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pH dependent synthesis of Zn(II) and Cd(II) coordination polymers with dicarboxyl-functionalized arylhydrazone of barbituric acid: photoluminescence properties and catalysts for Knoevenagel condensation

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Abstract

Four novel Zn(II) and Cd(II) compounds based on a dicarboxyl-functionalized arylhydrazone of barbituric acid ligand, 5-[2-{2,4,6-trioxotetrahydropyrimidin-5(2H)-ylidene}hydrazinyl]isophthalic acid (H₅L), namely [Zn(1κO:2κO':3κO''-H₃L)(H₂O)₂]_n (**1**), [Cd(1κO,O':2κO':3κO'',O'''-H₃L)(H₂O)₂]_n (**2**), [Zn(κN-H₃L)(H₂O)₃]_n·3H₂O (**3**) and [Cd(1κO,O':2κN-H₃L)(H₂O)₃]_n·4nH₂O (**4**), have been synthesized at different pH under hydrothermal conditions and characterized by elemental and thermogravimetric, FT-IR, and X-ray single-crystal diffraction analyses. Compounds **1** and **2** prepared in acidic medium are coordination polymers exhibiting double chain type one-dimensional (1D) structures, whereas **3** and **4** are obtained in basic medium. Compound **3** is a mononuclear Zn(II) complex containing three lattice water molecules, but in **4**, Cd(II) cations are bridged by H₃L²⁻ ligands to form an interesting zig-zag type 1D coordination polymer. The crystal structures of these compounds are stabilized by strong hydrogen bonding interactions, forming two and three-dimensional networks. The pH value of the reaction system plays a crucial role in the ligand deprotonation and in the assembly of the metal-organic polymers. These compounds act as effective heterogeneous catalysts, under mild conditions, for the Knoevenagel condensation reaction of different aldehydes with malononitrile and can be recycled at least five times without losing activity. Further, compounds **1-4** exhibit luminescent properties in the solid state at room temperature.

Keywords: Zinc, Cadmium, X-ray diffraction, Arylhydrazone of barbituric acid, Catalysis, Knoevenagel condensation

1. Introduction

Metal organic frameworks or coordination polymers (CPs) have a recognized importance owing to their wide range of potential applications in the growing fields of molecular storage, magnetism, electrical conductivity, sensor capability and catalysis.¹ The architectural diversities found in CPs results not only from covalent metal–ligand bonds, but also from weak non-covalent interactions, like hydrogen and halogen bonding, π -anion, π -cation and π -stacking interactions.² However, their synthesis in a truly rational manner continues to be a challenging task on account of the many factors that influence the product structures, such as nature of the ligand and metal, solvent,

reaction temperature, metal to ligand ratio, pH, etc.³ Particularly, the pH of the reaction medium can play a very important role in the construction of CPs,⁴ and its alteration can significantly affect the protonation level of the organic ligand resulting in architectural changes in the structures.⁵ The selection of the organic ligand is also crucial, namely for the control of topologies.⁶

In this context, Barbituric acid containing polydentate ligands are excellent candidates for the construction of novel structures and topologies because they have multiple coordination site and can adopt versatile conformations. Besides their pharmacological properties, barbiturates (pyrimidine-2,4,6(1*H*,3*H*,5*H*)-triones) are useful synthons for the non-covalent interactions assisted construction of supramolecular and coordination compounds.⁷ The modification of the pyrimidine moiety by introduction of different substituents to the C5 atom of the ring can change the nuclearity and the topology of the formed CPs.^{7c} Incorporation of a carboxyl-functionalized arylhydrazone moiety to the pyrimidine ring increases the donor centres of the ligand and its coordination versatility. Further, the presence of pyrimidine and carboxyl moieties in the ligand framework may affect the self-assembly process at different pH.

Based on the above considerations, we have synthesized, as a potential linker for CPs, the barbituric acid derivative 5-[2-{2,4,6-trioxotetrahydropyrimidin-5(2*H*)-ylidene}hydrazinyl] isophthalic acid (H₅L) (Scheme 1), which contains both amide and carboxylic acid groups. We have chosen such a type of linker taking into account the following factors: (a) the polydentate coordination sites may generate multidimensional structures; (b) this ligand contains an amide group which may be suitable to produce hydrogen bonded networks; (c) the deprotonation of H₅L may be affected by pH which will have an influence on the network topology.

Important applications of CPs concern their use in catalysis. Recently they been applied in heterogeneous catalysis⁸ in many organic reactions,⁹ *e.g.*, alkylation of aromatics,^{10a} carbonyl-ene and Diels-Alder reaction,^{10b} cyanotrimethylsilation,^{10c} isomerization of α -pinene oxide^{10d} and Mukaiyama-aldol reaction.^{10e} Acidic and basic polymers can exhibit high catalytic activity in condensation reactions like the Pechmann,¹¹ Knoevenagel¹² and Prins reactions.¹³ Recently, our group has reported various CPs which are catalytically active for the oxidation, nitroaldol and cyanosilylation reactions,¹⁴ and now we wish to extend our study to another type of reaction, the Knoevenagel condensation. This is one of the most useful C-C bond forming reactions, widely used in the synthesis of fine chemicals and pharmaceuticals.¹⁵ However, only few CPs have been reported¹⁶ which actively catalyse this reaction and there is still a great demand to develop new types of catalysts based on cheap and environmentally tolerable metal complexes that could be easily recyclable (hence forming an heterogeneous system) and could show high efficiency under mild conditions. Recently, Kitagawa *et al.*^{16a} and Zhou *et al.*^{16b} reported that amide functionalized MOFs are quite effective for the Knoevenagel condensation. Besides, some Zn-MOFs can also effectively catalyze this condensation in an heterogeneous way.^{16c-d} Thus, the development of suitable MOF (or CP) based catalysts for the Knoevenagel condensation is a topic of great interest.^{16e-g}

Hence, the two main objectives of the current work concern: (i) to synthesize Zn(II) and Cd(II) complexes, namely CPs, by using the 5-[2-{2,4,6-trioxotetrahydropyrimidin-5(2*H*)-ylidene}hydrazinyl]

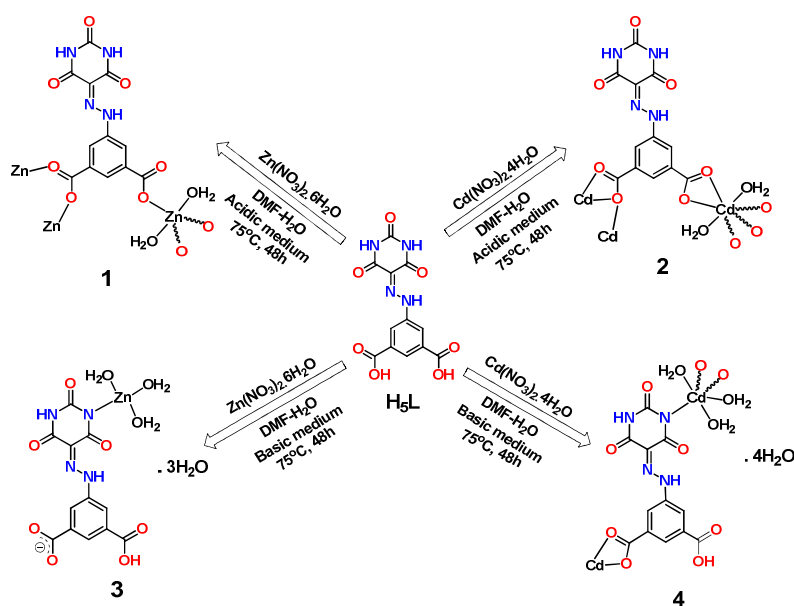
isophthalic acid (H_5L) linker at different pHs, under hydrothermal reaction conditions; (ii) to apply the synthesized complexes as heterogeneous catalysts for the Knoevenagel condensation reaction of different aldehydes with an active methylene compound; (iii) to study the photoluminescence properties of the complexes.

In this work, we have synthesized four different compounds, namely $[Zn(1\kappa O:2\kappa O':3\kappa O''-H_3L)(H_2O)_2]_n$ (**1**), $[Cd(1\kappa O,O':2\kappa O':3\kappa O'',O'''-H_3L)(H_2O)_2]_n$ (**2**), $[Zn(\kappa N-H_3L)(H_2O)_3]\cdot 3H_2O$ (**3**) and $[Cd(1\kappa O,O':2\kappa N-H_3L)(H_2O)_3]_n\cdot 4nH_2O$ (**4**), under solvothermal conditions at different values of pH which play a key role in the structural arrangement process. To our knowledge, no previous study on Zn(II) and Cd(II) coordination chemistry with 5-[2-{2,4,6-trioxotetrahydropyrimidin-5(2H)-ylidene}hydrazinyl]isophthalic acid (H_5L) has been reported. The heterogeneous catalytic properties of the obtained compounds (**1-4**) towards the Knoevenagel condensation reaction of malononitrile with various aldehydes have been successfully tested. In addition, the solid state photoluminescence properties of these compounds have also been investigated.

2. Results and Discussion

2.1 Syntheses and characterization

5-[2-{2,4,6-trioxotetrahydropyrimidin-5(2H)-ylidene}hydrazinyl]isophthalic acid (H_5L) was synthesized according to the procedure reported earlier.¹⁷ The solvothermal reaction of $Zn(NO_3)_2\cdot 6H_2O$ or $Cd(NO_3)_2\cdot 4H_2O$ with H_5L in DMF and water in acidic medium led to the formation of the double chain type 1D coordination polymer $[Zn(1\kappa O:2\kappa O':3\kappa O''-H_3L)(H_2O)_2]_n$ (**1**) or $[Cd(1\kappa O,O':2\kappa O':3\kappa O'',O'''-H_3L)(H_2O)_2]_n$ (**2**), respectively. But, when performed at a basic pH, the reaction produced the mononuclear zinc(II) complex $[Zn(\kappa N-H_3L)(H_2O)_3]\cdot 3H_2O$ (**3**) or the zig-zag one dimensional Cd(II) polymer $[Cd(1\kappa O,O':2\kappa N-H_3L)(H_2O)_3]_n\cdot 4nH_2O$ (**4**) (Scheme 1). Several attempts to obtain X-ray quality crystals at neutral pH medium failed.



Scheme 1 Syntheses of compounds **1-4**.

In the IR spectra of **1-4**, the characteristic strong bands of the coordinated carboxylate groups appear at 1585–1561 cm^{-1} for the asymmetric stretching and 1384–1360 cm^{-1} for the symmetric one.¹⁸ A medium broad band between 3418 and 3477 cm^{-1} is due to $\nu(\text{NH})$ of amide groups, whereas $\nu(\text{OH})$ of water molecules is in the 3377–3244 cm^{-1} region. Due to their insolubility in common solvents, the NMR spectra of these compounds could not be run, but they were characterized by IR spectroscopy, single crystal X-ray diffraction, elemental (see experimental section) and thermogravimetric analysis (supporting information, Figure S3).

2.2 Crystal structure analyses

According to the crystal structure analyses, **1-4** crystallize in different space groups (**1** and **2** in P-1, **3** in $P2_1/c$ and **4** in $C2/c$). Compounds **1** and **2** are similar double chain 1D CPs while **4** possesses a zig-zag type 1D chain. Compound **3** has a mononuclear structure. The variation of pH affects the formation of these frameworks. At acidic pH (2.0) the H_3L^{2-} ligand coordinates via carboxylate groups and the amide-N atoms remain protonated; but in basic medium the ligand coordinates via the deprotonated amide-N (for compound **3**) or via this atom and carboxylate-O atoms (for compound **4**).

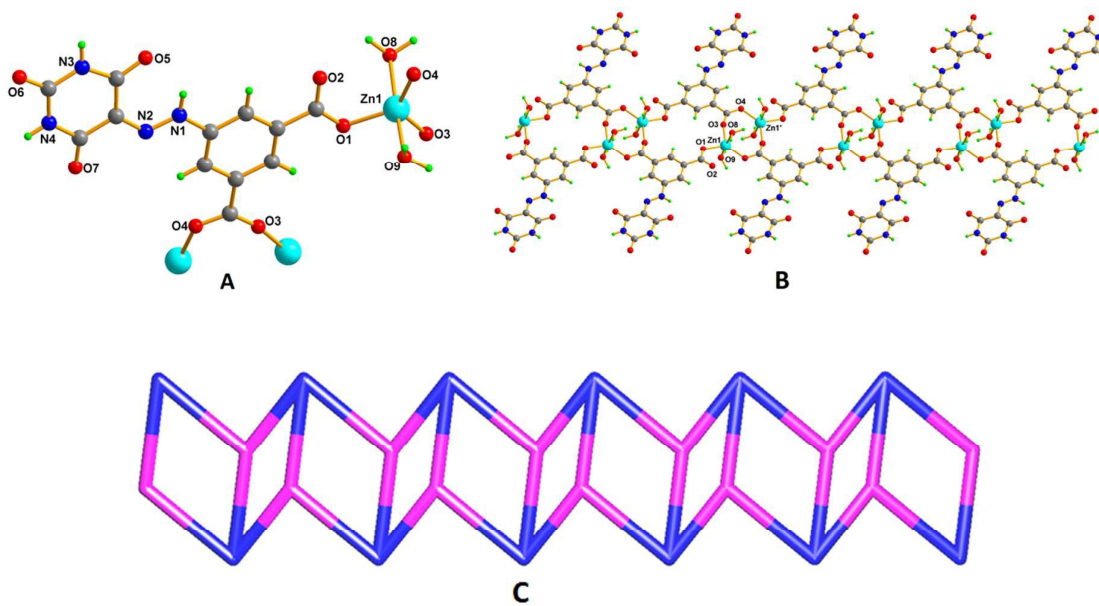


Figure 1: (A) The asymmetric unit of framework **1** with partial atom labelling scheme. (B) One dimensional structure of framework **1**. (C) Topological representation of frameworks **1** and **2**.

In all cases extensive H-bond interactions could be found that play a role towards the extension to 3D supramolecular frameworks. A list of selected hydrogen bonding interactions is presented in Table S2 (supporting information). Selected bond distances and angles are listed in Table S3 (supporting information).

The asymmetric unit of **1** contains one deprotonated ligand (H_3L^{2-}) and one Zn^{2+} ion along with two coordinated water molecules (Figure 1A). The Zn^{2+} ion has a trigonal bipyramidal ($\tau_5 = 0.76$)¹⁹ geometry and is involved in the dinuclear $\{\text{C}_2\text{O}_4\text{Zn}_2\}$ core by means of two *syn-syn*-type bridging

bidentate carboxylate groups [Zn1–O3, 1.964(2) Å and Zn1–O4, 1.964(2) Å], and in $\{C_{10}O_4Zn_2\}$ cores also with the involvement of non-bridging monodentate [Zn1–O1, 1.968(2) Å] carboxylate moieties (Figure 1B). Coordination sites are further occupied by the O-atoms of two coordinated water [Zn1–O8, 2.215(3) Å; Zn1–O9, 2.095(3) Å] molecules. The minimum Zn...Zn *intra-chain* distance is 3.8242(7) Å in **1**.

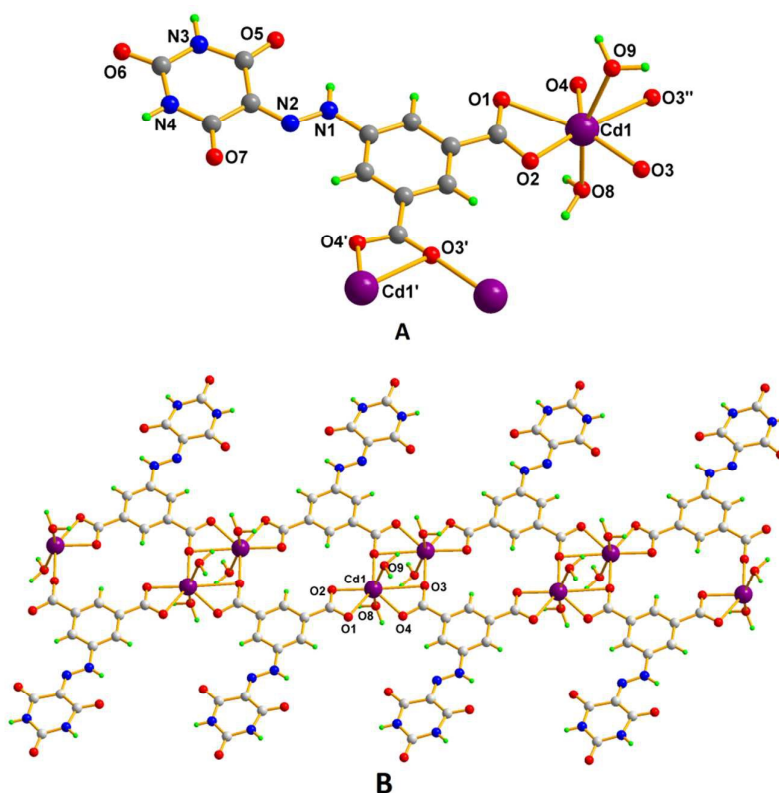


Figure 2: (A) The asymmetric unit of framework **2** with partial atom labelling scheme. (B) One dimensional double chain type structure of framework **2**.

The CP **2** has a similar structural arrangement to that of **1**. The asymmetric unit of **2** also contains one H_3L^{2-} ligand, one Cd^{2+} ion and two water molecules. The Cd(II) ion presents a distorted pentagonal bipyramidal environment which results from the chelating bidentate mode of two carboxylate groups from two H_3L^{2-} ligands and a bridging monodentate carboxylate moiety from another of such ligands [Cd1–O1; 2.525(2) Å, Cd1–O2, 2.231(2) Å; Cd1–O3, 2.244(2) Å and Cd1–O4, 2.209(2) Å], the coordination sphere being accomplished with two water molecules [Cd1–O8, 2.347(2) Å and Cd1–O9, 2.356(2) Å] (Figure 2A). The outcome of such organization is that the metal in CP **2** is involved in $\{Cd_2O_2\}$ and in $\{C_{10}Cd_2O_4\}$ dimetallic cores (Figure 2B). In this framework the minimum Cd...Cd distance is 3.8415(4) Å.

Topological analysis of frameworks **1** and **2** reveals that they have a 3-connected uninodal net with a topological type SP1-periodic net (Figure 1C).

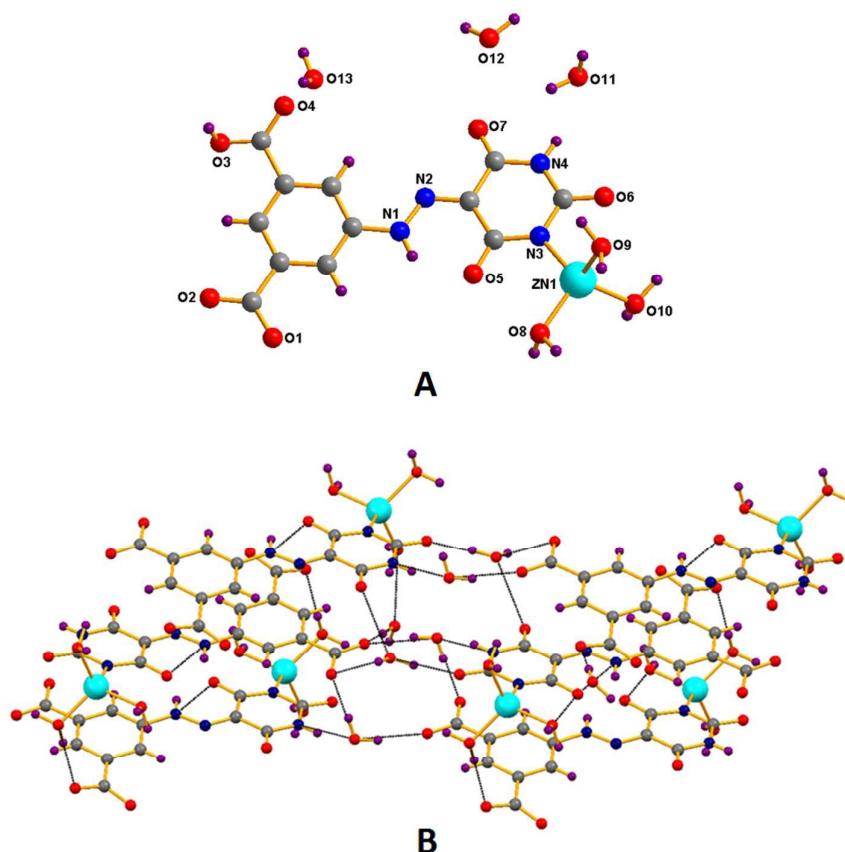


Figure 3: (A) The structure of compound **3** with partial atom labelling scheme. (B) Hydrogen bonded network of compound **3**.

The asymmetric units of **3** contains the zinc(II) ion coordinated by a deprotonated N-amide of the H_3L^{2-} ligand [Zn1-N3, 2.011(3) Å] and three water molecules [Zn1-O10 2.017(3) Å; Zn1-O8 2.021(3) Å; Zn1-O9 2.042(4) Å], as well as three crystallization water molecules (Figure 3A). The coordination geometry is tetrahedral ($\tau_4 = 0.94$).¹⁹ In the H_3L^{2-} ligand the carboxylate and carboxylic acid groups remain uncoordinated.

The single crystal analysis of **4** reveals a zig-zag type 1D framework constructed by Cd(II) ions and H_3L^{2-} ligands (Figure 4A). The asymmetric unit contains a Cd^{2+} ion, one deprotonated ligand (H_3L^{2-}), along with three coordinated water and one non-coordinated water molecule (Figure 4B). The Cd(II) centre displays a distorted octahedral geometry, the equatorial positions being occupied by the two oxygen atoms of a carboxylate from one H_3L^{2-} ligand [Cd1-O1, 2.446(5) Å and Cd1-O2, 2.415(5) Å], one amide nitrogen [Cd1-N3, 2.247(4) Å] and one water molecule [Cd1-O10, 2.296(6) Å]. The remaining two water molecules occupy the axial positions [Cd1-O8, 2.349(6) Å, and Cd1-O9, 2.338(6) Å].

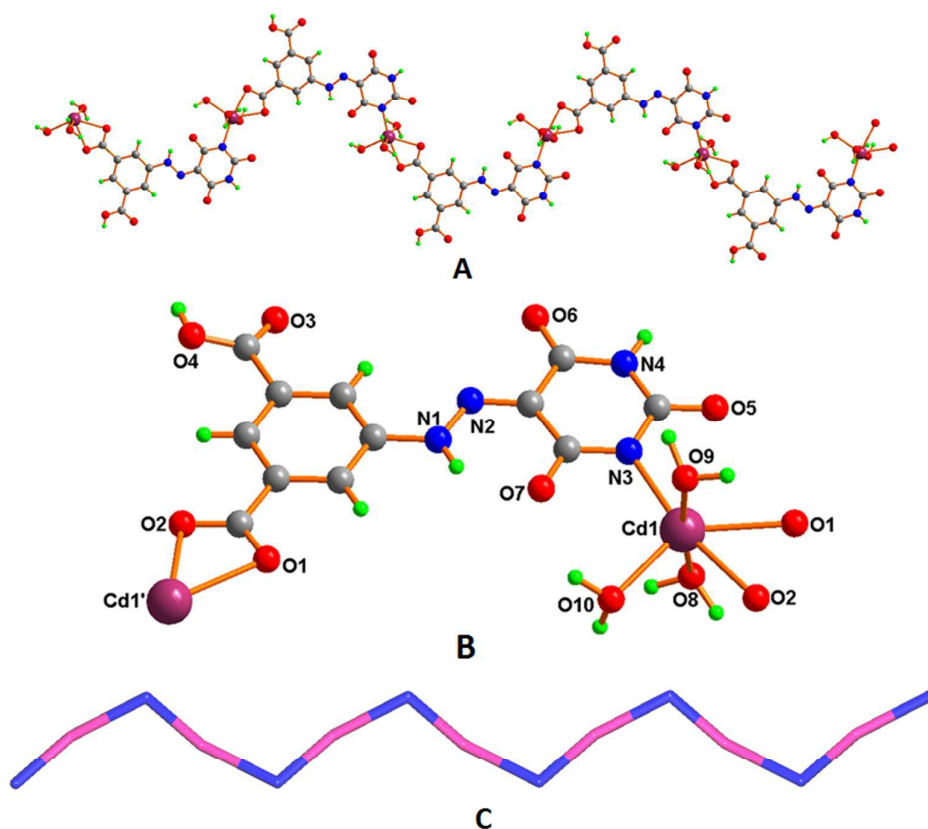
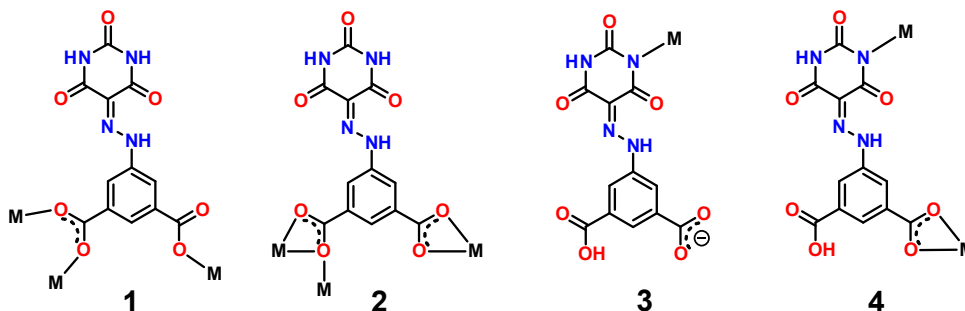


Figure 4: (A) One dimensional structure of framework **4**. (B) The structure of compound **4** with partial atom labelling scheme. (C) Node-and-linker-type description of the 1D coordination framework in **4**.

Topological analysis of framework **4** revealed that it has a 2-connected uninodal net with topological type 2C1 (Figure 4C).

In compounds **1-4** the organic ligand is almost plane, as well as the polymeric assemblies in **1, 2** and **4**. The co-planarity of H_3L^{2-} can be expressed by the angle between the least-square planes of the hetero- and the aromatic rings: 5.59° (**1**), 3.98° (**2**), 10.66° (**3**) and 5.22° (**4**).



Scheme 2 Coordination modes of H_3L^{2-} in **1-4**.

2.3 Comparison of the structures of 1–4 and pH-dependence

The structural differences of **1-4** reflect the extent and type of deprotonation of the 5-[2-(2,4,6-trioxotetrahydropyrimidin-5(2H)-ylidene)hydrazinyl]isophthalic acid (H_5L) ligand precursor. The linking fashions are illustrated in Scheme 2; the carboxylate groups adopt the unidentate, chelate, bridging and bridging chelating modes, whereas the deprotonated amide group shows the monodentate coordination. At acidic pH (**1** and **2**), the amide-N atoms of the ligand remain protonated, restricting themselves to coordination. The carboxylate groups coordinate to the metal ions via monodentate and bridging bidentate fashions (in case of **1**), or chelating plus bridging chelating bidentate modes (in case of **2**). Thus, 1D double chain type structures are formed in case of **1** and **2**.

With the increase of the pH value (10.0), compounds **3** and **4** are the obtained ones. In both of them one amide-N of the barbituric ring is deprotonated and coordinates in the monodentate fashion, while the other amide remains protonated. For compound **3**, both carboxylic acid and carboxylate groups of the ligand are uncoordinated and a mononuclear complex is obtained. But in **4** the carboxylate group coordinates to another Cd(II) ion in the chelating coordination mode, while the carboxylic group remains uncoordinated, generating a zig-zag type 1D structure. Therefore, taking into account the properties of H_5L , it is possible to construct derived CPs of different structural types based on pH-control, which plays a fundamental role in the formation of the resulting structure.

2.4 Photoluminescence studies

Luminescent compounds have gained a great deal of attention over the years and many CPs have been investigated and emerged as a new type of promising luminescent materials.²⁰ Therefore the luminescent properties of the free ligand precursor H_5L and complexes **1-4** have been investigated in the solid state at room temperature (Figure 5). The H_5L exhibits a weak emission at 522 nm ($\lambda_{ex} = 370$ nm), which could be attributed to the $\pi^*-\pi$ or π^*-n transitions.²¹ Complexes **1** and **2** exhibit emission characteristics similar to that of the free ligand. The emission peaks at 511 nm ($\lambda_{ex} = 370$ nm) in **1** and 514 nm ($\lambda_{ex} = 370$ nm) in **2** show a blue shift of ca. 8-10 nm, compared to that of the free ligand, which can be ascribed to the intra-ligand transition of the coordinated ligands.²² An analogous spectral pattern is observed for complex **3** ($\lambda_{em} = 492$, $\lambda_{ex} = 370$ nm) and **4** ($\lambda_{em} = 543$ nm, $\lambda_{ex} = 370$ nm), where the former shows a blue shift of ca. 30 nm and the latter exhibits a red shift of ca. 20 nm compared to that of the free ligand.

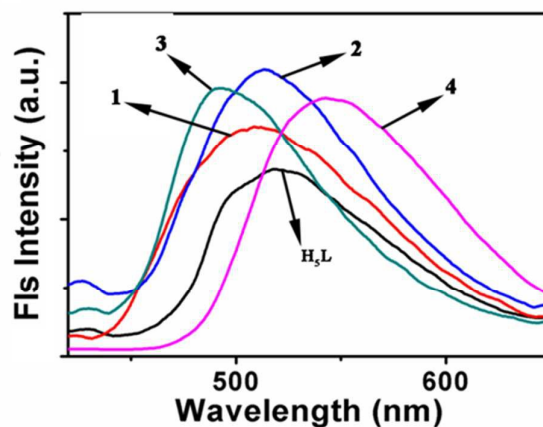


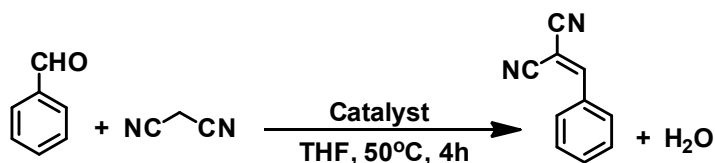
Figure 5 Solid state emission spectra of H_5L and complexes **1-4** at room temperature ($\lambda_{ex} = 370$ nm).

2.5 Catalytic application

The Knoevenagel condensation is one of the most useful C–C bond forming reactions.¹⁵ The condensation is usually catalysed by bases or acids and requires high reaction temperatures or microwave irradiation.²³ While various types of heterogeneous catalysts have been developed for such organic transformation,^{15,16} there is still a considerable interest in developing new ones, on account of their easy separation and reusability.

Therefore, we have tested the possible catalytic behaviour of our synthesised compounds **1-4** for such a condensation reaction. Tests performed with benzaldehyde and malononitrile in different solvents (THF, CH₃CN, EtOH, MeOH and H₂O) (Table 1, entries 7, 13-16) show that THF is the best one, leading to the highest yield (94%). The reactions under solvent-free conditions are much slower. Catalyst **3** is the most effective one, the catalytic performance following the order of **3>1>2>4** under the same experimental conditions (Table 1, entries 7, 21-23). Although the relationship between structure and catalytic activity is not clearly understood, the highest conversion shown by the compound **3** may be due its higher number of labile H₂O ligands and the easier accessibility of the zinc(II) centre to the substrate. In the other cases (**1**, **2** and **4**), the tight packing is unfavouring.

Consequently, the optimization of the reaction conditions (temperature, reaction time, amount of catalyst) was carried out in a model malononitrile–benzaldehyde system with **3** as the catalyst (Scheme 3, Table 1).



Scheme 3 Catalysed Knoevenagel condensation reaction of benzaldehyde with malononitrile.

The plot of yield *versus* time for the Knoevenagel condensation reaction of benzaldehyde and malononitrile with compound **3** is presented in Fig. 6A, showing that 4 h is the best reaction time.

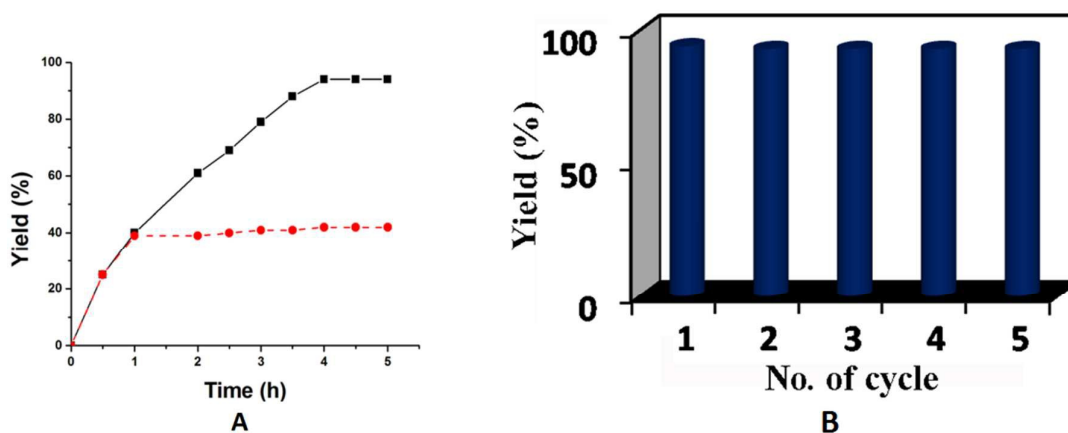


Fig. 6 (A) Plots of yield vs. time for the Knoevenagel condensation reaction of benzaldehyde and malononitrile in presence of catalyst **3** (black curve) and after filtering off the catalyst **3** (red curve). (B) Yield for five consecutive cycles of Knoevenagel condensation of benzaldehyde and malononitrile catalysed by **3**.

The reaction between benzaldehyde and malononitrile was also monitored in blank, as well as using free ligand precursor H_5L and the metal salts $Zn(NO_3)_2 \cdot 6H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$, instead of the catalysts (entries 24-27, Table 1). The reaction did not proceed at all in blank or in the presence of H_5L . Only 26 or 30% of product yield was obtained using $Zn(NO_3)_2 \cdot 6H_2O$ or $Cd(NO_3)_2 \cdot 4H_2O$ as catalyst, respectively. Moreover, the reaction performed by using 1:1 mixtures of H_5L and Zn(II) or Cd(II) salt led to only to yields of 25 or 31% (entries 28-29, Table 1).


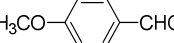
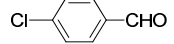
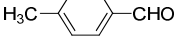
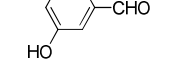
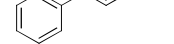
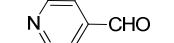
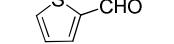
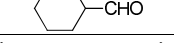
Table 1: Optimization of the parameters of the Knoevenagel condensation reaction between benzaldehyde and malononitrile with **3** as the catalyst^a

Entry	Catalyst	Time (h)	Amount of Catalyst (mol%)	T (°C)	Solvent	Yield (%) ^b	TON ^c
1	3	0.5	3.0	50	THF	25	8
2	3	1.0	3.0	50	THF	40	13
3	3	2.0	3.0	50	THF	61	20
4	3	2.5	3.0	50	THF	69	23
5	3	3	3.0	50	THF	79	26
6	3	3.5	3.0	50	THF	88	29
7	3	4.0	3.0	50	THF	94	31
8	3	4.5	3.0	50	THF	94	31
9	3	5.0	3.0	50	THF	94	31
10	3	4.0	1.0	50	THF	65	22
11	3	4.0	5.0	50	THF	93	31
12	3	4.0	7.0	50	THF	94	31
13	3	4.0	3.0	50	CH ₃ CN	82	27
14	3	4.0	3.0	50	EtOH	70	23
15	3	4.0	3.0	50	MeOH	75	25
16	3	4.0	3.0	50	H ₂ O	12	4
17	3	4.0	3.0	RT (22 °C)	THF	32	13
18	3	8.0	3.0	RT (22 °C)	THF	64	21
19	3	12.0	3.0	RT (22 °C)	THF	89	29
20	3	4.0	3.0	70 °C	THF	93	31
21	1	4.0	3.0	50	THF	84	28
22	2	4.0	3.0	50	THF	76	25
23	4	4.0	3.0	50	THF	80	27
24	Blank	4.0	-	50	THF	No Reaction	-
25	H ₅ L	4.0	3.0	50	THF	No Reaction	-
26	Zn(NO ₃) ₂ ·6H ₂ O	4.0	3.0	50	THF	26	9
27	Cd(NO ₃) ₂ ·6H ₂ O	4.0	3.0	50	THF	30	10
28	H ₅ L+ Zn(NO ₃) ₂ ·6H ₂ O	4.0	-	50	THF	25	-
29	H ₅ L+	4.0	-	50	THF	31	-

	Cd(NO ₃) ₂ ·6H ₂ O				
^a Reaction conditions unless stated otherwise: 3.0 mol% of catalyst 3 , solvent (THF) 1 mL, malononitrile (66 mg, 1.0 mmol) and benzaldehyde (0.50 mmol). ^b Calculated by ¹ H NMR. ^c Number of moles of product per mole of catalyst.					

The effects of temperature and catalyst amount were also monitored. At room temperature the reaction proceeds very slowly producing 89% yield after 12 h (entries 17-19, Table 1). However, increasing the temperature has a positive influence and the maximum yield (94%) was reached at 50 °C (entry 7, Table 1). Further temperature increase did not have any significant effect on the yield (entry 20, Table 1). Catalyst loading had a similar effect *i.e.*, its increase from 1.0 to 3.0 mol% increases the product yield from 65 to 94% (entries 7 and 10, Table 1), but further increase in the former had no significant effect on the latter (entries 11–12, Table 1).

We have also investigated the catalytic activity of **3** with different substituted aromatic, aliphatic, alicyclic and heterocyclic aldehydes in the reaction with malononitrile (Table 2). The highest yield was obtained by using *p*-nitrobenzaldehyde (100%), whilst the lowest one was for *p*-methoxybenzaldehyde (26%), suggesting that an electron-withdrawing substituent promotes the reactivity, relative to an electron-donor moiety, what can be related to the increase of the electrophilicity of the substrate in the former case. The yields for aliphatic, alicyclic and heterocyclic aldehydes are also good (66–79%).

Entry	Compound	Yield ^b (%)	TON ^c	ESI-MS (m/z, M ⁺)
1		100	33	200.24
2		42	14	185.26
3		89	30	189.85
4		35	12	169.78
5		68	23	171.65
6		60	20	181.56
7	Acetaldehyde	72	24	93.87
8	Propionaldehyde	66	22	107.54
9		75	25	156.89
10		71	24	161.67
11		79	26	161.32

^a Reaction conditions: 3.0 mol% of catalyst **3**, solvent (THF) 1 mL, malononitrile (66 mg, 1.0 mmol) and benzaldehyde (0.50 mmol). ^bCalculated by ¹H NMR. ^c Number of moles of product per mole of catalyst.

Leaching in general is a common phenomenon observed in the catalytic systems, leading to loss of activity. In order to test the possibility of leaching and the heterogeneity of our catalytic system, an experiment was performed following the procedure described by Sheldon *et al.*²⁴ After the reaction mixture was stirred for 1 h at 50 °C (only *ca.* 40 % conversion of benzaldehyde was then observed)

the catalyst was removed by filtration. The removal of the solid catalyst ceased the reaction completely (Fig. 6A), and no further conversion was observed even upon an extended time, supporting the heterogeneity of the catalyst with no appreciable leaching. Additionally, the filtrated solution, after the separation of the catalyst **3**, was evaporated to dryness and the amount of zinc determined was only 0.01% of that used in the reaction, thus ruling out any significant leaching of the catalyst.

In order to examine the reusability and stability of **3** during the catalytic process, it was recycled in five consecutive experiments and its catalytic activity was monitored. It remained almost the same (Figure 6B). FT-IR and powder X-ray diffraction of catalyst **3** taken before and after the reaction indicated that the structure of the solid was retained (Figure S1).

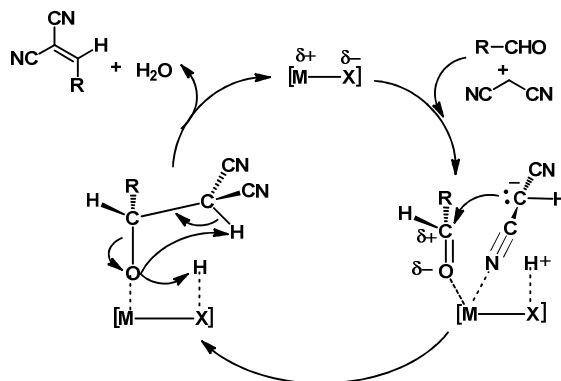
The efficiency of our catalyst in comparison with various CP catalysts for this kind of reaction is presented in Table 3. The obtained yield in our system is higher than that reported for a zinc(II) framework with a terephthalate derivative in which the reaction of benzaldehyde and malononitrile leads to an overall yield of 77% after 24 h reaction time at 70°C (*i.e.*, for a longer time and a higher temperature than in our case) (Table 3, entry 2).^{25a} Similarly, a 3D MOF built from nickel(II) ions and methanetetra benzoate ligands produced 78% yield after 6 h at 130°C (Table 3, entry 3).^{25b} Moreover, the reaction catalyzed by $[\text{Tb}(\text{BTATB})(\text{DMF})_2(\text{H}_2\text{O})]_n$ [BTATB = 4,4',4''-(benzene-1,3,5-triyltris(azanediyl))tribenzoate] produced 99% yield by using 4 mol% of catalyst at 60°C for 24 h, *i.e.*, longer time, higher temperature and higher catalyst amount than in our case (Table 3, entry 4).^{25c} At room temperature, our catalyst **3** led to a higher reaction yield than that reported for a Cd(II) MOF (Table 3, entries 5 and 6).^{25d} In comparison with other reported catalysts, ours have the advantages of being easy-to-prepare, rather cheap and highly active. Moreover, they are recyclable without appreciable loss of catalytic activity.

Entry	Catalyst	Amount of catalyst used (mol%)	Solvent/Temp/Time	Yield (%)	Ref.
1	$[\text{Zn}(\kappa\text{N-H}_3\text{L})(\text{H}_2\text{O})_3]\cdot 3\text{H}_2\text{O}$ (3)	3	THF/ 50 °C/ 5 h	94	This study
2	$[\text{Zn}_2\text{dobdc}]_n$	1	Toluene/ 70 °C/ 24 h	77	25a
3	$\{[\text{Ni}_4(\mu_6\text{-MTB})_2(\mu_2\text{-H}_2\text{O})_4(\text{H}_2\text{O})_4]\cdot 10\text{DMF}\cdot 11\text{H}_2\text{O}\}_n$	4	p-xylene/ 130 °C/ 6 h	78	25b
4	$[\text{Tb}(\text{BTATB})(\text{DMF})_2(\text{H}_2\text{O})]_n$	4	$\text{CH}_3\text{CN}/ 60\text{ °C}/ 24\text{ h}$	99	25c
5	$[\text{Zn}(\kappa\text{N-H}_3\text{L})(\text{H}_2\text{O})_3]\cdot 3\text{H}_2\text{O}$ (3)	3	THF/ RT/ 12 h	89	This study
6	$\{[\text{Cd}(\text{TPCT})_2(\text{SO}_4)_2]\text{DMF}\cdot 4\text{H}_2\text{O}\}_n$	4	$\text{CHCl}_3/\text{RT}/12\text{ h}$	80	25d

dobdc = 2,5-dioxidoterephthalate; MTB = methanetetra benzoate; BTATB = 4,4',4''-(benzene-1,3,5-triyltris(azanediyl))tribenzoate; TPCT = tri(pyridin-4-yl)cyclohexane-1,3,5-tricarboxamide

Among the four compounds (**1-4**), the zinc compounds (**3** and **1**) show higher catalytic activities than the cadmium complexes, which can be due to a higher Lewis acidic nature of Zn(II) ion. A possible mechanism for the Knoevenagel condensation catalyzed by **1-4** is presented in Scheme 4, on the basis of reported proposals.^{26,16g}

In the catalytic process it is assumed^{26,16g} that the zinc or cadmium centre (Lewis acid site) interacts with the carbonyl group of the benzaldehyde, increasing the electrophilic character of the carbonylic carbon atom, thus favouring the attack from the malononitrile. Similarly, the interaction of a cyano group of malononitrile with the Lewis acid metal site increases the acidity of its methylene moiety. The basic sites (carboxylate-O, amide-N or hydrazone-N) of our catalyst can abstract the proton from the methylenic compound to generate the corresponding nucleophilic species, which attacks the carbonyl group of benzaldehyde, with C–C bond formation and dehydration.



Scheme 4: Proposed catalytic cycle for the Knoevenagel condensation reaction catalyzed by **1-4** (M = Zn(II) or Cd(II) centre; X = O or N of a coordinated group).

3. Conclusion

In conclusion, four different zinc(II) and cadmium(II) compounds containing dicarboxyl-functionalized arylhydrazone of barbituric acid have been synthesized upon variation of pH under hydrothermal conditions, and structurally characterized. Compounds **1** and **2** have been obtained at acidic pH and they have one dimensional double chain-like structures. The metal ions are coordinated via ligand carboxylate groups and the amide functions remain protonated. However, compounds **3** and **4**, obtained under alkaline conditions, exhibit mononuclear and one dimensional zig-zag structures, respectively. In **3**, the Zn(II) ion is coordinated by a deprotonated amide-N whereas for **4** the Cd(II) centres are coordinated via both amide-N and carboxylate groups. These compounds show interesting zero dimensional and one dimensional structures with various topologies. The pH of the reaction system and the coordination modes of the arylhydrazone based ligand play pivotal roles in the formation of these structures. In addition, complexes **1-4** exhibit photoluminescence properties in the solid state at room temperature.

These compounds act as heterogeneous catalysts for the Knoevenagel condensation of aldehydes with malononitrile, at moderate temperature. Complex **3** is the most effective catalyst for this reaction. It effectively catalyzes the reaction of various aldehydes and malononitrile producing the corresponding benzylidenemalononitriles in high yields, which depend on the electrophilicity of the substrate. Moreover, the catalyst is stable and recyclable. This study provides further evidence that zinc(II) and Cd(II) coordination polymers containing arylhydrazone based ligand can be utilized as effective heterogeneous catalysts, under mild conditions, in this important organic reaction. Further explorations into the uses of this catalyst family in other organic transformations, as well as mechanistic investigations, are ongoing.

4. Experimental

The synthetic work was performed in air and at room temperature. All the chemicals were obtained from commercial sources and used as received. The infrared spectra (4000–400 cm^{-1}) were recorded on a Bruker Vertex 70 instrument in KBr pellets; abbreviations: s = strong, m = medium, w = weak, bs = broad and strong, mb = medium and broad. Carbon, hydrogen and nitrogen elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Thermal properties were analyzed with a Perkin-Elmer Instrument system (STA6000) at a heating rate of 5°C min^{-1} under a dinitrogen atmosphere. Powder X-ray diffraction (PXRD) was conducted in a D8 Advance Bruker AXS (Bragg Brentano geometry) theta-2theta diffractometer, with copper radiation ($\text{Cu K}\alpha$, $\lambda = 1.5406 \text{ \AA}$) and a secondary monochromator, operated at 40 kV and 40 mA. Flat plate configuration was used and the typical data collection range was between 5° and 40° . Emission spectra in solid state at room temperature were recorded on a Perkin Elmer Fluorescence Spectrometer (LS-55).

4.1 Syntheses

$[\text{Zn}(1\text{K}O:2\text{K}O':3\text{K}O''\text{-H}_3\text{L})(\text{H}_2\text{O})_2]_n$ (**1**)

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (29 mg, 0.10 mmol) and H_5L (32 mg, 0.10 mmol) [$\text{H}_5\text{L} = 5\text{-}[2\text{-}\{2,4,6\text{-trioxotetrahydropyrimidin-5(2H)\text{-ylidene}\}]\text{hydrazinyl}]\text{isophthalic acid}$] was dissolved in 2 mL of DMF and water (10 : 1). The pH of the solution was adjusted to 2.0 by the addition of HCl solution (1.0 M). The resulting mixture was sealed in an 8 mL glass vessel and heated at 75°C for 48 h. Subsequent gradual cooling to room temperature ($0.2^\circ\text{C min}^{-1}$) afforded light yellow crystals of **1**. Yield: 67% (based on Zn). Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_9\text{Zn}$ ($M = 419.61$): C, 34.35; H, 2.40; N, 13.35; Found: C, 34.22; H, 2.45; N, 13.02. FT-IR (KBr, cm^{-1}): 3477 (bs), 3377 (bs), 3029 (bm), 1719 (s), 1675 (s), 1611 (s), 1567 (s), 1525 (s), 1450 (s), 1401 (s), 1283 (m), 1261 (m), 1111 (w), 865(m), 799 (w), 779 (m), 522 (m), 495 (m).

$[\text{Cd}(1\text{K}O,O':2\text{K}O':3\text{K}O'',O'''\text{-H}_3\text{L})(\text{H}_2\text{O})_2]_n$ (**2**)

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (31 mg, 0.10 mmol) and H_5L (32 mg, 0.10 mmol) [$\text{H}_5\text{L} = 5\text{-}[2\text{-}\{2,4,6\text{-trioxotetrahydropyrimidin-5(2H)\text{-ylidene}\}]\text{hydrazinyl}]\text{isophthalic acid}$] were dissolved in 2 mL of DMF and water (10 : 1). The pH of the solution was adjusted to 2.0 by the addition of HCl solution (1.0 M). The resulting mixture was sealed in a capped glass vessel and heated to 75°C for 48 h. Subsequent gradual cooling to room temperature ($0.2^\circ\text{C min}^{-1}$) afforded yellow crystals of **2** in ca. 62% yield (based on Cd). Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{CdN}_4\text{O}_9$ ($M = 466.64$): C, 30.89; H, 2.16; N, 12.01; Found: C, 30.41; H, 2.01; N, 12.05. FT-IR (KBr, cm^{-1}): 3438 (bs), 3367 (bs), 3049 (bs), 2955 (bs), 1738 (s), 1691 (s), 1655 (s), 1633 (m), 1585 (m), 1528 (s), 1449 (m), 1386 (s), 1254 (s), 1139 (w), 1026 (w), 858 (s), 779 (m), 703 (s), 513 (s), 482 (s).

$[\text{Zn}(\text{K}N\text{-H}_3\text{L})(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$ (**3**)

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (29 mg, 0.10 mmol) and H_5L (32 mg, 0.10 mmol) [$\text{H}_5\text{L} = 5\text{-}[2\text{-}\{2,4,6\text{-trioxotetrahydropyrimidin-5(2H)\text{-ylidene}\}]\text{hydrazinyl}]\text{isophthalic acid}$] was dissolved in 2 mL of DMF and water (10 : 1). The pH of the solution was adjusted to 10.0 by the addition of 30% ammonium hydroxide solution. The resulting mixture was sealed in an 8 mL glass vessel and heated at 75°C for 48 h. It was subsequently cooled to room temperature ($0.2^\circ\text{C min}^{-1}$), affording plate-like yellow crystals of **3**. Yield: 71% (based on Zn). Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}_{13}\text{Zn}$ ($M = 491.67$): C, 29.31; H, 3.69;

N, 11.40; Found: C, 29.23; H, 3.52; N, 11.21. FT-IR (KBr, cm^{-1}): 3427 (bs), 3351 (bs), 3232 (bs), 3150 (bs), 1681 (s), 1623 (m), 1561 (s), 1510 (s), 1459 (s), 1393 (s), 1360 (s), 1287 (m), 1259 (s), 1100 (w), 885 (m), 821 (m), 785 (s), 548 (w), 490 (m).

[Cd(1κO,O':2κN-H₃L)(H₂O)₃]_n·4nH₂O (4)

A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (31 mg, 0.10 mmol) and H_5L (32 mg, 0.10 mmol) [$\text{H}_5\text{L} = 5\text{-}[2\text{-}\{2,4,6\text{-trioxotetrahydropyrimidin-5(2H)-ylidene}\} \text{hydrazinyl}] \text{isophthalic acid}$] were dissolved in 2 mL of DMF and water (10 : 1). The pH of the solution was adjusted to 10.0 by the addition of 30% ammonium hydroxide solution. The resulting mixture was sealed in an 8 mL glass vessel and heated at 75 °C for 48 h. It was subsequently cooled to room temperature (0.2 °C min^{-1}), affording yellow crystals of **4**. Yield: 58% (based on Cd). Anal. Calcd. for $\text{C}_{12}\text{H}_{20}\text{CdN}_4\text{O}_{14}$ ($M = 556.72$): C, 25.89; H, 3.62; N, 10.06; Found: C, 25.73; H, 3.41; N, 10.34. FT-IR (KBr, cm^{-1}): 3418 (bs), 3244 (bs), 1667 (s), 1614 (s), 1566 (s), 1506 (s), 1457 (m), 1384 (s), 1286 (m), 1259 (s), 1160 (m), 1103 (w), 812 (s), 777 (s), 731 (w), 531 (w), 491 (m).

4.2 Procedure for Knoevenagel condensation reaction catalyzed by the Zn(II) and Cd(II) coordination compounds

A reaction mixture of benzaldehyde (51 μL , 0.50 mmol), malononitrile (66 mg, 1.0 mmol) and catalyst (6.2 mg of **1**, 7.0 mg of **2**, 7.3 mg of **3** or 8.2 mg of **4**, 3 mol%) was placed in a capped glass vessel, and then 1 mL THF was added into it. The mixture was heated at 50 °C for 4 h, and subsequently quenched by centrifugation and filtration at room temperature. The filtrate was evaporated in vacuum to give the crude product [2-(Phenylmethylene) Malononitrile]. The residue was dissolved in CDCl_3 and analyzed by ^1H NMR. The ^1H -NMR spectra and the calculation of the yield for compound **3** in the Knoevenagel reaction is presented in the supporting information (Figure S2). The obtained m/z for 2-(phenylmethylene) malononitrile is 155.46 (M^+).

In order to perform the catalyst recycling experiments, the used catalyst (separated by centrifugation of the supernatant solution) was washed with THF and dried in air. It was then reused for the Knoevenagel condensation reaction as described above.

4.3 Crystal structure determinations

X-ray quality single crystals of the compounds were immersed in cryo-oil, mounted in a nylon loop and measured at room temperature (**1-4**). Intensity data were collected using a Bruker APEX-II PHOTON 100 diffractometer with graphite monochromated Mo-K α (λ 0.71069) radiation. Data were collected using phi and omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART²⁷ software and refined using Bruker SAINT^{27a} on all the observed reflections. Absorption corrections were applied using SADABS^{27a}. Structures were solved by direct methods by using the SHELXS-97 package^{27b} and refined with SHELXL-97^{27b}. Calculations were performed using the WinGX System-Version 1.80.03^{27c}. The hydrogen atoms attached to carbon atoms and to the nitrogen atoms were inserted at geometrically calculated positions and included in the refinement using the riding-model approximation; Uiso(H) were defined as 1.2Ueq of the parent nitrogen atoms or the carbon atoms for phenyl and methylene residues, and 1.5Ueq of the parent carbon atoms for the methyl groups. The hydrogen atoms of

coordinated water molecules were located from the final difference Fourier map and the isotropic thermal parameters were set at 1.5 times the average thermal parameters of the belonging oxygen atoms. The hydrogen atoms of the non-coordinated water were inserted in calculated positions by means of the CALC-OH routine of WinGX but their distances were fixed to achieve a reasonable result. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic ones for the remaining atoms were employed. PLATON/SQUEEZE^{27e} was used to correct the data and in compound **4** the potential volume of 1690 Å³ was found with 242 electrons per unit cell worth of scattering. The electron count suggests the presence of *ca.* 3 water molecules per asymmetric unit. Crystallographic data are summarized in Table S1 (Supplementary Information file) and selected bond distances and angles are presented in Table S2. CCDC 1422595-1422598 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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pH dependent synthesis of Zn(II) and Cd(II) coordination polymers with dicarboxyl-functionalized arylhydrazone of barbituric acid: photoluminescence properties and catalysts for Knoevenagel condensation

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Coordination polymers of Zn(II) and Cd(II) act as recyclable heterogeneous catalysts for Knoevenagel condensation reaction of aldehydes with malononitrile.

