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A 2D-layered Cd(II) MOF as an efficient heterogeneous catalyst for the **Knoevenagel reaction**

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ARTICLE INFO	A B S T R A C T
Keywords: 2D MOF Polytopic compartmental ligand Catalysis Heterogeneous Knoevenagel reaction	A Cd(II) coordination polymer based on a polytopic compartmental ligand was synthesized, and used as an efficient heterogeneous catalyst for the Knoevenagel reaction between benzaldehyde and malononitrile under mild reaction conditions. The solid catalyst was characterized using single crystal XRD, X-ray powder diffraction, SEM, TGA, UV diffuse reflectance, infrared spectroscopy and elemental analysis. The compound is a two-dimensional (2D) MOF with a grid structure. Topological analysis of the framework revealed that it is a 2,4-connected binodal net. The catalytic activity was tested between various benzaldehydes containing different substituents with malononitrile. The effect of reaction parameters such as solvent, time, reactant ratio and catalyst amount was investigated. Furthermore, the catalyst stability was examined through reusability experiments and it

is observed that the catalyst can be recycled at least five times without significant drop in its activity.

1. Introduction

Porous coordination polymers or metal organic frameworks (MOFs) are built from multi-functionalized organic molecules that are bound together by inorganic units. The advantageous features of these materials has caught increasing attention in recent years and turns out to be one of the fastest growing areas in synthetic chemistry and materials science. Compared to conventionally used porous inorganic materials, these metal-organic structures exhibit the potential for more flexible rational design, by controlling the size and the functionalization of the organic linkers and nodes [1,2]. Because of their unparalleled structural diversities, highly-ordered porous structure, high specific surface area and great structural designability, they have wide range of applications in the growing fields of molecular storage, drug delivery, sensing and catalysis [3–9].

The design and synthesis of MOFs with desired properties are of immense interest in heterogeneous catalysis [10]. As is known, the architectural diversities and pore surface properties of MOFs greatly depend on reactivity and flexibility of linkers and coordination modes of metal nodes, the designing of ligands with suitable functional groups is a key strategy for the construction of MOFs with required catalytic properties. The presence of multiple catalytic sites with appropriate coordination environments for metal ions also play a significant role in

enhancing the catalytic activities [11]. Compared to ditopic linkers based MOFs the polytopic compartmental linkers-based MOFs can more functionalize as heterogeneous catalysts due to the presence of multiple catalytic centers. Double hydrazone ligands, due to their specific geometry, including the different relative orientation of N-donors and the zigzag conformation of the spacer moiety (-CR=N-N=CR-) between the two terminal coordination groups, favors polymerization with novel network patterns not achievable by other rigid linking ligands, such as bipyridine and dicarboxylate ligands. All the known MOF linkers bind metal ion in a monodentate or bidentate coordination mode and a tetradentate spacer is never involved in metal coordination environment. The terminal nitrogens of these polytopic linkers have been shown to bind exodentate to metal nodes and the compartmental atoms lock by endodentate binding (Fig. 1).

As one of the most promising inorganic-organic hybrid materials for catalysis, MOFs function as solid catalysts or catalyst supports for several organic transformations such as Knoevenagel reaction, aldol condensation, oxidation, hydrogenation, Paal-Knorr reactions Suzuki crosscoupling, transesterification reaction, Friedel-Crafts alkylation, and epoxide ring-opening reaction [12-24]. Knoevenagel reaction is one of the most versatile reaction in organic chemistry and is widely employed for the condensation of aldehydes with active methylene compounds with numerous applications in the synthesis of useful chemicals as well as

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Fig. 1. Schematic representation of the design and construction of CP-Cd. (a) Structural formula of H₂DDIH and binding sites, (b) pictorial representation of the ligand and (c) self-assembly formation of CP-Cd.

heterocyclic compounds of biological significance [25,26]. The reaction is generally catalyzed by weak soluble bases in super-stoichiometric amounts. To address the problems of recyclability and high loading common with homogeneous base catalysts, efficient and recyclable solid base catalyst systems such as amine-functionalized mesoporous zirconia, cation-exchanged zeolites, chitosan hydrogel, amine-functionalized superparamagnetic nanoparticles, *etc.* have been utilized for these reaction [27–30]. However, most of these currently used methods suffer from one disadvantage or another which include, high-power microwaves, tedious preparation procedures, high reaction temperature as well as the use of toxic metals. Therefore, further development of new types of catalysts based on cheap and environmentally tolerable metal complexes that could be easily recyclable and could show high efficiency under mild conditions is desirable.

In the present paper, we wish to report the application of a Cd(II) MOF from a flexible dihydrazone linker as an efficient heterogeneous catalyst for the room temperature liquid phase Knoevenagel reaction. Detailed characterization of the MOF using various analytical methods, crystal structure, TG, PXRD, SEM *etc.* has also been performed. The catalyst stability was also ascertained by performing leaching and reusability experiments and a plausible mechanism has been proposed.

2. Experimental

2.1. Materials and methods

All reagents and solvents were purchased from commercial sources and were used without further purification. CHN analyses were done using an Elementar Vario EL III elemental analyzer. IR spectra were recorded using a KBr pellet method on a JASCO FT-IR-5300 Spectrometer in the 4000-400 $\rm cm^{-1}$ region. TGA analysis was carried out using a PerkinElmer STA6000/8000 under flowing nitrogen from 35 to 400 °C at a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) data were collected using a Bruker D8 Advance diffractometer system with Cu-Ka radiation. BET experiment was carried out using a Belsorp-mini II instrument (BEL Sorp II, Japan). Before the sorption experiment, sample was activated at 100 °C overnight. Solid state UV-Vis spectra were recorded using an Ocean Optics USB-4000 spectrometer and BaSO₄ as a reference. Scanning Electron Microscopy (SEM) micrographs were recorded using a JEOL Model JSM-6390LV instrument. Gas chromatography was conducted using an Agilent 7890-GC instrument using a flame ionization detector.

2.2. Synthesis of H_2 DDIH (1,2-diphenylethane-1,2-dione bisisonicotinylhydrazone)

Isonicotinic acid hydrazide (0.274 g, 2 mmol) was added to 20 mL DMF solution of 1,2-diphenylethane-1,2-dione (0.420 g, 1 mmol). The mixture was heated under stirring for 2 h at 60 °C. The white crystalline product obtained after slow evaporation of the solution was washed and dried in vacuum. $C_{26}H_{20}N_6O_2$ (H₂DDIH); Yield = 54% (0.246 g). Anal.

Calcd for $\rm H_2DDIH:$ C, 69.63; H, 4.49; N, 18.74%. Found: C, 69.92; H, 4.68; N, 18.93%.

2.3. Synthesis of $[Cd(DDIH)_2H_2O]_n$ (CP-Cd)

A solid mixture of cadmium acetate dihydrate, Cd(OAc)₂·2H₂O, (0.266 g, 1 mmol) and, 12-diphenylethane-1,2-dione bisisonicotinylhydrazone (H₂DDIH) (0.896, 2 mmol) was dissolved in 20 mL of DMF/THF (3:1 v/v) mixture. The solution was then heated to 80 °C for 45 min and cooled to room temperature. The mother liquor was kept for slow evaporation. After 5 days orange crystals were collected with a yield of 26% (0.156 g). Anal. Calcd. for $C_{26}H_{20}CdN_6O_3$: C, 54.13; H, 3.49; N, 14.57%. Found: C, 53.91; H, 3.62; N, 14.27%. IR spectrum (cm⁻¹): 3442 s, 1625 m, 1607 m, 1562 m, 1382 s, 1233 w, 1045 w, 710 m.

2.4. X-ray crystallography

Crystallographic data were collected with a Bruker SMART APEX II diffractometer with graphite monochromated Mo-Ka ($\lambda = 0.71073$ Å) Xray source. The unit cell dimensions were measured and the data collections were performed at 296 K. Bruker SMART software was used for data acquisition and Bruker SAINT Software for data integration [31]. Absorption corrections were carried out using SADABS based on Laue symmetry using equivalent reflections [32]. The structure was solved by direct methods and refined by full-matrix least-squares on F [2], including all reflections with the SHELXL-2018/3 software package [33]. All non-hydrogen atoms were refined with anisotropic displacement parameters and positions of hydrogen atoms were located in the difference Fourier maps and were placed in calculated positions with isotropic displacement parameters set to 1.2U_{eq} of the attached atom (1.5 for Me). The studied crystal was refined as a two-component twin and the twin data refinement was subsequently carried out with a scale factor of BASF = 0.2927. The site-occupancy factors [0.501 (6)/0.499 (6)] for the disordered atoms were refined using one common parameter. Their displacement parameters were refined using SIMU and DELU restraints and EADP instruction was used for the dummy atoms constrains. The possibility of spurious bonds was eliminated by PART instructions. All the drawings were made using, Diamond 3.2 k and Mercury 3.10.2 [34, 35]. The crystallographic data, refinement parameters, bond lengths and angles are summarized in Tables S1 and S2.

2.5. Catalytic studies

The condensation reaction of benzaldehyde derivatives and malononitrile was performed in a 10 mL beaker equipped with a magnetic stirrer. For each reaction, a benzaldehyde derivative (1.0 mmol), malononitrile (1.1 mmol), MeOH (5 mL), and a MOF catalyst (3 mol%) were placed in the 10 mL beaker. Then, the reaction mixture was stirred with a magnetic stirring bar at 400 rpm at room temperature. The reaction was monitored periodically by analyzing the sample by GC until completion of the reaction. The percentage conversion and selectivity were



Fig. 2. View (at the 50% probability level) of the asymmetric unit of CP-Cd with the atom numbering scheme.

determined by GC analysis. The product was confirmed by GC-MS analysis. Prior to the experiments, the sample was activated at 110 $^\circ\text{C}$ overnight.

To evaluate a potential influence of leaching of active species from the heterogeneous catalysts, the Knoevenagel condensation reaction was started as mentioned in the experimental procedure. Then a part of the reaction mixture was filtered to remove the catalyst at the reaction temperature and the obtained liquid phase was re-evaluated using the same starting material under the optimal catalytic conditions. In order to perform the catalyst recycling experiments, the used catalyst was separated by centrifugation, washed with acetone to remove any physisorbed reagents and dried in air. It is then reused for the next run. The above procedure was repeated four times.

3. Results and discussion

3.1. Structure and topology

The compound CP-Cd was isolated as orange air stable crystals by combination of H₂DDIH and Cd(OAc)₂ in mixed solvent system. It is worthwhile to point out that, in this reaction, the products do not depend on the ligand-to-metal ratio. The single-crystal X-ray structure of the compound was solved in an orthorhombic space group Iba2. The asymmetric unit is composed of one independent Cd(II) ion, deprotonated 1,2diphenylethane-1,2-dione bisisonicotinylhydrazone ligand, DDIH and one coordinated water molecule (Fig. 2). As shown in Fig. 3, Cd1 is sevencoordinated by four nitrogen atoms and two oxygen atoms from DDIH; oxygen atom from water molecule, revealing a distorted pentagonal bipyramidal geometry. The oxygen atoms and azomethine nitrogens in the equatorial plane around the metal center adopts a chelating coordination mode to generate a five membered Cd(II) containing ring. The terminal nitrogens which are axial to the equatorial plane are further linked to other Cd(II) centers to form a non-interpenetrating twodimensional network. The topology of the resulting structure can be defined as a (2,4) connected uninodal net with Schlafli symbol $\{3^{3}\cdot4^{4}\cdot5^{5}\cdot6^{2}\cdot7\}$ (Fig. 4). The hexagonal channels are running down the crystallographic 'c' axis (15.13 \times 4.3 Å). Packing fraction and total potential solvent area volume were calculated using PLATON program [36]. The packing index value of 43.7% and solvent area volume of 3389.93 $Å^3$, showed the complex to be potentially porous with wide solvent-accessible channels (Fig. 5). The metal connected infinite 2D grids are stacked parallel to each other along the 'a' axis with an ... ABAB ... arrangement.

3.2. Characterization and stability study

Experimental PXRD pattern of CP-Cd corroborated well with the simulated single crystal X-ray (SXRD) data (Fig. 6a). The sharp peak below 10° (with 20 of 8.38) indicates a highly crystalline material that clearly disclosed the phase purity of the bulk sample synthesized. The binding sites of the linker involved in coordination with the cadmium ions have been examined by the comparison of the infrared spectra of H₂DDIH and the complex (Fig. 6b). FTIR data for CP-Cd showed a sharp peak at 3442 cm⁻¹ corresponding to the O-H stretching vibration of coordinated water. The spectra of H₂DDIH exhibited bands at 3456 and 1658 cm⁻¹ due to the ν (N–H) and ν (C=O) vibrations respectively. The absence of these bands in the spectra of CP-Cd is consistent with the iminolization of the amide functionality and subsequent deprotonation of iminolic group and coordination of H₂DDIH to Cd(II) ion through iminolate oxygen atom. The band appearing at about 1382 cm⁻¹ is attributed to the ν (C–O) (iminolic) mode. The ν (C=N) band of the H₂DDIH (1594 cm^{-1}) has shifted to the higher wavenumber (1625 cm^{-1}) upon complexation which suggests the coordination of the azomethine nitrogen to cadmium. The compound CP-Cd showed band in the 1562 cm^{-1} region, assigned to newly formed C=N due to iminolization of the linker during complexation [37].

Thermal degradation investigations are necessary as many applications depend on their thermal stability [38]. As depicted in Fig. 6c, TGA analysis under dinitrogen atmosphere revealed that CP-Cd showed thermal stability up to ~300 °C followed by degradation of the organic moiety. Weight loss of about 3.1% between 60 and 100 °C suggests the escape of coordinated water molecule present in the MOF framework. It was also found that a sharp weight-loss step of over 55% was observed as the temperature increased from 300 to 400 °C, indicating the thermal decomposition of the CP-Cd in that temperature range. This TGA result ensured the applicability of the CP-Cd across a wide temperature range. The morphology of CP-Cd was observed by SEM. The SEM image exhibited a hexagonal shape with an average particle size of 15 μ M (Fig. 7).

3.3. Specific surface area and optical band gap

The gas adsorption-desorption study of CP-Cd was conducted to measure the porosity, but the sample did not respond (Fig. S1). The BET surface area is determined to be 4.85 m^2g^{-1} and the CO₂ adsorption isotherm shown adsorption of carbon dioxide gas up to 7.8 cm³g⁻¹ (Fig. S2). The data revealed very low surface area and porosity. Despite the stable framework and an adequate effective pore size, to our surprise no nitrogen or carbon dioxide and nitrogen adsorbates interact very strongly with the pore windows, which block other molecules from passing into the pore, as the framework has no other additional open channel along the 'a' and 'b' axes. Otherwise, as observed in SXRD data the offset packing of the 2D network perhaps blocks the through channels supporting the nonporous nature [39,40].

The optical band gap is closely related to its photocatalytic ability. In order to explore the photocatalytic ability of the compound, the measurements of diffuse reflectivity were performed to obtain the band gap (E_g), which was determined as the intersection point between the energy axis and the tangential line extrapolated from the linear portion of the adsorption edge in a plot of Kubelka-Munk function against energy E_g . The Kubelka–Munk function, F(R)=(1-R) [2]/2R, was obtained from the UV–Vis DRS data, where R is the reflectance of an infinitely thick layer at a given wavelength. As shown in Fig. 8, the compound **CP-Cd** showed a strong UV absorption around 325 nm. It suggests that the compound could efficiently utilize ultraviolet light and generate more electron under ultraviolet light irradiation [41]. The corresponding band gap energy (E_g) estimated from the steep absorption edge is 2.55 eV. The results clearly indicate that the compound is a potential wide gap semi-conductive material and probably a good candidate as a

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Fig. 3. (a) 2D capped stick view of the framework CP-Cd. (b) the Cd-centers are shown as purple coordination polyhedra (c) the distorted pentagonal bipyramidal geometry around Cd center. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 4. (a) 2D frameworks stacked parallel to each other along the 'a' axis (b) The topological network formed by CP-Cd. (c) Packing of layers with ... ABAB ... arrangement.



Fig. 5. (a) Perspective image showing the 3D structure of CP-Cd along 'c' axis (b) solvent accessible voids modelled using the program Mercury.

photocatalyst.

3.4. Catalytic study

Thermal and chemical stability of the framework, presence of labile H_2O ligand and infinite sheet structure of CP-Cd could offer a platform to accomplish heterogeneous catalytic reactions. Therefore, we have assessed the MOF, CP-Cd for its activity in the Knoevenagel reaction by studying the condensation of benzaldehyde with malononitrile to form benzylidene malononitrile as the principal product. Several reaction

factors, such as time, catalysts, temperature and solvents have been tested in order to reveal the most suitable parameters for the Knoevenagel condensation reaction. Consequently, the optimization of the reaction conditions (solvent, reactant ratio, reaction time, and the amount of catalyst) was carried out in a model malononitrile-benzaldehyde system. Substrate stoichiometry for the reaction has been chosen as 1:1.5 in the model catalytic reaction. As inspired by green chemistry principles, it was decided to carry out the reaction under room temperature conditions. Scheme 1 shows the representative Knoevenagel condensation reaction and details of the catalytic reaction procedure is provided in the



Fig. 6. (a) X-ray powder diffractogram of CP-Cd (b) comparison of FT-IR spectra of CP-Cd and H₂DDIH (c) TGA analysis of CP-Cd.



Fig. 7. SEM micrographs of CP-Cd.

Experimental section.

To gauge the catalytic efficiency, experiments were conducted in different solvents such as methanol, ethanol, ethyl acetate, acetonitrile and tetrahydrofuran. From Table 1, it can be deduced that methanol is the most suitable reaction solvent for further catalytic studies. Ethanol also gave satisfying yield. Tetrahydrofuran and acetonitrile gave comparable, but still lower yields of the desired product. Ethyl acetate gave very poor yield. The effect of reaction time in the Knoevenagel condensation shows that 15 min is the best reaction time.

The reaction has been further optimized to determine the best



Scheme 1. The Knoevenagel condensation reaction of benzaldehyde and malononitrile.

substrate ratio. Benzaldehyde versus malononitrile at molar ratios of 1:1, 1:1.5, 2:1, and 1:2 have been tested. The reaction rate at 1:1 ratio was low. Using the reagent molar ratio of 1:1.5, the reaction gave 96% conversion after 15 min, and then it could go to completion after 30 min with no trace amount of benzaldehyde being detected by GC. Further increase of the malononitrile nucleophile did not significantly accelerate the reaction rate. As a result, the 1:1.5 ratio of benzaldehyde and malononitrile was chosen as the optimal substrate ratio. Moreover, increasing the benzaldehyde molar ratio resulted in a significant drop in the reaction rate. It was observed that only 70% conversion was achieved for the reaction using 1 equiv of malononitrile and 1.5 equiv of benzaldehyde under same condition.

With such results in hand, we then decided to investigate the effect of catalyst concentration on reaction conversion. The catalyst concentration, with respect to the cadmium content in the CP-Cd, was studied in



Fig. 8. (a) Kubelka-Munk diffuse reflectance spectra and (b) Tauc plot for CP-Cd.

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Table 1

Optimization of the parameters for Knoevenagel reaction between benzaldehyde and malononitrile with **CP-Cd** as the catalyst^a.

Entry	Amount of catalyst (mol %)	Solvent	Time (min)	Conversion (%)
1	1.5 mol% CP-Cd	Methanol	15	85
2	1.5 mol% CP-Cd	Ethanol	15	83
3	1.5 mol% CP-Cd	Ethyl	15	32
		acetate		
4	1.5 mol% CP-Cd	THF	15	60
5	1.5 mol% CP-Cd	Acetonitrile	15	74
6	1.5 mol% CP-Cd	Methanol	20	87
7	2 mol% CP-Cd	Methanol	15	96
8	2.5 mol% CP-Cd	Methanol	15	97
9	3 mol% CP-Cd	Methanol	15	97
10	2 mol% CP-Cd (B:M =	Methanol	15	82
	1:1)			
11	2 mol% CP-Cd (B:M =	Methanol	15	70
	1.5:1)			
12	2 mol% CP-Cd (B:M =	Methanol	15	97
	1:2)			
13	Blank	Methanol	15	5
14	H ₂ DDIH	Methanol	15	10
15	Cd(OAc) ₂ ·H ₂ O	Methanol	15	28

^a All reactions except entries 10,11,12 were carried out at reactant ratio B:M = 1:1.5.

the range of 1.5–3 mol%. It was observed that quantitative conversion of benzaldehvde was achieved within 15 min at 2 mol% catalyst. Further increase in the former had no significant effect on reaction conversion. As expected, a lower reaction rate was observed for the reaction using 1.5 mol% catalyst. However, the reaction could afford a conversion of 93% after 30 min, and complete conversion of benzaldehyde was still obtained after 1 h. Decreasing the catalyst concentration to 1 mol% led to a significant drop in the reaction rate. The results indicated that the CP-Cd catalyst was quite active in the Knoevenagel reaction and best results were obtained in methanol as the solvent medium with 2 mol% catalyst along with substrates (benzaldehyde and malononitrile) in 1:1.5 stoichiometry at room temperature leading to 96% conversion within 15 min reaction time. The reaction between benzaldehyde and malononitrile was also monitored in blank, as well as using free ligand precursor H₂DDIH and the metal salt Cd(OAc)₂·2H₂O, instead of the catalysts. In the absence of the catalyst, the reaction showed trace yield at room temperature. Only 10-30% of product yield was obtained using Cd(OAc)₂·2H₂O or H₂DDIH as catalyst.

In order to determine the general applicability and efficiency of CP-Cd, we have also investigated the catalytic activity with different types of substituted aromatic aldehydes in the reaction with malononitrile applying the optimized reaction conditions based on the model reaction. The results summarized in Table 2 indicate that the MOF CP-Cd could convert all benzaldehyde derivatives studied to the corresponding condensation product effectively. The highest yield was obtained by using p-nitrobenzaldehyde (93%), whilst the lowest one was for pmethoxybenzaldehyde (56%). All other substituted benzaldehydes under the optimized reaction conditions gave 69-88%. The presence of a substituent on benzaldehyde such as an electron withdrawing or electron donating group has a profound effect on the product yield in the Knoevenagel condensation reaction. Electron-withdrawing substituent promotes the reactivity, relative to an electron-donor moiety. The results clearly demonstrate that CP-Cd possess the capacity for catalyzing the Knoevenagel reaction with a variety of aldehydes under ambient reaction conditions. Although the relationship between the structure and catalytic activity is not clearly understood, the high activity of CP-Cd may be due to the presence of labile H₂O ligands and the easier accessibility of the Cd(II) center to the substrate. As revealed from N2 and CO2 adsorption data, CP-Cd showed very low surface area and porosity. Hence, the condensation reaction by CP-Cd occurs on the surface of the catalyst.

Leaching is a crucial issue observed in the catalytic systems, leading to

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Table 2

Knoevenagel condensation reaction of various aldehydes with malononitrile with catalyst CP-Cd.

Sr. No	Substrate	Product	Yield (%)
1	СНО		96
2	FСНО	F-CN	80
3	СІ—		84
4	O ₂ N-CHO		93
5	О2N		88
6	но-Сно	HO	69
7	MeO		56

loss of activity due to the migration of active sites from solid support to the liquid phase. In order to examine the possibility of leaching and the heterogeneity of our catalytic system, an experiment was performed following the procedure described by Sheldon et al. [42] After the reaction mixture was stirred for 8 min (only ca. 50% conversion of benz-aldehyde was then observed) the solid catalyst was removed by filtration. The removal of the solid catalyst ceased the condensation reaction and negligible conversion was observed even upon an extended time, supporting the heterogeneity of the catalyst with no leaching of the active species (Fig. 9a).

Another point of great concern for most of solid catalysts is the recoverability as well as the reusability of the catalyst. MOF based catalysts are heterogeneous in nature and they can be easily separated from the catalytic system and show good catalytic performance, product yield and reusability. In order to evaluate the reusability and stability of CP-Cd during the Knoevenagel condensation, we have performed recycling tests in five consecutive experiments and its catalytic activity was monitored (Fig. 9b). It was observed that more than 90% conversion was still achieved at the fifth run. After the completion of five cycles, the catalyst was recovered by filtration and washed with acetone and dried. Furthermore, FT-IR and powder X-ray diffraction of CP-Cd taken before and after the reaction showed that the structure of the solid remained intact (Fig. 10).

The efficiency of our catalyst in comparison with various MOF based catalysts for the Knoevenagel condensation reaction with our investigation is presented in Table 3. The obtained yield in our system is par/better than that of the reported ones. Furthermore, our present study is conducted at room temperature with 15 min reaction time to achieve 96% conversion which makes the reaction energy efficient and eco-friendly. Table 3 reports Knoevenagel reaction investigated with longer reaction time, higher temperature and catalyst loading. In comparison with other reported catalysts, ours have the advantages of being easy-to-prepare, rather cheap, highly active and are recyclable without appreciable loss of catalytic activity.

A mechanism for the Knoevenagel reaction has been proposed. The labile water coordinated Cd(II) center acts as an active Lewis acidic



Fig. 9. (a) Plots of yield vs. time for the Knoevenagel condensation reaction of benzaldehyde and malononitrile in the presence of CP-Cd (black curve) and after filtering off the CP-Cd (red curve) (b) Catalyst recycling studies. Yield of five consecutive cycles. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 10. (a) Powder X-ray diffraction pattern and (b) FTIR spectra of CP-Cd before and after reaction.

Table 3

A comparison of catalytic activity of various MOFs in the Knoevenagel condensation reaction of benzaldehyde and malononitrile.

	MOF Catalyst	Catalyst mol%	Solvent	Time (h)	Temp (C°)	Conversion (%)	Ref
1	${[Cd(4-btapa)_2(NO_3)_2]\cdot 6H_2O\cdot 2DMF}_n$	4	Benzene	12	RT	98	[43]
2	$\{[Gd_2(L)_3(dmf)_4]\cdot 4DMF\cdot 3H_2O\}_n$	10	DCM	20 min	RT	96	[44]
3	[PbL ₂]·2DMF·6H ₂ O	3	CH ₃ CN	24	RT	100	[45]
4	ZIF-8	5	Toluene	6	RT	97	[46]
5	[Zn ₄ (TBCB)·(H ₂ O) ₆]·5DMAc		1,4 dioxane	4	90	99	[47]
6	TMU-5	2	Methanol	0.5	RT	68	[48]
7	UPC-30	10	DCM	5	RT	94	[49]
8	ZIF-9	5	Toluene	6	RT	99	[50]
9	Zn-MOF-NH ₂		DMF	4.5	80	98	[51]
10	CAU-1-NH ₂		Ethanol	7	40	98	[52]
11	$\{[Ni_4(\mu_6-MTB)_2(\mu_2-H_2O)_4(H_2O)_4]\cdot 10DMF\cdot 11H_2O\}_n$		p-Xylene	6	130	78	[53]
12	$\{[Zn(ADA)(L)]\cdot 2H_2O\}_n$		H ₂ O	1	RT	99	[52]
13	CAU-1-NH ₂		Ethanol	1	40	94	[54]
14	$[Zn(\kappa N-H_3L)(H_2O)_3]\cdot 3H_2O$	3	THF	5	50	94	[55]
15	[Zn ₂ dobdc] _n	1	Toluene	24	70	77	[56]
16	$\{[Ni_4(\mu_6-MTB)_2(\mu_2-H_2O)_4(H_2O)_4]\cdot 10DMF\cdot 11H_2O\}_n$	4	p-Xylene	6	130	78	[57]
17	[Tb(BTATB)(DMF) ₂ (H ₂ O)] _n	4	CH ₃ CN	24	60	99	[58]
18	$[Cd(DDIH)_2(H_2O)]_n$	3	Methanol	15 min	RT	95	present study

catalytic site. On the basis of crystal structure and previous reports [39, 58,59] a plausible mechanism of the Knoevenagel reaction on the Lewis acidic site is illustrated in Fig. 11. The reaction initiates from the attack of the polarized carbonyl oxygen from the aldehyde with the metal center, favoring the attack of malononitrile. Simultaneously, detachment of an acidic proton from the methylene group of malononitrile, give rise to carbonium anion intermediate. In the second step, the newly formed carbanion reacts with the carbonyl group of aromatic aldehyde *via* nucleophilic attack to give an intermediate. Lastly, the intermediate undergoes rearrangement and quickly converted to the benzylidenemalononitrile product after the absorption of one proton and loss of water.

4. Conclusion

In summary, a Cd(II) MOF has been synthesized with the reaction of cadmium acetate dihydrate and double hydrazone linker 1,2-diphenylethane-1,2-dione bisisonicotinylhydrazone. The linker is capable of coordinating Cd(II) center through endodentate and exodentate coordination and of generating novel coordination polymer. The MOF was characterized using a variety of different techniques and studied properties such as thermal and chemical stability, phase purity etc. The crystal structure of MOF revealed interesting two dimensional grid structure with uninodal topology. The semiconducting property of these MOF has also been reported. The compound acts as efficient heterogeneous



Fig. 11. Proposed catalytic cycle for the Knoevenagel condensation reaction catalyzed by CP-Cd (M = Cd(II) center; X = O of coordinated H_2O).

catalyst for the Knoevenagel condensation under mild reaction conditions. It effectively catalyzes the reaction of various aldehydes and malononitrile producing the corresponding benzylidenemalononitriles in high yields. Moreover, the catalyst could be recovered and reused up to five times without a significant degradation in catalytic activity. PXRD and FTIR measurements of the fresh and reused catalyst showed no structural changes and leaching experiment indicated no contribution of active Cd^{2+} species in the reaction solution during the course of the reaction, thus proving the catalyst stability under the present experimental conditions. It is apparent that the CP-Cd catalyst can be an alternative to other solid catalysts for the Knoevenagel reaction. Further explorations into the uses of this catalyst in other organic transformations, as well as mechanistic investigations, are ongoing.

CRediT authorship contribution statement

Lincy Tom: Conceptualization, Methodology, Investigation, Software, Writing - original draft, Funding acquisition. **M.R.P. Kurup:** Data curation, Visualization, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://do i.org/10.1016/j.jssc.2020.121846.

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