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Synthesized of mixed-metal MOF comprising two ligands used as a heterogeneous catalyst for Knoevenagel condensation reaction

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Abstract

A new mixed metal–organic framework [$Zn_{0.5}$ $Cd_{0.5}$ (NH_2BDC) (4-bpmbp)].2DMF (NH_2BDC = 2-amino terephthalate; 4-bpmbp = N4, N4'-bis (pyridine-4-ylmethylene)-biphenyl-4,4'-diamine DMF = N,N-dimethylformamide) (**Zn-Cd-MOF**) has been synthesized under solvothermal conditions using Cd^{2+} and Zn^{2+} salt, NH_2BDC as a rigid ligand and 4-bpmbp as pillar ligand. The material was characterized by Fourier transform infrared (FT-IR), powder X-ray diffraction (PXRD), and inductively coupled plasma (ICP) techniques. Furthermore, the catalytic behavior of Zn-Cd-MOF toward the Knoevenagel condensation reaction was investigated and good catalytic capability was achieved.

Keywords: MOF, mixed metal-organic framework, catalyst, Knoevenagel condensation.

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Introduction

Coordination chemistry is a new kind of molecular material and the mainstream of inorganic chemistry that has infinite metal ligand backbones connected by coordination bonds. It has a close correlation with other branches of chemistry like organic chemistry, materials chemistry, analytical chemistry, and so on [1, 2].

A series of crystalline advanced porous materials combined from metal ions as nodes held through coordination bonds by organic linkers, named Metal-organic frameworks (MOFs) [3,4]. Metal ions (like transition metals) are connected by organic ligands (like halides, carboxylates, phosphonates, cyanides, and pyridyl) [5,6,7].

Today, the synthesis and characterization of MOFs have been the subject of much research. Due to some advantages such as; high porosities and large surface areas [8], possess a wide range of application in various fields of science and technology.

MOFs can be prepared by several approaches such as solvothermal [8], hydrothermal [9], microwave-assisted [10], mechanochemical [11], electrochemical [12], and so on. The direct synthesis (solvothermal/hydrothermal) methods are the most commonly used process to design MOFs.

However, some characteristics like the limited electron transfer and chemical stability of MOFs during reaction restricted their applications, to address these restrictions, mixed-metal MOFs have been introduced. Mixed-metal MOFs are a new series of MOFs that have two (or more) various metal ions in their scaffolds, which could be synthesized by a one-pot reaction or post-synthetic procedure. In several applications (such as; gas sorption and storage, heterogeneous catalysis, luminescence and sensing, and so on.) the stability and affinity of MM-MOF improved and enhanced the active site of the material toward the primary monometallic MOF [13.14]. Because of these advantages, many research groups started studying MM-MOFs, for example; Zhang et al. introduced a series of bimetallic MOFs that were prepared with a one-pot synthesis method and showed that with induction of a second metal ion, the intrinsic characteristics (like thermal stability) could be tailored [15].

Usually, the oxygen-donor ligands lead to the two-dimensional (2D) sheet, and the N-donor ligands lead to the three-dimensional (3D) framework in the structure of pillared MOFs. According to this strategy, a wide range of MOFs with different topologies and tunable pores could be prepared. Previously, two pillared MOFs $\{[Zn(NH_2BDC)(4\text{-bpmbp})].2DMF\}n$ (TMU-25) and $\{[Cd(NH_2BDC)(4\text{-bpmbp})].2DMF\}n$ (TMU-26) were synthesized by Ghasempour *et al.* based on NH_2BDC and 4-bpmbp. Also, they reported the nano form of these frameworks. Interestingly, only one of them (TMU-25) was used as a heterogeneous catalyst for Knoevenagel condensation, because of its chemical stability in solvent media [16-17].

To enrich this field of research, we synthesized the mixed-metal MOF (MM-MOF) containing Zn and Cd with NH_2BDC and N4, N4'-bis (pyridine-4-ylmethylene)-biphenyl-4,4'-diamine ligand (4-bpmbp). Also, this novel MM-MOF was chemically stable in various solvent media, so it was used as an efficient and heterogeneous catalyst for the Knoevenagel condensation reaction.

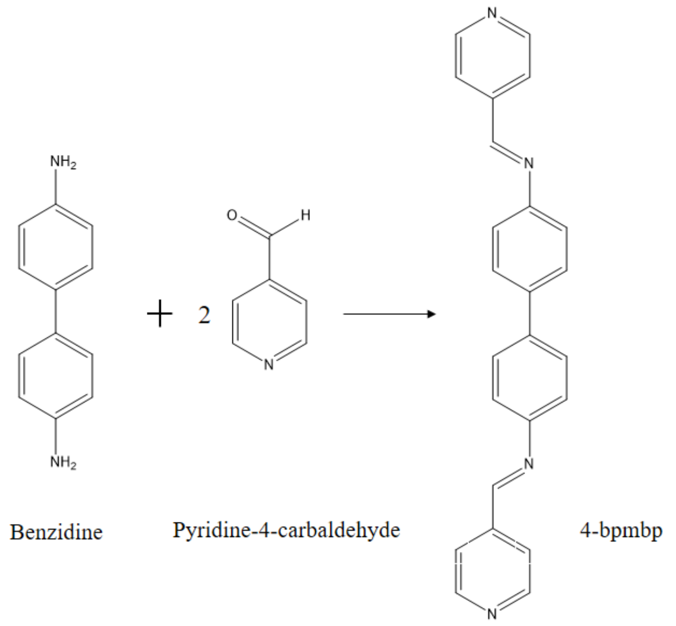
Experimental

Materials and characterization

All the reagents were purchased from commercial sources (Merck, Sigma Aldrich, and Biochem chemical companies) and used without purification. The elemental analysis (CHN) of Zn-Cd-MOF was obtained using a Thermo Finnigan FlashEA 1112 series. Powder X-ray diffraction (PXRD) patterns were collected by using a Rigaku Ultima iv diffractometer using Cu K_α radiation ($\lambda = 1.5406$ Å). FT-IR spectra were taken by Nexus 870 over the range of 600–4000 cm^{-1} and inductively coupled plasma (ICP) was performed by Perkin Elmer Analyst 100. Thermogravimetric analysis (TGA) was performed using a TGA Q50 thermogravimetric analyzer instrument (heating ramp of 20 °C/min) under an argon atmosphere. Gas chromatography (HP, Agilent 6890 N) equipped with a capillary column (HP-5) and a flame ionization detector (FID) was taken for quantitative analysis of products.

Synthesis of (4-bpmbp)

The N4, N4'-bis (pyridine-4-ylmethylene)-biphenyl-4, 4'-diamine ligand (4-bpmbp) was synthesized according to the previous reports without modification (Scheme 1). At first, 5 mmol of benzidine was dissolved in 15 mL ethanol, 10 mmol of pyridine-4-carbaldehyde was added to the previous solution, then two drops of formic acid were added to the mixture and it was stirred for 2 hours at ambient temperature. At last, the yellow solid was filtered and washed with ethanol [16].



Scheme 1. The synthesis procedure of as-synthesized 4-bpmbp.

Synthesis of Zn-Cd-MOF [$Zn_{0.5}$ $Cd_{0.5}$ (NH_2BDC)(4-bpmbp)].2DMF

The compound was synthesized by solvothermal reaction between $Zn(NO_3)_2.6H_2O$ (0.5 mmol), $Cd(NO_3)_2.2H_2O$ (0.5 mmol), and NH_2BDC (1 mmol) and 4-bpmbp (0.5 mmol), in DMF (15 ml). The mixture was stirred for 10 min at ambient conditions, transferred to a 20 ml Teflon-lined stainless-steel autoclave, and kept at 363 K for 72 h. After slow cooling to room temperature, crystals were collected by filtration, washed several times, and activated in a vacuum oven at 353 K.

In order to detect the amount of each metal ion, ICP analysis of Zn-Cd-MOF was conducted, and the Cd/Zn=1 of metal content was achieved.

Catalytic reaction

The Knoevenagel reaction is a famous condensation reaction for the preparation of the α,β-unsaturated ketone. This popular condensation is based on a nucleophilic addition of an active hydrogen compound to a carbonyl group, followed by the elimination of water. The final result of Knoevenagel is replacing a C=C double bond with a C=O bond (Scheme 2) [18].

The typical catalyst of this reaction is a basic amine, so amine functional MOFs such as $\{[Zn(Py_2TTz)(2\text{-}NH_2BDC)].(DMF)\}_n$ and $\{[Cd(Py_2TTz)(2\text{-}NH_2BDC)].(DMF)._{0.5}(H_2O)\}_n$ used as heterogeneous catalysts for this reaction [19].

Cd-Zn MOF has amine and imine functional groups, so could act as a heterogeneous catalyst with basic moieties.

General procedure for the catalytic Knoevenagel condensation reaction: the definite amount of activated Zn-Cd-MOF (as catalysts) was added to the solution of malononitrile (0.059 g, 0.9 mmol) and benzaldehyde (0.11 ml, 1.1 mmol) dissolved in 3 ml of solvent. Then the mixture was stirred at room temperature for specified times and the sampling was done. Finally, the filtrated samples were diluted with toluene (0.2 ml) and analyzed by gas chromatography (GC). At last, the filtrated catalysts were washed with methanol and dried for further analysis.

Scheme 2. Knoevenagel condensation reaction catalyzed by activated Zn-Cd-MOF.

In the first investigation, 30 mg of activated Zn-Cd-MOF catalyst was added to the malononitrile (0.059 g, 0.9 mmol) and benzaldehyde (0.11 ml, 1.1 mmol). As can be seen in Figure 1, while the reaction time was extended from 10 to 60 min, the conversion was increased from 76 to 92%.

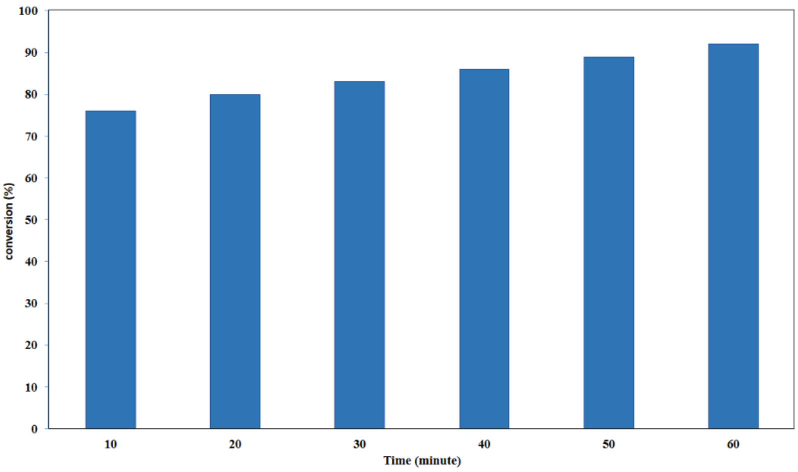


Figure 1. Time effect on Knoevenagel condensation reaction conditions: malononitrile (0.9 mmol), benzaldehyde (1.1 mmol), Zn-Cd-MOF catalyst (30 mg), Ethanol (3 ml), at room temperature.

The solvent effect is extremely significant in the Knoevenagel condensation reaction and also depends on the kind of catalysts, so different types of solvents were explored [20].

The results in Figure 2. Showed that the condensation occurred at all solvents in the presence of the activated Zn-Cd-MOF. The highest performance was achieved in protic solvents such as methanol and ethanol. Typically, polar solvents increase the solubility of precursor and ionic transition state and it improves the proton transfer of the catalyst. The Knoevenagel condensation conversion increased by polar solvents, these solvents enhanced the solubility of precursor and ionic transition state, so it caused the formation of a quasi-homogeneous media and improved the proton transfer of the catalyst [21, 22, 23].

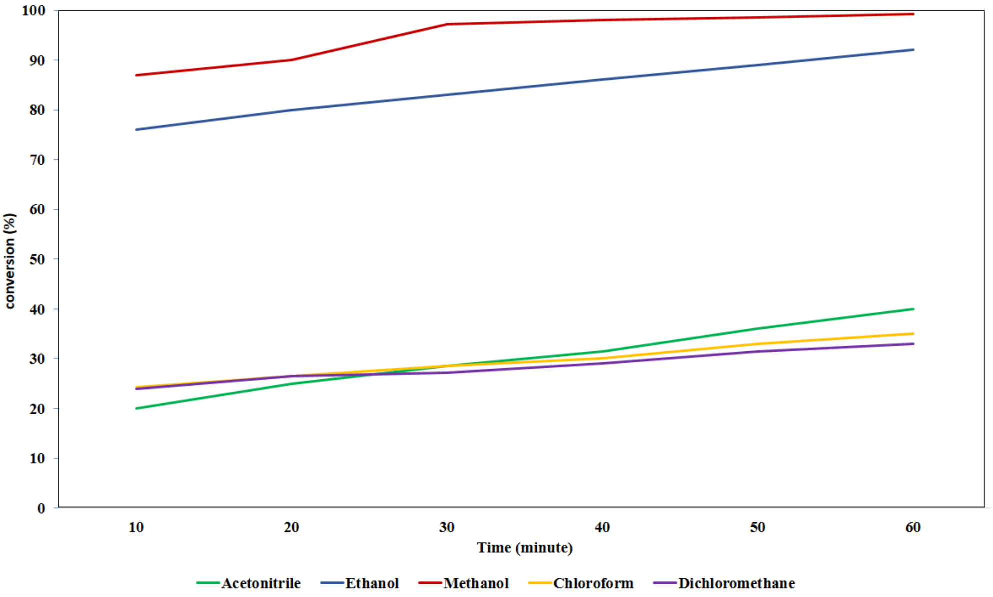


Figure 2. Knoevenagel condensation, Reaction conditions: malononitrile (0.9 mmol), benzaldehyde (1.1 mmol), Zn-Cd-MOF catalyst (30 mg), desired solvent (3 ml), at room temperature.

Finally, the effect of the catalyst amount was explored and the results are shown in Fig. 3. According to these results the reaction progress was insignificant by continuously increasing of catalyst from 10 to 30 mg, so 20 mg and 30 minutes were chosen as the optimized amount in methanol.

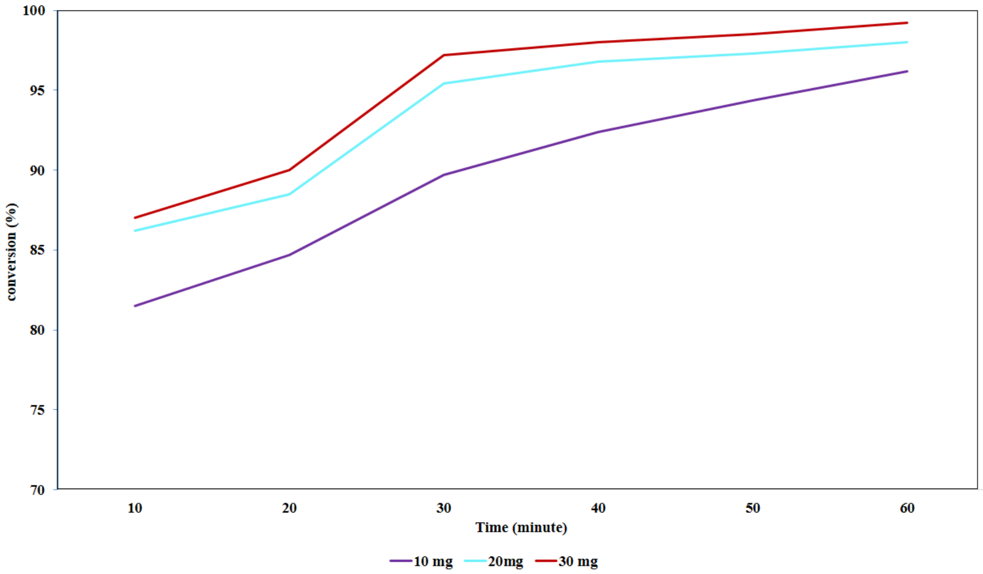


Figure 3. Knoevenagel condensation reaction over various amounts of Zn-Cd-MOF catalyst. Reaction conditions: malononitrile (0.9 mmol), benzaldehyde (1.1 mmol), and methanol (3 ml), at room temperature.

Since the recovery of the as-synthesized catalyst plays an important role in catalytic ability, the reused Zn-Cd-MOF was applied for Knoevenagel condensation in three runs. The results in Figure 4 suggested the catalytic stability and recyclability of **Zn-Cd-MO**F for Knoevenagel condensation after three steady reaction runs.

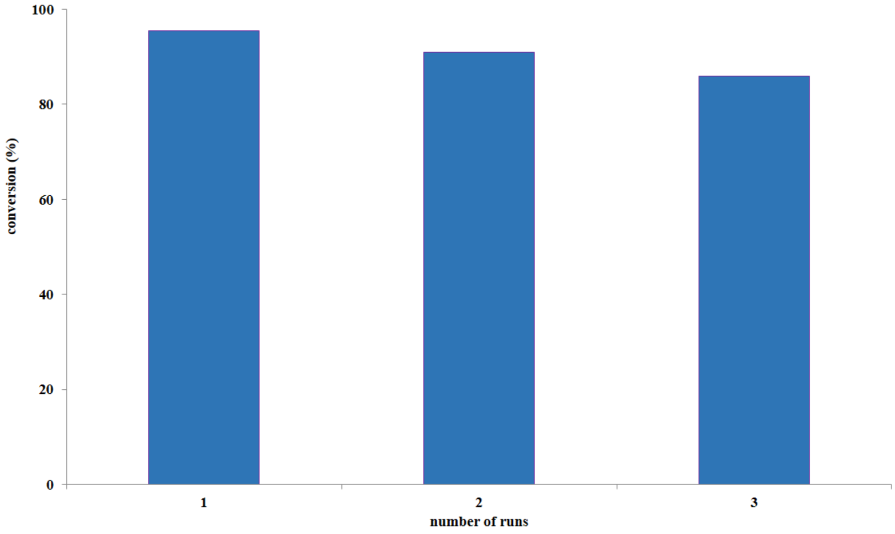
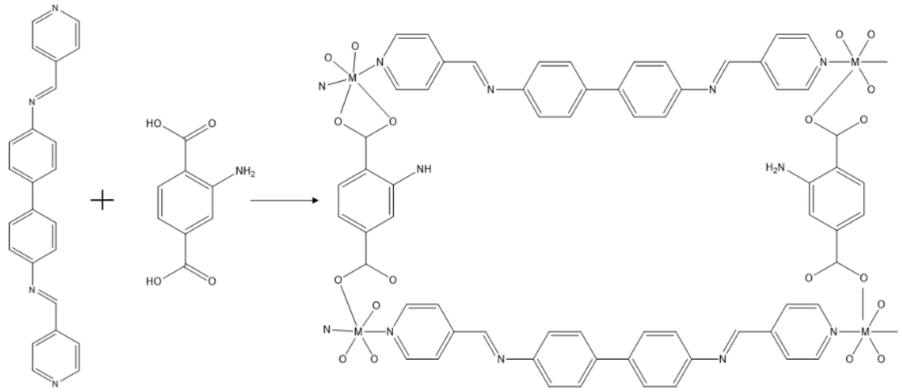


Figure 4. Knoevenagel condensation reaction using recycled Zn-Cd-MOF. Reaction conditions: catalyst (20 mg), malononitrile (0.9 mmol), benzaldehyde (1.1 mmol), and methanol (3 ml), in 30 minutes at room temperature.

Characterization

As shown in Scheme 1, 4-bpmbp was synthesized from the reaction of benzidine, and pyridine-4-carbaldehyde, in the presence of ethanol and formic acid. Afterward, the 4-bpmbp and NH_2BDC were used for the preparation of mixed metal MOF of Cd and Zn (Scheme 3).



Scheme 3. The synthesis procedure of Zn-Cd-MOF in the presence of metals (Zn and Cd).

The FT-IR spectra of as-synthesized 4-bpmbp and Zn-Cd-MOF are depicted in Fig. 4. The elimination of stretching vibration of N-H (at 3500 cm^{-1} corresponding to benzidine) and C=O (at 1740 cm^{-1} corresponding to pyridine-4-carbaldehyde) confirmed the coordination of two linkers in as-synthesized 4-bpmbp. Also, the good agreement between FTIR bonds of as-synthesized 4-bpmbp with reported bonds (which is summarized in Table 1) confirmed the accuracy of synthesis [16].

Table 1. Comparison of FTIR bonds of as-synthesized and reported 4-bpmbp.

As-synthesized 4-bpmbp (cm^{-1})	Reported 4-bpmbp (cm^{-1})
822	820
1210	1217
1408	1408
1490	1487
1605	1600
3419	3421

The presence of NH_2BDC in as-synthesized Zn-Cd-MOF is confirmed by symmetric and asymmetric vibrations of the carboxylate group which are observed as two strong bands at 1430 and 1565 cm^{-1}, respectively. Also, the bands at 3447 and 3330 cm^{-1} are related to the amine group in the NH_2-BDC ligand. Besides this, the weak band of Zn-Cd-MOF at 2925 cm^{-1} can be related to the aliphatic CH of the Schiff-base bond in the 4-bpmbp ligand. Finally, the desirable agreement between FTIR bonds of as-synthesized Zn-Cd-MOF with TMU-25 and TMU-26 which was reported previously is shown in Table 2 [16].

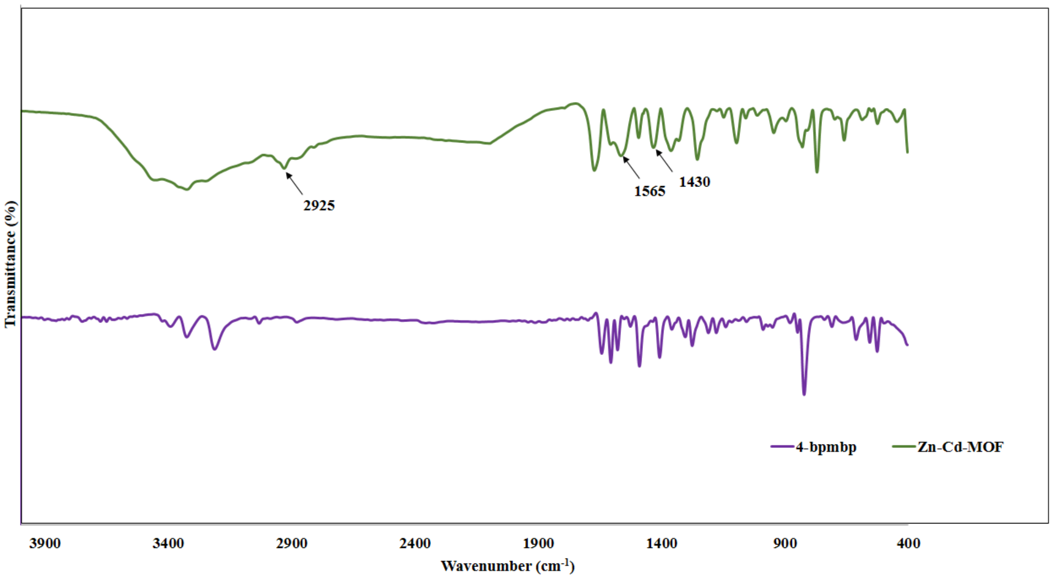


Figure 4. The FT-IR spectra for 4-bpmbp and as-synthesized Zn-Cd-MOF.

Table 2. Comparison of FTIR bonds of as-synthesized Zn-Cd-MOF with reported TMU-25 and TMU-26.

Reported TMU-25 (cm^{-1})	**Reported TMU-26 (cm^{-1})**	**As synthesized Zn-Cd-MOF (cm^{-1})**
659	660	660
767	773	770
830	831	830
1092	1092	1092
1254	1258	1255
1375	1371	1369
1427	---------	1429
1608	1557	1605
1672	1672	1672
2924	2929	2925
3445	3445	3445

The comparison between the PXRD pattern of as-synthesized Zn-Cd-MOF, simulated TMU-25, and simulated TMU-26 is shown in Fig. 4 [16]. The major peaks at 7.62, 8.73, 9.23, 11.15, and 17.81 are for the crystalline planes with Miller indices of (11-1), (210), (020), (300), (103), respectively. It clearly showed that the crystallinity of mixed metal MOF (Zn-Cd-MOF) was reduced however, the as-synthesized pattern confirmed the synthesis of Zn-Cd-MOF.

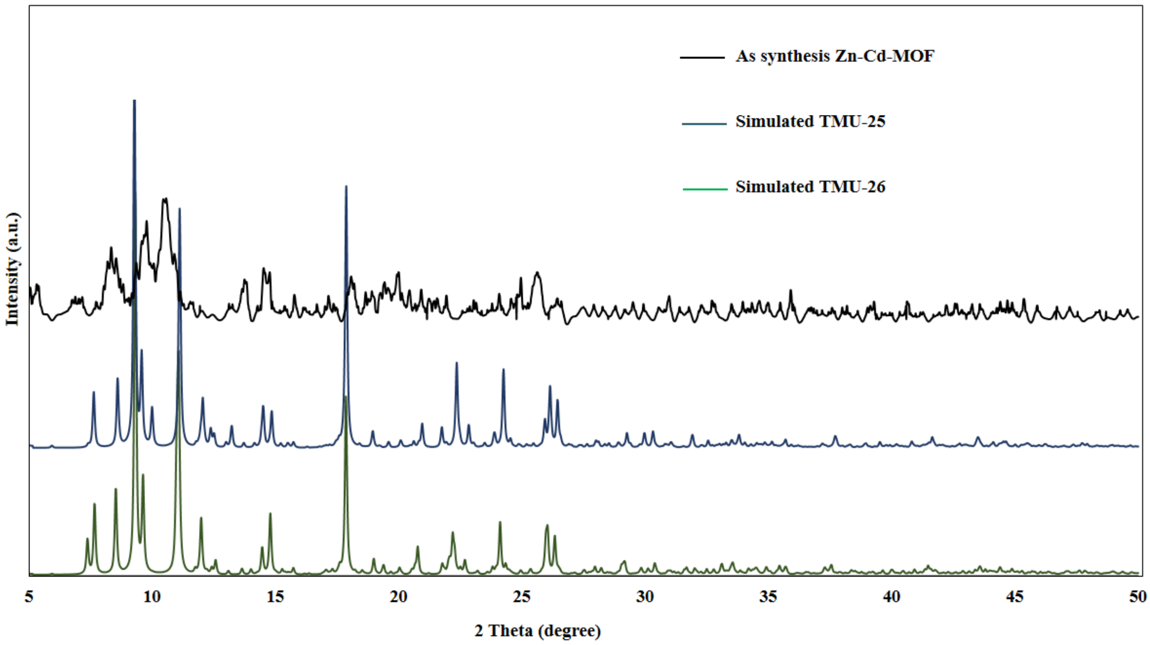


Figure 5. The PXRD patterns of simulated MOF-Zn and MOF-Cd and as-synthesized Zn-Cd-MOF.

Conclusion

Briefly, a long pillar ligand, N4,N4'-bis (pyridine-4-ylmethylene)-biphenyl-4,4'-diamine ligand (4-bpmbp) was prepared and used for the synthesis of mixed metal MOF (**Zn-Cd-MOF**). The novel as-synthesized **Zn-Cd-MOF** was chemically stable in various solvent media so could act as a heterogeneous catalyst. Also, it has basic moieties (amine and imine functional groups), and was used as a heterogeneous catalyst for Knoevenagel condensation reaction. Finally, different variable factors were optimized and the results reveal that 95.4% conversion was achieved after 30 minutes in the presence of 20mg of catalyst. The results reveal that it was a worthy and reusable catalyst for such a reaction.

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