



Zr MOF Catalysts

Diastereoselective Synthesis of Pyranoquinolines on Zirconium-Containing UiO-66 Metal-Organic Frameworks

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Abstract: The Zr terephthalate MOFs UiO-66 and UiO-66-NH₂ have been found to be highly diastereoselective catalysts for the synthesis of a pyrano[3,2-*c*]quinoline through an inverse electron-demand aza-Diels–Alder [4+2] cycloaddition of an aryl imine (formed in situ from aniline and benzaldehyde) and 3,4-

dihydro-2*H*-pyran in one pot, affording the corresponding *trans* isomer in diastereomeric excesses of 90–95 %. The solids are stable under the reaction conditions and can be reused at least three times without significant loss of activity or diastereoselectivity.

Introduction

Metal-organic frameworks (MOFs) are crystalline porous materials constructed of metal ions or metal oxo clusters connected by multitopic organic ligands into extended one-, two-, or three-dimensional frameworks. Their strictly regular and tunable porous systems and huge surface areas of thousands of square meters per gram, together with the possibility of introducing different functionalities at the metal nodes and organic linkers or inside the pores (either by direct synthesis or through post-synthetic modification of pre-formed MOFs) make them very promising candidates for applications in, for example, gas separation^[1-3] and heterogeneous catalysis.^[4-7] In particular, the high tunability of the composition, structure, and intra-cavity chemical environment of MOFs are invaluable for the design and synthesis of highly chemo-, regio-, and enantioselective MOFs for use as catalysts for the synthesis of high-added-value chemicals.

Tetrahydroquinoline derivatives are an important class of heterocyclic compounds with a wide variety of biological activities, such as anti-allergic,^[8] anti-inflammatory,^[9] anti-arrhythmic,^[10] anti-malarial,^[11] anti-tumor,^[12] and anti-oxidant activity.^[13] Among them, pyrano[3,2-*c*]quinolines (hereafter PQs) form the core of various natural bioactive alkaloids, such as simulenoline, huajiaosimuline, flindersine, veprisine, and oricine.^[14,15] In our ongoing research into the application of metalorganic frameworks (MOFs) as heterogeneous catalysts for the synthesis of high-added-value chemicals, we have recently reported that (tetrahydro)quinoline derivatives can be readily pre-

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a sappointing information and Okcipity norm the dataons) for this analytic are available on the WWW under http://dx.doi.org/10.1002/ejic.201600372. pared by using bifunctional heterogeneous catalysts based on Pd or Pt species encapsulated inside Cr-MIL-101 MOFs through a tandem nitroarene reduction and intramolecular reductive amination of nitrocinamaldehyde.^[16] Nonetheless, one of the most important synthetic routes for preparing six-membered nitrogen heterocycles including (tetrahydro)quinolines is the so-called Povarov reaction.^[17] This reaction consists of an inverse electron-demand aza-Diels–Alder [4+2] cycloaddition of an aryl imine (formed in situ from aniline and an aldehyde) and electron-rich alkenes. In particular, by using 3,4-dihydro-2*H*-pyran (hereafter DHP) as the electron-rich dienophile, the corresponding PQ can be obtained, usually as a pair of *cis* and *trans* diastereoisomers, the ratio depending on the synthesis conditions used (Scheme 1).

Various homogeneous and heterogeneous acid catalysts, including SnCl₂,^[18] SbCl₃ doped on hydroxyapatite (SbCl₃-HPA),^[19] tungstophosphoric acid supported on nanosized MCM-41 (TPA/MCM-41),^[20] perchloric acid adsorbed on silica gel (HClO₄-SiO₂),^[21] GdCl₃,^[22] and ferric sulfate,^[23] have been reported for the synthesis of tetrahydropyranoguinolines. However, some of the methods used so far suffer from limitations such as the use of large amounts of catalyst (up to 50 mol-%), very low diastereoselectivities, or poor catalyst reusability. Herein we will show that Zr-containing MOFs bearing acid sites can be efficiently used as recoverable heterogeneous acid catalysts for the synthesis of PQs, affording high activities and excellent diastereoselectivities towards the trans (exo) isomer 6. In reports of research related to the present work, some authors have indeed demonstrated that various MOFs bearing acid functionalities can catalyze the Diels-Alder reactions (both normal and inverse-demand) of various substrates.^[24-29]

In the present work we used Zr-containing MOFs of the UiO-66 type to catalyze the synthesis of a PQ. These MOFs belong to a highly robust family of compounds formed by Zr_6 hexameric oxo-aggregate units connected by 12 linear dicarboxylate molecules in close-cubic packing that define octahedral and tetrahedral pores, both of which are accessible through triangu-







Scheme 1.

lar windows with free openings of about 6 Å (in the case of UiO-66 with terephthalate linkers), as shown schematically in Figure 1.^[30] However, this ideal structure of UiO-66-type MOFs is frequently interrupted by the occurrence of defects, mainly associated with linker deficiencies, that leads to a connectivity of the Zr₆ units lower than the expected value of 12 and to the formation of Zr⁴⁺ ions having coordinative unsaturation.^[31] There is now clear evidence that coordinatively unsaturated Zr⁴⁺ sites associated with defects are mainly responsible for the well-known acidic character of these compounds, as has already been shown for a number of acid-catalyzed reactions.^[32–35]



Figure 1. Pictorial view of the UiO-66 MOF structure showing the Zr_6 oxoaggregates (left) and their close-cubic packing (center) to form octahedral and tetrahedral cavities (right), both of which are accessible through triangular faces (evidenced by bold lines).

Results and Discussion

Synthesis of PQs Over Zr-MOFs

When an acetonitrile solution of aniline, benzaldehyde, and DHP was placed in contact with Zr-containing UiO-66-type MOFs (3.6 mol-% Zr with respect to aniline), the imine intermediate **3** was immediately obtained, which was gradually converted into the desired *cis* and *trans* PQs **5** and **6**, respectively. As an example, Figure 2 shows the kinetic evolution of products obtained when UiO-66 was used as the catalyst. Thus, after 22 h of reaction time, the final yield of the PQ obtained was 83 % with an excellent diastereoselectivity; the *trans/cis* diastereomeric excess (*de*) was 94 % (as determined by ¹H NMR spectroscopy). Besides PQ and the intermediate imine, a minor sideproduct (below 5 % yield) was also detected, which was identified as the aza-Michael addition product of aniline and DHP. When acetonitrile was replaced by other solvents, either polar (ethanol, *N*,*N*-dimethylformamide) or apolar (toluene, hexane, chloroform), the final yield of the PQ product was considerably lower or even negligible. As expected, no PQ was obtained in the absence of catalyst. Table 1 summarizes the results obtained with various MOFs and other acid catalysts taken from the literature for comparison.



Figure 2. Conversion of aniline 1 on UiO-66 (\blacksquare) and evolution of the products: intermediate imine 3 (\blacktriangle) and PQs 5 and 6 ().

According to the XRD and ICP-OES analyses of the solid catalyst recovered after the reaction (see Figure S1 in the Supporting Information), UiO-66 was found to be stable under the reaction conditions and was reusable for at least three catalytic cycles without significant loss of activity or diastereoselectivity (Table 1, entries 1–3).

Compared with UiO-66, UiO-66-NH₂ afforded slightly better results in terms of PQ yield in a shorter reaction time (Table 1, entry 4 and Figure S3 in Supporting Information), as well as affording an excellent diastereomeric ratio. UiO-66-NH₂ was also found to be stable and reusable without loss of activity under the reaction conditions. In comparison, $ZrCl_4$ (entry 7) was found to be much more active for the aza-Diels–Alder reaction than both Zr-MOFs, yielding 85 % PQ in only 15 min under the same reaction conditions. However, the product was obtained as a mixture of *trans* and *cis* isomers in a ratio of 73:27, which



Table	1.	Synthesis	of	PQs	over	various	solid	acid	catalysts.	[a
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	Catalyst	[Cat.] [mol-%]	Time [h]	Yield of PQ [mol-%]	<i>de</i> ^[b] [%]
1	UiO-66	3.8	10 (22)	75 (83)	94
2	UiO-66 1st reuse	3.8	22	77	92
3	UiO-66 2nd reuse	3.8	22	75	91
4	UiO-66-NH ₂ (45 nm)	3.8	3 (10)	74 (88)	88
5	UiO-66-NH ₂ (60 nm)	3.8	3 (22)	32 (77)	90
6	UiO-66-NH ₂ (130 nm)	3.8	22	<5	-
7	ZrCl ₄	3.8	0.25	85	46
8	(Cr)-MIL-101	3.8	24	<5	-
9	(AI)-MIL-101-NH ₂	3.8	24	<5	-
10	(Fe)-MIL-101-NH ₂	3.8	24	<5	-
11	SnCl ₂ •2H ₂ O ^[18]	10	1.8	95	40
12	SbCl ₃ -HAP, ^{[19][c]}	1.6	2.5	85	100
13	TPA/MCM-41 ^[20]	0.5	2.25	88	16
14	HCIO ₄ -SiO ₂ ^[21]	5	0.25	95	78
15	GdCl ₃ ^[22]	25	12	84	22
16	Fe ₂ (SO ₄) ₃ •xH ₂ O, ^{[23][c]}	10	1.5	87	56
17	NbCl ₅ ^[36]	10	0.5	85	90
18	Sml ₂ ^[37]	20	5	88	46
19	InCl ₃ ^[38]	20	0.5	80	18
20	LiBF ₄ ^[39]	20	1.5	88	70
21	CuBr ₂ ^[40]	50	2	76	58

[a] Reaction conditions with the Zr-MOF catalysts: Aniline (1 mmol), benzaldehyde (1.2 mmol), DHP (2 mmol), acetonitrile (0.5 mL), Zr-MOF (3.8 mol-% Zr), r.t.. [b] Diastereomeric excess: [(*trans – cis*)/(*trans + cis*)] × 100. [c] The reaction was carried out by heating at reflux in acetonitrile.

corresponds to a considerably lower diastereomeric excess of only 46 %.

To put into context the results obtained with the Zr-MOFs, we also compared our catalytic results with other solid catalysts described in the literature. In particular, concerning the diastereoselectivity, the results obtained with the Zr-MOFs rivaled those obtained with NbCl₅ and HClO₄-SiO₂, and were clearly surpassed only by SbCl₃-HAP (Table 1, entry 12). However, with these exceptions, Zr-MOFs largely outperformed most of the solid acid catalysts reported so far in the literature. Altogether, considering their good activity, excellent diastereoselectivity, and easy reusability, the Zr-containing MOFs studied in the present work emerge as convenient and reusable solid acid catalysts for the synthesis of PQs from amine, aldehyde, and DHP in one pot at room temperature with excellent diastereoselectivity.

Considering the dimensions of the PQs relative to the pore openings of the Zr-MOFs, it is evident that the Povarov threecomponent coupling reaction can only take place at the external surface of the solid catalyst. In agreement with this, three different UiO-66-NH₂ samples with particle sizes ranging from 45 to 130 nm (see Figure S2 in the Supporting Information) showed significant differences in catalytic activity, which decreased with increasing particle size, as expected. Thus, the turnover frequency (TOF) for the formation of PQ calculated after 3 h of reaction was 6.5 h^{-1} for the sample with the smallest particles (45 nm). This value was reduced to less than half when we used a sample containing particles with an average size of 60 nm (2.8 h^{-1}), whereas a UiO-66-NH₂ sample with particles of 130 nm was almost inactive for the formation of PQ (compare entries 4-6 in Table 1). If only simple geometric considerations (surface-to-volume ratio) are taken into account, one would ex-



pect much smaller differences in the catalytic activities of the samples with 45 and 60 nm particles, of around 33 %. Therefore, the higher activity of the sample with the smallest particles probably reflects a higher number of defects (in the form of linker deficiencies) located at the external surface compared with the sample with particles of 60 nm. It is worth mentioning that thermogravimetric analysis of the samples can provide an estimation of the overall number of linker defects (both internal and external) following the method proposed by Valenzano et al.^[31] Therefore, because we did not observe significant differences in the total amounts of defects in these two samples (ca. 8 % in both cases), our catalytic results suggest that these defects are not equally distributed among the internal and external surfaces of the MOFs from one sample to another (see Table S1 in the Supporting Information and the discussion therein).

To circumvent the limitations of product diffusion when narrow-pore Zr-MOFs were used as catalysts, we turned our attention to metal-organic compounds with pores in the mesoporous range. In particular, we considered trivalent metal (Fe³⁺, Cr³⁺, and Al³⁺) terephthalates of the MIL-101 family. This is a family of highly robust compounds featuring mesoporous cavities (ca. 3-3.5 nm) accessible through pentagonal and hexagonal windows of 1.2-1.5 nm, which are large enough to allow diffusion of very large molecules. Moreover, these materials are known to exhibit Lewis acid properties arising from coordinative unsaturation of the trivalent cations in the MIL-101structure, which, in principle, could also catalyze the Povarov reaction leading to PQs. However, when these MIL-101 materials were used as catalysts, there was hardly any formation of PQ (maximum yields below 5-10 %) under the mild reaction conditions used (room temperature and only 3.8 mol-% M³⁺ with respect to aniline). This result probably reflects the lower polarizing power (Z^2/r ratio) and thus the lower Lewis acidity of Fe³⁺, Cr³⁺, and Al³⁺ cations with respect to the Zr⁴⁺ ions present in the UiO-66-type compounds. Therefore, in the light of our catalytic results, Zr⁴⁺ ions (with coordinative unsaturation due to ligand defects in the structure^[33]) are strong enough acids to activate the intermediate imine, thus increasing the electrophilic character of the carbonyl carbon (coming from benzaldehyde) and facilitating the attack of the electron-rich DHP dienophile. In contrast, the M³⁺ ions in MIL-101 would not be capable of activating the intermediate imine enough to trigger the Diels-Alder cycloaddition at room temperature.

Proposed Mechanism

The Povarov reaction leading to PQs is actually a domino twostep reaction consisting of an aza-Diels–Alder [4+2] cycloaddition (aza-D–A) followed by a tautomeric 1,3-hydrogen shift to yield the final tetrahydroquinoline molecule in which the aromatic ring is regenerated (Scheme 2).

There is still some controversy over the mechanism of the aza-D-A reaction, as to whether it is a concerted or a stepwise reaction.^[36,41,42] It is generally accepted that the use of strong electrophilically activated azadienes and strong nucleophilically activated ethylenes favors a two-step reaction. Activation of the







Scheme 2.

azadiene can either be achieved by protonation of the imine by Brønsted acids or by the coordination of the N atom to strong Lewis acids, whereas the presence of electron-releasing groups in the ethylene increases its nucleophilic character. The first step consists of the nucleophilic attack of C6 of the ethylene on C1 of the imine (the attack on C4 being energetically very unfavorable). The formation of this C1–C6 single bond can take place from two approaching directions (*endo* and *exo*), which will eventually determine the formation of either the *cis* or *trans* PQ isomer. The second step of the aza-D–A reaction consists of the ring-closing reaction with the formation of the C4–C5 single bond.

In the particular case of the Povarov reaction catalyzed by Zr-MOF, the following mechanism can be hypothesized (Scheme 3). In the first step, the in situ formed imine is coordinated to the coordinatively unsaturated Zr ions of the MOF, most probably associated with missing linker defects. This coordination activates the electrophilic character of the imine, thereby favoring nucleophilic attack by DHP. The presence of bulky substituents in the Lewis acid coordinated to the imine can introduce important steric hindrance, which would favor the formation of the *trans* isomer through the *exo* approach of the DHP molecule. In this sense, the MOF can be considered as



Scheme 3.

a "macroligand" of the Zr ions, which would explain the high diastereomeric selectivity observed. A similar mechanism has been proposed by da Silva et al. to explain the diastereoselect-ivity of the NbCl₅-catalyzed Povarov reaction,^[36] and steric hindrance has also been claimed to be the factor influencing the outcome of a reaction by controlling the orientation of its intermediates.^[43]

Once the aza-D-A product has been formed, the ensuing 1.3-hydrogen shift reaction takes place leading to the final PO product. Again, this reaction can be considered either a concerted or a stepwise process. However, the direct (concerted) 1,3-hydrogen shift is very unfavorable due to the formation of a very strained four-membered transition state.^[41] Given the acidic character of the hydrogen atom involved in the tautomerization, the presence of a basic species or protic solvents (such as water) is expected to accelerate the reaction. Therefore, the presence of amino groups in UiO-66-NH₂ may be responsible for the higher catalytic activity observed for this catalyst compared with UiO-66 by either participating directly in the tautomerization reaction or by favoring the adsorption of water generated during the formation of imine in close proximity to the Zr catalytic sites. In this sense, it has been reported by Walton and co-workers that amino groups in the terephthalate linkers indeed favor water adsorption on the material.^[44]

Conclusions

In this work we have shown that UiO-66-type metal-organic frameworks containing coordinatively unsaturated Zr⁴⁺ ions associated with linker vacancies are highly diastereoselective heterogeneous catalysts for the inverse electron-demand hetero-Diels–Alder cycloaddition (Povarov reaction) of an imine and DHP leading to a *trans*-pyrano[3,2-*c*]quinoline with diastereomeric excesses of around 90–95 %. This diastereoselectivity clearly outperforms most of the solid Lewis acid catalysts reported so far, with the sole exception of SbCl₃-HAP.^[19] Both, UiO-66 and UiO-66-NH₂ compounds, prepared with terephthalic and aminoterephthalic ligands, respectively, are stable under the very mild reactions conditions used (room temperature) and can be reused at least three times without significant loss of activity or diastereoselectivity.

The relatively small pores of UiO-66 materials with respect to the dimensions of PQs prevent the reaction from occurring inside the pores of the MOFs, so only the active centers located at the external surface of the particles contribute to the observed activity. Accordingly, as the average particle size of UiO-66-NH₂ increases from 45–60 nm, the calculated TOFs decrease from 6.5–2.8 h⁻¹.

Experimental Section

Synthesis of UiO-66 and UiO-66-NH₂: All syntheses were performed according to the procedure reported by Kandiah et al.⁽⁴⁵⁾ Briefly, $ZrCl_4$ (750 mg) and either terephthalic acid (740 mg; UiO-66) or aminoterephthalic acid (800 mg; UiO-66-NH₂) were dissolved in DMF (90 mL; Zr/ligand/DMF molar ratio of 1:1:220) and the solution was kept in a closed round-bottomed flask in an oil bath at





80 °C for 12 h without stirring, followed by another 24 h at 100 °C. The resulting materials were recovered by filtration and washed thoroughly with fresh DMF. Then the solids were washed three times by soaking them in dichloromethane for 3 h. Finally, the solid was recovered by filtration and dried under vacuum at room temperature. X-ray diffraction (Phillips X'Pert, Cu- K_{α} radiation) was used to confirm the expected structure type and high crystallinity of the materials.

Catalytic Studies: In a typical catalytic reaction, aniline (93 mg, 1 mmol), benzaldehyde (127 mg, 1.2 mmol), and 3,4-dihydro-2Hpyran (168 mg, 2 mmol) in acetonitrile (0.5 mL) were added at room temperature to the MOF (3.6 mol-% Zr with respect to aniline) in a 3 mL batch reactor with a magnetic stirrer. The progress of the reaction was monitored by GC (Varian 3900 with 30 m \times 0.25 mm BS5-SGE column) and GC–MS (Agilent 6890 with 30 m \times 0.25 mm HP-5 column and Agilent mass selective detector 5973) using dodecane as internal standard. After each cycle, the solid catalysts were recovered by centrifugation and Soxhlet-washed overnight with acetonitrile and dried at 60 °C before reuse. The crystallinity of the recovered material was determined by XRD and compared with that of the fresh material. The diastereoisomeric excesses of the products were determined by ¹H NMR spectroscopy (Variant Unity 300 Plus Gemini at 300 MHz, in CDCl₃) from the integrated intensities of the peaks at δ = 3.65 ppm (td, J = 11.5, 2.5 Hz, 1 H) for the *trans* isomer and at δ = 3.36 (td, J = 11.3, 2.9 Hz, 1 H) and 5.33 ppm (d, J = 5.6 Hz, 1 H) for the *cis* isomer in the ¹H NMR spectra of the crude reaction mixtures.

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Zr MOF Catalysts

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 Diastereoselective Synthesis of Pyranoquinolines on Zirconium-Containing UiO-66 Metal-Organic Frameworks



Zirconium-containing UiO-66-type compounds catalyze the Povarov reaction between an imine and dihydropyran at room temperature to give *trans*-pyrano[3,2-*c*]quinoline with diastereomeric excesses of 90–95 %. The solids are stable and reusable catalysts that show no significant loss of activity or diastereoselectivity.

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