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Zinc and Cadmium Complexes of Pyridinemethanol Carboxylates: Metal Carboxylate Zwitterions and Metal–Organic Frameworks

Yan Liu,[a] Shi-Xin Lin,[a] Ru-Jie Niu,[a] Quan Liu,*[b] Wen-Hua Zhang,*[a] and David J. Young[c]

Abstract: Hetero-functional lactone furo[3,4-b]pyridin-5(7H)-one (**L₁**) undergoes a coordination-induced ring-opening reaction with $Zn(NO_3)_2{\cdot}6H_2O$ to yield zwitterionic $[Zn(\mathbf{L_1'})_2(H_2O)_2]$ (**1**, **L₁'** = 2-(hydroxymethyl)nicotinate) with an uncoordinated carboxylate. The same reaction with $Cd(NO_3)_2{\cdot}4H_2O$ provides a two-dimensional (2D) network of $[Cd(\mathbf{L_1'})_2]_n$ (**3**) with the carboxylates coordinated to Cd^{2+} propagating the assembly. The corresponding reactions of $Zn(NO_3)_2{\cdot}6H_2O$ and $Cd(NO_3)_2{\cdot}4H_2O$ with 2-(hydroxymethyl)isonicotinic acid (H**L₂**) generated zwitterionic $[Zn(\mathbf{L_2})_2(H_2O)_2]$ (**2**) and 2D network $[Cd(\mathbf{L_2})_2]_n{\cdot}nDMF$ (**4**, DMF = N, N'-dimethylformamide), respectively. Complexes **1**−**4** are weakly emissive, giving ligand-centered emissions at 409 nm (**1**), 412/436 nm (**2**), 404 nm (**3**), and 412/436 nm (**4**) in $CHCl_3$ solutions upon excitation at 330 nm. This work points to the potential of using 'hidden' functionalities widely found in small organic molecules and natural products for the construction of coordination complexes with new functionality and potential applications.

Introduction

Metal–organic frameworks (MOFs) as a subset of coordination chemistry have experienced an explosion of interest over the last two decades.[1] Prepared by the self-assembly of metal ions and organic ligands, these unique materials have a variety of applications, including gas adsorption/separation,[2] analyte sensing,[3] catalysis,[1b, 1d, 4] and in biological systems.[5] This plethora of diverse uses is due to an almost limitless number of structural patterns by the combination of different metal sources and ligands. The porosity of some MOFs allows for guest species to diffuse into the inner space of the material to accomplish guest/metal/ligand exchange and ligand functionalization, further enriching the structural library.[6] Some flexible MOFs are also susceptible to structural variation while retaining their chemical composition when exposed to external stimuli, leading to the observation of some unusual behaviors such as breathing and negative gas adsorption.[7]

Most pristine MOFs are prepared by a one-pot assembly in solution, and usually involving hydrothermal conditions. This "black-box" method necessarily precludes the observation of the potentially interesting meta-stable phases that can significantly contribute to our understanding of MOF-shaping processes. We wondered if this hurdle could be at least partially overcome by employing hetero-functional ligands that permit observation of the coordination reactions in sequence before the ultimate MOF formation.

In this regard, we were interested in exploring MOFs supported by 2-pyridylmethanol carboxylate conjugated ligands.[3c, 8] Our initial interest in these compounds arises from earlier observations that 2-pyridinemethanol and its derivatives are able to support intriguing and diverse homo-/hetero-metallic cluster species under mild conditions, including Mn_2/Ir_2,[9] Ni_4/Ni_3Gd,[10] Mn_4Ca,[11] $Ni_7/Co_7/Co_6Na$,[12] Mn_{25},[13] among others. These clusters, as well as some mononuclear species, have applications as single-molecular magnets,[10c, 12-13] cluster models related to biological oxygen-evolving complexes[11] and synthetic water oxidation electrocatalysts.[9] Our use of 2-pyridylmethanol carboxylates for isolating MOFs bearing large cluster secondary building units (SBUs) unexpectedly leads to the isolation of MOFs with rod-shaped SBUs, similar to those found in MOF-74 and isoreticular networks.[3c, 8a] More recently, we have also reported the reaction of a porphyrin-based 2-pyridylmethanol ligand with Co(II) salt to provide a two-dimensional (2D) MOF wherein only half of the alcoholic oxygens were used for coordination to the Co^{2+} center, leaving the MOF with sufficient reactive 2-pyridylmethanol moieties on the surface for possible further reactions.[14]

During our previous studies, we found that metal carboxylate zwitterionic complexes of Co(II), Ni(II), Cu(II), and Zn(II), were readily isolable *en route* to the corresponding MOFs.[8] These zwitterions formed likely because of the strong chelation of the 2-pyridylmethanol moiety, coupled with the instability of metal-carboxylate bonds for these particular metal ions (especially Zn) in water,[15] as well as the intrinsic driving force to form neutral molecular species in solution.

In the present work, we have extended the study to isomeric 2-pyridylmethanol carboxylate ligands anticipating synergistic coordination of the two functionalities to yield new MOF patterns. We employed the same synthetic methodology as previously described for 2-(hydroxymethyl) isonicotinate (*iso*-hmnH, H**L₂**) and 6-(hydroxymethyl)nicotinate (hmnH) in the attempted synthesis of 2-(hydroxymethyl)nicotinate (Scheme 1).[8b]

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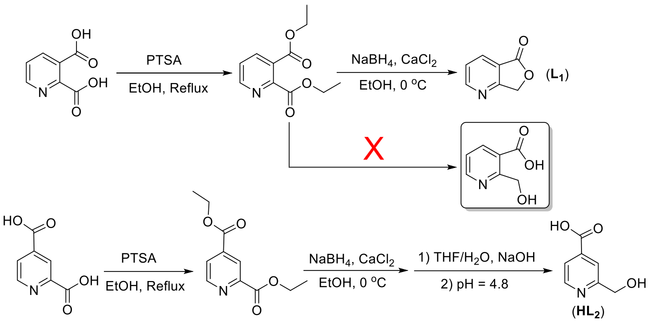
However, a lactone furo[3,4-b]pyridin-5(7H)-one (**L$_1$**) was formed by intramolecular esterification. The subsequent reactions of **L$_1$** and H**L$_2$** with $Zn(NO_3)_2{\cdot}6H_2O$ yielded zwitterions [Zn(**L$_1$'**)$_2$(H_2O)$_2$] (**1**, **L$_1$'** = 2-(hydroxymethyl)nicotinate) and [Zn(**L$_2$**)$_2$(H_2O)$_2$] (**2**) [8a] featuring un-coordinated carboxylates, while their corresponding reactions with $Cd(NO_3)_2{\cdot}4H_2O$ yielded 2D MOFs [Cd(**L$_1$'**)$_2$]$_n$ (**3**) and [Cd(**L$_2$**)$_2$]$_n$·nDMF (**4**, DMF = N, N'-dimethylformamide) featuring coordinated carboxylates that propagate the assembly. The formation of the zwitterion **1** through the coordination-driven ring-opening of lactone may point to an opportunity of using 'hidden' functionalities found in synthetic or naturally occurring species for the construction of coordination complexes with new properties and applications.



Scheme 1. Synthesis of **L$_1$** and H**L$_2$**.

Results and Discussion

We initially targeted the ligand 2-(hydroxymethyl)nicotinic acid wherein the N, –CH_2OH, and –COOH functionalities are aligned to achieve cooperative coordination and potentially yield MOFs sustained by new cluster SBUs (Scheme 1). However, the reduction step provided a white fibrous crystalline solid of lactone furo[3,4-b]pyridin-5(7H)-one (**L$_1$**) from intramolecular esterification in *ca* 25% yield. Both **L$_1$** and H**L$_2$** were spectroscopically characterized and their solid-state structures verified by single-crystal X-ray crystallography (Figure 1).

Reactions of **L$_1$** and H**L$_2$** with $Zn(NO_3)_2{\cdot}6H_2O$ in a DMF/H_2O mixed solvent yielded zwitterions [Zn(**L$_1$'**)$_2$(H_2O)$_2$] (**1**) and [Zn(**L$_2$**)$_2$(H_2O)$_2$] (**2**).[8] By contrast, their similar reactions using $Cd(NO_3)_2{\cdot}4H_2O$ as the metal source provided 2D MOFs of [Cd(**L$_1$'**)$_2$]$_n$ (**3**) and [Cd(**L$_2$**)$_2$]$_n$·nDMF (**4**). We reason that the Zn^{2+} preference for the zwitterionic complex formation and the Cd^{2+} preference for 2D matrices is due to their different binding affinities for the ligands relative to H_2O. The Zn(II)-carboxylate bond is susceptible to hydrolysis as observed for many Zn(II)-based MOFs, such as the iconic MOF-5.[15] On the other hand, Cd(II)-carboxylate coordination is comparatively more stable in water.[3c, 6g, 8b, 16] These small differences in coordination stabilities, though widely acknowledged, are rarely studied and compared in a systematic manner for coordination complexes and MOFs.

Zwitterionic complexes **1** and **2**, and 2D MOFs **3** and **4** were stable under aerobic conditions and in common organic solvents, such as CH_2Cl_2, $CHCl_3$, MeOH, EtOH, MeCN, and DMF. These compounds, together with their constituent ligands **L$_1$** and H**L$_2$** were accordingly characterized by Fourier transform infrared (FT-IR), microanalysis, electrospray ionization mass spectrometry (ESI-MS), powder X-ray diffraction (PXRD, Figure S1, Supporting Information), and thermogravimetric analysis (TGA, Figure S2, Supporting Information). The experimental PXRD of **1**–**4** matched those simulated from the X-ray single-crystal data, indicating the bulk phase purity of these compounds. TGA curves showed that MOF **3** is stable until around 350 °C (Figure S2a, Supporting Information), while the DMF-solvated MOF **4** lost DMF solvate between 170–315 °C. The total solvent loss of 16.2% (Figure S2b, Supporting Information) agrees well with the calculated value from the X-ray structure (14.9%) and microanalysis results. The structures of **L$_1$**, H**L$_2$**, and **1**–**4** were further authenticated by single-crystal X-ray crystallographic analysis.

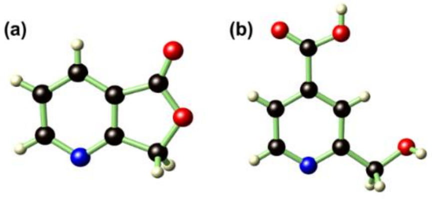


Figure 1. The single molecular structure of **L$_1$** (a) and H**L$_2$** (b). Colour legend: C (black), H (light-yellow), N (blue), O (red).

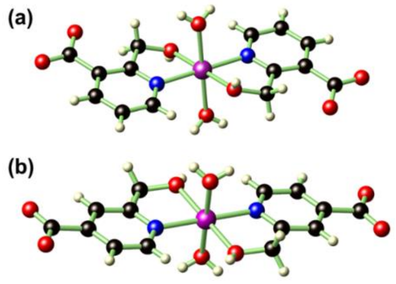


Figure 2. The zwitterionic structure of **1** (a) and **2** (b). Colour legend: Zn (magenta), C (black), H (light-yellow), N (blue), O (red).

Both ligands **L$_1$** (Figure 1a) and H**L$_2$** (Figure 1b) crystallize in the monoclinic space group $P2_1/n$ and $P2_1/c$. Ligand **L$_1$** is a lactone without conventional hydrogen-bonding donors but stabilized by non-conventional C−H···N and C−H···O hydrogen-bonding to give a three-dimensional (3D) network (Figure S3a and Table S2, Supporting Information). By contrast, ligand H**L$_2$** is rich in hydrogen-bonding donors, such as the alcoholic –OH, carboxylic –OH, and water –OH donors, as well as the hydrogen-bonding acceptors such as N, O$_{water}$, and carboxylic C=O, resulting in a 2D hydrogen-bonded network structure (Figure S3b and Table S2, Supporting Information).

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The zwitterionic structures of **1** (Figure 2a) and **2** (Figure 2b)[8a] crystallize in the monoclinic $P2_1/n$ and orthorhombic *Pbca* space groups and are isomeric in the location of the free and deprotonated carboxylates for charge balance. Pairs of alcoholic –OH, N and coordinated H_2O were mutually *trans* in both complexes, resembling those found in *trans*-Co(*iso*-hmnH)$_2$(H_2O)$_2$, *trans*-Ni(*iso*-hmnH)$_2$(H_2O)$_2$, and *trans*-Zn(3,2,4-hpbH)$_2$(H_2O)$_2$ (3,2,4-hpbH = 3-(2-(hydroxymethyl)pyridin-4-yl) benzoate).[8b] In **1**, the two C–O bond distances of 1.227(3) Å and 1.238(3) Å (Table S1, Supporting Information) for the uncoordinated carboxylates are nearly identical, indicating that they are conjugated and the complex is zwitterionic. Zwitterionic **1** features a complicated 3D structure as stabilized by various hydrogen-bonding interactions between alcohol –OH and water –OH as donors, and the free, uncoordinated –COO as acceptors (Figure S3c and Table S2, Supporting Information).

MOF **3** crystallizes in the monoclinic space group *C2/c*. In **3**, each Cd^{2+} is chelated by a pair of 2-pyridylmethanol moieties in addition to a pair of monodentate carboxylates in the *cis* configuration (Figure 3a), thus defining a distorted octahedron geometry. Each **L₁'** ligand, in turn, bridges two Cd centers to form a 2D grid (Figure 3c).

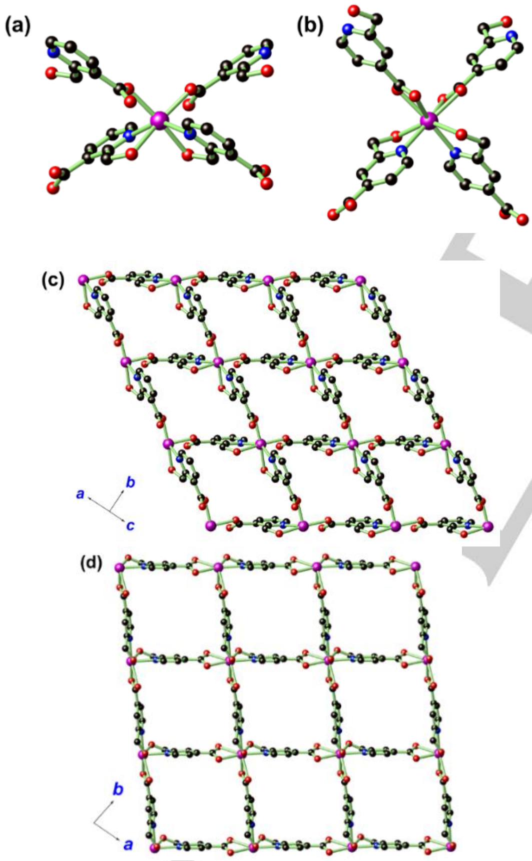

Figure 3. Views of the full coordination sphere of Cd in MOFs **3** (a) and **4** (b), as well as their 2D grid structures looking along the crystallographic [102] (**3**, c) and *c* directions (**4**, d). Colour codes: Cd (dark magenta), C (black), N (blue), O (red).

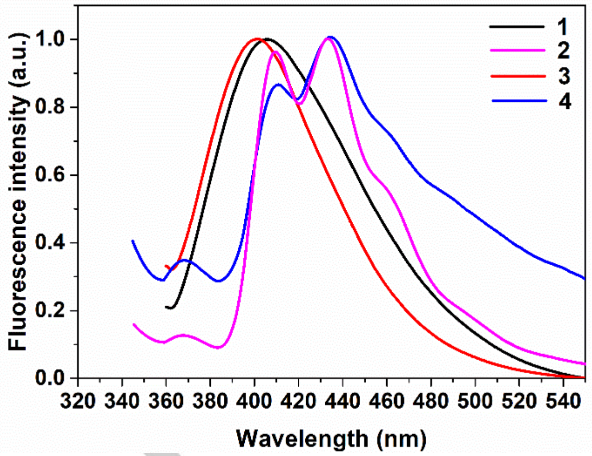

Figure 4. Normalized emission spectra of zwitterions **1** (black) and **2** (light pink) and MOFs **3** (red) and **4** (blue) suspended in $CHCl_3$ at an excitation wavelength of 330 nm.

MOF **4** also crystallizes in the monoclinic space group *C2/c*. Each Cd^{2+} in **4** is chelated by a pair of 2-pyridylmethanol moieties which is a similar arrangement to that of **3** (Figure 3b). The Cd-O distance of 2.4779(9) Å and Cd-N distance of 2.3439(10) Å are similar to those identified in MOF **3** (2.3458(17) Å for Cd-O and 2.3441(18) Å for Cd-N, Table S1, Supporting Information). However, in **4**, the distances between Cd and the two O atoms of the coordinated carboxylates are 2.5872(9) Å and 2.3393(8) Å, contrasting with 2.2809(16) Å and 3.0821(16) Å in **3**, and suggesting a chelating coordination of the carboxylate in **4**. Thus each Cd^{2+} is eight-coordinate and associated with four **L₂** ligands. Each **L₂** ligand, in turn, bridges two Cd^{2+} centers to give a 2D grid (Figure 3d) with connectivity resembling that of MOF **3**.

The 2D layers of both **3** and **4** are packed in ABAB fashion supported by the inter-layer hydrogen-bonding between the alcoholic –OH as the donor and the carboxylate as the acceptor (Figures S3d and S3e, Supporting Information). While MOF **3** is non-porous, MOF **4** features voids of 552.2 Å^3 per cell which corresponds to 30.2% of the total cell volume. This void volume is occupied by DMF solvates as revealed by Platon.[15]

Crystalline powders of **L₁**, H**L₂**, zwitterions **1** and **2**, and MOFs **3** and **4** were dissolved or suspended in $CHCl_3$ for photoluminescence measurements. Upon excitation at 330 nm, **L₁** and H**L₂** gave rise to weak emissions at 400 nm (**L₁**) and 412/435 nm (H**L₂**) (Figure S4, Supporting Information). The emissions of zwitterion **1** (409 nm) and MOF **3** (404 nm) resemble that of **L₁**, whereas the nearly identical emissions of zwitterion **2** (412/436 nm) and MOF **4** (412/436 nm) resemble that of H**L₂** (Figure 4), suggesting ligand-centered emissions for all four coordination compounds, facilitated by the d^{10} electronic configurations of Zn^{2+} and Cd^{2+} that resists both oxidation and reduction.[3f, 17]

Neither MOFs **3** or **4** adsorbs N_2 at 77 K (Figures S5a and S5b, Supporting Information), presumably due to the large kinetic size of N_2 (3.64 Å). MOF **3** does not adsorb CO_2 (Figure S5c, Supporting Information) while MOF **4** adsorbed 32.9 $cm^3\ g^{-1}$ CO_2 (1.47 $mmol\ g^{-1}$, 6.50 wt% at standard temperature and pressure, STP, Figure S5d, Supporting Information) which is low compared to most MOFs, such as [Zn(*iso*-hmn)] (1.63 $mmol\ g^{-1}$; 7.23 wt% at STP),[8a] and Mn(2,6-ndc) (3.0 $mmol\ g^{-1}$; 13.0 wt% at STP; ndc = 2,6-naphthalenedicarboxylate).[18]

Conclusions

In summary, we have prepared a pyridyl-fused lactone and 2-pyridinemethanol carboxylate ligand, as well as their corresponding metal zwitterions (for Zn) and 2D MOFs (for Cd). The variation of the product outcome likely originates from the different coordination stabilities Zn and Cd toward carboxylate, relative to H_2O. Zwitterion and MOF preparation from a lactone is an interesting route and may point to some new coordination chemistry using abundant synthetic and naturally occurring molecules such as Lamellarin D, Camptothecin, and D-Glucuronic acid lactone. One possible application might be the development of drug-based Trojan-horse coordination complexes. These temporarily altered drug molecules could exhibit different, and hopefully lower toxicity than their unmodified progenitors. The coordination bond is often unstable in the complex, and aqueous environment of a biological system may induce the release of the therapeutic species in a sustained and more-or-less predictable manner.

Experimental Section

Ligand H**L₂** and [Zn(**L₂**)₂(H₂O)₂] (**2**) were synthesized following our reported procedures.[8] $Zn(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$ and other reagents were obtained from commercial sources and used as received. FT-IR spectra were measured on a Varian 1000 FT-IR spectrometer as KBr disks (400–4000 cm^{-1}). Elemental analyses for C, H, and N were performed on a Carlo-Erba CHNO-S microanalyzer. High-resolution mass spectra (HRMS-ESI) were obtained on a MicroTM or a Micro YA263 Q-TOF mass spectrometer. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo Star System at a heating rate of 5 °C min^{-1} under a nitrogen gas flow in an Al_2O_3 pan. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 GADDS micro-diffractometer equipped with a VANTEC-2000 area detector using φ rotation. The N_2 and CO_2 adsorption isotherms for MOFs **3** and **4** were measured at 77 K (liquid nitrogen) and room temperature using a BELSORP-max (BEL, Japan). Single crystals of MOFs **3** and **4** (around 100 mg for each sample) were ground into fine powders and washed with $CHCl_3$ several times, before further dynamic vacuum at 100 °C for 12 hours prior to gas adsorption studies.

Synthesis of furo[3,4-b]pyridin-5(7H)-one (L_1)

Step 1. 2,3-Pyridinedicarboxylic acid (25.25 g, 0.15 mol) was mixed with *p*-toluenesulfonic acid monohydrate (60.35 g, 0.32 mol, 2.1 eq) in EtOH (1 L). The solution was refluxed at 100 °C for 5 days and then cooled to r.t. The solvent was evaporated and saturated Na_2CO_3 (73.98 g, 0.70 mol) carefully added. The residue was extracted with $CHCl_3$ twice and the extracts combined, washed with brine 3 times and dried over anhydrous $MgSO_4$. Chromatographic purification on silica using EA/hexane (2:1, *v*/*v*) as eluent yielded 2,3-diethylcarboxypyridine as a light-yellow oil. Yield 30.96 g, 91.8%. ^1H NMR (400 MHz, $CDCl_3$): δ 8.73–8.74 (m, 1H), 8.16–8.18 (m, 1H), 7.44–7.47 (m, 1H), 4.34–4.47 (m, 4H), 1.34–1.42 (m, 6H). $^{13}C\ \{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 167.0, 165.9, 152.3, 151.9, 138.2, 127.0, 125.3, 62.7, 14.7.

Step 2. $CaCl_2$ (0.83 g, 7.5 mmol) was added portion-wise with stirring to a degassed solution of 2,3-diethylcarboxypyridine (1.67 g, 7.5 mmol) and $NaBH_4$ (0.19 g, 5.0 mmol) in EtOH (75 mL) at 0 °C. The resulting mixture was stirred for 2.5 h at the same temperature and quenched with concentrated H_2SO_4 (2 drops). The mixture was stirred for 3 h and left stand overnight. White precipitate of $CaSO_4$ was removed by filtration and the solvent evaporated. Brine was added and the mixture extracted with $CHCl_3$, followed by solvent evaporation and column chromatography purification (EA/hexane, 2:1, *v*/*v*) to give light-yellow crystalline fibres of furo[3,4-b]pyridin-5(7H)-one (**L₁**, 0.25 g, 25%). High quality colourless block crystals were grown by slow evaporation of **L₁** in CH_2Cl_2/EtOH or CH_2Cl_2/hexane. ^1H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, J = 4.2 Hz, 1H), 8.19 (d, J = 7.7 Hz, 1H), 7.46–7.49 (m, 1H), 5.31 (s, 2H) $^{13}C\ \{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 167.2, 156.0, 139.0, 134.7, 124.6, 120.5, 71.0. Anal. Calcd. (%) for $C_7H_5NO_2$: C 62.22, H 3.73, N 10.37; found: C 62.25, H 3.46, N 10.16. IR (KBr pellet): 3506(w), 3076 (w), 2966 (w), 2941 (w), 2768 (w), 2526 (w), 2447 (w), 2282 (w), 2083 (w), 1992 (w), 1974 (w), 1955 (w), 1875 (w), 1769 (s), 1649 (sh), 1605 (s), 1589 (s), 1475 (s), 1458 (s), 1421 (s), 1371 (s), 1357 (s), 1301 (s), 1266 (s), 1241 (s), 1196 (m), 1184 (s), 1099 (s), 1050 (s), 1001 (s), 963 (sh), 866 (w), 822 (m), 748 (s), 698 (s), 601 (m), 506 (w), 468 (s), 406 (w) cm^{-1}.

Synthesis of [Zn(L₁')₂(H₂O)₂] (1)

$Zn(NO_3)_2{\cdot}6H_2O$ (29.8 mg, 0.1 mmol) in 2 mL H_2O was added to **L₁** (27.0 mg, 0.2 mmol) and the mixture heated at 120 °C for 3 days and then slowly cooled to r.t. to give a colourless solution, which was filtered and slowly evaporated to give colourless, platelet crystals. These crystals were filtered, washed with H_2O and dried under vacuum. Yield: (13.0 mg, 32 % based on Zn). Anal. Calcd. (%) for $C_{14}H_{16}N_2O_8Zn$: C 41.45, H 3.98, N 6.91; found: C 41.89, H 3.73, N 6.89. IR (KBr pellet): 3195(s, br), 2775 (s), 2642 (s), 2576 (sh), 2484 (sh), 1923 (w), 1805 (w), 1611 (s), 1570 (s), 1477 (s), 1421 (s), 1379 (s), 1271 (m), 1240 (m), 1197 (m), 1155 (m), 1112 (m), 1074 (m), 1043 (s), 1006 (sh), 866 (s), 805 (s), 777 (s), 718 (s), 635 (s), 571 (m), 489 (w), 451 (w), 438 (w) cm^{-1}.

Synthesis of [Cd(L₁')₂]ₙ (3)

$Cd(NO_3)_2{\cdot}4H_2O$ (15.5 mg, 0.05 mmol) and **L₁** (13.5 mg, 0.1 mmol) were added to a Pyrex glass tube (10 cm in length and 0.5 cm in diameter) followed by DMF/H_2O (1 mL/2 mL). The tube was sealed and heated in an oven at 120 °C for three days and gradually cooled to ambient temperature at a rate of 5 °C min^{-1}. The colourless crystals formed were filtered, washed with DMF and dried under vacuum. Yield: (8.1 mg, 39 % based on Cd). Anal. Calcd. (%) for $C_{14}H_{12}CdN_2O_6$: C 40.36, H 2.90, N 6.72; found: C 40.78, H 2.91, N 6.93. IR (KBr pellet): 3432 (br), 3164 (br), 2963 (w), 2929 (w), 1773 (s), 1607 (m), 1590 (m), 1475 (m), 1458 (w), 1400 (s), 1385 (s), 1357 (w), 1301 (w), 1266 (w), 1138 (s), 1058 (s), 1001 (m), 823 (w), 751 (m), 617 (w), 537 (w), 468 (w), 401 (w) cm^{-1}.

Synthesis of [Cd(L₂)₂]ₙ·nDMF (4)

$Cd(NO_3)_2{\cdot}4H_2O$ (31 mg, 0.1 mmol) and ethyl 2-(hydroxymethyl)isonicotinate (the precursor of **HL₂**, 36 mg, 0.2 mmol) were dissolved in DMF/H_2O (4 mL/4 mL) and heated at 125 °C for 72 h in a DURAN glass bottle. The light-yellow crystals formed were filtered and washed with DMF. Yield: (25.0 mg, 51 % based on Cd). Anal. Calcd. (%) for $C_{17}H_{19}CdN_3O_7$: C 41.69, H 3.91, N 8.58; found: C 41.88, H 3.91, N 7.90. IR (KBr pellet): 3178 (s), 2923 (s), 2850 (s), 2729 (w), 1735 (w), 1638 (s), 1599 (s), 1559 (s), 1462 (s), 1379 (s), 1329 (s), 1281 (s), 1256 (s), 1215 (w), 1116 (m), 1063 (s), 1018 (m), 898 (w), 882 (m), 818 (s), 787 (s), 737 (m), 702 (s), 632 (w), 595 (w), 569 (w), 494 (w), 420 (w) cm^{-1}.

X-ray crystallography

Crystallographic measurements were made on a Bruker AXS APEX II diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å). Absorption and other corrections were applied using SADABS.[19] All crystal structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with the SHELXTL-2016 program.[20] For H**L₂**, **1**, **3** and **4**, the hydrogen atoms on the alcoholic O–H were located from the difference Fourier map with their O–H distances restrained to O–H = 0.83 Å and thermal parameters constrained to $U_{iso}(H) = 1.2U_{eq}(O)$. For **4**, some spatially delocalized electron density in the lattice was found and initially modeled as disordered DMF molecules. However, such modeling gave high atomic displacement parameters and short contacts between some of the disordered atoms with the latter prompting A-level alerts in the Platon checkCIF routine.[21] The solvent contribution was then modeled using SQUEEZE in the Platon program suite.[22] A total of 157 electrons were calculated for each cell, which corresponds to 3.92 DMF molecules. The correct formula of **4** can thus be written approximately as $[Cd(\mathbf{L_2})_2]_n \cdot nDMF$ (Z = 4). Crystallographic data for $\mathbf{L_1}$, H$\mathbf{L_2}$, **1**, **3**, and **4** have been deposited in the Cambridge Crystallographic Data Center (CCDC) as supplementary publication numbers 1851500–1851504. These data can be obtained free of charge either from the CCDC via www.ccdc.cam.ac.uk/data_request/cif or from the Supporting Information. A summary of the key crystallographic data for $\mathbf{L_1}$, H$\mathbf{L_2}$, **1**, **3** and **4** are listed in Table 1, and selected bond distances and angles for $\mathbf{L_1}$, H$\mathbf{L_2}$, and **1**–**4** are listed in Table S1 (Supporting Information).

Table 1. Summary of crystallographic data for $\mathbf{L_1}$, H$\mathbf{L_2}$, **1**, **3**, and **4**.

Compounds	$\mathbf{L_1}$	H$\mathbf{L_2}$	**1**	**3**	**4**
Formula	$C_7H_5NO_2$	$C_{14}H_{16}N_2O_7$	$C_{14}H_{16}N_2O_8Zn$	$C_{14}H_{12}CdN_2O_6$	$C_{14}H_{12}CdN_2O_6$
FW	135.12	324.29	405.66	416.66	416.66
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$C2/c$	$C2/c$
a (Å)	3.9376(3)	7.1153(9)	8.0129(7)	13.6320(9)	14.0656(7)
b (Å)	6.8834(4)	27.746(3)	11.1371(10)	8.2693(6)	12.5058(6)
c (Å)	22.4069(15)	7.4756(9)	8.6477(7)	13.6886(9)	10.8846(6)
α (º)	90.00	90.00	90.00	90.00	90.00
β (º)	91.641(2)	106.634(4)	107.705(2)	118.2690(10)	107.1520(10)
γ (º)	90.00	90.00	90.00	90.00	90.00
V (Å^3)	607.07(7)	1414.1(3)	735.17(11)	1359.04(16)	1829.47(16)
Z	4	4	2	4	4
ρ_{calc}, g cm^{-3}	1.478	1.523	1.833	2.036	1.513
μ, mm^{-1}	0.111	0.124	1.722	1.643	1.221
$F(000)$	280	680	416	824	824
Total reflns.	22350	22769	10036	2515	13017
Uniq. reflns.	2897	2506	1347	1287	2183
Reflns. (I ≥ 2σ(I))	2349	2312	1183	1274	2142
R_{int}	0.0289	0.0462	0.0233	0.0128	0.0228
Parameters	91	226	127	108	108
R_1[a]	0.0519	0.0814	0.0240	0.0192	0.0139
wR_2[b]	0.1455	0.0812	0.0592	0.0491	0.0348
GOF[c]	1.098	1.152	1.074	1.191	1.080
ρ_{max}/ρ_{min}, e Å^{-3}	0.325/–0.285	0.286/–0.382	0.442/–0.412	0.342/–1.092	0.438/–0.449

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b] $wR_2 = \{\Sigma[\omega(F_o^2-F_c^2)^2]/\Sigma[\omega(F_o^2)^2]\}^{1/2}$, and [c] $GOF = \{\Sigma[\omega(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections, and p the total number of parameters refined.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carboxylates • lactones • metal−organic frameworks • ring-opening reactions • zwitterions

[1] a) J. Zhu, P. M. Usov, W. Xu, P. J. Celis-Salazar, S. Lin, M. C. Kessinger, C. Landaverde-Alvarado, M. Cai, A. M. May, C. Slebodnick, D. Zhu, S. D. Senanayake, A. J. Morris, *J. Am. Chem. Soc.* **2018**, *140*, 993−1003; b) J. Zhu, P.-Z. Li,

W. Guo, Y. Zhao, R. Zou, *Coord. Chem. Rev.* **2018**, *359*, 80−101; c) X. Zhao, S. Shimazu Matthew, X. Chen, X. Bu, P. Feng, *Angew. Chem. Int. Ed.* **2018**, *57*, 6208−6211; d) W. Zhang, B. Zheng, W. Shi, X. Chen, Z. Xu, S. Li, R. Chi Yonggui, Y. Yang, J. Lu, W. Huang, F. Huo, *Adv. Mater.* **2018**, *30*, 1800643; e) W. Zhang, J. Lu, X. Gao, P. Li, W. Zhang, Y. Ma, H. Wang, B. Tang, *Angew. Chem. Int. Ed.* **2018**, *57*, 4891−4896; f) J.-D. Xiao, L. Han, J. Luo, S.-H. Yu, H.-L. Jiang, *Angew. Chem. Int. Ed.* **2018**, *57*, 1103−1107; g) B. Tu, Q. Pang, H. Xu, X. Li, Y. Wang, Z. Ma, L. Weng, Q. Li, *J. Am. Chem. Soc.* **2017**, *139*, 7998−8007; h) Q.-G. Zhai, X. Bu, X. Zhao, D.-S. Li, P. Feng, *Acc. Chem. Res.* **2017**, *50*, 407−417; i) P.-Q. Liao, N.-Y. Huang, W.-X. Zhang, J.-P. Zhang, X.-M. Chen, *Science* **2017**, *356*, 1193−1196; j) J. A. do Nascimento Neto, A. K. S. M. Valdo, C. C. da Silva, F. F. Guimarães, L. H. K. Queiroz Júnior, L. J. Q. Maia, R. C. de Santana, F. T. Martins, *J. Am. Chem. Soc.* **2019**, *141*, 3400−3403.

[2] a) Y. Wang, W. Liu, Z. Bai, T. Zheng, A. Silver Mark, Y. Li, Y. Wang, X. Wang, J. Diwu, Z. Chai, S. Wang, *Angew. Chem. Int. Ed.* **2018**, *57*, 5783−5787; b) N. Prasetya, A. A. Teck, B. P. Ladewig, *Sci. Rep.* **2018**, *8*, 2944; c) S. Mukherjee, A. V. Desai, S. K. Ghosh, *Coord. Chem. Rev.* **2018**, *367*, 82−126; d) M. Meckler Stephen, E. Bachman Jonathan, P. Robertson Benjamin, C. Zhu, R. Long Jeffrey, A. Helms Brett, *Angew. Chem. Int. Ed.* **2018**, *57*, 4912−4916; e) G. Liu, V. Chernikova, Y. Liu, K. Zhang, Y. Belmabkhout, O. Shekhah, C. Zhang, S. Yi, M. Eddaoudi, W. J. Koros, *Nat. Mater.* **2018**, *17*, 283−289; f) M. J. Lee, H. T. Kwon, H.-K. Jeong, *Angew. Chem. Int. Ed.* **2018**, *57*, 156−161; g) M.-Y. Chao, W.-H. Zhang, J.-P. Lang, *Molecules* **2018**, *23*, 755; h) Y. Deng, Y. Zhao, X.-D. Zhang, Y.-S. Kang, W.-Y. Sun, *Micropor. Mesopor. Mater.* **2016**, *231*, 163−170; i) Y.-L. Li, D. Zhao, Y. Zhao, P. Wang, H.-W. Wang, W.-Y. Sun, *Dalton Trans.* **2016**, *45*, 8816−8823; j) K. Chen, Y.-S. Kang, L. Luo, Y. Zhao, P. Wang, Q. Liu, Y. Lu, W.-Y. Sun, *Polyhedron* **2014**, *79*, 239−249; k) M.-H. Yu, B. Space, D. Franz, W. Zhou, C. He, L. Li, R. Krishna, Z. Chang, W. Li, T.-L. Hu, X.-H. Bu, *J. Am. Chem. Soc.* **2019**, *141*, 17703−17712; l) X.-Y. Hou, X.-L. Yan, X. Wang, S. n. Li, Y. Jiang, M. Hu, Q.-G. Zhai, *Cryst. Growth Des.* **2018**, *18*, 6035−6045; m) X.-J. Kong, T. He, Y.-Z. Zhang, X.-Q. Wu, S.-N. Wang, M.-M. Xu, G.-R. Si, J.-R. Li, *Chem. Sci.* **2019**, *10*, 3949−3955.

[3] a) Z.-Z. Lu, R. Zhang, Y.-Z. Li, Z.-J. Guo, H.-G. Zheng, *J. Am. Chem. Soc.* **2011**, *133*, 4172−4174; b) W. Yan, C. Zhang, S. Chen, L. Han, H. Zheng, *ACS Appl. Mater. Interfaces* **2017**, *9*, 1629−1634; c) F.-L. Yuan, Y.-Q. Yuan, M.-Y. Chao, D. J. Young, W.-H. Zhang, J.-P. Lang, *Inorg. Chem.* **2017**, *56*, 6522−6531; d) H.-L. Chen, R.-T. Li, K.-Y. Wu, P.-P. Hu, Z. Zhang, N.-H. Huang, W.-H. Zhang, J.-X. Chen, *Talanta* **2020**, *210*, 120596; e) B.-P. Xie, G.-H. Qiu, B. Sun, Z.-F. Yang, W.-H. Zhang, J.-X. Chen, Z.-H. Jiang, *Inorg. Chem. Front.* **2019**, *6*, 148−152; f) Y.-X. Shi, F.-L. Hu, W.-H. Zhang, J.-P. Lang, *CrystEngComm* **2015**, *17*, 9404−9412; g) H. Wang, W. P. Lustig, J. Li, *Chem. Soc. Rev.* **2018**, *47*, 4729−4756; h) Z. Hu, B. J. Deibert, J. Li, *Chem. Soc. Rev.* **2014**, *43*, 5815−5840; i) B. Chen, L. Wang, Y. Xiao, F. R. Fronczek, M. Xue, Y. Cui, G. Qian, *Angew. Chem. Int. Ed.* **2009**, *48*, 500−503; j) M.-H. Yu, T.-L. Hu, X.-H. Bu, *Inorg. Chem. Front.* **2017**, *4*, 256−260.

[4] a) K. Yuan, T. Song, D. Wang, X. Zhang, X. Gao, Y. Zou, H. Dong, Z. Tang, W. Hu, *Angew. Chem. Int. Ed.* **2018**, *57*, 5708−5713; b) D. Yang, M. A. Ortuño, V. Bernales, C. J. Cramer, L. Gagliardi, B. C. Gates, *J. Am. Chem. Soc.* **2018**, *140*, 3751−3759.

[5] a) C. Doonan, R. Riccò, K. Liang, D. Bradshaw, P. Falcaro, *Acc. Chem. Res.* **2017**, *50*, 1423−1432; b) R. Riccò, W. Liang, S. Li, J. J. Gassensmith, F. Caruso, C. Doonan, P. Falcaro, *ACS Nano* **2018**, *12*, 13−23; c) G.-H. Qiu, Z.-H. Weng, P.-P. Hu, W.-J. Duan, B.-P. Xie, B. Sun, X.-Y. Tang, J.-X. Chen, *Talanta* **2018**, *180*, 396−402; d) L. Qin, Z.-Y. Sun, K. Cheng, S.-W. Liu, J.-X. Pang, L.-M. Xia, W.-H. Chen, Z. Cheng, J.-X. Chen, *ACS Appl. Mater. Interface* **2017**, *9*, 41378−41386; e) S.-P. Yang, S.-R. Chen, S.-W. Liu, X.-Y. Tang, L. Qin, G.-H. Qiu, J.-X. Chen, W.-H. Chen, *Anal. Chem.* **2015**, *87*, 12206−12214.

[6] a) A. W. Stubbs, L. Braglia, E. Borfecchia, R. J. Meyer, Y. Román- Leshkov, C. Lamberti, M. Dincă, *ACS Catal.* **2018**, *8*, 596−601; b) C. Zhao, X. Dai, T. Yao, W. Chen, X. Wang, J. Wang, J. Yang, S. Wei, Y. Wu, Y. Li, *J. Am. Chem. Soc.* **2017**, *139*, 8078−8081; c) J. Ma, A. P. Kalenak, A. G. Wong-Foy, A. J. Matzger, *Angew. Chem. Int. Ed.* **2017**, *56*, 14618−14621; d) J. A. Boissonnault, A. G. Wong-Foy, A. J. Matzger, *J. Am. Chem. Soc.* **2017**, *139*, 14841−14844; e) C. Liu, C. Zeng, T.-Y. Luo, A. D. Merg, R. Jin, N. L. Rosi, *J. Am. Chem. Soc.* **2016**, *138*, 12045−12048; f) Y. Ma, R. Matsuda, H. Sato, Y. Hijikata, L. Li, S. Kusaka, M. Foo, F. Xue, G. Akiyama, R. Yuan, S. Kitagawa, *J. Am. Chem. Soc.* **2015**, *137*, 15825−15832; g) Z.-X. Zhang, N.-N. Ding, W.-H. Zhang, J.-X. Chen, D. J. Young, T. S. A. Hor, *Angew. Chem. Int. Ed.* **2014**, *53*, 4628−4632.

[7] a) S. Bureekaew, H. Sato, R. Matsuda, Y. Kubota, R. Hirose, J. Kim, K. Kato, M. Takata, S. Kitagawa, *Angew. Chem. Int. Ed.* **2010**, *49*, 7660−7664; b) S. K. Elsaidi, M. H. Mohamed, D. Banerjee, P. K. Thallapally, *Coord. Chem. Rev.* **2018**, *358*, 125−152; c) J.-P. Zhang, H.-L. Zhou, D.-D. Zhou, P.-Q. Liao, X.-M. Chen, *Nat. Sci. Rev.* **2018**, *5*, 907−919; d) T. D. Bennett, A. K. Cheetham, A. H. Fuchs, F.-X. Coudert, *Nat. Chem.* **2016**, *9*, 11−16; e) H. Li, M. R. Hill, *Acc. Chem. Res.* **2017**, *50*, 778−786.

[8] a) M. Armaghan, X. J. Shang, Y. Q. Yuan, D. J. Young, W. H. Zhang, T. S. A. Hor, J. P. Lang, *ChemPlusChem* **2015**, *80*, 1231−1234; b) M. Armaghan, W. Y. J. Lu, D. Wu, Y. Wei, F.-L. Yuan, S. W. Ng, M. M. Amini, W.-H. Zhang, D. J. Young, T. S. A. Hor, J.-P. Lang, *RSC Adv.* **2015**, *5*, 42978−42989.

[9] a) T. K. Michaelos, D. Y. Shopov, S. B. Sinha, L. S. Sharninghausen, K. J. Fisher, H. M. C. Lant, R. H. Crabtree, G. W. Brudvig, *Acc. Chem. Res.* **2017**, *50*, 952−959; b) W. Li, S. W. Sheehan, D. He, Y. He, X. Yao, R. L. Grimm, G. W. Brudvig, D. Wang, *Angew. Chem. Int. Ed.* **2015**, *54*,

11428−11432; c) L. S. Sharninghausen, S. B. Sinha, D. Y. Shopov, B. Choi, B. Q. Mercado, X. Roy, D. Balcells, G. W. Brudvig, R. H. Crabtree, *J. Am. Chem. Soc.* **2016**, *138*, 15917−15926.

[10] a) Y.-Q. Yuan, F.-L. Yuan, F.-L. Li, Z.-M. Hao, J. Guo, D. J. Young, W.-H. Zhang, J.-P. Lang, *Dalton Trans.* **2017**, *46*, 7154−7158; b) W.-H. Zhang, N. B. Sulaiman, P. X. S. Tio, T. S. A. Hor, *CrystEngComm* **2011**, *13*, 2915−2922; c) P. Wang, S. Shannigrahi, N. L. Yakovlev, T. S. A. Hor, *Dalton Trans.* **2014**, *43*, 182−187.

[11] a) J. S. Kanady, P.-H. Lin, K. M. Carsch, R. J. Nielsen, M. K. Takase, W. A. Goddard, T. Agapie, *J. Am. Chem. Soc.* **2014**, *136*, 14373−14376; b) E. Y. Tsui, R. Tran, J. Yano, T. Agapie, *Nat. Chem.* **2013**, *5*, 293−299.

[12] a) J. Zhang, P. Teo, R. Pattacini, A. Kermagoret, R. Welter, G. Rogez, T. S. A. Hor, P. Braunstein, *Angew. Chem. Int. Ed.* **2010**, *49*, 4443−4446; b) R. Pattacini, P. Teo, J. Zhang, Y. Lan, A. K. Powell, J. Nehrkorn, O. Waldmann, T. S. A. Hor, P. Braunstein, *Dalton Trans.* **2011**, *40*, 10526−10534.

[13] T. C. Stamatatos, K. A. Abboud, W. Wernsdorfer, G. Christou, *Angew. Chem. Int. Ed.* **2007**, *46*, 884−888.

[14] R.-J. Niu, W.-F. Zhou, Y. Liu, J.-Y. Yang, W.-H. Zhang, J.-P. Lang, D. J. Young, *Chem. Commun.* **2019**, *55*, 4873−4876.

[15] a) J. A. Greathouse, M. D. Allendorf, *J. Am. Chem. Soc.* **2006**, *128*, 13312−13312; b) P. L. Feng, J. J. Perry IV, S. Nikodemski, B. W. Jacobs, S. T. Meek, M. D. Allendorf, *J. Am. Chem. Soc.* **2010**, *132*, 15487−15489.

[16] a) M.-Y. Chao, J. Chen, Z.-M. Hao, X.-Y. Tang, L. Ding, W.-H. Zhang, D. J. Young, J.-P. Lang, *Cryst. Growth Des.* **2019**, *19*, 724−729; b) M.-Y. Chao, J. Chen, D. J. Young, W.-H. Zhang, J.-P. Lang, *Dalton Trans.* **2018**, *47*, 13722−13729.

[17] a) B. D. McCarthy, E. R. Hontz, S. R. Yost, T. Van Voorhis, M. Dincă, *J. Phys. Chem. Lett.* **2013**, *4*, 453−458; b) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* **2012**, *112*, 1105−1125; c) M. D. Allendorf, C. A. Bauer, R. K. Bhakta, R. J. T. Houk, *Chem. Soc. Rev.* **2009**, *38*, 1330−1352; d) Y.-X. Shi, W.-X. Li, H.-H. Chen, D. J. Young, W.-H. Zhang, J.-P. Lang, *Chem. Commun.* **2017**, *53*, 5515−5518; e) B. Wu, W.-H. Zhang, Z.-G. Ren, J.-P. Lang, *Chem. Commun.* **2015**, *51*, 14893−14896; f) C.-N. Lü, M.-M. Chen, W.-H. Zhang, D.-X. Li, M. Dai, J.-P. Lang, *CrystEngComm* **2015**, *17*, 1935−1943.

[18] H. R. Moon, N. Kobayashi, M. P. Suh, *Inorg. Chem.* **2006**, *45*, 8672−8676.

[19] Bruker, *APEX2, SAINT and SADABS. Bruker ACS Inc., Madison, Wisconsin, USA.* **2014**.

[20] G. Sheldrick, *Acta Crystallogr., Sect. C* **2015**, *71*, 3−8.

[21] A. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7−13.

[22] A. L. Spek, *Acta Crystallogr., Sect. C* **2015**, *71*, 9−18.

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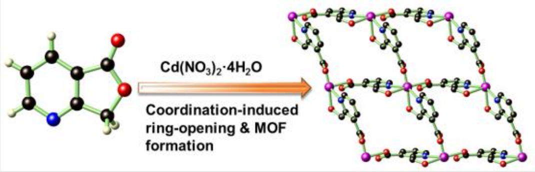

Zn-based zwitterions of $[Zn(\mathbf{L_1'})_2(H_2O)_2]$ (**1**, $\mathbf{L_1'}$ = 2-(hydroxymethyl)nicotinate) and $[Zn(\mathbf{L_2})_2(H_2O)_2]$ (**2**, H$\mathbf{L_2}$ = 2-(hydroxymethyl)isonicotinic acid), and Cd-based MOFs of $[Cd(\mathbf{L_1'})_2]_n$ (**3**) and $[Cd(\mathbf{L_2})_2]_n$·nDMF (**4**) have been synthesized and characterized. Complexes **1**−**4** exhibit ligand-centered emissions at 409 nm (**1**), 412/436 nm (**2**), 404 nm (**3**), and 412/436 nm (**4**) in $CHCl_3$ solutions upon excitation at 330 nm.

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Zinc and Cadmium Complexes of Pyridinemethanol Carboxylates: Metal Carboxylate Zwitterions and Metal–Organic Frameworks