# pH-Tuned Modulation of 1D Chain to 3D Metal–Organic Framework: Synthesis, Structure and Their Useful Application in the Heterogeneous Claisen–Schmidt Reaction

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The role of pH in the formation of metal–organic frameworks (MOFs) has been studied on magnesium-based carboxylate framework systems  $[Mg(Pdc)(H_2O)_3]_n$  (1) and  $[Mg(Pdc)(H_2O)]_n$  (2) (Pdc = pyridine-2,3-dicarboxylate). The investigation reveals the formation of two different compounds of one- or three-dimensions starting from the same reaction mixture that differs only in pH. Isolated compounds have been characterized by IR and elemental analysis; both compounds were also successful-

## Introduction

Molecular engineering has now reached a highly diversified level of sophistication and considerable maturity with a rich knowledge of how to attain control over the structure of the materials. Self-assembly processes that deal with metal ions have attracted a great deal of attention in the field of supramolecular chemistry and crystal engineering with a view to the development of novel multifunctional materials, thereby exploiting the bridging potential of different organic linkers and the geometry of the metal ions.<sup>[11]</sup> An essential feature of selfassembly is the use of modular building blocks that contain sufficient structural information to guide the self-assembling pathways. A metal ion together with ligands contain a variety of structural information to guide the self-assembly reaction, and a number of interesting self-assembled systems have been reported in the past decade.<sup>[2]</sup>

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ly characterized by single-crystal X-ray diffraction. This study shows that the gradual increase in pH helps to construct a higher-dimensional network. Catalytic activity of compounds 1 and 2 was tested for the Claisen–Schmidt reaction. Compound 2 was successfully dehydrated to produce a coordinately unsaturated compound 2 a, which shows higher catalytic activity than 1 or 2 in heterogeneous medium.

To create the desired framework and functionality in a hybrid solid, it is important to control and understand the external factors, such as temperature, pH and solvent that govern the crystallization process and the overall stability of crystals. The pioneering study by Cheetham et al. systematically studied the role of temperature in the formation of the various cobalt succinate phases by keeping the same reaction mixture but at different temperatures.<sup>[3]</sup> This result spawned a series of studies to develop new materials by tuning reaction parameters. Rao et al. successfully developed the temperaturecontrolled progressive assembly of Zn oxalates and Ni succinates.<sup>[4]</sup> Bu and his co-workers successfully demonstrated a new temperature-dependent system based on the camphorate anion.<sup>[5]</sup> In another report, Mahata et al. showed a remarkable example of time- and temperature-controlled open-framework synthesis.<sup>[6]</sup> Recently Yao et al. added a new series of triazole-based frameworks by varying the reaction temperature, solvent and molar ratio.<sup>[7]</sup> A similar type of system was also developed by Kitagawa and co-workers during their study of the formation of cobalt pyridinedicarboxylates.<sup>[8]</sup> Maji et al. synthesized 1D to 3D frameworks by controlling only reaction temperature.<sup>[9]</sup> Natarajan et al. studied the influence of time and temperature in controlled open-framework synthesis.<sup>[10]</sup>

The pH of the reaction medium is also one of the most important factors in preparing framework materials. The influence of pH on the coordinated geometry of the transition metal and the coordinated mode of ligands has been studied, and the pH-controlled synthesis of transition-metal coordination polymers has been reported.<sup>[11]</sup> To observe the vital role of pH in the synthesis of MOFs, Zhao et al. showed the synthesis of four Zn-based carboxylate frameworks.<sup>[12]</sup> In another study,

Matsumoto et al. successfully showed an interconversion of monomer to oligomer by varying the pH of the medium.<sup>[13]</sup> In a recent study, Mathur et al. developed a new series of 1D to 3D Cd complexes controlled by acids.<sup>[14]</sup> In addition to the MOFs, this variation technique has also been used to produce various kinds of polyoxometalates (POMs). Ozeki and co-workers produced different types of high-nuclear Mo-based aggregation by tuning the pH.<sup>[15]</sup> Cao et al. have added a new series of silver-based POMs by maintaining the pH of the medium.<sup>[16]</sup>

At the same time, environmentally friendly heterogeneous catalytic processes are receiving increasing attention in the chemical industry. The design of highly active solid Lewis acid or base catalysts that are capable of catalyzing C-C bond-formation reactions is a challenge. The main drawbacks of using acids or bases in homogeneous catalysis are separation difficulties, corrosion of the equipment and generation of a large amount of waste. To overcome these disadvantages, several efforts have been made to adapt heterogeneous catalytic systems with controlled basic properties to increase the efficacy of the process. MOFs are currently being investigated as heterogeneous catalysts for this type of acid-base catalytic reactions.<sup>[17]</sup> When the coordination sphere of metal centres has one exchangeable position not compromised by the crystal structure of the MOF, then these metallic nodes can act as Lewis acid sites to promote organic reactions.<sup>[18]</sup>

Herein, we report a new approach for the pH-controlled synthesis of two MOFs,  $[Mg(Pdc)(H_2O)_3]_n$  (1) and  $[Mg(Pdc)(H_2O)]_n$ (2) (Pdc = pyridine-2,3-dicarboxylate). Compound 1 is a 1D zigzag chain material. Compound 2 has a 3D framework structure and readily undergoes dehydration to form the dehydrated active species 2a. The catalytic activity of 1, 2 and 2a has been studied in the Claisen–Schmidt reaction under heterogeneous base-free conditions. Compound 2a is catalytically more active than 1 or 2. To the best of our knowledge, compound 2 or 2a is the first reported magnesium-containing 3D MOF that catalyzes the Claisen–Schmidt reaction under heterogeneous base-free conditions.

## **Results and Discussion**

## X-ray crystal structure of $\{[Mg(Pdc)(H_2O)_3]_n$ (1)

Compound 1 crystallized in the space group  $Pca2_1$  with Z=4. In the asymmetric unit of compound 1, the metal centre is in distorted-octahedral geometry (ORTEP diagram is shown in Figure S1 of the Supporting Information). The basal plane of the central metal ion is formed by the two oxygen atoms from two water molecules (O2 and O3) and one nitrogen atom from the pyridyl ring (N8) and one monodentate carboxylate oxygen atom (O4). The axial positions are occupied by one oxygen atom from a water molecule (O1) and one oxygen atom from another carboxylate ligand (O14). The Mg–O and Mg–N bond lengths are in the range of 2.0399(11)–2.1636(12) and 2.222(13) Å (Table 1), respectively, which are in good agreement with the previous reports.<sup>[19]</sup> The metal centres are connected with each other by the carboxylate part of the Pdc ligand to form a helical linear 1D infinite chain parallel to the

Table 1. Selected bond lengths [Å] and angles [°] of compounds 1 and 2. $^{\rm [a]}$				
Compound 1		Compound 2		
	Bond lengths			
Mg–O1	2.0507(18)	Mg–O1	2.112(2)	
Mg–O2	2.1634(17)	Mg–O2	2.0700(19)	
Mg–O3	2.0418(16)	Mg–N6	2.226(2)	
Mg–O4	2.0398(16)	Mg— <sup>ii</sup> O12	2.045(2)	
Mg–N8	2.2221(17)	Mg- <sup>iii</sup> O13	2.045(2)	
Mg <sup>_i</sup> O14	2.0661(17)	Mg- <sup>iv</sup> O3	2.0780(19)	
	Bond	angles		
01-Mg-O2	83.89(6)	O1-Mg-O2	97.71(7)	
O1-Mg-O3	84.81(7)	O1-Mg-N6	172.24(8)	
01-Mg-04	95.40(7)	01-Mg- <sup>ii</sup> 012	84.59(7)	
O1-Mg-N8	87.28(6)	01-Mg- <sup>iii</sup> 013	85.06(7)	
01-Mg- <sup>i</sup> O14	165.15(7)	O1-Mg- <sup>iv</sup> O3	89.21(7)	
O2-Mg-O3	94.34(6)	O2-Mg-N6	74.76(7)	
O2-Mg-O4	170.89(7)	O2-Mg- <sup>ii</sup> O12	92.40(8)	
O2-Mg-N8	94.18(6)	O2-Mg- <sup>iii</sup> O13	95.04(8)	
02-Mg- <sup>i</sup> O14	84.03(6)	O2-Mg- <sup>iv</sup> O3	172.83(8)	
O3-Mg-O4	94.64(7)	"O12-Mg-N6	93.73(7)	
O3-Mg-N8	167.69(7)	<sup>iii</sup> O13-Mg-N6	97.33(7)	
O3-Mg- <sup>i</sup> O14	87.53(7)	<sup>iv</sup> O3-Mg-N6	98.25(7)	
O4-Mg-N8	76.71(6)	"O12-Mg-""O13	167.97(8)	
O4-Mg- <sup>i</sup> O14	97.89(6)	<sup>iv</sup> O3-Mg- <sup>ii</sup> O12	86.36(8)	
<sup>i</sup> O14-Mg-N8	102.19(6)	<sup>iv</sup> O3-Mg- <sup>iii</sup> O13	87.39(8)	
[a] Symmetry codes: i) $1/2-x$ , y, $1/2+z$ . ii) $-x$ , $-1/2+y$ , $3/2-z$ . iii) $1-x$ , $-1/2+y$ , $3/2-z$ . iv) x, $1/2-y$ , $-1/2+z$ .				

crystallographic c axis (Figure 1). In the crystal packing these chains are strongly bonded to each other by the hydrogen bonding mediated through the coordinated water molecules and the stability of this 1D chain compound is also gained by



**Figure 1.** a) Crystal structure of compound **1** propagating along the *c* axis. b) Topological view of the 1D zigzag chain in compound **1**.

the intramolecular hydrogen bonds through the carboxylate oxygen atoms and the water molecules: O1–H1A···O14 [x+ 1/2, -y, z], O1–H1B···O5 [-x+1/2, y, z–1/2], O2–H2A···O15 [x +1/2, -y+1, z], O2–H2B···O5 [x+1/2, -y, z], O3–H3A···O2 [-x+1, -y, z+1/2], O3–H3B···O15 [x+1/2, -y, z].

## X-ray crystal structure of $[Mg(Pdc)(H_2O)]_n$ (2)

X-ray structure analysis reveals that compound **2** crystallizes in the space group  $P2_1/c$  with Z=4. In the asymmetric unit there is one type of metal centre, Mg. The Mg centre is in distorted-



octahedral geometry. The basal plane is formed by the one nitrogen atom (N6), two *syn-anti*-bridged oxygen atoms (O2 and O3) from the carboxylate and one oxygen atom from the water molecule (O1). The axial positions are occupied by two *anti--anti*-bridged oxygen atoms from two different carboxylates (O12 and O13) (ORTEP diagram is shown in Figure S2 of the Supporting Information; bond lengths and angles have been collated in Table 1). These metal centres are bridged by the carboxylate group of the Pdc ring and ultimately form a nonporous 3D network (Figure 2). The calculation of the sol-



Figure 2. Three-dimensional polyhedral view of compound 2.

vent accessible void (SAV) from PLATON did not give any porosity within the network of compound **2** even after removal of the coordinated water molecules. To gain deeper insight into the structure of **2**, a topological analysis was performed by reducing the multidimensional structure to a simple node-and-linker net. Topological analysis of **2** by means of TOPOS<sup>[20]</sup> revealed that this compound is a binodal 4-*c* 3D net with the Schläfli symbol { $4^2.6^3.8$ } (Figure 3).



Figure 3. Three-dimensional simplified topological view of compound 2.

#### Thermogravimetric analysis

TG analysis was carried out to study the stability of the frameworks. TG analysis of compounds 1 and 2 was performed using powdered samples from room temperature to  $800^{\circ}C$  CHEMPLUSCHEM Full Papers

under a nitrogen atmosphere (Figure S3 in the Supporting Information). Compounds 1 and 2 showed a two-step mass loss. TG measurements confirm that compounds 1 and 2 are thermally stable up to about 150 °C. During the first step, a slow mass loss (22.23 wt%) of compound 1 between 145 and 250 °C corroborates the theoretical value of mass loss (22.17 wt%) of three coordinated water molecules. The TG curve indicates that compound 2 starts to lose water molecules at about 150°C and completes dehydration at about 210°C. The mass loss of about 9.0 wt% (theoretical value 8.7 wt%) shown in the range 150-210 °C of compound 2 corresponds to the loss of one coordinated water molecule present in the compound. Thereafter the TG curves remain flat up to about 350°C for 1 and 2, thus indicating no mass loss in this temperature range. On further heating, the TG curves show continuous mass loss, thus indicating the decomposition of compounds.

### Conversion of compound 2 to form the dehydrated framework 2 a

Crystal-structure analysis showed that compound 2 contains one coordinated water molecule on each magnesium site. TG analysis clearly indicates that 2 loses its coordinated water molecule on heating to produce a dehydrated product that is stable up to about 350 °C. The required quantity of dehydrated product (2a) of compound 2 was collected from the TG analyzer in several batches after heating to 250 °C. Dehydration was also achieved by heating compound 2 at 200 °C under vacuum (10<sup>-3</sup> torr) for one hour. The powder X-ray diffraction patterns of the dehydrated species (2a) and 2 corroborate well, thus indicating phase purity and framework stability of 2 after dehydration (Figure S5 in the Supporting Information). We attempted the dehydration of compound 2 in a controlled manner to achieve single-crystal-to-single-crystal transformation, but the single crystallinity of 2 was lost upon dehydration. In addition, it was not possible to form a single crystal of the dehydrated product (2 a) by the solution route.

#### **Catalytic Claisen–Schmidt reactions**

The aldol reaction, in which the carbonyl group undergoes nucleophilic attack by the same or a different type of carbonyl compound to give a  $\beta$ -hydroxy carbonyl compound, belongs to the most general and versatile organic reactions to form C–C bonds. [Cu<sub>3</sub>(btc)<sub>2</sub>] (btc=1,3,5-benzene tricarboxylate) has been reported as a general catalyst for the synthesis of pyrimidine chalcones through an aldol condensation under mild reaction conditions in toluene with a few drops of concentrated sulfuric acid.<sup>[21]</sup>

The Claisen–Schmidt reaction is an aldol condensation between an aromatic aldehyde and a ketone that leads to a conjugated enone as the final product through the formation of carbon–carbon bonds. The most studied example of the Claisen–Schmidt condensation is the reaction of benzaldehyde with acetophenone to form chalcones (1,3-diarylpropenones). Chalcone and its derivatives have gained increasing attention owing to numerous pharmacological applications, for example, as anticancer and antihyperglycemic agents.<sup>[22]</sup> A high yield of acetalized product was observed using  $[Cu_3(btc)_2]$  as catalyst at room temperature in methanol.<sup>[18a]</sup> MIL-101 was used as catalyst for the self-condensation of acetone to give mesityl oxide as the product.<sup>[23]</sup> The catalytic activity of UiO-66 and UiO-66(NH<sub>2</sub>) was tested for the cross-aldol reaction between benzaldehyde and heptanal for the formation of jasminaldehyde under solvent-free conditions.<sup>[24]</sup>

Among various magnesium compounds that are used as mediators or catalysts for several organic reactions,<sup>[25]</sup> magnesium oxide is a versatile catalyst for carbon-carbon bond-formation reactions.<sup>[26]</sup> Magnesium oxide nanoparticles have also recently been employed in the catalytic aldol condensation reaction.<sup>[27]</sup> It was proposed that the surface –OH and O<sup>2-</sup> of these oxide crystallites are expected to trigger the carbon-carbon bond-formation reaction.<sup>[27]</sup> However, little attention has been paid to using magnesium carboxylates in C-C bond-formation reactions owing to their limited synthetic procedure and hygroscopic nature.<sup>[28]</sup> Recently two 3D porous magnesium carboxylate framework materials have been synthesized through a hydrothermal route and their activity in heterogeneous aldol reaction was tested in the presence of triethylamine in THF.<sup>[11, 19a]</sup> Two 2D magnesium carboxylate compounds have also been reported that catalyzed the aldol reaction under heterogeneous base-free conditions.<sup>[19b,c]</sup> Sometimes calcined MOFs are a superior catalyst in aldol reactions to their parent compounds.<sup>[19a,c]</sup> Here, the catalytic activity of 1, 2 and 2a has been studied in a Claisen-Schmidt reaction under heterogeneous base-free conditions (Scheme 1). Compound 2 is the first



Scheme 1. Claisen–Schmidt reaction under base-free conditions.

report of a 3D magnesium-containing MOF that catalyzes the Claisen–Schmidt reaction under heterogeneous base-free conditions.

Catalytic reactions were performed in the presence of an excess amount of ketone for the effective use of aldehyde.<sup>[29]</sup> Reactions occur at room temperature and were performed in THF. The performance of catalysts **1** and **2** was very similar (Table 2). However, when calcined species (**2a**) were employed as catalyst, the yield of the reaction increased remarkably (Table 2). It can be anticipated that after **2** loses the coordinated water on heating, the metal centres of the framework compound become coordinatively unsaturated. These metal sites are now accessible to the reactant molecules and give a high yield of product. But in the case of **1**, it was not stable in the reaction medium after dehydration and therefore catalytic activity of calcined **1** was not measured. With an increase in the

<b>Table 2.</b> Solvent effect on Claisen–Schmidt reactions of <i>p</i> -nitrobenzalde-hyde with acetone catalyzed by compounds 1, 2 and $2a$ . <sup>[a]</sup>				
Compound	Solvent	Product type	lsolated yield [wt %]	Selectivity [wt %]
1	THF	β-aldol product	22 <sup>[b]</sup>	100
2	THF	β-aldol product	28 <sup>[b]</sup>	100
2a	THF	β-aldol product	69 <sup>[b]</sup>	100
2a	THF	β-aldol product	78 <sup>[c]</sup>	100
2a	THF/water (9:1)	β-aldol product	40 <sup>[c]</sup>	100
2a	no solvent	$\beta$ -aldol product	46 <sup>[c]</sup>	100
[a] Reaction conditions: <i>p</i> -nitrobenzaldehyde (2 mmol), acetone (3 mmol), solvent (3 mL), catalyst (5 mg), temperature ( $0-5$ °C). Yields were isolated after 6 h of reaction. [b] Reactions were performed under open atmosphere. [c] Reactions were performed under an inert atmosphere.				

reaction temperature, the  $\beta$ -aldol product transformed into benzylidene ketone (condensed product). Generally, it is easier to obtain the condensed product than the  $\beta$ -aldol product. Therefore, we were interested in isolating the yield in  $\beta$ -aldol form. The catalytic reactions were performed in THF, THF/water and solventless conditions (Table 2). The best result was obtained in THF. For 1 and 2, it did not matter whether the reaction was carried out in the open or under an inert atmosphere. The same yield was obtained in both cases. In the case of 2a, however, a small change in the yield of the product was noticed between the open atmosphere and inert atmosphere (Table 2). The yield obtained under inert atmosphere was higher than that in open atmosphere. In an open atmosphere, the absorption of water molecules from the atmosphere will result in the deactivation of some active sites and can cause low yield of the product. To further explore the versatility of the calcined species as a selective catalyst for the aldol reaction and the effect of substituents on the aldol reaction, different types of aldehydes and ketones were used as substrates in the THF medium under an inert atmosphere (Table 3). In all the above conditions aldehydes were converted to their respective  $\beta$ -aldols as the sole product. In this study we noticed that  $\beta$ aldol products did not undergo further transformation to form unsaturated carbonyl compounds. Generally the  $\beta$ -aldol product undergoes dehydration to give a conjugated enone in the Claisen–Schmidt reaction.<sup>[30]</sup> The yield of the  $\beta$ -aldol product decreases from *p*-nitrobenzaldehyde to *m*-nitrobenzaldehyde through o-nitrobenzaldehyde. It might be realized that the nitro substituent at the ortho and para position affords both a negative inductive effect and a negative mesomeric effect, which increases electrophilicity of the C=O group of nitrobenzaldehydes, but substitution at the meta position affords only the negative inductive effect. Between p-nitrobenzaldehyde and o-nitrobenzaldehyde, more steric crowding at the ortho position might lead to low conversion for the ortho variety. An aldol-condensation reaction catalyzed by nonporous crystalline magnesium oxide showed 75% conversion for p-nitrobenzaldehyde and acetone in 24 hours under heterogeneous conditions.<sup>[27]</sup> In the case of chloro-substituted benzaldehydes, the yield of the  $\beta$ -aldol product decreases from *o*-chlorobenzalde-



Entry	Ketone	Aldehyde	Major product	lsolated yield [wt %]	TON <sup>[b]</sup>
1	acetone	CHO NO <sub>2</sub>	O OH	78	59
2	acetone		O OH NO <sub>2</sub>	72	54
3	acetone		O OH NO <sub>2</sub>	68	51
4	acetone	CHO		75	57
5	acetone	СНО	O OH CI	71	54
6	acetone	СНО	O OH	66	50
7	acetone	СНО	O OH	55	42
8	acetone	OMe	O OH OMe	50	38
9	acetone	CHO Me	O OH	44	33
10	acetophenone		O OH NO2	75	57
11	cyclopentanone		O OH NO2	71	54

pability of the catalytically active alkaline earth-metal centre to accommodate an external ligand to its coordination site, which gives rise to the metal complex intermediate species.[33] Magnesium has highest Lewis acidity in the series so it can easily fulfil first requirement.[33] The the second requirement is achieved by the removal of water molecules from the coordination sphere in compound 2. Carbonyl-group oxygen possibly becomes coordinated to the Lewis acidic magnesium in the intermediate stage. Subsequently, the carbon-carbon bond forms with concomitant coordination of the carbonyl group of the aldehyde or with noncoordinated aldehyde.[17,31]

To ascertain that the catalysis is indeed heterogeneous, we performed a hot filtration test. To test if the metal was leached out from the solid catalyst during the reaction, the liquid phase of the reaction mixture was collected by filtration after approximately 40% completion of the reaction and the residual activity of the supernatant solution after separation of the catalyst was studied. The supernatant solution was kept under reaction conditions for another eight hours and the composition of the solution was analyzed from time to time. No progress

hyde to *p*-chlorobenzaldehyde through *m*-chlorobenzaldehyde owing to the decreasing effect of the negative inductive effect. However, in the presence of an electron-donating group in the ring, such as methyl, the yield decreases significantly and demonstrates the lowest conversion. Interestingly, in the case of *p*-methoxybenzaldehyde the yield was still good. Presumably, the methoxy group can interact with Mg<sup>2+</sup> and facilitate the reaction.<sup>[31]</sup> The Claisen–Schmidt reaction was also performed for acetophenone and cyclopentanone; however, the yield decreases from acetone to acetophenone to cyclopentanone.

catalyst (5 mg). Yields were isolated after 6 h of reaction. [b] Turnover number.

We propose a mechanism for the magnesium MOF-mediated aldol condensation reaction on the basis of the calcium MOF-catalyzed heterogeneous hydrogenation reaction and zinc-catalyzed aldol condensation reaction reported earlier.<sup>[31,32]</sup> Taking this type of mechanism into account, two different kinds of requirements are needed: (1) Lewis acidity, which favours the formation of the intermediate species and (2) the caof the reaction was observed during this period, which excludes the presence of active species in solution. This result suggests no leaching of magnesium from the solid catalyst during reactions. Furthermore, atomic absorption spectrometric analysis (sensitivity up to 0.001 ppm) of the supernatant solution of the reaction mixture collected by filtration confirms the absence of magnesium ions in the liquid phase.

To determine the stability of the catalyst, we characterized the recovered materials. After completion of the catalytic reaction, solid catalyst was recovered by centrifugation, washed thoroughly with dichloromethane, and dried. The recovered catalyst was then subjected to X-ray powder diffraction and FTIR analysis. Comparison of X-ray diffraction patterns (Figures S4 and S5 in the Supporting Information) and FTIR profiles (Figures S6 and S7) of the pristine compound and recovered catalyst convincingly demonstrates that the structural integrity of the compound was retained after the reaction.



For the recycling study, aldol condensation reactions were performed using *p*-nitrobenzaldehyde. After the first cycle of the reactions, the catalyst was recovered by centrifugation. The recovered catalyst was then washed several times with dichloromethane and activated under vacuum at 200 °C. The performance of the recycled catalyst in C–C coupling reactions was studied for up to five successive runs (Figure 4). The catalytic efficacy of the recovered catalyst remained almost the same in each run.



**Figure 4.** Catalytic performance of compound **2a** in different catalytic cycles using *p*-nitrobenzaldehyde.

The advantages of our system are that the catalytic reaction was carried out in the absence of any added base so there is no corrosion problem involved in the process. Reactants were converted to their respective product with a high yield and 100% selectivity over a short time, which demonstrates that the surface of the catalyst is highly active.

## Conclusion

In summary, we have synthesized two novel compounds by tuning the pH of the medium,  $[Mg(Pdc)(H_2O)_3]_n$  (1) and  $[Mg(Pdc)(H_2O)]_n$  (2), and structurally characterized these compounds by means of single-crystal X-ray diffraction analysis. Compound 1 has a 1D chain structure, whereas 2 has a 3D structure. These compounds behaved like heterogeneous catalysts in the Claisen–Schmidt reaction in the absence of any external base. The dehydrated compound 2a was found to catalyze the Claisen–Schmidt reaction more effectively than the hydrated compound 2. The catalysts were easily recovered by centrifugation after reaction and could be reused after washing. The recovered catalyst exhibited no significant loss of catalytic activity, either due to leaching of the active species or degradation of its structure.

## **Experimental Section**

#### Materials

Magnesium nitrate hexahydrate, pyridine-2,3-dicarboxylic acid and substituted benzaldehydes were purchased from Aldrich and were used as received. Other chemicals were purchased from local sources. Benzaldehyde, acetone and tetrahydrofuran were dried and distilled before use. Benzaldehyde was kept over NaA molecular sieves to trap possible traces of benzoic acid.

#### Physical measurements

Elemental analysis was performed with a Perkin–Elmer 240C elemental analyzer. Fourier-transformed infrared spectra of powdered samples suspended in KBr pellets were measured in the range of 400–4000 cm<sup>-1</sup> with a Mattson Mod 7000 spectrometer. The powder X-ray diffraction (XRD) patterns of the samples were recorded with a Scintag XDS-2000 diffractometer using Cu<sub>Kα</sub> radiation. TG analysis was performed with a Perkin–Elmer (SINGAPORE) Pyris Diamond TGA unit. The heating rate was programmed at  $5^{\circ}$ Cmin<sup>-1</sup> with a protecting stream of N<sub>2</sub> flowing at a rate of 20 mLmin<sup>-1</sup>. The metal content of the samples was estimated with a Varian Techtron AA-ABQ atomic absorption spectrometer.

#### Synthesis of compounds 1 and 2

 $[Mg(Pdc)(H_2O)_3]_n$  (1) and  $[Mg(Pdc)(H_2O)]_n$  (2) were synthesized through a hydrothermal route. The compounds were obtained as colourless block crystals in a Teflon-lined Parr acid digestion bomb at 160 °C for three days followed by slow cooling at the rate of 5°Ch<sup>-1</sup> to room temperature. The initial reaction mixture was prepared by mixing magnesium nitrate hexahydrate and pyridine-2,3dicarboxylic acid in a 2:1 ratio in water. The pH of the medium was then adjusted to 5 and 7 by mixing a dilute NaOH solution to obtain 1D and 3D framework compounds, respectively. The yield was about 35 and 45% (based on the metal) for 1 and 2, respectively. For the characterization of the bulk compounds, elemental analysis and an IR spectroscopic study were undertaken. IR (KBr disk) for 1:  $\tilde{\nu} = 1644$ , 1533 ( $\upsilon_{as}(CO_2^{-})$ ), 1468 ( $\upsilon_s(CO_2^{-})$ ), 1403, 1375  $(v_s(C-O))$ , 3600–3280 cm<sup>-1</sup> (brs) (v(O-H)); elemental analysis calcd (%) for [Mg(Pdc)(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> (1): C 34.52, H 3.69, N 5.75; found: C 33.85, H 3.89, N 5.98. IR (KBr) for **2**:  $\tilde{\nu} = 1635$ , 1589 ( $\upsilon_{as}(CO_2^{-})$ ), 1468  $(\upsilon_s(CO_2^{-}))$ , 1412, 1384  $(\upsilon_s(C-O))$ , 3500–3280 cm<sup>-1</sup> (brs)  $(\upsilon(O-H))$ ; elemental analysis calcd (%) for [Mg(Pdc)(H<sub>2</sub>O)]<sub>n</sub> (2): C 40.51, H 2.41, N 6.75; found: C 40.85, H 2.50, N 6.89.

#### X-ray crystallography

X-ray diffraction data for **1** and **2** were collected at 150(2) K with a Bruker SMART APEX II CCD X-ray diffractometer using graphitemonochromated Mo<sub>Ka</sub> radiation ( $\lambda = 0.71073$  Å). Determination of integrated intensities and cell refinement were performed with the SAINT<sup>[34]</sup> software package using a narrow-frame integration algorithm. An empirical absorption correction<sup>[35]</sup> (SADABS) was applied. All the structures were solved by direct methods and refined using the full-matrix least-squares technique against  $F^2$  with anisotropic displacement parameters for non-hydrogen atoms using the programs SHELXS97 and SHELXL97.<sup>[36]</sup> The hydrogen atoms were located from the difference Fourier maps and were refined isotropically. In the final difference Fourier maps there were no remarkable peaks except for the ghost peaks that surrounded the metal centres. A summary of crystal data and relevant refinement parameters for compounds **1** and **2** is given in Table 4.

#### **Catalytic reaction**

The catalytic reactions were carried out in a glass batch reactor according to the following procedure. Ketone (3 mmol), tetrahydro-

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Table 4. Crystal data and structure refinement parameters of compounds 1 and 2.			
Compound	1	2	
formula	C <sub>7</sub> H <sub>9</sub> MgNO <sub>7</sub>	C₂H₅MgNO₅	
formula weight	243.46	207.43	
T [K]	150(2)	150(2)	
crystal system	orthorhombic	monoclinic	
space group	Pca2 <sub>1</sub>	P2 <sub>1</sub> /c	
a [Å]	16.1285(11)	6.2574(9)	
<i>b</i> [Å]	6.7987(4)	10.5311(15)	
с [Å]	8.4646(6)	11.1893(14)	
β [°]	-	91.947(5)	
V [Å <sup>3</sup> ]	928.17(11)	736.92(18)	
Ζ	4	4	
$ ho_{ m calcd}  [ m g  cm^{-3}]$	1.742	1.870	
absorption coefficient [mm <sup>-1</sup> ]	0.215	0.234	
F(000)	504	424	
intervals of reflection indices	$-20 \le h \ge 20, -8 \le k \ge 8, -10 \le l \ge 10$	$-8 \le h \ge 4, -14 \le k \ge 12, -12 \le l \ge 14$	
measured reflections	14 105	3827	
reflections with $(l > 2\sigma(l))$	1878	1456	
independent reflections	1911	1788	
final R indices $(I > 2\sigma(I))^{[a]}$	$R_1 = 0.0235, wR_2 = 0.0591$	$R_1 = 0.0586, wR_2 = 0.1471$	
<i>R</i> indices (all data) <sup>[a]</sup>	$R_1 = 0.0240, wR_2 = 0.0594$	$R_1 = 0.0678, wR_2 = 0.1566$	
R <sub>int</sub>	0.0346	0.0278	
goodness of fit on $F^2$	1.069	1.081	
largest diff. peak/hole [e Å <sup>-3</sup> ]	0.263/-0.156	1.494/-0.426	
$[a] R_1 = \Sigma   F_o  -  F_c   / \Sigma  F_o, wR_2 = [\Sigma w( F_o  -  F_c )^2] / \Sigma [w(F_o^2)]^{1/2}.$			

furan (3 mL) and catalyst (5 mg) were added to a round-bottomed flask. It was then placed in an ice bath with temperature maintained between 5 and 10 °C. Aldehyde (2 mmol) was added to this solution and the reaction mixture was stirred for six hours (Scheme 1). Reactions were carried out at room temperature. For isolation of the products at the end of the catalytic reaction, the catalyst was first removed by centrifugation, filtered and finally concentrated under vacuum. The residue was purified by column chromatography over silica gel (mesh 60–120) by using *n*-hexane/ ethyl acetate mixture as eluent to obtain the desired product. The product was analyzed by <sup>1</sup>H NMR spectroscopy and elemental analysis, and the data were compared with those of authentic samples.

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**Multidimensional**: Two novel magnesium-containing metal-organic frameworks (MOFs) have been synthesized by using magnesium ions and pyridine-2,3dicarboxylic acid in a medium at different pH values. They have a 1D chain or 3D framework structure and catalyze the Claisen–Schmidt reaction efficiently (see scheme).



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pH-Tuned Modulation of 1D Chain to 3D Metal–Organic Framework: Synthesis, Structure and Their Useful Application in the Heterogeneous Claisen–Schmidt Reaction