Zr-AzoBDC	H ₂ -AzoBDC	ZrOCl ₂
Yield	17	28	66	<2	32

Scheme 1 Reactions of benzoic acid with methylamine.

of carboxylic acid and amine coupling derivatives. The isolated product yields are presented in Table 2.

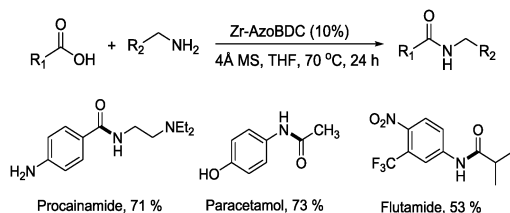
Reasonable yields were achieved for acid derivatives with both activating and deactivating substituents at different substituted positions (entries 1–4). The amidation of more reactive acids (*i.e.* aliphatic carboxylic acids) achieved excellent yields even at 2–5 mol% catalyst loading (entries 5 and 6). Additionally, cross-coupling reactions of benzoic acid with substituted benzylamine derivatives were also investigated. As is shown, desired products were also obtained in relatively high yields (entries 7–10). Finally, the optimized catalytic conditions were extended to the direct amidation of benzoic acid with piperidine, a secondary amine source. The desired product was realized in 48% yield (entry 11), thus, effectively demonstrating the exceptional catalytic activity of Zr-AzoBDC over a wide range of substrates.

The use of homogeneous catalysts in pharmaceutical synthesis often represents a major problem regarding the removal of

Table 2 Reaction scope with respect to coupling partners^a

$\text{R}_1\text{-COOH} + \text{R}_2\text{-NH}_2 \xrightarrow[\text{4\AA MS, THF, 70 }^\circ\text{C, 24 h}]{\text{Zr-AzoBDC (2-10\%)}} \text{R}_1\text{-CO-NH-R}_2$				
Entry	Acids	Amines	Product	Yield (%)
1		Bn-NH ₂		78
2		Bn-NH ₂		37
3		Bn-NH ₂		39
4		Bn-NH ₂		55
5 ^b		Bn-NH ₂		97
6 ^c		Bn-NH ₂		81
7				75
8				80
9		4-MeO-Bn-NH ₂		68
10		4-Cl-Bn-NH ₂		71
11				48

^a Reaction conditions: carboxylic acid derivatives (1 mmol), amine derivatives (1.5 mmol), catalyst (10 mol%), and activated 4 Å molecular sieves (0.5 g) in dry solvent at 70 °C in a sealed tube under an Ar atmosphere. ^b Catalyst (5 mol%). ^c Catalyst (2 mol%).



Scheme 2 Synthesis of bioactive amide-containing compounds by the heterogeneous Zr-AzoBDC catalyst.

contaminated metals.²³ To further expand on the potential of Zr-AzoBDC to be used in practical applications, we utilized this heterogeneous catalyst in the synthesis of pharmaceutically relevant amides possessing bioactivity (Scheme 2). Specifically, procainamide, an antiarrhythmic agent, was efficiently synthesized from the respective carboxylic acid. Previously, either the protection of the aromatic amine group or a 2-step synthetic process, including amidation of nitroarenes followed by hydrogenation, was required.²⁴ Similarly, paracetamol was obtained directly from acetic acid and 4-aminophenol in 73% yield through utilization of Zr-AzoBDC. Finally, a reasonable yield was achieved in the synthesis of flutamide, an oral and non-steroidal antiandrogen drug mainly used for prostate cancer treatment. It is noted that these drugs were previously synthesized by reacting amines with acid anhydrides or acyl halides.²⁵ One can argue that increased efficiency in such reactions makes the chemical processes more “green” by reducing the amount of steps in the synthetic sequences and in the resulting purification.

In conclusion, we have reported the synthesis of Zr-AzoBDC constructed from an azobenzene-4,4'-dicarboxylate (4-Az) linker and a $Zr_6O_4(OH)_4(CO_2)_{12}$ cluster. This structure exhibited exceptional catalytic activity toward direct amidation of benzoic acids under mild conditions (10 mol% catalyst loading, THF, 70 °C). The heterogeneous nature of Zr-AzoBDC enabled it to be recycled and re-applied to new reactions (5 times) without degradation in catalytic activity. Furthermore, the substrate scope of Zr-AzoBDC was demonstrated to be widely applicable to various substituted carboxylic acid and amine derivatives for the synthesis of bioactive amide compounds.

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