Supporting Information (SI)

Coordination Polymers from Biphenyl-Dicarboxylate Linkers: Synthesis, Structural Diversity, Interpenetration, and Catalytic Properties

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S1
**General Methods.** All chemicals and solvents were obtained from commercial suppliers. 3,3′-Dihydroxy-(1,1′-biphenyl)-4,4′-dicarboxylic acid (H$_4$L$_1$) and 4,4′-dihydroxy-(1,1′-biphenyl)-3,3′-dicarboxylic acid (H$_4$L$_2$) were acquired from Jinan Henghua Sci. & Tec. Co., Ltd. C/N/H analyses were run on an Elementar Vario EL elemental analyzer. Bruker EQUINOX 55 spectrometer was used for recording the FTIR spectra (KBr discs). LINSEIS STA PT1600 thermal analyzer was used for thermogravimetric (TGA) measurements (heating rate: 10°C/min; N$_2$ flow). PXRD (powder X-ray diffraction) analyses were carried out on a Rigaku-Dmax 2400 diffractometer (Cu-Kα radiation, λ = 1.54060 Å). Solid-state excitation and emission spectra were measured on an Edinburgh FLS920 fluorescence spectrometer under ambient temperature. Solution $^1$H NMR spectra were recorded on a JNM ECS 400M spectrometer.

**Synthesis and analytical data for 1–9.**

$[\text{Co}_2(\mu_2-H_2L_1)_2(\text{phen})_2(H_2O)_4]$ (1). A mixture of CoCl$_2$·6H$_2$O (0.2 mmol, 47.6 mg), H$_4$L$_1$(0.2 mmol, 54.8 mg), phen (0.2 mmol, 40.0 mg), and NaOH (0.4 mmol, 16.0 mg) in H$_2$O (10 mL) was stirred for 15 min at ambient temperature. It was then sealed in a Teflon-lined stainless steel reactor (25 mL) and heated at 160 °C for 3 days, followed by a slow cooling to ambient temperature (10 °C/h). Pink block-shaped crystals were isolated manually, washed with distilled water, and dried in air to give product 1. Yield: 54% (based on H$_4$L$_1$). Calcd for C$_{52}$H$_{40}$Co$_2$N$_4$O$_{16}$: C 57.05, H 3.68, N 5.12%. Found: C 57.29, H 3.66, N 5.10%. IR (KBr, cm$^{-1}$): 3435w, 3076 w, 1625 m, 1577 s, 1512 m, 1485 w, 1425s, 1349 m, 1225 w, 1189 w, 1157 w, 1141 w, 1101 w, 1033 w, 962 w, 865 m, 850 w, 810 w, 726 m, 670 w, 641 w.

$[\text{Mn}(\mu_4-H_2L_1)(\text{phen})_4]_n$·4nH$_2$O (2). A mixture of MnCl$_2$·4H$_2$O (39.6 mg, 0.2 mmol), H$_4$L$_1$(0.2 mmol, 54.8 mg), phen (40.0 mg, 0.2 mmol), NaOH (16.0 mg, 0.4 mmol), and H$_2$O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h$^{-1}$. Yellow crystals of 2 were isolated manually, and washed with distilled water. Yield: 46% (based on H$_4$L$_1$). Anal. Calcd for C$_{52}$H$_{40}$Mn$_2$N$_4$O$_{16}$: C 57.29, H 3.66, N 5.10%. Found: C 57.58, H 3.72, N 5.15%. IR (KBr, cm$^{-1}$): 3067 w, 1625 m, 1580 s, 1517 m, 1445 s, 1369 s, 1313 w, 1233 w, 1185 w, 1154 w, 1101 w, 1045 w, 962 w, 869 m, 845 w, 814 w, 786 w, 726 m, 705 w, 665 w, 637 w.

$[\text{Zn}(\mu_2-H_2L_1)(2,2′\text{-bipy})(H_2O)]_n$ (3). A mixture of ZnCl$_2$ (27.3 mg, 0.20 mmol), H$_4$L$_1$(0.2 mmol, 54.8 mg), 2,2′-bipy (31.2 mg, 0.2 mmol), NaOH (16.0 mg, 0.4 mmol), and H$_2$O (10 mL) was stirred at room temperature for 15
min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h⁻¹. Colorless block-shaped crystals of \(3\) were isolated manually, washed with distilled water and dried (yield 51% based on \(\text{H}_4\text{L}_1\)). Anal. Calcd for \(\text{C}_{24}\text{H}_{18}\text{ZnN}_2\text{O}_7\): C, 56.32; H, 3.54; N, 5.47. Found: C, 56.47; H, 3.52; N, 5.44%. IR (KBr, cm⁻¹): 3435 w, 3043 w, 1632 m, 1580 s, 1513 w, 1489 m, 1433 s, 1357 m, 1333 m, 1249 w, 1229 m, 1185 w, 1157 w, 1105 w, 1057 w, 1026 w, 961 w, 869 m, 817 w, 769 m, 729 w, 709 w, 670 w, 629 w.

\([\text{Cd}(\mu_2\text{-H}_2\text{L}_1)(2,2′\text{-bipy})(\text{H}_2\text{O})]_n\) (4). A mixture of \(\text{CdCl}_2\cdot\text{H}_2\text{O}\) (40.2 mg, 0.20 mmol), \(\text{H}_4\text{L}_1\) (0.2 mmol, 54.8 mg), bipy (31.2 mg, 0.2 mmol), NaOH (16.0 mg, 0.4 mmol), and \(\text{H}_2\text{O}\) (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h⁻¹. Colorless block-shaped crystals of \(4\) were isolated manually, washed with distilled water and dried (yield 46% based on \(\text{H}_4\text{L}_1\)). Anal. Calcd for \(\text{C}_{24}\text{H}_{18}\text{CdN}_2\text{O}_7\): C, 51.58; H, 3.25; N, 5.01. Found: C, 51.39; H, 3.28; N, 5.03%. IR (KBr, cm⁻¹): 3416 w, 3060 w, 1625 m, 1585 s, 1517 m, 1429 s, 1385 s, 1225 w, 1141 w, 1105 w, 1045 w, 905 w, 850 m, 773 w, 726 m, 665 w, 641 w.

\([\text{Mn}_2(\mu_2\text{-H}_2\text{L}_1)(\mu_2\text{-4,4′-bipy})_2]_n\cdot4\text{nH}_2\text{O}\) (5). A mixture of \(\text{MnCl}_2\cdot4\text{H}_2\text{O}\) (39.6 mg, 0.2 mmol), \(\text{H}_4\text{L}_1\) (0.2 mmol, 54.8 mg), 4,4′-bipy (31.2 mg, 0.2 mmol), NaOH (16.0 mg, 0.4 mmol), and \(\text{H}_2\text{O}\) (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h⁻¹. Yellow block-shaped crystals of \(5\) were isolated manually, washed with distilled water and dried (yield 44% based on \(\text{H}_4\text{L}_1\)). Anal. Calcd for \(\text{C}_{48}\text{H}_{38}\text{Mn}_2\text{N}_4\text{O}_{16}\): C, 55.61; H, 3.69; N, 5.40. Found: C, 55.74; H, 4.67; N, 5.38%. IR (KBr, cm⁻¹): 3143 m, 1605 m, 1577 s, 1516 w, 1493 w, 1425 m, 1353 s, 1249 w, 1154 w, 1069 w, 1029 w, 1002 w, 957 w, 857 m, 805 m, 777 w, 726 m, 674 w, 650 w.

\([\text{Zn}(\mu_2\text{-H}_2\text{L}_1)(\mu_2\text{-4,4′-bipy})_2]_n\) (6). Synthesis of \(6\) was similar to \(5\) except using \(\text{ZnCl}_2\) (27.3 mg, 0.20 mmol) instead of \(\text{MnCl}_2\cdot4\text{H}_2\text{O}\). Colorless block-shaped crystals of \(6\) were isolated manually, washed with distilled water and dried (yield 43% based on \(\text{H}_4\text{L}_1\)). Anal. Calcd for \(\text{C}_{24}\text{H}_{16}\text{ZnN}_2\text{O}_6\): C, 58.37; H, 3.27; N, 5.67. Found: C, 58.53; H, 3.25; N, 5.68%. IR (KBr, cm⁻¹): 1616 s, 1577 s, 1489 m, 1421 s, 1389 m, 1333 s, 1229 w, 1157 w, 1069 w, 1029 w, 1014 w, 962 w, 865 m, 814 m, 729 w, 705 w, 673 w, 641 w.

\([\text{Zn}(\mu_2\text{-H}_2\text{L}_2)(\text{phen})]_n\) (7). A mixture of \(\text{ZnCl}_2\) (27.3 mg, 0.20 mmol), \(\text{H}_4\text{L}_2\) (54.8 mg, 0.20 mmol), phen (40.0 mg, 0.20 mmol), NaOH (16.0 mg, 0.40 mmol), and \(\text{H}_2\text{O}\) (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h⁻¹. Colorless block-shaped crystals of \(7\) were isolated manually, washed with distilled water and dried (yield 53% based on \(\text{H}_4\text{L}_2\)). Anal. Calcd for \(\text{C}_{26}\text{H}_{16}\text{ZnN}_2\text{O}_6\): C, 60.31; H, 3.11; N, 5.41.
Found: C, 60.53; H, 3.13; N, 5.38%. IR (KBr, cm\(^{-1}\)):\ 1630 w, 1556 s, 1470 s, 1415 s, 1362 w, 1288 w, 1242 m, 1146 w, 1106 w, 1047 w, 981 w, 936 w, 874 m, 836 w, 774 w, 720 w, 698 w, 641 w.

\([Cd(\mu_3-H_2L_2)(phen)]_n\) (8). A mixture of CdCl\(_2\)H\(_2\)O (40.2 mg, 0.2 mmol), H\(_4\)L\(_2\) (54.8 mg, 0.20 mmol), phen (40.0 mg, 0.20 mmol), NaOH (16.0 mg, 0.40 mmol), and H\(_2\)O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h\(^{-1}\). Colorless block-shaped crystals of 8 were isolated manually, washed with distilled water and dried (yield 45% based on H\(_4\)L\(_2\)). Anal. Caled for C\(_{26}\)H\(_{16}\)CdN\(_2\)O\(_6\): C, 55.29; H, 2.86; N, 4.96. Found: C, 55.16; H, 2.84; N, 4.97%. IR (KBr, cm\(^{-1}\)):\ 1626 w, 1560 s, 1514 w, 1481 w, 1419 s, 1374 w, 1324 w, 1282 w, 1241 w, 1220 w, 1196 w, 1162 w, 1146 w, 1096 w, 1043 w, 997 w, 914 w, 868 w, 831 s, 724 m, 699 w, 641 w.

\([Cu(\mu_2-H_2L_2)(\mu_2-4,4′-bipy)(H_2O)]_n\) (9). A mixture of CuCl\(_2\)2H\(_2\)O (34.1 mg, 0.2 mmol), H\(_4\)L\(_2\) (54.8 mg, 0.20 mmol), 4,4’-bipy (31.2 mg, 0.20 mmol), NaOH (24.0 mg, 0.60 mmol), and H\(_2\)O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h\(^{-1}\). Green needle-shaped crystals of 9 were isolated manually, washed with distilled water and dried (yield 43% based on H\(_4\)L\(_2\)). Anal. Caled for C\(_{24}\)H\(_{17}\)CuN\(_2\)O\(_7\): C, 56.64; H, 3.37; N, 5.50. Found: C, 56.75; H, 3.40; N, 5.48%. IR (KBr, cm\(^{-1}\)):\ 3434 w, 3100 w, 1627 w, 1564 s, 1471 m, 1407 s, 1358 w, 1286 w, 1246 w, 1157 w, 1069 w, 944 w, 872 m, 852 w, 820 m, 727 w, 695 w, 647 w. 

![compound 1](image1.png)  ![compound 2](image2.png)
Figure S1. Transmittance (%) FTIR spectra of compounds 1–9.
Figure S2. PXRD patterns of compounds 1–9 at room temperature. Black patterns correspond to the experimental data obtained using the as-synthesized bulk samples. Red patterns were simulated from the single crystal X-ray data (CIF files).

Luminescent Properties. The emission spectra of compounds 1–9, H₄L₁ and H₂L₂ were recorded in the solid state
at room temperature (Fig. S3). The spectra of H₄L₁ and H₄L₂ disclose two weak emission bands centered at 470 and 483 nm. In contrast to H₄L₁ and H₄L₂, zinc(II) and cadmium(II) derivatives feature bands of a more pronounced intensity with maxima in the 440–458 nm range, namely 457 nm for 3, 440 nm for 4, 458 nm for 6, 455 nm for 7, and 445 nm for 8. These bands are associated with an intraligand π–π* or n–π* transitions of main carboxylate ligand. S1–S3

An enhanced luminescence of 3, 4, and 6–8 vs. H₄L₁ and H₄L₂ is likely due to the coordination of ligands to Zn(II) or Cd(II), which may strengthen the rigidity of ligands and diminish a loss of energy from radiationless decay. S3–S5 However, compounds 1, 2, 5, and 9 display very weak luminescence and almost no emission, which is probably attributed to the fluorescence quenching of Co²⁺, Mn²⁺, and Cu²⁺ by the ligands present in these compounds. S6–S9

**Figure S3.** Solid-state emission spectra of 1–9, H₄L₁ and H₄L₂ at room temperature (λₑₓ = 316 nm).
Figure S4. Typical $^1$H NMR spectrum of the reaction mixture with integration of signals for determination of the Henry reaction products (conditions of Table 3, entry 7; 4-nitrobenzaldehyde substrate, catalyst 3).

Calculation of the product yield and selectivity based on the data of Figure S4

Yield:

Total amount of compounds: 4-nitrobenzaldehyde + anti + syn = 1.00 + 3.52 + 4.38 = 8.90.

Percentage of the unreacted 4-nitrobenzaldehyde: $(1/8.90) \times 100 = 11.2\%$.

Conversion of 4-nitrobenzaldehyde = yield of beta-nitroalkanols = 100−11.2= 88.8\%.

Selectivity:

Selectivity toward anti product: $3.52/(3.52 + 4.38) \times 100 = 45\%$.

Selectivity toward syn product: $4.38/(3.52 + 4.38) \times 100 = 55\%$. 

**Figure S5.** Accumulation of product vs. time in the Henry reaction of 4-nitrobenzaldehyde with nitroethane catalysed by 3. Reaction conditions are those of Table 3, entries 1–7.

**Figure S6.** Catalyst recycling experiments (five reaction runs) in the Henry reaction of 4-nitrobenzaldehyde with nitroethane catalyzed by 3. Reaction conditions are those of Table 3, entry 7. Figures above the bars correspond to product yields in %.
**Figure S7.** PXRD patterns for 3: simulated (red), before (black) and after (blue) catalysis.

**Figure S8.** Proposed catalytic cycle for Henry reaction catalyzed by 3.
### Table S1. Selected bond lengths [Å] and angles [°] for compounds 1–9.\(^a\)

| 1 | 2.0418(12) | 2.1838(13) | 2.0866(13) |
|---|-------------|-------------|-------------|
| Co(1)-O(1) | Co(1)-O(5)i | Co(1)-O(7) | |
| Co(1)-O(8) | 2.1384(14) | 2.1319(16) | 2.1225(15) |
| O(1)-Co(1)-O(7) | 95.42(6) | 170.89(6) | 93.64(6) |
| O(1)-Co(1)-N(1) | 93.01(6) | 169.66(6) | 78.08(6) |
| O(8)-Co(1)-O(1) | 87.43(6) | 86.62(6) | 92.19(6) |
| N(1)-Co(1)-O(8) | 99.76(6) | 82.53(5) | 87.00(5) |
| N(2)-Co(1)-O(5)i | 98.88(5) | 88.16(6) | 167.55(5) |

| 2 | 2.0870(16) | 2.2087(13) | 2.1005(15) |
|---|-------------|-------------|-------------|
| Mn(1)-O(1) | Mn(1)-O(2)i | Mn(1)-O(7) | |
| Mn(1)-O(10)i | 2.2014(13) | 2.3077(17) | 2.3044(17) |
| Mn(2)-O(4)i | 2.1973(14) | 2.0966(17) | 2.1959(14) |
| Mn(2)-O(11) | 2.0919(16) | 2.3011(18) | 2.3043(19) |
| O(1)-Mn(1)-O(7) | 108.37(8) | 87.78(6) | 99.39(6) |
| O(1)-Mn(1)-O(2)i | 97.98(8) | 88.63(6) | 168.18(5) |
| O(1)-Mn(1)-N(2) | 163.05(7) | 88.56(7) | 88.57(6) |
| N(2)-Mn(1)-O(2)i | 82.92(6) | 90.96(7) | 160.65(7) |
| N(1)-Mn(1)-O(10)i | 80.06(6) | 89.55(6) | 72.10(6) |
| O(11)-Mn(2)-O(5)iv | 102.29(8) | 97.62(6) | 90.12(7) |
| O(11)-Mn(2)-O(4)i | 86.97(6) | 100.64(6) | 167.18(6) |
| O(11)-Mn(2)-N(3) | 164.20(8) | 93.51(8) | 82.10(6) |
| O(4)i-Mn(2)-N(3) | 90.23(6) | 91.86(7) | 165.66(7) |
| O(8)v-Mn(2)-N(4) | 85.64(6) | 82.24(6) | 72.35(7) |

| 3 | 1.9897(17) | 2.0413(15) | 2.0096(16) |
|---|-------------|-------------|-------------|
| Zn(1)-O(1) | Zn(1)-O(4) | Zn(1)-O(7) | |
| Zn(1)-N(1) | 2.1127(19) | 2.095(2) | |
| O(1)-Zn(1)-O(7) | 120.27(8) | 90.39(7) | 91.23(7) |
| O(1)-Zn(1)-N(2) | 120.65(7) | 119.06(9) | 89.81(7) |
| N(1)-Zn(1)-O(1) | 94.816(6) | 95.65(7) | 167.79(8) |
| N(1)-Zn(1)-N(2) | 78.04(7) | | |

| 4 | 2.3964(19) | 2.457(3) | 2.474(2) |
|---|-------------|-------------|-------------|
| Cd(1)-O(1) | Cd(1)-O(2) | Cd(1)-O(3) | |
| Cd(1)-O(5)i | 2.3476(19) | 2.273(2) | 2.357(2) |
| Cd(1)-N(2) | 2.363(2) | | |
| O(8)-Cd(1)-O(5)i | 100.37(8) | 91.28(9) | 150.14(7) |
| O(8)-Cd(1)-N(2) | 155.26(9) | 88.97(9) | 70.56(8) |
| O(1)-Cd(1)-O(8) | 98.05(8) | 78.98(7) | 126.78(7) |
| O(1)-Cd(1)-N(2) | 106.24(8) | 89.29(8) | 131.90(7) |
| O(2)-Cd(1)-N(1) | 75.07(8) | 101.51(8) | 52.96(7) |
| O(4)i-Cd(1)-O(8) | 83.56(8) | 53.88(7) | 101.03(8) |
| O(4)i-Cd(1)-N(2) | 83.64(8) | 131.99(7) | 171.81(10) |

| 5 | 2.351(4) | 2.222(3) | 2.212(3) |
|---|-------------|-------------|-------------|
| Mn(1)-O(1) | Mn(1)-O(2) | Mn(1)-O(5) | |
| Mn(1)-O(5)i | 2.504(3) | 2.256(3) | 2.259(4) |
| Mn(1)-N(2)i | 2.256(4) | | |
| O(1)-Mn(1)-O(5)i | 136.79(12) | 56.65(13) | 166.54(13) |
| O(6)i-Mn(1)-O(2) | 139.39(13) | 87.70(14) | 89.50(15) |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|-----------------------|--------------|-----------------------|--------------|-----------------------|--------------|
| O(5)-Mn(1)-O(1)       | 1.488(12)    | O(5)-Mn(1)-O(2)       | 0.92(13)     | O(5)-Mn(1)-O(5)i     | 0.74(12)     |
| O(5)-Mn(1)-O(6)i      | 1.284(13)    | O(5)-Mn(1)-N(1)       | 0.89(14)     | N(2)ii-Mn(1)-O(5)    | 0.89(15)     |
| O(1)-Mn(1)-O(6)i      | 0.827(12)    | O(5)i-Mn(1)-O(6)i     | 0.54(11)     | N(1)-Mn(1)-O(6)      | 0.923(13)    |
| N(1)-Mn(1)-O(1)       | 0.902(15)    | N(1)-Mn(1)-O(5)i      | 0.92(12)     | O(1)-Mn(1)-N(2)ii    | 0.893(16)    |
| N(2)ii-Mn(1)-O(5)i    | 0.894(13)    | N(2)-Mn(1)-O(6)i      | 0.90(13)     | N(1)-Mn(1)-N(2)      | 0.176(15)    |
| Zn(1)-O(1)            | 1.964(4)     | Zn(1)-O(4)            | 1.922(4)     | Zn(1)-N(1)           | 2.055(4)     |
| Zn(1)-N(2)            | 2.059(5)     |                        |              |                       |              |
| O(1)-Zn(1)-N(1)       | 1.313(2)     | O(1)-Zn(1)-N(2)       | 1.016(2)     | O(1)-Zn(1)-O(4)      | 1.028(2)     |
| O(4)-Zn(1)-N(1)       | 0.996(18)    | O(4)-Zn(1)-N(2)       | 1.211(2)     | N(2)ii-Zn(1)-N(1)    | 1.027(18)    |
| Zn(1)-O(1)            | 2.038(3)     | Zn(1)-O(2)            | 2.329(4)     | Zn(1)-O(5)i         | 1.939(3)     |
| Zn(1)-N(1)            | 2.078(5)     | Zn(1)-N(2)            | 2.072(5)     |                       |              |
| N(1)-Zn(1)-O(2)       | 0.913(15)    | N(1)-Zn(1)-N(2)       | 0.802(16)    | N(2)-Zn(1)-O(2)      | 1.349(15)    |
| O(1)-Zn(1)-N(1)       | 1.373(16)    | O(1)-Zn(1)-N(2)       | 0.987(15)    | O(1)-Zn(1)-O(2)      | 0.597(13)    |
| O(5)i-Zn(1)-N(1)      | 1.103(15)    | O(5)i-Zn(1)-N(2)      | 1.295(15)    | O(5)i-Zn(1)-O(1)     | 1.091(15)    |
| O(5)i-Zn(1)-O(2)      | 1.955(14)    |                        |              |                       |              |
| Cd(1)-O(1)            | 2.343(6)     | Cd(1)-O(2)            | 2.348(6)     | Cd(1)-O(4)i         | 2.346(6)     |
| Cd(1)-O(5)i           | 2.220(6)     | Cd(1)-N(1)            | 2.300(7)     | Cd(1)-N(2)           | 2.368(7)     |
| N(1)-Cd(1)-N(2)       | 0.717(2)     | N(1)-Cd(1)-O(1)       | 0.912(2)     | N(1)-Cd(1)-O(2)      | 1.026(3)     |
| N(1)-Cd(1)-O(4)i      | 0.913(2)     | O(1)-Cd(1)-N(2)       | 1.567(2)     | O(1)-Cd(1)-O(2)      | 0.554(2)     |
| O(4)-Cd(1)-O(1)       | 0.834(2)     | O(4)-Cd(2)-N(2)       | 1.120(2)     | N(2)-Cd(2)-O(4)i    | 1.112(2)     |
| O(4)-Cd(2)-O(2)       | 1.360(2)     | O(5)i-Cd(2)-N(1)      | 1.555(2)     | O(5)i-Cd(2)-N(2)     | 0.897(3)     |
| O(5)i-Cd(2)-O(1)      | 1.108(2)     | O(5)i-Cd(2)-O(2)      | 0.998(2)     | O(5)i-Cd(2)-O(4)i   | 0.794(2)     |
| Cu(1)-O(1)            | 1.939(2)     | Cu(1)-O(4)i           | 2.184(3)     | Cu(1)-O(7)          | 1.953(2)     |
| Cu(1)-N(1)            | 2.000(3)     | Cu(1)-N(2)            | 2.019(3)     |                       |              |
| O(1)-Cu(1)-O(7)       | 0.916(10)    | O(1)-Cu(1)-N(1)       | 1.6524(12)   | N(1)-Cu(1)-O(7)     | 0.909(11)    |
| N(2)-Cu(1)-O(1)       | 0.8618(10)   | N(2)-Cu(1)-O(7)       | 1.6814(12)   | N(1)-Cu(1)-N(2)     | 0.883(11)    |
| O(1)-Cu(1)-O(4)i      | 0.9964(10)   | O(7)-Cu(1)-O(4)i      | 0.9770(11)   | N(1)-Cu(1)-O(4)i   | 0.944(11)    |
| N(2)-Cu(1)-O(4)i      | 0.9416(11)   |                        |              |                       |              |

*aSymmetry transformations used to generate equivalent atoms: i – x+2, –y+1, –z+1 for 1; ii x+1, –y+1, –z+1; iii x, y+1, z; iv x, y, z+1; v x, y, z+1 for 2; vi x+3/2, y, z+1/2 for 4; vii x+1, y, z+1/2; vii x, y+1, z for 5; vii x+1/2, y+1/2, z+1/2 for 7; vii x+1/2, y+1/2, z+1/2; vii x, –y+2, z+1/2 for 8; vii x+1, –y+1, –z+1 for 9.*
Table S2. Hydrogen bonds in crystal packing [Å, °] of 1–9.

| Compound | D-H…A       | $d$(D-H) | $d$(H…A) | $d$(D…A) | $\angle$DHA | Symmetry code |
|----------|-------------|----------|----------|----------|-------------|---------------|
| 1        | O(3)-H(1) – O(2) | 0.820    | 1.879    | 2.599    | 145.93      |               |
|          | O(7)-H(1W) – O(4) | 0.880    | 1.797    | 2.624    | 155.58      | -x+2, -y+1, -z+1 |
|          | O(7)-H(2W) – O(2) | 0.796    | 2.125    | 2.860    | 153.63      |              |
|          | O(8)-H(3W) – O(2) | 0.842    | 2.092    | 2.884    | 156.62      |               |
|          | O(8)-H(4W) – O(4) | 0.806    | 1.869    | 2.674    | 177.04      | -x+1, -y+1, -z+1 |
| 2        | O(3)-H(1) – O(2) | 0.820    | 1.831    | 2.551    | 145.64      |               |
|          | O(6)-H(2) – O(4) | 0.820    | 1.856    | 2.574    | 145.49      |               |
|          | O(9)-H(5) – O(8) | 0.820    | 1.829    | 2.545    | 145.08      |               |
|          | O(12)-H(8) – O(10) | 0.820  | 1.858    | 2.569    | 144.38      |               |
| 3        | O(3)-H(1) – O(2) | 0.820    | 1.817    | 2.537    | 145.72      |               |
|          | O(6)-H(2) – O(5) | 0.820    | 1.808    | 2.537    | 147.25      |               |
|          | O(7)-H(1W) – O(2) | 0.932    | 1.766    | 2.681    | 166.11      | -x+1, y+1/2, -z+3/2 |
|          | O(7)-H(2W) – O(5) | 0.877    | 1.807    | 2.640    | 177.04      | -x+2, -y+3/2, z+1/2 |
| 4        | O(3)-H(1) – O(2) | 0.820    | 1.833    | 2.555    | 146.05      |               |
|          | O(6)-H(2) – O(5) | 0.820    | 1.756    | 2.505    | 150.94      |               |
|          | O(8)-H(1AA) – O(5) | 0.871   | 2.112    | 2.848    | 141.78      |              |
|          | O(8)-H(1AB) – O(1) | 0.870   | 1.999    | 2.752    | 144.19      | x+1/2, -y+3/2, z |
| 5        | O(3a)-H(3a) – O(1) | 0.820    | 1.906    | 2.595    | 141.05      |               |
|          | O(3b)-H(3b) – O(1) | 0.820    | 1.903    | 2.619    | 145.17      |               |
|          | O(4a)-H(4a) – O(2) | 0.820    | 1.906    | 2.528    | 131.83      |               |
|          | O(1b)-H(4b) – O(2) | 0.820    | 1.907    | 2.621    | 144.90      |               |
|          | O(7a)-H(7a) – O(6) | 0.820    | 1.901    | 2.607    | 143.77      |               |
|          | O(7b)-H(7b) – O(6) | 0.820    | 1.922    | 2.610    | 140.85      |               |
| 6        | O(3)-H(3) – O(2) | 0.820    | 1.793    | 2.522    | 147.28      |               |
|          | O(6)-H(6) – O(5) | 0.820    | 2.030    | 2.567    | 122.60      |               |
| 7        | O(3)-H(3) – O(2) | 0.820    | 1.874    | 2.593    | 145.61      |               |
|          | O(6)-H(6) – O(4) | 0.820    | 1.843    | 2.566    | 146.35      |               |
| 8        | O(3)-H(3) – O(1) | 0.820    | 1.910    | 2.584    | 138.89      |               |
|          | O(6)-H(6) – O(5) | 0.820    | 1.814    | 2.535    | 145.86      |               |
| 9        | O(3)-H(3) – O(2) | 0.820    | 1.869    | 2.590    | 146.02      |               |
|          | O(6)-H(6) – O(5) | 0.820    | 1.856    | 2.566    | 144.26      |               |
|          | O(7)-H(1W) – O(2) | 0.850    | 1.869    | 2.719    | 179.94      |               |
|          | O(7)-H(2W) – O(5) | 0.850    | 1.735    | 2.585    | 179.92      | x, y+1, z+1   |
Table S3. Comparison of related catalytic systems for the Henry reaction between 4-nitrobenzaldehyde and nitroethane.\(^a\)

| Entry | Catalyst | Solvent  | Time (h) | Temp. (°C) | Product yield (%) |
|-------|----------|----------|----------|------------|------------------|
| 1     | [Zn(µ₂-H₂L₁)(2,2'-bipy)(H₂O)]ₙ (3) | CH₃OH    | 12       | 70         | 89               | This work       |
| 2     | [[Cu₂(L₆)(H₂O)₂][DMF]₂(H₂O)]ₙ (activated) | −        | 48       | 50         | 81               | 82              |
| 3     | [{Cu(L₇)·DMF·H₂O}]ₙ | H₂O      | 40       | 75         | 98               | 83              |
| 4     | [Zn(L₈)·H₂O]₂ | CH₃OH    | 48       | 70         | 97               | 85              |
| 5     | [Zn(L₉)·H₂O]₂ | H₂O      | 48       | 70         | 93               | 86              |

\(^a\)Linkers in coordination polymer catalysts: H₄L₁: 5,5’-(piperazine-1,4-diyl)diisophthalic acid; H₂L₆: 5-{(pyridin-4-ylmethyl)-amino} isophthalic acid; H₂L₇: 5-benzamidoisophthalic acid; H₂L₈: 3,3’-{(pyridine-2,6-dicarbonyl)-bis(azanediyl)} dibenzoic acid.

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