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1 Introduction

Metal-organic frameworks, sometimes called multidimensional porous coordination polymers, compose a large and successively expanding group of micro- and mesoporous materials. In these porous compounds, crystalline three-dimensional structures are covalently formed by combining inorganic parts (metal ions) with organic parts (linkers).^{1,2} The obvious feature of MOFs is that they exhibit the greatest flexibility of structure and property compared to other crystalline nanoporous materials such as zeolites and mesoporous molecular sieves.³ The main reason is that MOFs benefit from the combination of inorganic and organic structural building units and the feasibility of modifications (both before and after the synthesis). Actually, MOFs are the bridge of the gap between pure organic and inorganic materials; hence, they are the interesting materials with numerous potential applications including gas adsorption/separation, sensing, biomedical applications, and catalysis.^{4,5} Among these



Sima Aryanejad, 回 a Ghodsieh Bagherzade*a and Maryam Moudib

This study focused on the synthesis of a new manganese-based metal-organic framework and the investigation of its application aspects. A Mn-MOF nanostructure, namely UoB-4, was prepared using a Schiff base organic linker (H₂bbda: 4,4'-[benzene-1,4-diylbis(methylylidenenitrilo)]dibenzoic acid) under ultrasound irradiation. The structure of the as-synthesized UoB-4 was characterized *via* PXRD, TGA, CHNO, ICP, TEM, BET, and FTIR techniques. The catalytic performance of UoB-4 was evaluated in the reactions of Hantzsch for the synthesis of 1,4-dihydropyridines and alcohol oxidation. The products of both reactions were obtained with high yields under green conditions. A recycling study of UoB-4 revealed that it can be used as a recoverable stable heterogeneous catalyst without significant loss in performance. In the next step of this study, the efficiency of UoB-4 was evaluated, showing the biological potential as an antibacterial agent. Its antibacterial activity was tested against *Bacillus cereus* and *Escherichia coli in vitro* by determining the diameter of the inhibition zone in the disc diffusion method. The results indicated the acceptable activity of UoB-4 was greater towards Gram-positive bacteria (*B. cereus*) compared to that towards Gram-negative one (*E. coli*). These results open the mentality that there is the synthesis possibility of Mn-based MOFs with various application aspects and high performance.

different applications of MOFs, the catalytic activity is the most rapidly growing one. The main reasons for this are the intrinsic properties of MOFs such as high density, uniform dispersion of active sites, and readily accessible active sites due to the highly porous structure that greatly facilitates the diffusion and transport of the substrates and products. Therefore, MOFs effectively incorporate the advantages of both homogeneous and heterogeneous catalysts, with amazing reaction efficiency and recyclability.⁶

Multi-component reactions in one-pot syntheses play an important role in modern synthetic chemistry since they not only reveal a higher selectivity and atom economy, but also allow the construction of molecules of more varieties and complexities.⁷ Furthermore, multicomponent reactions are accompanied by many advantages such as the simple procedure, energy saving and reduced waste.^{8,9} Multicomponent reactions in making heterocyclic compounds are powerful tools in the drug-discovery process as they can offer the suitable synthesis of libraries of drug-like compounds in a single procedure.¹⁰ The one-pot multicomponent condensation reaction between aldehyde aromatic, β -ketoesters and ammonium acetate has been recognised as a suitable synthesis method of 1,4-dihydropyridine (1,4-DHP). They have attracted remarkable interest because of their promising pharmacological and therapeutic activities



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^a Department of Chemistry, Faculty of Sciences, University of Birjand, Birjand, 97175-615, Iran. E-mail: gbagherzade@gmail.com, bagherzade@birjand.ac.ir; Fax: +98 56 32345192; Tel: +98 56 32345192

^b Department of Biology, Faculty of Sciences, University of Birjand, Birjand, 97175-615, Iran

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such as serving as integral backbones of several calcium channel blockers, vasodilation, bronchodilation, and geroprotective, hepatoprotective, and antidiabetic functions.^{11,12} In addition, 1,4-DHPs are already commercial products and among the most widely used drugs (e.g. amlodipine,¹³ isradipine,¹⁴ lacidipine,¹⁵ nitrendipine,¹⁶ nifedipine¹⁷ and nimodipine B18). Due to the aforementioned advantages of 1,4-DHPs in the biological and chemical worlds, many efforts have already been made toward the synthesis of these compounds.¹⁹⁻²¹ Nevertheless, the optimization of 1,4-DHP preparation can be important and should be predominantly based on the development of more effective and selective catalysts. According to the extraordinary properties of MOFs, they can help a lot for the progress in the synthesis of useful chemical compounds; however, there have been only a few reports about the usage of MOFs as heterogeneous catalysts for the preparation 1,4-DHPs. In 2014, Morsali and co-workers reported the utilization of IRMOF-3 as a catalyst in the Hantzsch condensation reaction for the synthesis of 1,4-DHPs.²² Recently, the same research group has also presented their studies on the use of Cd-MOFs as reusable catalysts.²³ In another search, Hajiashrafi et al. have developed a new catalytic system based on Er-MOFs that displayed excellent selectivity and good yield for this reaction.²⁴ With respect to the significance of 1,4-DHPs as pharmaceutical compounds and the few reports on MOFs that have been used for their preparation, this research work aimed at the introduction of a new MOF as a heterogeneous catalyst for the improvement of 1,4-DHP synthesis methods. Therefore, we have herein synthesized novel, flexible, microporous Mn-MOF nanostructures (UoB-4) under ultrasound irradiation as a procedure, which better meets the ecological requirements. In addition, the results indicated that Mn-MOFs can be used as suitable, efficient and green catalysts for the Hantzsch condensation of aldehydes and β-ketoesters with ammonium acetate without any solvent, salts and additives, with good to excellent yields of DHPs.

In the course of our continuing investigation on the catalytic activity of MOFs, the successful use of different MOFs with a Schiff base linker to catalyze alcohol oxidation reactions under green conditions was reported.^{25–27} In this study, the catalytic use of UoB-4 nanostructures has also been explored in the catalytic oxidation of primary/secondary alcohols to afford corresponding carbonyl compounds with a high percentage of conversion and good selectivity. The obtained results exhibited that UoB-4 nanostructures are high-efficiency recyclable versatile heterogeneous catalysts for the Hantzsch and alcohol oxidation reactions under mild and green conditions.

As mentioned above, the excellent properties of MOFs enhance their application potentials in various fields. Our interest in expanding the functional aspects of MOFs led to the investigation of UoB-4 efficiency in the biomedical field as an anti-bacterial reagent. For this purpose, commercially available strains of *Bacillus cereus* (Gram-positive) and *Escherichia coli* (Gram-negative) were used, and the anti-bacterial performance of UoB-4 nanostructures was investigated based on the standard zone of the inhabition test. The results indicated that UoB-4 exhibits a strong antibacterial activity against the growth of microorganisms.

2 Experimental

2.1 Materials and measurement

All the chemicals were obtained from a commercial source and used without further purification. The ligand (H₂bdda: 4,4'-[benzene-1,4-diylbis-(methylylidenenitrilo)]dibenzoic acid) was synthesized according to our reported procedure.²⁵ Elemental analyses of C, H, N, and O were performed using a PerkinElmer CHNS-O elemental analyzer. Inductively coupled plasma atomic emission spectroscopic (ICP-AES) analysis was conducted using an OPTIMA 7300DV. Thermogravimetric analysis (TGA) was obtained using a Shimadzu Thermoanalyzer between 30 and 710 °C at a heating rate of 10 °C min⁻¹ in a nitrogen atmosphere. Infrared (IR) samples were prepared as KBr pellets, and the spectra were recorded in the range of 400–4000 cm^{-1} using a NICOLET system. Transmission electron microscopic (TEM) analysis was performed using a Philips CM120 electron microscope. The Brunauer-Emmett-Teller (BET) surface area and pore sizes of the UoB-4 were measured using N2 adsorption/desorption isotherms at 77 K using a Belsorp mini II instrument. Powder X-ray diffraction (PXRD) was conducted using an X'Pert Pro MPD diffractometer equipped with a Cu-K α (λ = 1.54060 Å) radiation source between $2\theta = 2^{\circ}$ and $2\theta = 50.0^{\circ}$. The progress of the reactions and purity of the products were analysed by TLC on silica gel polygram SILG/UV254 plates. ¹H-NMR (CDCl₃) spectra were recorded using a Bruker UltraShield[™] spectrometer at 400 MHz.

2.2 Synthesis of nanoscale Mn-MOFs (UoB-4)

At first, NaOH 10% (1 mL) was added to an H₂bdda (0.372 g, 1 mmol) solution in deionized water (20 mL), whereupon the system was stirred for 5 minutes at room temperature to obtain a clear yellow solution. Then, a solution of Mn(acac)₂ (0.704 g, 2 mmol) in deionized water (10 mL) was added dropwise to the obtained mixture under ultrasonic irradiation at room temperature for 15 minutes and was kept under the same condition for 30 minutes. The resulting green precipitate was collected by centrifugation and washed three times with ethanol. The obtained products were dried in an oven at 100 °C and made Mn₃(bdda)₂ acac₂·5H₂O. Anal. calcd for: C: 54.22%; H: 4.8%; N: 4.68% and Mn: 13.8%; found: C: 54.35%; H: 3.8%; N: 5.48% and Mn: 13.79%.

2.3 The general catalytic Hantzsch reaction procedure

A mixture of aldehyde (1.0 mmol), ammonium acetate (1.2 mmol), 1,3-dicarbonyl (2.0 mmol), and UoB-4 (1.5 mol%) without any organic solvents as green conditions was stirred at 65 °C for an appropriate time. The reaction progress was surveyed by thin-layer chromatography (TLC) using EtOAc/n-hexane (1:3) as the eluent. After completion of the reaction, the catalyst was removed by centrifugation. A pure product was obtained by recrystallization from alcohol–water. The products were identified by comparing their melting points with those

previously reported because the products are known compounds. The spectral data for the selected compounds are as follows:

Diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate. Pale yellow solid; IR (KBr, cm⁻¹) ν : 3340 (N–H str), 3034 (Ar–H), 2953 (C–H str of CH₃), 1755 (C=O, ester), 802 (Ar–H). ¹H NMR (400 MHz, CDCl₃): δ = 7.30–7.28 (2H, m, Ar–H), 7.23–7.19 (2H, m, Ar–H), 7.15–7.11 (1H, m, Ar–H), 5.58 (1H, brs, NH), 5.00 (1H, s, aryl –CH), 4.15–4.03 (4H, m, –*CH*₂CH₃), 2.34 (6H, s, –CH₃), 1.23 (t, *J* = 7.2 Hz, 6H, –CH₂*CH*₃); ¹³C NMR (100 MHz, CDCl₃) δ : 167.6, 147.7, 143.7, 128.0, 127.8, 126.1, 104.2, 59.7, 39.6, 19.6, 14.2.

Diethyl-4-(4-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate. Pale yellow solid; IR (KBr, cm⁻¹) ν : 3352 (N–H str), 3026 (Ar–H), 2961 (C–H str of CH₃), 1742 (C=O, ester), 823 (Ar–H). ¹H NMR (400 MHz, CDCl₃) δ : 7.18 (2H, d, *J* = 8.4 Hz, Ar–H), 6.73 (2H, d, *J* = 8.4 Hz, Ar–H), 5.99 (1H, s, NH), 4.92 (1H, s, aryl –CH), 4.14–4.02 (4H, m, –*CH*₂CH₃), 3.73 (3H, s, –OCH₃), 2.29 (6H, s, –CH₃), 1.22 (6H, t, *J* = 7.2 Hz, –CH₂*CH*₃); ¹³C NMR (100 MHz, CDCl₃) δ : 167.7, 157.8, 143.8, 140.3, 128.9, 113.1, 104.1, 59.6, 55.0, 38.6, 19.4, 14.2.

Diethyl-4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate. Pale yellow solid; IR (KBr, cm⁻¹) ν : 3332 (N–H str), 3074 (Ar–H), 2942 (C–H str of CH₃), 1741 (C==O, ester), 837 (C–Cl), 787 (Ar–H). ¹H NMR (400 MHz, CDCl₃) δ : 7.21 (2H, d, J = 8.4 Hz, Ar–H), 7.16 (2H, d, J = 8.4 Hz, Ar–H), 6.24 (1H, s, NH), 4.96 (1H, s, aryl –CH), 4.14–4.02 (4H, m, –*CH*₂CH₃), 2.28 (6H, s, –*C*H₃), 1.21 (6H, t, J = 7.2 Hz, –*C*H₂*C*H₃); ¹³C NMR (100 MHz, CDCl₃) δ : 167.5, 146.3, 144.3, 131.5, 129.3, 127.8, 103.4, 59.7, 39.1, 19.3, 14.1.

2.5 The general catalytic alcohol oxidation reaction procedure

In a typical experiment, UoB-4 nanostructures (3 mol%) and TBHP (2 mmol) were placed in a vessel containing benzyl alcohol (1 mmol) under solvent-free conditions. The reaction mixture was vigorously stirred at 45 °C. Upon reaction completion, monitored by TLC, the catalyst was removed from the mixture of reaction by centrifugation. The products were purified on a silica gel plate to give pure products. For the identification of the final products, their physical data were compared with those of authentic samples, because all of them are known.

2.6 Anti-bacterial activity

The antibacterial test was conducted based on the disk diffusion test²⁸ to examine the antibacterial performance of UoB-4

nanostructures against *Bacillus cereus* (ATCC 13061) and *Escherichia coli* (ATCC 25922DQ) as model Gram (+) and Gram (-) bacteria. First, the bacterial strains were cultivated on nutrient agar plates at 37 °C for 24 h and then stored at 4 °C for future use. Solid agar nutrient plates were prepared by dissolving 15.0 g L⁻¹ agar powder, 5.0 g L⁻¹ tryptone, 2.5 g L⁻¹ yeast extract, and 1.0 g L⁻¹ glucose in deionized water in a 500 mL capacity Erlenmeyer flask. The obtained mixture was heated and stirred until the agar dissolved. For adjusting the pH of the solution to 7.0 ± 0.1, sodium hydroxide or hydrochloric acid was utilized. After that, the sterile nutrient agar was poured, cooled to room temperature, and then was autoclaved at 121 °C under a pressure of 15 psi for 20 minutes.

A fresh bacterial suspension of *Bacillus cereus* and *Escherichia coli* (200 mL, containing 5×10^7 colony-forming units (CFU) mL⁻¹) was spread on the prepared agar plates. The plates were dried, and the holes (7 mm diameter) were punched with the sterile tip over them. UoB-4 (1 mg) was directly disposed of onto the holes of agar plates, after which the plates were incubated at 37 °C for 48 h. The antibacterial activity was observed after incubating based on the inhibition surrounding the spotted compound. The growth inhibition zone was reported in centimeters, and the procedure was repeated two times.

3 Results and discussions

3.1 Syntheses and characterization

Ultrasound irradiation was used as a facile procedure for the synthesis of UoB-4 nanostructures. The reaction of manganese(π) acetylacetonate with H₂bdda, which was synthesized according to the procedure reported earlier, in the presence of water and NaOH leads to the formation of [Mn₃(bdda)₂acac₂·5H₂O] (Scheme 1).

Thermogravimetric analysis (Fig. 1a) indicated that dehydration of UoB-4 nanostructures occurred at 300 $^{\circ}$ C with a weight loss of 6.66% (calcd: 6.53%). The weight loss has been followed by the expulsion of organic components.

 N_2 adsorption-desorption measurement was performed to evaluate the textural properties of UoB-4 nanostructures, and the results are shown in Fig. 1b. The structure of UoB-4 exhibits the type IV isotherm with an H_1 hysteresis loop, which is the typical characteristic of the material with cylindrical mesopores.



Scheme 1 Synthesis of UoB-4 nanostructures under ultrasonic irradiation in water as a solvent.



Fig. 1 (a) TGA curve; (b) N_2 adsorption-desorption isotherms; and (c) pore width of UoB-4 nanostructures.

Through the N₂ isotherm, the specific surface area and pore value were determined as 127 m² g⁻¹ and 0.17 cm³ g⁻¹, respectively. Furthermore, the pore-size distribution, calculated by Barret–Joyner–Halenda (BJH), revealed an approximately narrow pore size distribution in the range of 2–10 nm with a peak maximum of 8 nm (Fig. 1c).

The morphology of UoB-4 nanostructures was investigated using the TEM images (Fig. 2a). The images exhibit that nanoparticles are framework structures with uniform size and morphology. Moreover, it can be obviously shown that the UoB-4 nanostructures are monodispersed without any amorphous components. The TEM images were used to draw the particle size distribution, based on which the average diameter of nanostructures was obtained to be 59 nm (Fig. 2b).

The XRD pattern of UoB-4 nanostructures is illustrated in Fig. 3. The sharp reflections appearing at the low angel $(2\theta < 10)$ confirmed a high degree of mesoscopic ordering. It is noteworthy that the XRD pattern of UoB-4 is similar to the reported simulated pattern of IRMOF-74.²⁹ Therefore, it can be concluded that both the structures (UoB-4 & IRMOF-74) are isostructural.

More information about the structure of UoB-4 nanostructures was achieved using FT-IR spectra (Fig. 4). A broad and strong peak at 3400 cm⁻¹ is attributed to the stretching vibrations of the coordinated water molecules. Moreover, the band at 1690 cm⁻¹ established the presence of the coordinated acetylacetonate ligand. The asymmetric stretching of carboxylate groups (-COO-) of UoB-4 appeared at 1595 and 1530 cm⁻¹ and the symmetric stretching of carboxylate groups appeared at 1399 cm⁻¹. The difference in the symmetric and asymmetric stretching vibrations of carboxylate groups ($\Delta \nu$) can be applied



Fig. 2 (a) TEM image of the 4UoB-4 nanostructures and (b) particle size distribution histogram.



Fig. 3 XRD pattern of UoB-4 nanostructures.

for determining the coordination modes of carboxylate groups to metal.³⁰ Thus, the carboxylate groups coordinated to Mn as a bridging mode based on the obtained $\Delta \nu$ values. The O–H vibration of adsorbed water and the C–O stretching appeared around 3350 and 1172 cm⁻¹, respectively.

3.2 Catalytic activity

3.2.1 Hantzsch reaction. The presence of azomethine group and metal–carboxylate in the UoB-4 nanostructure caused to investigate its behavior as a catalyst in the synthesis of Hantzsch 1,4-dihydropyridines (Scheme 1). To optimize the conditions of the catalytic reaction, benzaldehyde, ethyl aceto-acetate and ammonium acetate were selected as model substrates. Several parameters such as the nature of solvent, temperature and the amount of catalyst were investigated and the obtained results are presented in Table 1 (Scheme 2).

First, the effect of the nature of the solvent on the yield of 1,4-DHPs was studied in the presence of UoB-4 in various solvents (entries 1–4). The model reaction occurred more efficiently under solvent-free conditions with respect to the solvent medium, as the catalysts and reagents are in more significant proximity to each other when a solvent is not employed. Consequently, performing the reaction under these conditions is accompanied by advantages such as simple reactors, and simple and efficient workup procedures that are often more environmentally friendly. Next, the effect of the



Fig. 4 (a) FTIR spectrum of UoB-4 and (b) the suggested geometry around the Mn center.

Table 1 Screening of factors in the synthesis of 1,4-DHPs via theHantzsch reaction by UoB-4 nanostructures^a

Entry	Solvent	Temp. (°C)	Catalyst (mol%)	$\operatorname{Yield}^{b}(\%)$	
1	H_2O	65	1.5	43	
2	EtOH	65	1.5	54	
3	EtOAc	65	1.5	40	
4	_	65	1.5	97	
5	_	65	_	10	
6	_	65	0.5	30	
7	_	65	1	44	
8	_	65	1.5	97	
9	_	65	2	97	
10	_	r.t.	1.5	40	
11	_	45	1.5	60	
12	_	65	1.5	97	
13	_	80	1.5	98	

^{*a*} Reaction conditions: benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol), urea (1.2 mmol), 30 min. ^{*b*} Yields of product isolated.



Scheme 2 Synthesis of 1,4-DHP by UoB-4 nanostructures.

amount of catalysts on the yield of 1,4-DHPs was studied (entries 5–9). Initially, when the model reaction was carried out in the presence and absence of UoB-4 nanostructures, the yield of product was 97% and 10%, respectively. The results indicated that UoB-4 as a catalyst is very effective to promote the given reaction. Upon increasing the amount of UoB-4 from 0.5 to 1.5 mol%, the yield of the product was improved, whereas a further increase of up to 2 mol% had no impressive effect on it. The effect of temperature on the reaction efficiency was also investigated by carrying out the model Hantzsch reaction using optimal amounts of UoB-4 at different temperatures (entries 10–13). The product yield increased from 40 to 97% in the presence of UoB-4 when the temperature of the model reaction changed from room temperature to 65 $^{\circ}$ C. However, when the reaction temperature was further increased to over 85 $^{\circ}$ C, the reaction efficiency did not change significantly.

With the experimental results in hand, the scope of the Hantzsch reaction was developed using different aldehydes with electron-donating/withdrawing substituent groups and β -ketoesters under optimized reaction conditions. All reactions proceeded smoothly to afford the corresponding 1,4-DHPs within the short reaction time in good to high yields (Table 2).

 Table 2
 Preparation of 1,4-DHPs via the Hantzsch reaction in the presence of the UoB-4 nanocatalyst



					$M.p.^{b}$ (°C)	
Entry	R_1	\mathbf{R}_2	Time (min)	Yield ^a (%)	Found	Reported
1	Н	Et	30	97	157-158	157-159
2	$4-NO_2$	Et	20	96	134-136	135-136
3	4-CN	Et	20	94	165-166	165-167
4	4-Me	Et	30	85	139-141	139-140
5	4-OMe	Et	40	90	143-145	145
6	4-Cl	Et	35	93	144 - 145	144-146
7	$2 - NO_2$	Et	25	91	168-170	169
8	2-OMe	Et	40	81	156-158	142
9	Ph	Me	30	95	195-197	196-197
10	$4-NO_2$	Me	25	97	168-169	168
11	4-CN	Me	25	96	226-227	225-227
12	4-Me	Me	35	84	172-174	175
13	4-OMe	Me	35	81	186-188	188
14	4-Cl	Me	30	90	197–199	198

 a Isolated yields. b The physical data of all products were compared with those reported in the literature. 24,31,32

It could be noticed that the aromatic aldehyde electronwithdrawing substituent groups (NO2, CN) were fairly more active than the electron-donor ones (OMe, Me) in terms of the reaction time or the product yield. It is also notable that the sterically demanding ortho-substituted aromatic aldehydes afforded the corresponding products in high yields (entries 7 and 8). These observations strongly establish excellent efficiency and powerful activity of the present catalyst for a broad range of substrates to produce different derivatives of 1,4-DHPs, which are applicable and important in drug chemistry.

The uniqueness of the UoB-4 nanostructures is rationalized based on their selectivity in 1,4-DHP synthesis over the other existing system, which is displayed by comparison with the previously reported homogeneous and heterogeneous catalysts (Table 3). The present catalyst exhibits a better catalytic activity in the Hantzsch reaction in terms of catalyst load, reaction time, temperature, and non-solvent conditions which afford the favorable conditions for green chemistry. In analogy, UoB-4 nanostructures are highly stable, reusable, and scalable catalysts for the synthesis of 1,4-DHPs.

3.2.2 Alcohol oxidation reaction. Our research group has dedicated the past few years to some catalytic oxidation reactions, particularly alcohol oxidation with MOF nanostructures as catalysts. According to the previous reports, the manganese complexes were proven to be efficient catalysts in alcohol oxidation.⁴¹⁻⁴⁴ However, UoB-4 nanostructures, as MOFs synthesized based on Mn, exhibited high catalytic activity. These findings indicated a possibility that UoB-4 could promote alcohol oxidation reactions. In an attempt to expand the application of MOFs, UoB-4 nanostructures were employed to the oxidation of a series of primary and secondary alcohols.

First, benzyl alcohol was chosen as a model substrate to screen the optimal conditions, and the main results are summarized in Table 4. It should be noted that no significant progress of reaction took place without the manganese catalyst or in the presence of the precursor salt. Furthermore, benzyl alcohol oxidation was performed in various solvents under solvent-free conditions (entries 1-5). The best result based on the product yield was obtained under solvent-free conditions, which is in line with the green chemistry. The reason for this observation could be the exposed catalytic sites under solventfree conditions. Then, the model reaction was carried out under solvent-free conditions at room temperature, 45 and 65 °C

Table 4 Screening reaction conditions^a

			JoB-4 (x mol%) TBHP (y mmol)		≥0
Entry	Solvent	Temp. (°C)	Catalyst (mol%)	TBHP (mmol)	$\operatorname{Yield}^{b}(\%)$
1	H_2O	45	3	2	23
2	EtOH	45	3	2	70
3	EtOAc	45	3	2	50
4	CH_3CN	45	3	2	63
5	_	45	3	2	90
6	_	r.t.	3	2	47
7	—	45	3	2	90
8	_	65	3	2	70
9	_	45	1	2	45
10	_	45	2	2	70
11	_	45	3	2	90
12	_	45	4	2	91
13	_	45	3	0.5	32
14	_	45	3	1	50
15	_	45	3	1.5	72
16	_	45	3	2	90
17	_	45	3	3	70

^a Reaction conditions: benzyl alcohol (1 mmol), 75 min. ^b Yields of product isolated.

(entries 6-8). The product yield was increased up to 45 $^{\circ}C$ and was decreased significantly at 65 °C. The reduction in the product yield could be due to the decomposition of TBHP to molecular water and tert-butanol in the presence of UoB-4 at evaluated temperatures. As a result, 45 °C was selected the as optimum reaction temperature. To determine the amount of catalysts, the benzyl alcohol oxidation was performed with a different amount of UoB-4 at 45 °C without any solvent. Increasing the amount of the catalyst up to 3 mol% led to improved yields, but the more increasing of it had no important effect on the product yield (entries 9-12). Further investigation disclosed that the amount of oxidizing agents is crucial to the product yield (entries 13-17). When the oxidation of the model reaction was carried out using 0.5, 1, 1.5 and 2 mmol of tert-butyl hydroperoxide, the yield of the product increased as the concentration of tert-butyl hydroperoxide increased. However, using more than 3 mmol oxidizing agents had the opposite effect on the product yield that it could be due to over-oxidation.

The ability of different single oxygen donors such as NaIO₄, H₂O₂, oxone, and TBHP was examined in the oxidation of

Table 3	Comparison	of the	catalytic	activity	of	UoB-4	with	formerly	reported	catalysts
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Entry	Catalyst	Time	Catalyst amount	Temperature	Solvent	Yield (%)	Ref.
1	Ce(SO ₄) ₂ ·4H ₂ O	15 min	4 mol%	R.T.	EtOH/H ₂ O	60	33
2	PdNiRu@GO	45 min	6 mg	70 °C	DMF	93	34
3	Zr-SBA-16	3 h	6 mmol%	80 °C	EtOH	77	35
4	SBA-SO ₃ H	25 min	10 mol%	R.T.	EtOH	86	36
5	Triton-X-100	2.5 h	10 mol%	R.T.	H_2O	95	37
	Fe-C-O-Mo alloy	2.5 h	0.1 mol%	Reflux	EtOH	96	38
6	H5BW12O40	45 min	10 mol%	Reflux	EtOH	94	39
7	Er-MOF	4 h	40 mg	70 °C	EtOH	92	24
8	IRMOF-3	5 min	4 mol%	Reflux	Solvent free	90	22
9	MIL-101-SO ₃ H	8 h	20 wt%	60 °C	EtOH	99	40
10	UoB-4	30 min	1.5 mol%	65 °C	Solvent free	97	This work

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 Table 5
 Screening the nature of oxidants^a

Entry	Oxidant	Time (min)	$\operatorname{Yield}^{b}(\%)$
1	H_2O_2	75	63
2	Oxone	120	20
3	$NaIO_4$	90	23
4	TBHP	75	90

 a Reaction conditions: benzyl alcohol (1 mmol), oxidant (2 mmol), UoB-4 (3 mol%), S. F., 45 $^\circ C.$ b Yields of product isolated.

benzyl alcohol in the presence of UoB-4 under solvent-free conditions at 45 $^{\circ}$ C. The results indicated that TBHP is the best oxygen source because of its good oxidation conversion (Table 5).

After the optimized conditions were established, this catalytic system was applied for the oxidation of a wide variety of primary and secondary alcohols to the corresponding carbonyl compounds. As shown in Table 6, good to excellent yields were accomplished in both primary and secondary alcohols. Clearly, the electron nature of the substituents on the aromatic ring of primary alcohols displayed no obvious effect on this transformation, because the products were obtained in high yields.

3.2.3 Reusability. To further evaluate the potential for industrial applications of UoB-4 nanostructures, their recyclability was examined for use with successive batches of fresh benzyl alcohol (for alcohol oxidation reaction)/benzaldehyde, ammonium acetate and 1,3-dicarbonyl (for the Hantzsch reaction). Both reactions were performed using optimized conditions. After the reaction completion, the nanostructures were recovered and then used as catalysts for the fresh batch of substrates. This procedure was repeated for a total of five runs using the same nanostructures, and the product yields were obtained from each run. However, the reaction yields progressively decreased, but they remained appropriate for both reactions even after five reuse cycles of UoB-4 nanostructures. FT-IR analysis of reused UoB-4 indicated that there is no significant change in terms of the internal structure (Fig. 5).

3.3 Antibacterial activity (performance)

In the last decades, antibacterial agents have attracted considerable attention because of the appearance of contagious diseases caused by pathogenic bacteria. Moreover, researchers have recently increased their studies to find out new antibacterial agents due to the increased resistance of bacteria to old antibacterial compounds.45 Despite the widespread use of MOFs in storage/adsorption gas and drug delivery, the usage of them as antibacterial reagents has rarely been reported.46 MOFs, with unique properties such as long-term stability, and high thermal and optical resistance, are very suitable candidates for use as antibacterial compounds. Therefore, we decided that the antibacterial efficiency of UoB-4 nanostructures should be investigated. As a proof of concept, Gramnegative bacteria, Escherichia coli, and Gram-positive bacteria, Bacillus cereus, were selected as model microorganisms at a concentration of 80 µL by a disk diffusion susceptibility test. The diameters of the inhibition zones against E. coli and B. cereus were approximately 180 and 280 mm, in the presence





 a Reaction conditions: substrate (1 mmol), TBHP (2 mmol), UoB-4 (3 mol%), S. F., 45 $^\circ \rm C.$ b Yields of product isolated.



Fig. 5 (left) Catalyst recyclability test for Hantzsch and alcohol oxidation reactions. (right) FTIR spectra of UoB-4: (a) fresh, (b) after Hantzsch reaction; and (c) after alcohol oxidation.



Fig. 6 Agar plate diffusion experiment to estimate the antibacterial activity on (right) *B. cereus*, and (left) *E. coli* with UoB-4 nanostructures.

of UoB-4 nanostructures, respectively (Fig. 6). This initial experiment revealed that UoB-4 nanostructures can be effective in this medium and can inhibit the growth of both used microorganisms. UoB-4 was more effective at inhibiting the growth of *B. cereus* compared to *E. coli*. It may be due to the difference of Gram-positive and Gram-negative bacteria in the susceptibility to UoB-4 nanostructures, because of their distinction in the cell structure, physiology, and metabolism.

4 Conclusion

In summary, new Mn-MOF, UoB-4, nanostructures have been successfully prepared and characterized, and their application aspects have been verified. UoB-4 demonstrated an excellent activity

as a nanocatalyst for the multi-component and oxidation reactions as the two type of different them. It exhibited high catalytic activity for the green synthesis of 1,4-DHPs under solvent free conditions via the Hantzsch reaction. In addition, UoB-4 was demonstrated to be an efficient catalyst for the various primary/secondary alcohol oxidations when TBHP was used as an oxidant under solvent-free conditions. The catalysis protocols displayed in this work offer several advantages such as good to excellent yields, mild and green reaction conditions, short reaction times, and eco-friendly synthesis. These nanostructures showed suitable recyclability with no significant yield decrease after five runs. The antibacterial activity of UoB-4 was also examined as another applied aspect of UoB-4, which revealed a strong activity against both Gram-positive (B. cereus) and -negative (E. coli) bacteria. Given its performance, UoB-4 nanostructures, as a substance that is easily synthesized, can be effective materials for various applications.

Conflicts of interest

There are no conflicts to declare.

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