# Cd$^{II}$ MOFs Constructed Using Succinate and Bipyridyl Ligands: Photoluminescence and Heterogeneous Catalytic Activity

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Four Cd$^{II}$ MOFs, [Cd$_2$(μ-succinate)$_2$(H$_2$O)$_2$]·H$_2$O (**1A**), [Cd$_2$(μ-succinate)$_2$(μ-4,4'-bpy)$_2$]·H$_2$O (**1B**), [{Cd$_2$(μ-succinate)$_2$}(μ-bpa)$_2${Cd(H$_2$O)$_2$}(NO$_3$)$_2$]·H$_2$O (**2**), and [Cd(μ-succinate)(μ-bpp)$_2$]·2H$_2$O (**3**), with various bipyridyl ligands (4,4'-bipyridine (4,4'-bpy), 1,2-bis(4-pyridyl)ethane (bpa), and 1,3-bis(4-pyridyl)propane (bpp)) were prepared, and their structures were determined using X-ray crystallography. The structures and dimensionalities of Cd$^{II}$–(succinate) compounds varied depending on the auxiliary ligands. Heterogeneous catalytic activity for transesterification reactions, photoluminescence and the thermal stabilities of these compounds were also examined.

**Key Words :** Cd$^{II}$ MOFs, Succinate, Photoluminescence, Heterogeneous catalysts, Transesterification

## Introduction

Dicarboxylates have been commonly used in MOFs (Metal-Organic Frameworks), providing structures of various dimensionalities with different coordination modes and pore sizes. The rigid aromatic dicarboxylates[1-12] have been the most popular choice for the synthesis of MOFs, and flexible cyclohexane-dicarboxylates[13,14] have also been used. α,ω-alkane dicarboxylates, comprising a particular group of flexible dicarboxylates, have been shown to be particularly suitable as ligands in MOFs with various topologies. Though less frequently employed in MOFs than aromatic dicarboxylates, a few examples of MOFs featuring α,ω-alkane dicarboxylates have been reported.[15-20] A systematic investigation of MOFs containing these α,ω-alkane (or alkene) dicarboxylates is warranted and important.

We recently reported on Cu-MOFs constructed of flexible α,ω-alkane dicarboxylates, glutarate and bipyridyl ligands[21] and on Zn-MOFs containing flexible α,ω-alkane dicarboxylates, malonate, and bipyridyl pillars.[22] Two of the Cu-MOFs possessed very similar pore shapes with controllable pore dimensions, exhibited good selectivity for CO$_2$ over N$_2$ and H$_2$, and one of them was shown to be an efficient, mild, and easily recyclable heterogeneous catalyst for transesterification reactions.[21] The Zn-MOFs containing malonates and bipyridyl pillars formed three-dimensional (3-D) frameworks and catalyzed the heterogeneous transesterification of phenyl acetate.[22] We reported a CO$_2$-selective, dynamic 2-D MOF system, [Zn(glu)(μ-bpe)]·2H$_2$O (glu = glutarate, bpe = 1,2-bis(4-pyridyl)ethylene), and it showed a structural transformation of the framework upon desolvation.[23] We also used five flexible α,ω-alkane (or alkene) dicarboxylates



**Scheme 1.** Chemical structures of various bipyridyl ligands.

(succinate, fumarate, glutarate, adipate, and muconate) for the formation of 2-D or 3-D Zn$^{II}$ frameworks.[24]

As an extension of our previous works, we used a flexible succinate with various bipyridyl ligands (4,4'-bipyridine (4,4'-bpy), 1,2-bis(4-pyridyl)ethane (bpa), and 1,3-bis(4-pyridyl)propane (bpp), Scheme 1) to prepare new functional Cd-MOFs with interesting structures and potential applications.

## Experimental

**Materials.** Succinic acid, 1,2-bis(4-pyridyl)ethane, 4,4'-trimethylene dipyridine, 4,4'-bipyridine, acetone, acetonitrile, methanol, ethanol, 4-nitrophenyl acetate, phenyl acetate, 4-methylphenyl acetate, 4-nitrophenyl benzoate, phenyl benzoate, 4-chlorophenyl benzoate, 4-methylphenyl benzoate, vinyl acetate, methylacetate, methylbenzoate, methyl acetate, NH$_4$OH, and Cd(NO$_3$)$_2$·6H$_2$O were purchased from Sigma-Aldrich and were used as received.

**Instrumentation.** Elemental analysis for carbon, nitrogen, and hydrogen was performed using a vario MACRO (Elemental Analysensysteme, Germany) at the Laboratory Center of Seoul National University of Science and Technology, Korea. For IR measurements, KBr pellets were produced, and the IR spectra were measured on a BIO RAD FTS 135 spectrometer. Thermogravimetric analyses (TGA) were performed on a Shimadzu TA50 integration thermal analyzer.

Product analysis for the transesterification reactions was performed on either a Hewlett-Packard 5890 II Plus gas chromatograph interfaced with Hewlett-Packard Model 5989B mass spectrometer or on a Donam Systems 6200 gas chromatograph equipped with a FID detector using a 30-m capillary column (Hewlett-Packard, HP-1, HP-5, and Ultra 2). The emission/excitation spectra were recorded on a Perkin–Elmer LS45 fluorescence spectrometer. Powder X-ray diffraction patterns (PXRD) were obtained using a Rigaku MiniFlex (operated at 30 kV and 15 mA with a scan speed of 2°/min and step-size of 0.02).

**Synthesis of [Cd$_2$($\mu$-succinate)$_2$(H$_2$O)$_2$]·H$_2$O (1A) and [Cd$_2$($\mu$-succinate)$_2$($\mu$-4,4'-bpy)$_2$]·H$_2$O (1B).** 9.5 mg (0.08 mmol) of succinic acid, 25.2 mg (0.08 mmol) of Cd(NO$_3$)$_2$·4H$_2$O and 20.8 µL (0.16 mmol) of NH$_4$OH were dissolved in 4 mL of H$_2$O, and a 4 mL ethanol solution of 4,4'-bipyridine (12.7 mg, 0.08 mmol) was carefully added. IR (KBr): $\nu$ (cm$^{-1}$) = 1526 (m), 1408 (m), 1330 (w), 1219 (w), 1069 (w), 1046 (w), 809 (m), 672 (m), 579 (s).

**Synthesis of [{Cd$_2$($\mu$-succinate)$_2$}($\mu$-bpa)$_2${Cd(H$_2$O)$_2$}-(NO$_3$)$_2$]·H$_2$O (2).** 11.9 mg (0.1 mmol) of succinic acid, 25.2 mg (0.1 mmol) of Cd(NO$_3$)$_2$·4H$_2$O and 26.0 µL (0.2 mmol) of NH$_4$OH were dissolved in 4 mL of H$_2$O, and a 4 mL ethanol solution of 1,2-bis(4-pyridyl)ethane (38.0 mg, 0.2 mmol) was carefully added. The yield was 78.6 mg (60.5%) for **2**. The bulk purity of sample of **2** was examined using powder XRD (see Figure S1 in Supporting Information). IR

(KBr): $\nu$ (cm$^{-1}$) = 1529 (s), 1414 (m), 1328 (w), 1231 (w), 1069 (w), 827 (m), 809 (m), 676 (s). Anal. Calc. for C$_{44}$H$_{50}$Cd$_3$N$_8$O$_{17}$ (1300.15), 2: C, 40.65; H, 3.88; N, 8.62%. Found: C, 40.54; H, 3.92; N, 8.35%.

**Synthesis of [Cd($\mu$-succinate)($\mu$-bpp)$_2$]·2H$_2$O (3).** 11.9 mg (0.1 mmol) of succinic acid, 25.2 mg (0.1 mmol) of Cd(NO$_3$)$_2$·4H$_2$O and 26.0 µL (0.2 mmol) of NH$_4$OH were dissolved in 4 mL of H$_2$O, and a 4 mL solution of 4,4'-trimethylene dipyridine (31.9 mg, 0.2 mmol) in acetone, methanol, acetonitrile was carefully added. The yield was 48.8 mg (73.8%) for **3**. The bulk purity of sample of **3** was examined using powder XRD (see Figure S2 in Supporting Information). IR (KBr): $\nu$ (cm$^{-1}$) = 1563 (s), 1422 (s), 1296 (w), 1222 (w), 1012 (m), 884 (m), 812 (m), 603 (m), 571(s). Anal. Calcd. for C$_{30}$H$_{32}$CdN$_4$O$_6$ (661.07) 3: C, 54.50; H, 4.89; N, 8.48. Found: C, 54.78; H, 5.03; N, 8.14%.

**Catalytic Activity of 3.** Ester (0.05 mmol) and **3** (7.56 × 10$^{-3}$ mmol) were added into methanol (1 mL) and shaken at 50 °C (450 rpm). Then, 20 µL aliquots were withdrawn periodically from the reaction mixture, and the reaction conversion was monitored by GC/MS. All reactions were performed at least three times, and the average conversion yields are presented. The yields were based on the formation of the products: methyl acetate or methyl benzoate.

**X-ray Crystallography.** The X-ray diffraction data for all four compounds were collected on a Bruker SMART APX diffractometer equipped with a monochromator in the

**Table 1.** Crystallographic Data for **1-3**

| | 1A | 1B | 2 | 3 |
|---|---|---|---|---|
| Empirical formula | C$_8$H$_{18}$Cd$_2$O$_{13}$ | C$_{28}$H$_{24}$Cd$_2$N$_4$O$_9$ | C$_{44}$H$_{48}$Cd$_3$N$_8$O$_{17}$ | C$_{30}$H$_{16}$CdN$_4$O$_6$ |
| Formula weight | 547.02 | 785.31 | 1298.10 | 640.87 |
| T (K) | 293(2) | 170(2) | 293(2) | 293(2) |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Space group | $P2_1$/c | Cmca | $C2$/c | $C2$/c |
| a (Å) | 15.329(3) | 11.707(2) | 23.859(5) | 21.964(4) |
| b (Å) | 12.707(3) | 15.551(3) | 8.735(2) | 11.241(2) |
| c (Å) | 8.395(2) | 15.881(3) | 29.497(6) | 24.961(5) |
| $\alpha$ (°) | 90.00 | 90.00 | 90.00 | 90.00 |
| $\beta$ (°) | 95.48(3) | 90.00 | 112.35(3) | 97.84(3) |
| $\gamma$ (°) | 90.00 | 90.00 | 90.00 | 90.00 |
| Volume (Å$^3$) | 1627.8(6) | 2891.2(1) | 5686(2) | 6105(2) |
| Z | 4 | 4 | 4 | 8 |
| Density (calc.) (Mg/m$^3$) | 2.232 | 1.804 | 1.516 | 1.394 |
| Absorption coeff. (mm$^{-1}$) | 2.675 | 1.531 | 1.181 | 0.761 |
| Crystal size (mm$^3$) | 0.15 × 0.10 × 0.08 | 0.44 × 0.04 × 0.04 | 0.15 × 0.15 × 0.02 | 0.20 × 0.10 × 0.10 |
| Reflections collected | 8728 | 7483 | 15321 | 15913 |
| Independent reflections | 3127 [R(int) = 0.0295] | 1442 [R(int) = 0.0471] | 5534 [R(int) = 0.0552] | 5856 [R(int) = 0.1179] |
| Data / restraints / parameters | 3127 / 10 / 239 | 1442 / 6 / 114 | 5534 / 3 / 337 | 5856 / 34 / 329 |
| Goodness-of-fit on F$^2$ | 0.951 | 1.070 | 1.002 | 1.062 |
| Final R indices [I > 2$\sigma$(I)] | R$_1$ = 0.0231, wR$_2$ = 0.0501 | R$_1$ = 0.0267, wR$_2$ = 0.0619 | R$_1$ = 0.0515, wR$_2$ = 0.1355 | R$_1$ = 0.0749, wR$_2$ = 0.1782 |
| R indices (all data) | R$_1$ = 0.0313, wR$_2$ = 0.0521 | R$_1$ = 0.0287, wR$_2$ = 0.0626 | R$_1$ = 0.0778, wR$_2$ = 0.1500 | R$_1$ = 0.1482, wR$_2$ = 0.2168 |
| Extinction coefficient | 0.0027(2) | – | – | 0.0012(2) |
| Largest diff. peak and hole (e.Å$^{-3}$) | 0.627 and −0.430 | 0.373 and −0.566 | 1.279 and −0.598 | 0.765 and −0.522 |

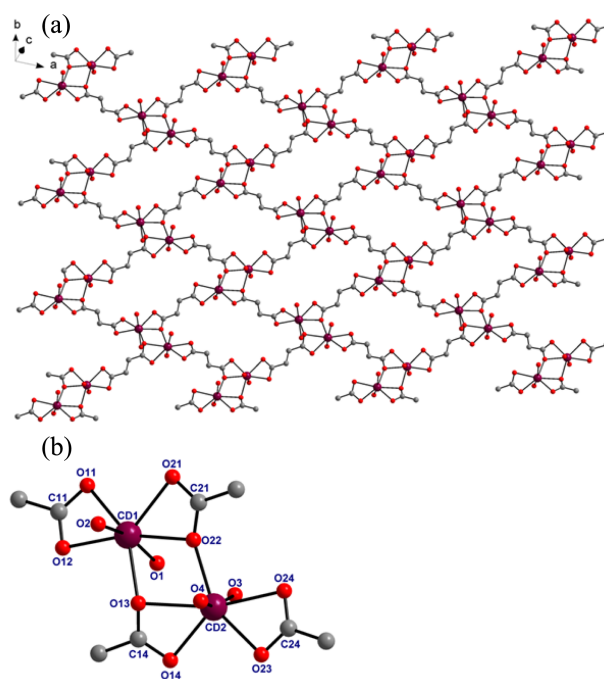**Table 2.** Selected Bond Distances and Angles for **1-3**

| | 1A | 1B | 2 | 3 |
|---|---|---|---|---|
| Cd-O$_{succ}$ | 2.340(2)-2.490(2) Å | 2.290(3)-2.459(4) Å | 2.322(4)-2.532(4) Å | 2.401(6)-2.459(6) Å |
| Cd-O$_{water}$ | 2.266(2)-2.352(2) Å | – | 2.360(4) Å | – |
| Cd-N | – | 2.309(3) | 2.298(4)-2.325(5) Å | 2.362(6)-2.396(7) Å |
| N$_{axial}$-Cd-N$_{axial}$ | – | 171.5(1)° | 169.5(2), 179.997(1)° | 177.9(2)° |
| O$_{water}$-Cd-O$_{water}$ | 164.92(8), 164.16(9)° | | | |

Mo Kα (λ = 0.71073 Å) incident beam. Each crystal was mounted onto a glass fiber. The CCD data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHEXTL V6.12.[24] All hydrogen atoms were placed in the calculated positions. The crystallographic data for **1-3** are provided in Table 1. Selected bond distances and angles are listed in Table 2. Crystallographic data for the structures reported here have been deposited with CCDC (CCDC reference numbers are 955456 for **1A**, 963398 for **1B**, 955457 for **2**, and 955458 for **3**). These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk.
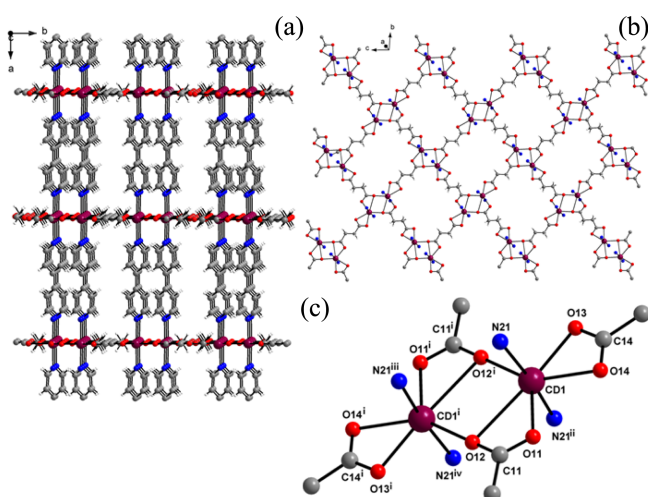
## Results and Discussion

**Synthesis and General Characterization.** The structures of Cd$^{II}$-succinate complexes containing various bipyridyls were investigated. The infrared spectra of **1-3** were fully consistent with their formulations. Very strong, slightly broadened bands at ≈ 1600 cm$^{-1}$ and ≈ 1400 cm$^{-1}$ indicated asymmetric and symmetric C=O stretching modes, respectively, of the ligated succinate moieties.[25-27] The absence of bands in the ≈ 1710 cm$^{-1}$ region indicates full deprotonation of all carboxylate groups in **1-3**,[25-27] which is consistent with the results of the X-ray analysis.

**[Cd$_2$(μ-succinate)$_2$(H$_2$O)$_2$]·H$_2$O (1A).** The asymmetric unit contains two Cd$^{II}$ ions, two succinate ligands, two aqua ligands and a water solvent molecule. Dinuclear Cd$_2$ units are connected by succinate ligands to form a 2-D layer (Figure 1). Two asymmetric Cd$^{II}$ ions in a dinuclear unit are bridged by two carboxylates from two succinate ligands in chelating/bridging coordination (η$^2$:η$^1$:μ$_2$) modes. The other side of a carboxylate coordinates to other Cd$^{II}$ ions in a chelating (η$^1$:η$^1$) coordination mode. Each Cd$^{II}$ ion is also coordinated by two aqua ligands, and the coordination geometry of a Cd$^{II}$ ion is a distorted pentagonal bipyramid with five carboxylate oxygen atoms and axial aqua atoms. The pentagonal bipyramidal geometries of two asymmetric Cd1 and Cd2 are differently distorted with different bond distances and bond angles. The Cd1-O$_{succinate}$ and Cd2-O$_{succinate}$ bond distances are 2.340(2)-2.490(2) Å and 2.281(2)-2.485(2) Å, respectively. The Cd1-O$_{water}$ distances are 2.266(2) and 2.317(2) Å, and Cd2-O$_{water}$ distances are 2.273(2) and 2.352(2) Å. The O$_{water}$-Cd1-O$_{water}$ and O$_{water}$-Cd2-O$_{water}$ bond angles are 164.92(8) and 164.16(9)°, respectively (Table 2).
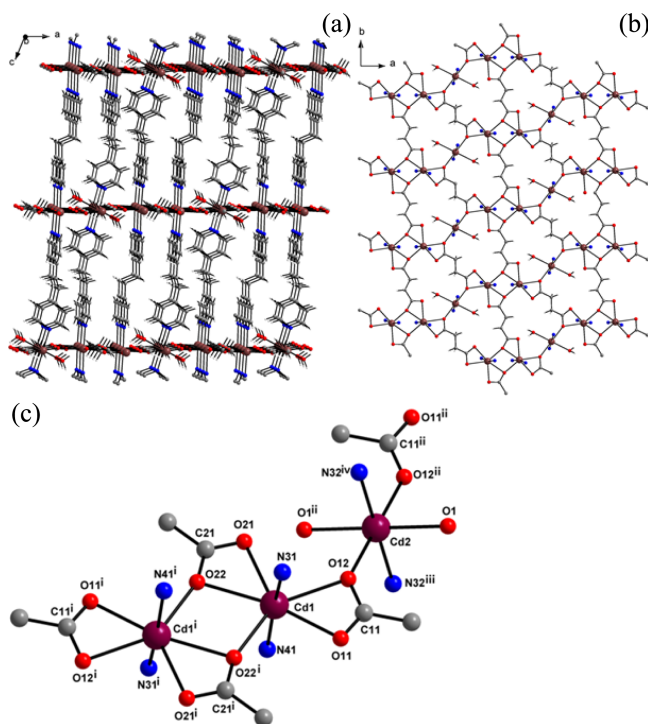


**Figure 1.** (a) Crystal structure of [Cd$_2$(μ-succinate)$_2$ (H$_2$O)$_2$]·H$_2$O **1A**. All solvent molecules were omitted for clarity. (b) The coordination environment around a Cd$_2$ unit.

**[Cd$_2$(μ-succinate)$_2$(μ-4,4'-bpy)$_2$]·H$_2$O (1B).** The asymmetric unit contains a Cd$^{II}$ ion, a succinate ligand, a 4,4'-bpy and a water solvent molecule. Two succinate ligands connect two Cd$^{II}$ ions to form a dinuclear unit, and these dinuclear units are further bridged by the other succinate ligands to form a 2-D sheet (Figure 2). The coordination modes of the carboxylates for each succinate are both chelating/bridging (η$^2$:η$^1$:μ$_2$) and chelating (η$^1$:η$^1$) modes. The 2-D sheets are further connected by 4,4'-bpy ligands to form a 3-D framework (Figure 2). The 3-D frameworks are 2-fold interpenetrated. The PLATON analysis indicates a small void volume (5.9%, 169.7 Å$^3$/2891.2 Å$^3$ for solvent-free 3-D framework). The geometry of the Cd$^{II}$ ion is a distorted pentagonal pyramid constructed by five carboxylate oxygen atoms and two bpa nitrogen atoms. The structure indicated a 7-connected uninodal net with a Schläfli symbol of 3$^3$·4$^{13}$·5$^4$·6 assuming a Cd$^{II}$ ion act as a node without any simplication based on by TOPOS analysis (version 4.0).[28] The Cd-O$_{succinate}$ bond distances range from 2.290(3) to 2.459(4) Å, and the Cd-N distance is 2.309(3) Å. The N-Cd-N bond angle is 171.46(13)° (Table 2).

**Figure 2.** (a) Crystal structure of [Cd$_2$(μ-succinate)$_2$(μ-4,4'-bpy)$_2$]·H$_2$O **1B** along the *c* axis. All solvent molecules were omitted for clarity. (b) A 2-D sheet of Cd$^{II}$-succinate. (c) The coordination environment around a Cd$_2$ unit. Symmetry operations: (i) x, 1−y, 2−z, (ii) −x, y, z, (iii) x, 1−y, 2−z, (iv) −x, 1−y, 2−z.
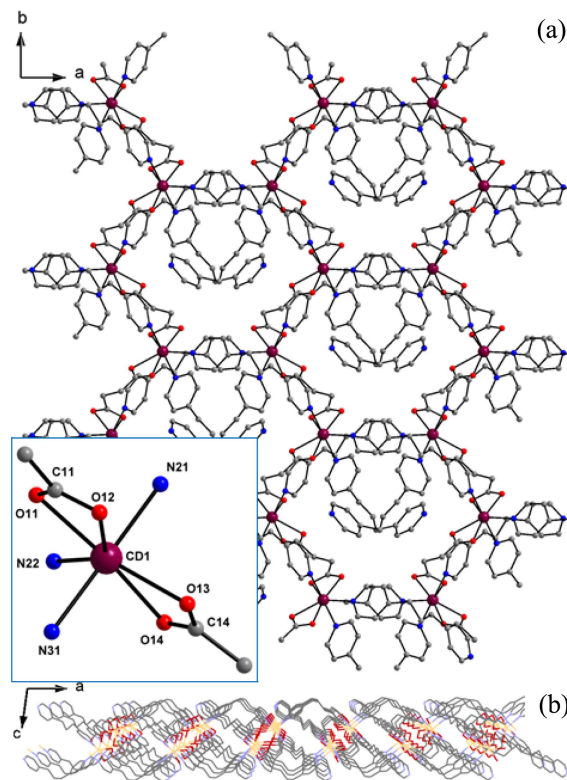
**[{Cd$_2$(μ-succinate)$_2$}(μ-bpa)$_2${Cd(H$_2$O)$_2$}(NO$_3$)$_2$]·H$_2$O (2).** Two succinate ligands connect two Cd$^{II}$ ions *via* a chelating/bridging (η$^2$:η$^1$:μ$_2$) coordination mode; these dinuclear units are further bridged by the other succinate ligands in a chelat-

ing coordination mode, and one of the chelating carboxylate oxygen atoms also coordinates to another Cd(H$_2$O)$_2$$^{2+}$ ion to form a 2-D sheet (Figure 3). The asymmetric unit also contains two NO$_3$$^−$ counter-anions and a water molecule. The coordination of each carboxylate is chelating/bridging (η$^2$:η$^1$:μ$_2$), and a succinate bridges four Cd$^{II}$ ions. These sheets are connected by bpa ligands to form a 3-D framework (Figure 3). The solvent-free 3-D framework comprises 17.6% (998.5 Å$^3$/5686.0 Å$^3$) of the void volume of **2** based on the PLATON analysis. The geometry of a Cd$^{II}$ ion in a dinuclear unit is a distorted pentagonal pyramid constructed by five carboxylate oxygen atoms and two bpa nitrogen atoms, and the geometry of Cd$^{II}$ in Cd(H$_2$O)$_2$$^{2+}$ is an octahedron constructed by two carboxylate oxygen atoms, two water oxygen atoms, and two bpa nitrogen atoms. The structure indicated a 8- and 10-connected 2-nodal net with Schläfli symbols of {3$^{11}$·4$^{24}$·5$^9$·6}2{3$^8$·4$^{18}$·5·6} assuming two Cd$^{II}$ ions act as 2 nodes without any simplication based on by TOPOS analysis. The N-Cd-N bond angle is 169.47(18)°. The Cd-O$_{succinate}$ bond distances range from 2.322(4) to 2.532(4) Å, the Cd-N distances range from 2.298(4) to 2.325(5) Å, and the Cd-O$_{water}$ distance is 2.360(4) Å (Table 2).

**[Cd(μ-succinate)(μ-bpp)$_2$]·2H$_2$O (3).** The asymmetric unit contains a Cd$^{II}$ ion, a succinate, two bpp, and two water solvent molecules. The succinate and bpp ligands bridge



**Figure 3.** (a) Crystal structure of [{Cd$_2$(μ-succinate)$_2$}(μ-bpa)$_2${Cd(H$_2$O)$_2$}(NO$_3$)$_2$]·H$_2$O **2** along the *b* axis. All anions and solvent molecules were omitted for clarity. (b) A 2-D sheet of Cd$^{II}$-succinate. (c) The coordination environment around Cd$^{II}$ ions. Symmetry operations: (i) −x, −y, −z, (ii) 0.5−x, 0.5−y, −z, (iii) x, −y, −0.5+z, (iv) 0.5−x, 0.5−y, 0.5−z.



**Figure 4.** (a) Crystal structure of [Cd(μ-succinate)(μ-bpp)$_2$]·2H$_2$O **3** along the *c* axis. Inset is the coordination environment around a Cd$^{II}$ ion. (b) The channels of **3** along *b* axis. The disordered atoms, all solvent molecules, and hydrogen atoms were omitted for clarity.

Cd$^{II}$ ions to form a thick 2-D sheet containing a dangling bpp ligand on the Cd$^{II}$ ion (Figure 4(a)). Each carboxylate coordinates to a Cd$^{II}$ ion in a chelating ($\eta^1$:$\eta^1$) mode. The geometry of a Cd$^{II}$ ion is a distorted pentagonal bipyramid consisting of four carboxylate oxygen atoms and one bpp nitrogen atom on the equatorial positions and two bpp nitrogen atoms on the axial positions (Fig. 4(a)). **3** has channels along the *b* axis as shown in Figure 4(b). The N$_{axial}$-Cd-N$_{axial}$ bond angle is 177.9(2)°. The Cd-O$_{succinate}$ bond distances range from 2.401(6) to 2.459(6) Å, and the Cd-N distances range from 2.362(6) to 2.396(7) Å (Table 2).
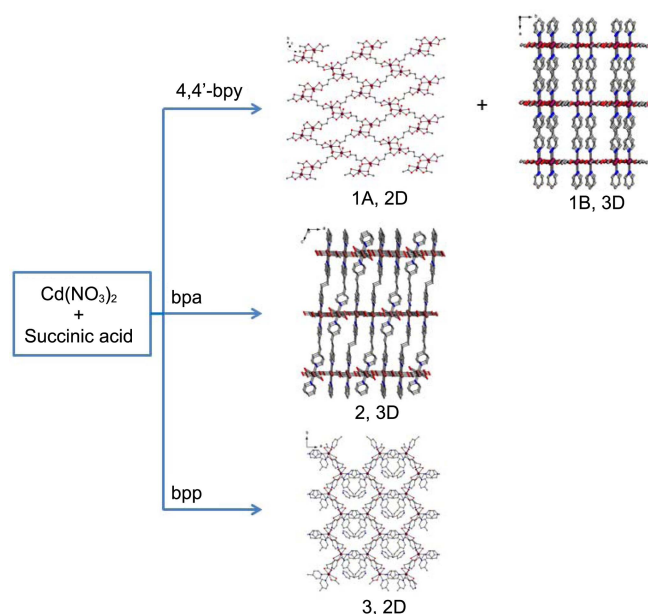
We previously investigated coordination polymers containing malonates with various bipyridyl ligands. The malonates presented similar 3-D frameworks with the general formula [{Zn(H$_2$O)($\mu$-malonate)}$_2$($\mu$-bipyridyl)], in which the malonate ligands bridge three Zn ions to form two-dimensional layers, and these layers are connected by bipyridyl pillars to form 3-D frameworks.[21] In contrast, the succinates presented various structures with Cd$^{II}$ ions depending on the bipyridyl assistant ligands.

Four Cd$^{II}$ coordination polymers containing succinate ligands and various bipyridyl ligands are shown in Scheme 2. Succinate ligands with 4,4'-bpy produced two different structures under the same experimental conditions: one shows a two-dimensional Cd$^{II}$-succinate sheet without 4,4'-bpy ligands (**1A**), and the other shows a three-dimensional framework containing two-dimensional Cd$^{II}$-succinate sheets connected by 4,4'-bpy (**1B**). The bpa produced a 3-D framework (**2**), and bpa connects the 2-D Cd$^{II}$-succinate sheets to form a 3-D framework. Both **1B** and **2** show 2-D Cd$^{II}$-succinate layers connected by bipyridyl pillars, so they can be called as pillared-layer structures. The bpp produced a 2-D sheet (**3**), and both bpp and the succinate ligands bridge Cd$^{II}$ ions to form a 2-D sheet. The coordination modes of two carbox-
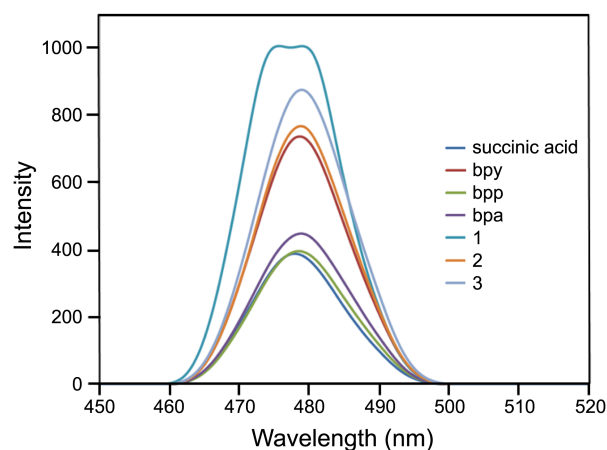
ylates of a succinate are chelating/bridging ($\eta^2$:$\eta^1$:$\mu_2$) and chelating ($\eta^1$:$\eta^1$) in **1A** and **1B**, both carboxylates are in chelating/bridging modes in **2**, and both are in chelating modes in **3**. The coordination geometry of a Cd$^{II}$ ion in **1** and **3** is distorted pentagonal pyramidal, and **2** possesses both octahedral and pentagonal pyramidal geometries of Cd$^{II}$ ions. Thus, the coordination geometry and coordination mode play important roles in the structure construction. The PLATON analysis indicates a small void volume for **1B** and 17.6% of the void volume for **2**; both compounds did not show any gas sorption properties.

**Thermogravimetric Analysis.** To study the thermal stabilities of these complexes, thermogravimetric analyses (TGA) of **2** and **3** were performed. The TGA curve of **2** exhibited 4.13% weight loss within the temperature range of 26-148 °C, which is consistent with the removal of three water molecules (calcd. 4.16%, Figure S3). The second weight loss of 9.53% in the temperature range of 148-258 °C is consistent with the loss of two nitrates (calcd. 9.53%). The third gradual weight loss of 42.51% within the temperature range 258-308 °C is consistent with the loss of three coordinated 1,2-bis(4-pyridyl)ethane (calcd. 42.51%). For **3**, a 5.50% weight loss was observed in the range of 24-91 °C, corresponding to the removal of two water molecules (calcd. 5.45%) (Figure S4). The second gradual weight loss of 60.00% in the temperature range of 91-327 °C corresponds to the loss of two coordinated 4,4'-trimethylene dipyridines (calcd. 59.98%).

**Photoluminescence Property.** Considerable attention has focused on luminescent coordination complexes because of their potential applications as chemical sensors, their photochemistry, and their potential use in electroluminescence displays.[29-32] Previous studies have shown that coordination polymers containing cadmium and zinc exhibit photoluminescent properties.[32-34] Therefore, the photoluminescent spectra of **1** (a mixture of **1A** and **1B**), **2**, **3**, succinic acid, and free ligands were investigated in the solid state at room temperature (Figure 5). The emissions for **1-3** were found to be similar to those of the free bipyridyl ligands ($\lambda_{max}$ = 478 nm).



**Scheme 2.** Cd$^{II}$ MOFs containing succinates and various bipyridyl ligands.



**Figure 5.** Solid-state photoluminescent spectra of **1**, **2**, **3**, succinic acid, 4,4'-bpy, bpa, and bpp at room temperature.
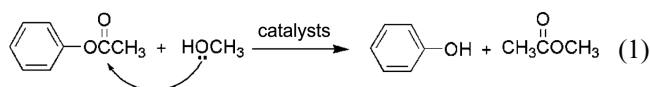
**Table 3.** Transesterification of esters by methanol in the presence of **3** at 50 °C[a]

| Entry | Substrate | **3** (time/day)[b] |
|-------|-----------|---------------------|
| 1 | 4-nitrophenyl acetate | 0.6 |
| 2 | 4-fluorophenyl acetate | 2 |
| 3 | phenyl acetate | 6 |
| 4 | 4-methylphenyl acetate | 4 |
| 5 | 4-chlorophenyl benzoate | 10 |
| 6 | phenyl benzoate | 14 |
| 7 | 4-methylphenyl benzoate | 10 |
| 8 | vinyl acetate | 0.8 |

[a]All esters were completely converted to the corresponding products: methyl acetate and methyl benzoate. Reaction conditions: esters, 0.05 mmol; catalyst, $1.23 \times 10^{-3}$ mmol for **3**, methanol (1 mL). [b]Time necessary for the complete conversion of substrate to product.

Upon complexation, the emissions of the complexes were not shifted compared to the free bpa, bpp, and bpy ligands, and succinic acid. Therefore, the emissions of **1-3** appear to be attributed to the π-π* intraligand florescence.[30,31,35] These results suggest that **1-3** could be possible candidates for a potential hybrid inorganic-organic photoactive material.[32]

**Catalytic Transesterification Reactions by 3.** Transesterification reactions, one of the effective methods for the synthesis of esters, are important in the field of organic synthesis in academia, as well as in industrial laboratories.[36-38] Therefore, we tested the catalytic transesterification reactions using **2** and **3** and found that **3** performed the most efficient catalytic transesterification. The reaction consisting of phenyl acetate and methanol in the presence of **3** produced methyl acetate quantitatively under neutral conditions within 6 days (eq. 1; see entry 3 of Table 3), while minimal transesterification occurred without the polymeric compound **3**. This efficient reactivity is comparable to the catalytic system reported previously in Cd-containing polymeric compounds.[39-43]



Furthermore, we examined the reusability of **3**. After the reaction completed, the compound was recovered by filtration and thoroughly washed with methanol for future runs. The recovered compound was used for a new reaction batch of phenyl acetate and found to exhibit almost the same catalytic activity for the transesterification reaction (see Table S1). **3** showed excellent reusability over 5 cycles without showing any significant loss of catalytic activity.

These promising results led us to examine the transesterification of other esters, including *p*-substituted phenyl acetates and benzoates, in the presence of **3**. These results are also presented in Table 3. This catalyst was very active toward *p*-nitrophenyl acetate and *p*-fluorophenyl acetate (both containing electron-withdrawing groups), which underwent transesterification in 0.6 and 2 days, respectively (entry 1).

4-Methylphenyl acetate showed somewhat slow reactivity (entry 4). The benzoates underwent slower transesterification than acetates (entries 5-8). Importantly, vinyl acetate, which is widely used as a precursor for ester synthesis, was also efficiently converted to the product methyl acetate by **3** within 0.8 days (entry 8), suggesting that this catalytic system can be useful for preparing various esters by transesterification. Moreover, these results offer the opportunity to use the many Cd-containing polymeric compounds reported to date as potential catalysts for transesterification reactions.

**Conclusion**

Four Cd[II] coordination polymers, $[Cd_2(\mu\text{-succinate})_2(H_2O)_2]\cdot H_2O$, $[Cd_2(\mu\text{-succinate})_2(\mu\text{-4,4'-bpy})_2]\cdot H_2O$, $[\{Cd_2(\mu\text{-succinate})_2\}(\mu\text{-bpa})_2\{Cd(H_2O)_2\}(NO_3)_2]\cdot H_2O$, and $[Cd(\mu\text{-succinate})(\mu\text{-bpp})_2]\cdot 2H_2O$, with various bipyridyl ligands have been prepared. 4,4'-bpy and bpa connect the two-dimensional Cd[II]-succinate sheets to form three-dimensional frameworks. The bpp and succinate ligands bridge Cd[II] ions to form a two-dimensional sheet. The coordination polymer **3** appears to be an efficient, mild and easily recyclable transesterification catalyst. The photoluminescence properties of these compounds indicate that they may be good candidates for luminescent materials.

**References**

1. Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341*, 1230444.
2. Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724.
3. Li, J.-R.; Ma, Y.; McCarthy, M. C.; Sculley, J.; Yu, J.; Jeong, H.-K.; Balbuena, P. B.; Zhou, H.-C. *Coord. Chem. Rev.* **2011**, *255*, 1791.
4. Liu, J.; Thallapally, P. K.; McGrail, B. P.; Brown, D. R.; Liu, J. *Chem. Soc. Rev.* **2012**, *41*, 2308.
5. Yoon, M.; Srirambalaji, R.; Kim, K. *Chem. Rev.* **2012**, *112*, 1196.
6. Farrusseng, D.; Aguado, S.; Pinel, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 7502.
7. Lun, D. J.; Waterhouse, G. I. N.; Telfer, S. G. *J. Am. Chem. Soc.* **2011**, *133*, 5806.
8. Farha, O. K.; Shultz, A. M.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. *J. Am. Chem. Soc.* **2011**, *133*, 5652.
9. Cychosz, K. A.; Wong-Foy, A. G.; Matzger, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 6938.
10. Gu, J.-M.; Kim, S.-J.; Kim, Y.; Huh, S. *CrystEngComm* **2012**, *14*, 1819.
11. Jiang, H.-L.; Tatsu, Y.; Lu, Z.-H.; Xu, Q. *J. Am. Chem. Soc.* **2010**, *132*, 5586.

12. Jiang, H.-L.; Xu, Q. *Chem. Commun.* **2011**, 3351.
13. Lee, Y. J.; Kim, E. Y.; Kim, S. H.; Jang, S. P.; Lee, T. G.; Kim, C.; Kim, S.-J.; Kim, Y. *New J. Chem.* **2011**, *35*, 833 and references therein.
14. Kim, E. Y.; Park, H. M.; Kim, H.-Y.; Kim, J. H.; Hyun, M. Y.; Lee, J. H.; Kim, C.; Kim, S.-J.; Kim, Y. *J. Mol. Struct.* **2011**, *994*, 335 and references therein.
15. Dey, R.; Haldar, R.; Maji, T. K.; Ghoshal, D. *Cryst. Growth Des.* **2011**, *11*, 3905.
16. Farnum, G. A.; Martin, D. P.; Sposato, L. K.; Supkowski, R. M.; LaDuca, R. L. *Inorg. Chim. Acta* **2010**, *363*, 250.
17. Demir, S.; Kantar, G. K.; Topcu, Y.; Li, Q. *Transition Met. Chem.* **2012**, *37*, 257.
18. Chen, B.-Q.; Han, L.; Wu, B.-L.; Wu, M.-Y.; Huang, Y.-G.; Hong, M.-C. *Chinese J. Struct. Chem.* **2006**, *25*, 527.
19. Bowden, T. A.; Milton, H. L.; Slawin, A. M. Z.; Lightfoot, P. *Dalton Trans.* **2003**, 936.
20. Kim, J.-S.; Kim, H.; Ree, M. *Chem. Mater.* **2004**, *16*, 2981.
21. Hwang, I. H.; Bae, J. M.; Kim, W.-S.; Jo, Y. D.; Kim, C.; Kim, Y.; Kim, S.-J.; Huh, S. *Dalton Trans.* **2012**, *41*, 12759.
22. Hyun, M. Y.; Hwang, I. H.; Lee, M. M.; Kim, H.; Kim, K. B.; Kim, C.; Kim, H.-Y.; Kim, Y.; Kim, S.-J. *Polyhedron* **2013**, *53*, 166.
23. Hwang, I. H.; Bae, J. M.; Hwang, Y.-K.; Kim, H.-Y.; Kim, C.; Huh, S.; Kim, S.-J.; Kim, Y. *Dalton Trans.* **2013**, *42*, 15645.
24. Hwang, I. H.; Kim, H.-Y.; Lee, M. M.; Na, Y. J.; Kim, J. H.; Kim, H.-C.; Kim, C.; Huh, S.; Kim, Y.; Kim, S.-J. *Cryst. Growth Des.* **2013**, *13*, 4815.
25. Bruker, SHELXTL/PC. Version 6.12 for Windows XP, Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
26. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley & Sons: New York, 1986.
27. Tao, J.; Tong, M.-L.; Chen, X.-M. *J. Chem. Soc., Dalton Trans.* **2000**, 3669.

28. Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *CrystEngComm* **2004**, *6*, 377. http://www.topos.ssu.samara.ru (accessed May 1, 2013).
29. Chen, W.; Wang, J.-Y.; Chen, C.; Yue, Q.; Yuan, H.-M.; Chen, J.-S.; Wang, S.-N. *Inorg. Chem.* **2003**, *42*, 944.
30. Lee, S.Y.; Park, S.; Kim, H. J.; Jung, J. H.; Lee, S. S. *Inorg. Chem.* **2008**, *47*, 1913.
31. Wei, Y.; Yu, Y.; Wu, K. *Cryst. Growth Des.* **2007**, *7*, 2262.
32. Chen, X. L.; Zhang, B.; Hu, H.-M.; Fu, F.; Wu, X.-L.; Qin, T.; Yang, M.-L.; Xue, G.-L.; Wang, J.-W. *Crystal Growth Des.* **2008**, *8*, 3706.
33. Allendrof, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. *Chem. Soc. Rev.* **2009**, *38*, 1330.
34. Lu, W.-G.; Jiang, L.; Feng, X.-L.; Lu, T.-B. *Cryst. Growth Des.* **2006**, *6*, 564.
35. Yang, E.-C.; Zhao, H.-K.; Ding, B.; Wang, X.-G.; Zhao, X.-J. *Cryst. Growth Des.* **2007**, *7*, 2009.
36. Lin, M.-H.; RajanBabu, T. V. *Org. Lett.* **2000**, *2*, 997.
37. Grasa, G. A.; Kissling, R. M.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 3583.
38. Grasa, G. A.; Guveli, T.; Singh, R.; Nolan, S. P. *J. Org. Chem.* **2003**, *68*, 2812.
39. Kim, J. H.; Bae, J. M.; Lee, H. G.; Kim, N. J.; Jung, K. D.; Kim, C.; Kim, S.-J.; Kim, Y. *Inorg. Chem. Commun.* **2012**, *22*, 1.
40. Eom, G. H.; Kim, J. H.; Jo, Y. D.; Kim, E. Y.; Bae, J. M.; Kim, C.; Kim, S.-J.; Kim, Y. *Inorg. Chim. Acta* **2012**, *387*, 106.
41. Song, Y. J.; Kwak, H.; Lee, Y. M.; Kim, S. H.; Lee, S. H.; Park, B. K.; Jun, J. Y.; Yu, S. M.; Kim, C.; Kim, S.-J.; Kim, Y. *Polyhedron* **2009**, *28*, 1241.
42. Kim, S. H.; Park, B. K.; Song, Y. J.; Yu, S. M.; Koo, H. G.; Kim, E. Y.; Poong, J. I.; Lee, J. H.; Kim, C.; Kim, S.-J.; Kim, Y. *Inorg. Chim. Acta* **2009**, *362*, 4119.
43. Shin, J. W.; Bae, J. M.; Kim, C.; Min, K. S. *Inorg. Chem.* **2013**, *52*, 2265.