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A magnesium-based multifunctional metal–organic framework: synthesis, thermally induced structural variation, selective gas adsorption, photoluminescence and heterogeneous catalytic study†

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Three magnesium based carboxylate framework systems were prepared through a temperature-dependent synthesis. The compounds were synthesized by a hydrothermal method and characterized by single crystal X-ray diffraction analysis. A stepwise increase in the temperature of the medium resulted a stepwise increase in the dimensionality of the network, ultimately leading to the formation of a new 2D layered alkaline earth metal–organic framework (MOF) compound, $\{[Mg_2(HL)_2(H_2O)_4]\cdot H_2O\}_n$ (**1**) (H_3L = pyrazole-3,5-dicarboxylate). Compound **1** selectively adsorbs hydrogen (H_2) (*ca.* 0.56 wt% at 77 K) over nitrogen at 1 atm and demonstrates a strong blue fluorescent emission band at 480 nm (λ_{max}) upon excitation at 270 nm. Notably, the 2D framework compound efficiently catalyzes the aldol condensation reactions of various aromatic aldehydes with ketones in a heterogeneous medium under environmentally friendly conditions. The catalyst can be recycled and reused several times without any significant loss of activity.

Introduction

The last few decades have witnessed the proliferation of diverse disciplines of crystal engineering and the design of advanced multi-functional materials, exploiting the bridging potential of different organic linkers and the geometry of the metal ions.[1] The research in the area of the fabrication of metal–organic frameworks (MOFs) continues to be intriguing by virtue of their unique topology and tunable properties.[2] For the desired framework and functionality in a hybrid solid, it is of importance to control and understand the external factors, such as temperature, pH and solvent, that govern the crystallization process and the overall stability of the crystal.[3,4] Metal carboxylates are particularly interesting because they exhibit open-framework structures and their carboxylate groups act as a linker between inorganic moieties.[5] Dicarboxylates have found applications in the diverse field of designing the coordination polymer arrays, as they are useful building blocks for porous networks containing metal ions throughout the periodic system.[6] The ligand H_3L (H_3L = 3,5-pyrazoledicarboxylic acid) has six potential donor sites involving the two nitrogen atoms of the pyrazole ring and the four carboxylate oxygens from two carboxylate groups when it is fully deprotonated and exhibits a multiple coordination motif with the metal center.[4,7] A variety of coordination compounds using this ligand have been synthesized and reported in the literature and the majority of the compounds are concerned with transition metals and rare earth cations.[7,8] In comparison to the reports on the coordination behavior of other metals, studies on alkaline earth metals are scanty.[9] Fromm *et al.* have recently reviewed the chemistry of the coordination polymers of the s-block metal ions.[9a] The avoidance of using the alkaline earth cations as building blocks arises from their unpredictable coordination numbers and geometries, as no ligand field stabilization effects govern their coordinative bonding, and their tendency to form solvated metal centers which leads to the formation of typical alternating $[M(H_2O)_6]L$ (M = alkaline earth metal, L = ligand) organic–inorganic ionic layers.[10] As a result, the chemistry of the alkaline earth metals has remained largely an unexplored area.

The lack of intrinsically useful properties (*i.e.* magnetism or variable oxidation states) might appear to make alkaline earth metals less interesting. Nevertheless, the alkaline earth metals have some advantages for applications in materials science; they are non-toxic, cheap and generally soluble to aqueous

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†Electronic supplementary information (ESI) available: a table for the intermolecular contacts and the solvent effect in the aldol condensation reactions, a plot for TGA and DTA, the CO_2 adsorption isotherm at 273 K, solid state UV-VIS spectra, ^1H NMR of all products of known compounds and the elemental analysis study of the isolated products. CCDC number 943160 for **1**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51509e

preparation. For these reasons alkaline earth salts are the preferred formulations for a host of commercial materials, including many common pharmaceuticals, dyes and pigments.[9] In this context some recent studies concerning alkaline earth metal complexes deserve to be mentioned.[3j,4,11–16] MOFs formed by light main-group metals such as Mg^{2+} and Al^{3+} may play an important role in exhibiting a promising hydrogen storage capacity, owing to their low framework density, high specific surface area and tuneable surface structures on which hydrogen molecules can be adsorbed.[12] Platero-Prats *et al.* studied alkene hydrogenation and ketone hydrosilylation reactions using alkaline earth sulfonate metal–organic compounds under homogeneous conditions.[13a] The same reactions were studied in heterogeneous conditions over an alkaline earth carboxylate metal–organic framework.[13b] Lin *et al.* studied the Michael addition of α,β-unsaturated γ-butyrolactam using a 3,3′-Ph_2-BINOL-Mg catalyst which showed a direct asymmetric vinylogous Michael addition with a high yield and an excellent enantioselectivity.[14] Brinkmann *et al.* employed calcium and strontium amides as precatalysts for the intermolecular hydroamination of styrenes and dienes.[15] Homogeneous catalysts, however, suffer from the problems of recycling as their separation from the reaction mixture is troublesome. Recycling the catalyst is a task of great economic and environmental advantage in the chemical and pharmaceutical industries.

In the course of our continuing investigation on the catalytic uses of MOFs,[4,17] we have successfully employed alkaline earth metal-based MOFs to catalyze the aldol condensation reaction under heterogeneous conditions in presence of triethylamine.[4,17e] Recently, we have developed a barium-based MOF which successfully catalyzed the aldol condensation reaction under heterogeneous base-free conditions.[17f] The further exploration of alkaline earth metal based MOFs afforded a new 2D MOF involving magnesium and 3,5-pyrazoledicarboxylic acid [H_3L], namely $\{[Mg_2(HL)_2(H_2O)_4]\cdot H_2O\}_n$ (**1**). Herein, we wish to report a new approach for the temperature-controlled synthesis of MOFs involving magnesium and H_3L. Interestingly, compound **1** features a layered 2D framework structure which is photoluminescent and capable of adsorbing hydrogen selectively. To best of our knowledge compound **1** is the first example of a magnesium based framework compound that catalyzes the aldol condensation reaction under heterogeneous base-free conditions. Notably, 2D layered alkaline earth metal frameworks rarely adsorb hydrogen selectively over nitrogen gas.

Experimental

Materials

Magnesium nitrate hexahydrate, 3,5-pyrazoledicarboxylic acid monohydrate, cyclopentanone, acetophenone and substituted benzaldehydes were purchased from Aldrich and were used as received. Other chemicals were purchased from Merck (India). The liquid aldehydes were distilled before use. Benzaldehyde was kept over NaA molecular sieves to trap possible traces of benzoic acid.

Physical measurements

Elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer. The Fourier transformed infrared spectra of the KBr pellets were measured using a Perkin-Elmer RX I FT-IR spectrometer. The powder X-ray diffraction (XRD) patterns of the sample were recorded with a Scintag XDS-2000 diffractometer using CuKα radiation at the desired temperature. TG analysis was performed on a Perkin-Elmer (SINGAPORE) Pyris Diamond TGA unit. The heating rate was programmed at 5 °C min^{-1} with a protecting stream of N_2 flowing at a rate of 150 ml min^{-1}. The metal content of the sample was estimated on a Varian Techtron AA-ABQ atomic absorption spectrometer. Gas sorption isotherms were measured in the pressure range of 0–1 bar using an Autosorb iQ (Quantachorme Inc., USA) gas sorption system. For all isotherms, warm and cold free space correction measurements were performed using ultrahigh purity He gas (99.999% purity). N_2 and H_2 isotherms at 77 K were measured in a liquid nitrogen bath using UHP-grade gas sources.

The synthesis of the compound 1. $\{[Mg_2(HL)_2(H_2O)_4]\cdot H_2O\}_n$ (**1**) was synthesized through a hydrothermal route. The initial reaction mixture was prepared as follows: pyrazole-3,5-dicarboxylic acid monohydrate (0.087 g, 0.5 mmol) first dissolved in 5 ml of milliQ water and the pH of the solution was adjusted to 4 by mixing a weak base, sodium azide. To this, magnesium nitrate hexahydrate (0.256 g, 1 mmol) was added and the final mixture was stirred for half an hour. Compound **1** was obtained as colorless block crystals in a 20 ml capacity teflon-lined acid digestion bomb, at 210 °C for 3 days followed by slow cooling to room temperature. The yield was *ca.* 63% based on the metal. The mononuclear complex $[Mg(HL)(H_2O)_4]$ and its dinuclear congener $[Mg(HL)(H_2O)_3]_2$ were obtained at 170 °C and 190 °C, respectively. Notably, these two were converted to **1** when they were treated hydrothermally in a 25 ml teflon-lined Parr acid digestion bomb at 210 °C for 3 days in water. For characterization of the bulk compound, elemental analyses and IR spectroscopic studies were undertaken. Anal. calcd for $\{[Mg_2(HL)_2(H_2O)_4]\cdot H_2O\}_n$ **1**; C = 26.85, H = 3.15, N = 12.54, found C = 26.8, H = 3.1, N = 12.5. Selected IR peaks (KBr disk, ν, cm^{-1}): 1632, 1556 [ν_{as} (CO_2^-)], 1497, 1460, 1431 [ν_s (CO_2^-)], 1358, 1234 [ν_s (C–O)], and 3163–3430 s br [ν (O–H)].

X-ray crystallography

The X-ray diffraction data for **1** were collected at 293(2) K on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The determination of the integrated intensities and cell refinement were performed with the SAINT[18] software package using a narrow-frame integration algorithm. An empirical absorption correction[19] (SADABS) was applied. The structure was solved by direct methods and refined using the full-matrix least-squares technique against F^2 with anisotropic displacement

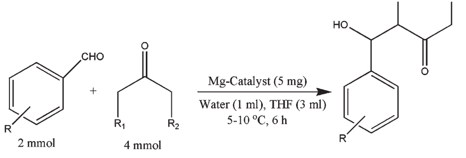
Table 1 Crystal data and structure refinement parameters of compound **1**

Compound	**1**
Formula	$C_{10}H_{14}N_4O_{13}Mg_2$
Formula weight	446.87
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	*C*2/*c*
a (Å)	12.5972(3)
b (Å)	10.0305(3)
c (Å)	13.8663(4)
β (°)	94.483(10)
Volume (Å^3)	1746.73(8)
Z	4
Calculated density (Mg m^{-3})	1.699
Absorption coefficient (mm^{-1})	0.219
F(000)	920
Intervals of reflection indices	$-16 \le h \ge 15$, $-13 \le k \ge 9$, $-16 \le l \ge 18$
Measured reflections	7243
Reflections with $[I > 2\sigma(I)]$	1886
Independent reflections	2025
Final *R* indices $[I > 2\sigma(I)]$	$R_1 = 0.0407$, w$R_2 = 0.1086$
R indices (all data)	$R_1 = 0.0425$, w$R_2 = 0.1105$
R_{int}	0.0199
Goodness of fit on F^2	1.143
Largest diff. peak and hole (e Å^{-3})	0.425, −0.673

parameters for non-hydrogen atoms with the programs SHELXS97 and SHELXL97.[20] The hydrogen atoms were placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. In the final difference Fourier maps there were no remarkable peaks except the ghost peaks surrounding the metal centers. A summary of the crystal data and the relevant refinement parameters for compound **1** is given in Table 1.

Catalytic reaction

The catalytic reactions were carried out in a glass batch reactor according to the following procedure. Ketone (4 mmol), water (1 ml), tetrahydrofuran (3 ml) and catalyst (5 mg) were placed in a round bottom flask. This was then placed in an ice-bath and the temperature was maintained at 5–10 °C. To this solution, aldehyde (2 mmol) was added and the reaction mixture was stirred for 6 h (Scheme 1). To isolate the products at the end of the catalytic reaction, the catalyst was first separated out by filtration and then the filtrate was extracted four times with dichloromethane (5 ml). The organic layers thus collected were first treated with brine solution, dried over anhydrous Na_2SO_4, filtered and finally concentrated in a vacuum. The residue was purified by column chromatography over silica gel (mesh 60–120) using a *n*-hexane–ethyl acetate mixture as the eluent to get the desired product. The products were analyzed by ^{1}H NMR spectroscopy and elemental analysis, and the data were compared with those of the authentic samples.



Scheme 1 The aldol condensation reaction catalyzed by compound **1**.

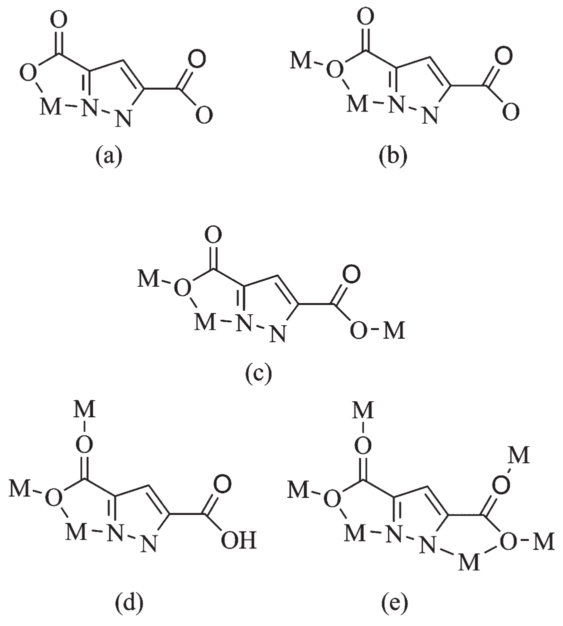
Results and discussion

The synthesis and the temperature dependent structural transformation

With much promise for versatility, the H_3L ligand contains three different types of hydrogen atom, one heterocyclic amine hydrogen atom and two carboxylic protons. The hydrogen of the carboxylate group adjacent to the imine group is easier to remove as it forms a stable chelating complex with the metal center. The hydrogen atom attached to the imine nitrogen dissociates less readily than the carboxylate hydrogen atoms. As the ligand possesses multidonor coordination sites involving both nitrogen atoms and carboxylate oxygen atoms, it exhibits a variety of coordination modes to the bridge metal ions (Scheme 2). Three different types of coordination mode of the carboxylate oxygen atoms of H_3L can be achieved at pH 4 (keeping other conditions unaltered) by merely varying the temperature (see ESI; Fig. S1†). A detailed description of the temperature dependent structural transformation is given in the ESI.†

X-ray structure of compound 1

Upon the hydrothermal treatment of the mixture of pyrazole-3,5-dicarboxylic acid monohydrate and magnesium nitrate hexahydrate at 210 °C, the new kind of 2D framework compound crystallized in the space group *C*2/*c* with *Z* = 4, with one molecule of water of crystallization. The ORTEP diagram with the atom-numbering scheme is shown in Fig. 1. Selected bond



Scheme 2 The metal coordination modes of pyrazole-3,5-dicarboxylic acid.

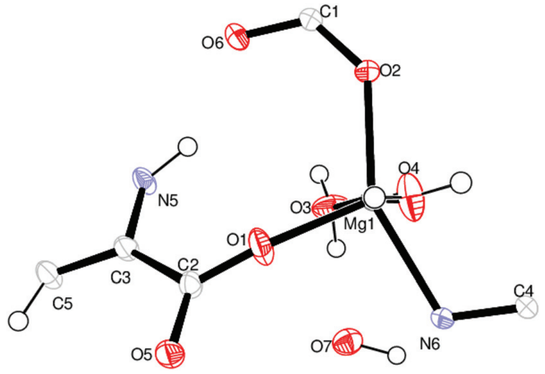


Fig. 1 The ORTEP diagram of compound **1** with 40% ellipsoid probability.

Table 2 Selected bond lengths (Å) and angles (°) for compound **1**

Bond lengths		Bond angles	
Mg1–O1	2.0094(11)	O1–Mg1–O2	111.42(5)
Mg1–O2	2.0556(10)	O1–Mg1–O3	92.46(5)
Mg1–O3	2.0308(12)	O1–Mg1–O4	83.26(5)
Mg1–O4	2.0776(13)	O1–Mg1–^{a}O2	167.16(5)
Mg1–^{a}O2	2.1542(11)	O1–Mg1–N6	99.03(5)
Mg1–N6	2.2094(12)	O2–Mg1–O3	88.72(5)
		O2–Mg1–O4	93.98(5)
		O2–Mg1–^{a}O2	76.22(4)
		O2–Mg1–N6	149.64(4)
		O3–Mg1–O4	175.54(5)
		O3–Mg1–^{a}O2	98.27(4)
		O3–Mg1–N6	92.45(5)
		O4–Mg1–^{a}O2	85.84(4)
		O4–Mg1–N6	87.02(5)
		^{a}O2–Mg1–N6	73.59(4)

Symmetry codes: (a) $3/2 - x$, $1/2 - y$, $1 - z$.

distances and bond angles are collated in Table 2. The basic unit of compound **1** consists of an Mg1 center with distorted octahedral geometry. The basal plane of **1** is generated by a chelating bidentate pyrazole carboxylate ligand (O2 and N6) and two oxygen atoms from the other two pyrazole carboxylate ligands (O1 and O2*, * = $3/2 - x$, $1/2 - y$, $1 - z$), while the oxygen atom O2 and its symmetry-related O2* bridge two Mg^{II} centers in a μ_2-bridging mode leading to the formation of Mg_2-diad (Mg_2O_2). The remaining two apical positions are occupied by water molecules (O3 and O4) (Fig. 2). The Mg–O (carboxylate) bond distances range from 2.009(11) to 2.154(11) Å which are in agreement with the Mg–O bond lengths observed in other magnesium carboxylate complexes.[3j,4] Each pyrazole-3,5-dicarboxylato ligand coordinates to three alkaline earth metal centers through two carboxylato oxygen atoms and one pyrazolate nitrogen atom (Fig. 2) to give rise to a 2D net (Fig. 3). The Mg_2O_2 SBUs formed *in situ* are bridged by organic HL^{2-} linkers. A topological analysis of compound **1** revealed that this compound is a 5-nodal 3,4-c 2D net with the Schläfli symbol $\{3.14^2\}\{3.4.5\}2\{4^2.6.142.15\}\{4^2.6\}$, consisting of four different kinds of three-coordinated nodes of HL^{2-} ligands with the point symbol $\{3.4.5\}$, $\{3.14^2\}$, $\{3.4.5\}$, $\{4^2.6\}$ for C1, C2, N1, and O1 respectively and a four-coordinated node of the Mg(II) centers with the point symbol $\{4^2.6.14^2.15\}$ (Fig. 4).[21] The uncoordinated water molecules are entrapped within the layer of the two-dimensional network by hydrogen bonding and non-bonding attractions (Fig. 5). Additional reinforcements to the network structure are achieved by intramolecular and intermolecular hydrogen bonding among the carboxylate oxygen atoms, pyrazolate imine protons and water molecules (Fig. 5 and ESI; Table S1†).

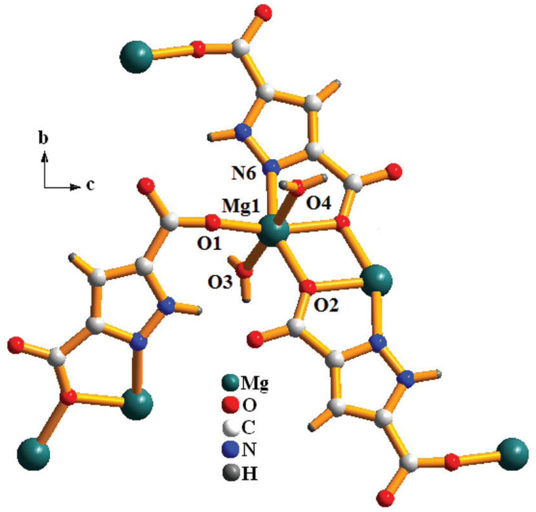


Fig. 2 The segment of compound **1**, showing the local coordination environment of the magnesium(II) ion.

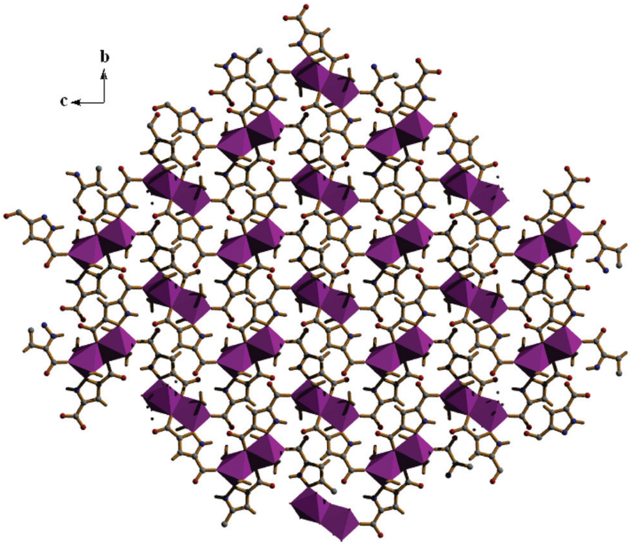


Fig. 3 The 2D network of compound **1**.

Thermogravimetric analysis

The thermogravimetric analysis of **1** was performed using a powdered sample in a nitrogen atmosphere. The TG measurement confirms that compound **1** was thermally stable up to ~130 °C (ESI; Fig. S2†). The TG curve indicates that **1** starts to

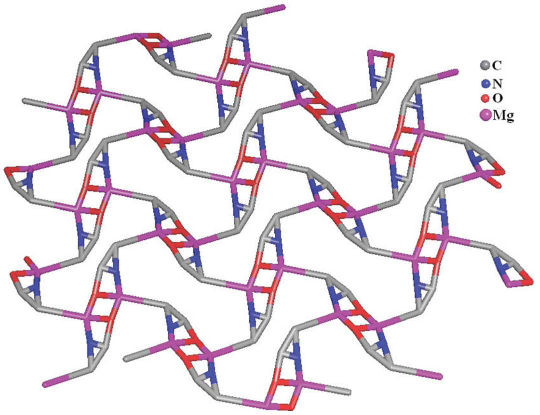


Fig. 4 The topological view of compound **1**.

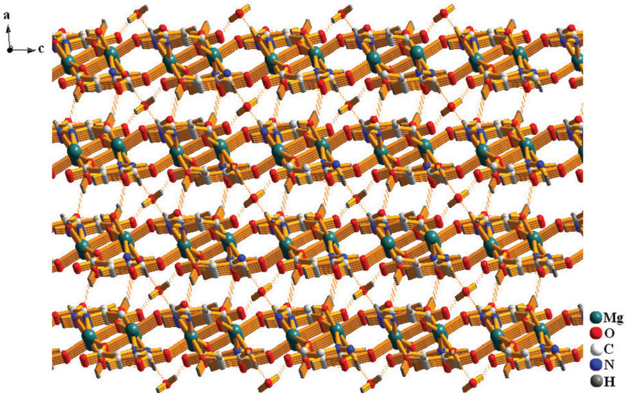


Fig. 5 The hydrogen bonded 3D network in compound **1**.

lose water molecules at ~130 °C and dehydrates completely at around 285 °C. The mass loss of ~20.0% shown in the range 130–285 °C is in agreement with the theoretical value for mass loss of 20.0%, which corresponds to the loss of one crystalline and four coordinated water molecules. No clear steps were observed between the loss of the crystalline and coordinated water molecules. The corresponding DTA curve of compound **1** shows three endothermic peaks ~165 °C, ~227 °C and ~280 °C. The first endothermic peak seems to correspond to the loss of the crystalline water molecules, as the coordinated water molecules bind the metal center more tightly. Thereafter the TG curve shows a small plateau up to ~330 °C indicating that no mass loss occurred in this temperature range. Finally the compound decomposes steadily showing no clear steps in the TG curve; the corresponding DTA curve exhibits a small exothermic peak in this region.

Gas sorption study

Gas sorption measurements were undertaken to understand the porous nature of compound **1** and to verify if the compound exhibits any preference in adsorption amongst the small molecule gasses. Prior to the sorption experiments, the samples were outgassed at the desired temperature (80 °C) for 3 h under vacuum (10^{-3} Torr). The adsorption and desorption isotherms of **1** are shown in Fig. 6. The sorption studies confirmed that compound **1** demonstrates very interesting selective adsorption of H_2 over N_2. The hydrogen uptake of compound **1** reached about 0.6 wt% at the adsorbate pressure of 1 atm. This is comparable to the corresponding value of hydrogen uptake in other similar Mg-based MOFs.[21] The adsorption of these small molecule gases follows the type I isotherms. On approaching a sorbate pressure close to 1 atm. $\{[Mg_2(HL)_2(H_2O)_4]\cdot H_2O\}_n$ **1** exhibits a significantly higher amount of hydrogen uptake (*ca.* 63 $cm^3\ g^{-1}$) in comparison to nitrogen (*ca.* 6 $cm^3\ g^{-1}$). The big difference in the gas uptake of compound **1** (more than ten folds higher for H_2 than N_2 at 77 K with the adsorbate pressure of 1 atm) underscores the potential of using Mg-based MOFs for the selective separation of H_2 over N_2. Such a preferential hydrogen uptake over nitrogen might be attributed to the small inter layer separations (2.71→3.60 Å) which permit only H_2 molecules (kinetic diameters of 2.89 Å) to enter into the layers, blocking the entrance for the N_2 molecules (kinetic diameters of 3.64 Å). The selective adsorption of H_2 over N_2 for microporous MOFs including alkaline earth metal frameworks has been reported previously which looks promising for the utilization of these MOFs in gas separation.[22,23] Morris and coworkers evaluated the kinetic separation of O_2 and N_2 on Cu(mcbdc) (mcbdc = 5-methoxycarbonyl-benzene-1,3-dicarboxylate) that features a 2D structure containing two different channels with hydrophilic and hydrophobic surfaces, respectively.[24] It was found that the adsorption of N_2 in this MOF is significantly slower than that of O_2, which was attributed to a kinetic effect. The selective adsorption of H_2 over N_2 is another important concern because of its potential application for H_2 enrichment from N_2/H_2 exhaust mixtures in ammonia synthesis.[23c,f] $\{[Mg_2(HL)_2(H_2O)_4]\cdot H_2O\}_n$ **1** adsorbs no hydrogen at 298 K and its carbon dioxide uptake is only ~8 $cm^3\ g^{-1}$ at standard temperature and pressure (STP) (see ESI; Fig. S3†).

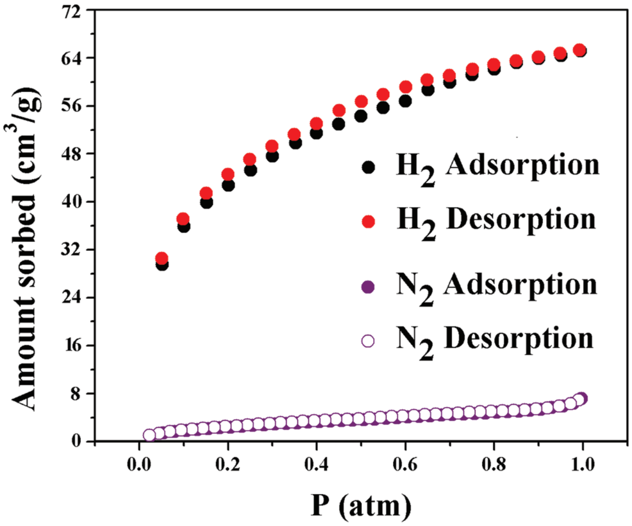


Fig. 6 The H_2 and N_2 adsorption–desorption isotherm of compound **1** at 77 K.

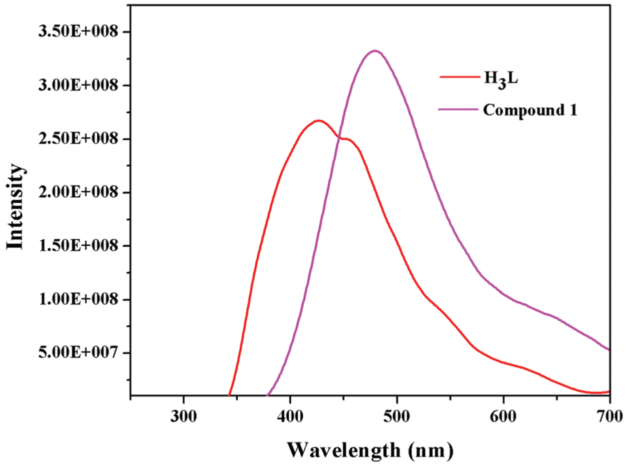


Fig. 7 The solid state photoluminescence spectra of H_3L and compound **1**.

Photoluminescence study

It is established that the photoluminescence properties of a luminescent ligand significantly enhance upon complex formation with alkaline earth metals.[25] The electronic and photoluminescence spectra (Fig. 7) of the H_3L ligand and compound **1** are measured in the solid state as well as in DMSO (see also ESI; Fig. S4–S6†). The ligand displayed a very strong blue fluorescent emission (λ_{max} = 425 nm in the solid state and λ_{max} = 350 nm in DMSO) in the solid state as well as in DMSO upon excitation at 270 nm which is probably due to the $\pi^* \rightarrow \pi$ electronic transition. The shift of the fluorescent emission of H_3L in the solid state in comparison to that in DMSO may be due to the solvent effect. In the case of compound **1**, the emission band was found at 480 nm (λ_{max}) with a higher intensity and is red-shifted by ~55 nm. The red-shift of the emission spectra observed in compound **1** in comparison with the corresponding free ligand, may be attributed to the deprotonation of the ligand in the complex.[26] The photoluminescence properties of the alkaline earth metals could have potential applications in fluorescent materials.[27]

Catalytic aldol condensation reactions

Environmentally friendly heterogeneous catalytic processes are increasingly receiving attention in the chemical industry. Designing highly active solid Brønsted-type basic catalysts which are capable of catalyzing C–C bond formation reactions is a challenge. The main drawbacks of using NaOH or KOH as homogeneous catalysts are separation difficulties, corrosion in the equipment and the generation of a large amount of waste. In order to overcome these disadvantages several efforts have been made to arrange new catalytic systems with controlled basic properties in order to increase the efficacy of the process. Garcia *et al.* have recently reviewed the condensation reactions of carbonyl groups when using metal–organic frameworks as the solid catalyst.[28] Among the various magnesium compounds which are used as mediators or catalysts for several organic reactions,[29] magnesium oxide is a versatile catalyst for carbon–carbon bond formation reactions.[30] Magnesium oxide nano-particles also have been employed in the catalytic aldol condensation reaction.[18] It was proposed that the surface –OH and O^{2-} of these oxide crystals are expected to trigger the carbon–carbon bond formation reactions.[31] However, little attentions have been paid in using magnesium carboxylates in C–C bond formation reactions due to their limited synthetic procedure and hygroscopic nature.[16] Magnesium pyrazole-3,5-dicarboxylate with a variety of structures (0D monomer to 3D polymer) catalyzed the aldol condensation reaction under homogeneous and heterogeneous conditions in presence of triethylamine.[4] Triethylamine is also to some extent corrosive which should preferably be avoided. In contrast the catalytic activity of compound **1** has been studied in the aldol condensation reaction under heterogeneous base-free conditions (Scheme 1).

The catalytic reactions were performed in the presence of a large excess of ketone to prevent the self-condensation of the aldehyde as well as for the effective use of the aldehyde.[32] Reactions were performed in a THF–water mixture medium. The temperature of the medium was maintained in the range of 5–10 °C throughout the reaction. With the increasing reaction temperature, the β-aldol product transformed to benzylidene ketone (the condensed product). The catalytic reactions were performed in different ratios of THF to H_2O (see ESI; Table S2†). The best result was obtained in a 3 : 1 THF–H_2O mixture and the results of the aldol condensation reactions are summarized in Table 3. In all of the above conditions, the aldehydes were converted to their respective β-aldols as the sole product. In this study we noticed that the β-aldol products did not undergo further transformation to form unsaturated carbonyl compounds. Generally, the β-aldol product undergoes a dehydration to give a conjugated enone in the aldol condensation reaction.[33] The aldol condensation reaction catalyzed by nonporous crystalline magnesium oxide showed a 75% conversion for *p*-nitrobenzaldehyde and acetone in 24 h under heterogeneous conditions.[31] The yield of the β-aldol product decreased from *p*-nitrobenzaldehyde to *m*-nitrobenzaldehyde through *o*-nitrobenzaldehyde. It may 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 the electrophilicity of the >C=O group of the nitrobenzaldehyde. The substitution at the *meta* position affords only the negative inductive effect. Between *p*-nitrobenzaldehyde and *o*-nitrobenzaldehyde, more steric crowding at the *ortho* position may lead to a lower conversion for the *ortho* variety. In the case of the chloro substituted benzaldehydes, the yield of the β-aldol product decreased from *o*-chlorobenzaldehyde to *p*-chlorobenzaldehyde through *m*-chlorobenzaldehyde. On the other hand in the presence of an electron donating group in the ring, such as methyl, the yield decreases significantly and the lowest conversion was demonstrated. Interestingly in case of *p*-methoxy-benzaldehyde, the yield was still very good. Presumably the methoxy group may interact with Mg^{2+} and facilitate the reaction.[34] For acetophenone and cyclopentanone a

Table 3 The reactions of various aromatic aldehydes and ketones catalyzed by compound **1**[a]

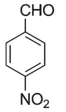
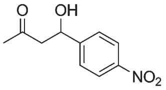
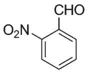
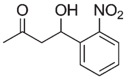
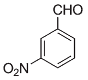
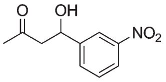
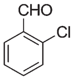
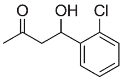
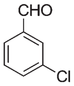
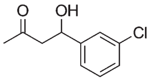
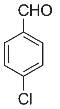
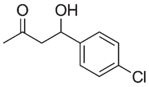
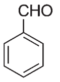
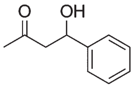
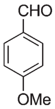
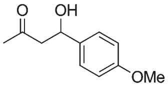
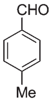
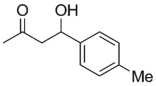
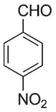
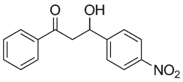
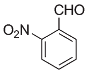
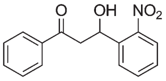
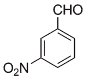
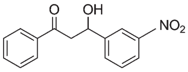
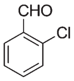
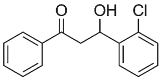
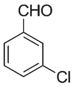
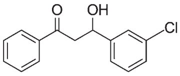
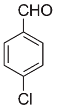
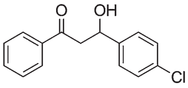
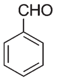
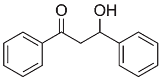
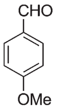
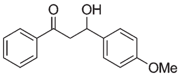
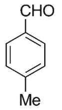
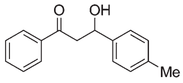
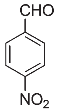
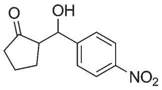
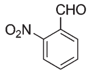
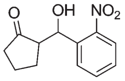
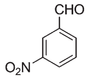
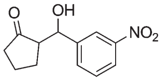
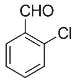
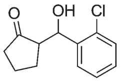
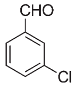
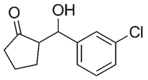
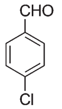
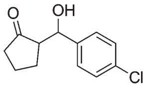
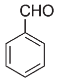
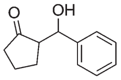
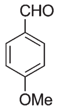
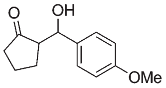
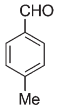
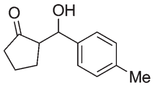
Entry	Ketone	Aldehyde	Major product	Isolated yield (wt%)	TON
1	Acetone			82, 80[b]	120, 117[b]
2	Acetone			77	112
3	Acetone			70	100
4	Acetone			80	109
5	Acetone			74	102
6	Acetone			69	92
7	Acetone			58	84
8	Acetone			52	79
9	Acetone			46	65
10	Acetophenone			78, 75[b]	116, 114[b]
11	Acetophenone			71	110
12	Acetophenone			65	97
13	Acetophenone			75	106
14	Acetophenone			70	96
15	Acetophenone			66	87
16	Acetophenone			50	79
17	Acetophenone			44	72

Table 3 *(Contd.)*

Entry	Ketone	Aldehyde	Major product	Isolated yield (wt%)	TON
18	Acetophenone			37	61
19	Cyclopentanone			75, 74[b]	112, 109[b]
20	Cyclopentanone			70	107
21	Cyclopentanone			64	96
22	Cyclopentanone			74	102
23	Cyclopentanone			70	94
24	Cyclopentanone			65	84
25	Cyclopentanone			51	74
26	Cyclopentanone			45	69
27	Cyclopentanone			36	59

[a] Reaction conditions: aldehyde (2 mmol), ketone (4 mmol), tetrahydrofuran (3 ml), water (1 ml) and catalyst (5 mg); temperature = 5–10 °C. Yields were isolated after 6 h of reaction. [b] Fifth cycle.

similar trend in the yield of the β-aldol products were observed but overall, the yield decreased from acetone to cyclopentanone through acetophenone.

To ascertain that the catalysis was 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 ~40% completion of reaction and the residual activity of the supernatant solution after separation from the catalyst was studied. The supernatant solution was kept under the reaction conditions for another 8 h and the composition of the solution was analyzed from time to time. No progress of reaction was observed during this period, which excludes the presence of the active species in the solution. This result suggests that there was no leaching of Mg from the solid catalyst during the reaction. In addition, an atomic absorption spectrometric analysis (sensitivity up to 0.001 ppm) of the supernatant solution of the reaction mixture thus collected by filtration confirms the absence of magnesium ions in the liquid phase.

To check the stability of the catalyst, we characterized the recovered material. After the completion of the catalytic reaction, the solid catalyst was recovered by centrifugation, washed thoroughly with dichloromethane and dried. The recovered catalyst was then subjected to X-ray powder diffraction analysis. A comparison of the X-ray diffraction patterns (Fig. 8) of the pristine compound and the recovered catalyst convincingly demonstrates that the structural integrity of the compound was retained after the aldol condensation reaction.

For the recycling study, the aldol condensation reactions were performed using *p*-nitrobenzaldehyde. After the first cycle of reactions, the catalyst was recovered by centrifugation. The recovered catalyst was then washed several times with dichloromethane and dried under vacuum. The performance of the recycled catalyst in the C–C coupling reactions in up to five

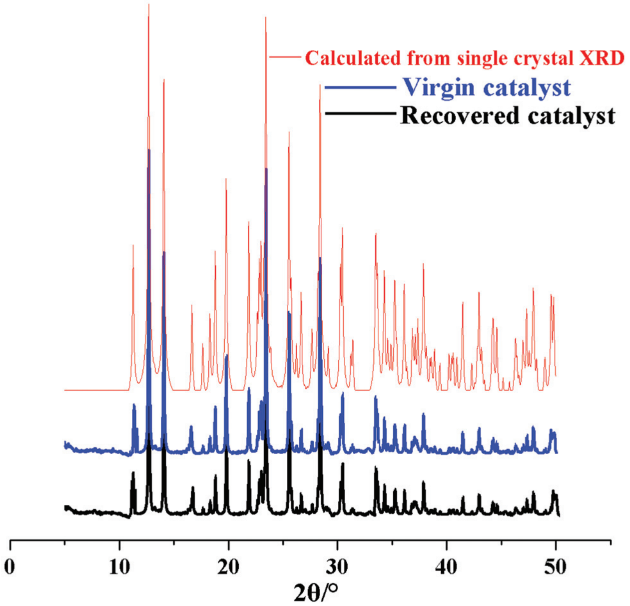


Fig. 8 The X-ray powder pattern of the pristine catalyst and the recovered catalyst for **1**.

successive runs was studied (Table 3). The catalytic efficacy of the recovered catalyst remained almost the same in each run.

The advantages of our system are that the catalyst is not air or moisture sensitive; hence, there is no need to carry out the reaction in an inert atmosphere. The catalyst can easily be recovered by filtration and can be reused several times without any significant loss of catalytic activity. The catalytic reaction was carried out in the absence of any added base so there is no corrosion problem involved in the process. The reactants were converted to their respective product with a high yield and a 100% selectivity in a short time duration, which demonstrates that the surface of the catalyst is highly active.

Conclusion

In summary we have synthesized a new two-dimensional alkaline earth metal–organic framework (MOF) compound, $\{[Mg_2(HL)_2(H_2O)_4]\cdot H_2O\}_n$ (**1**) through a hydrothermal route. Synthetically we are able to correlate this framework with two low dimensional compounds by tuning the temperature of the medium. **1** exhibits very good solid state photoluminescence properties at room temperature and a selective hydrogen-sorption property over nitrogen. The framework compound demonstrates excellent catalytic activity in the aldol condensation reactions towards various aromatic aldehydes and displays a good yield of the products with a high selectivity in a short reaction time under heterogeneous conditions. Notably, the catalyst can be recycled and reused several times without any significant loss of activity. Further investigations regarding the application of the alkaline earth metal based frameworks towards gas sorption and catalytic reactions are currently being investigated in our laboratory.

Acknowledgements

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