Supporting Information (SI)

Coordination Polymers Constructed from an Adaptable Pyridine-Dicarboxylic Acid Linker: Assembly, Diversity of Structures, and Catalysis

Xiaoyan Cheng,† Lirong Guo,*,† Hongyu Wang,† Jinzhong Gu,*,† Ying Yang,† Marina V. Kirillova,‡ and Alexander M. Kirillov*,‡

†State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, People’s Republic of China
‡Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001, Lisbon, Portugal

*To whom correspondence should be addressed. Tel.: +86-931-8915196; E-mail: gujzh@lzu.edu.cn; guolr@lzu.edu.cn; kirillov@tecnico.ulisboa.pt; Tel.: +351-218419396.

Contents

| Section                                                                 | Page |
|------------------------------------------------------------------------|------|
| General Methods                                                       | S2   |
| Synthesis and analytical data for 1–8                                   | S2   |
| Figure S1 FTIR spectra of compounds 1–8                                 | S4   |
| Figure S2 PXRD patterns of compounds 1–8                               | S6   |
| Figure S3 X-ray photoelectron spectroscopy (XPS) spectrum of 6.        | S7   |
| Figure S4 Typical 1H NMR spectra of the reaction mixtures (and product yield calculation) | S8   |
| Figure S5 Accumulation of product vs. time in the Knoevenagel condensation | S14  |
| Figure S6 Catalyst recycling experiments                               | S14  |
| Figure S7 PXRD patterns for 4                                          | S15  |
| Scheme S1 Plausible mechanism for the Knoevenagel condensation reaction catalyzed by 4 | S15  |
| Table S1 Selected bond lengths and angles for compounds 1–8            | S16  |
| Table S2 Hydrogen bonds in crystal packing of 1–8                      | S17  |
| Table S3 Reaction attempts for the synthesis of CPs                    | S18  |
| Table S4 Porosity and gas sorption data for 4                          | S19  |
| Table S5 Comparison of various catalysts in the Knoevenagel condensation of benzaldehyde and propanedinitrile | S20  |
**General Methods.** All chemicals and solvents were obtained from commercial suppliers. 4,4'-(Pyridine-3,5-diyl)dibenzoic acid (H$_2$pdba) was 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 the 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). Solution $^1$H NMR spectra were recorded on a JNM ECS 400M spectrometer.

**Synthesis and Analytical Data for 1–8.**

$[Mn(\mu_4-pdba)(H_2O)]_n$ (1). A mixture of MnCl$_2$$\cdot$4H$_2$O (39.6 mg, 0.20 mmol), H$_2$pdba (63.8 mg, 0.20 mmol), NaOH (16.0 mg, 0.40 mmol), and H$_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}$. Yellow block-shaped crystals of 1 were isolated manually, washed with distilled water and dried (yield 65% based on H$_2$pdba). Anal. Calcd for C$_{19}$H$_{13}$MnNO$_5$: C, 58.48; H, 3.36; N, 3.59. Found: C, 58.61; H, 3.38; N, 3.57%. FTIR (KBr, cm$^{-1}$): 3195 w, 3006 w, 2898 w, 2811 w, 1600 s, 1584 m, 1546 s, 1439 w, 1394 s, 1332 w, 1217 w, 1196 w, 1109 w, 1014 w, 941 w, 891 w, 862 w, 813 w, 792 m, 747 w, 710 w, 689 w, 648 w.

$\{[M(\mu_3-pdba)(phen)]\cdot2H_2O\}_n$ (M = Co, 2; Ni, 3). A mixture of CoCl$_2$$\cdot$6H$_2$O or NiCl$_2$$\cdot$6H$_2$O (0.20 mmol), H$_2$pdba (63.8 mg, 0.20 mmol), phen (40.0 mg, 0.20 mmol), NaOH (16 mg, 0.40 mmol), and H$_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}$. Red (2) or green (3) block-shaped crystals of 2 and 3 were isolated manually, washed with distilled water and dried (yield 56% for 2; 50% for 3, based on H$_2$pdba). Anal. Calcd for C$_{31}$H$_{23}$CoN$_3$O$_6$: C, 62.84; H, 3.91; N, 7.09. Found: C, 62.57; H, 3.93; N, 7.06%. FTIR (KBr, cm$^{-1}$): 3422 w, 3063 w, 1596 s, 1546 s, 1514 w, 1423 s, 1378 s, 1320 w, 1237 w, 1167 w, 1101 w, 1014 w, 982 w, 911 w, 871 w, 841 w, 788 m, 710 w, 668 w, 644 w.

$\{[Cu_2(\mu_3-pdba)_2(bipy)]\cdot2H_2O\}_n$ (4). A mixture of CuCl$_2$$\cdot$2H$_2$O (34.1 mg, 0.20 mmol), H$_2$pdba (63.8 mg, 0.20 mmol), 2,2’-bipy (31.2 mg, 0.20 mmol), NaOH (16 mg, 0.40 mmol), and H$_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. Blue block-shaped crystals of 4 were isolated manually, washed with distilled water and dried (yield 43% based on H₂pdba). Anal. Calcd for C₄₈H₃₂Cu₂N₄O₁₆: C, 60.44; H, 3.59; N, 5.87. Found: C, 60.23; H, 3.58; N, 5.89%. FTIR (KBr, cm⁻¹): 3459 w, 3075 w, 1608 s, 1554 w, 1443 w, 1386 s, 1361 w, 1242 w, 1188 w, 1163 w, 1138 w, 1105 w, 1056 w, 1011 w, 920 w, 866 w, 817 w, 784 m, 771 w, 709 w, 668 w, 635 w.

\[[\text{Co}(\mu_3\text{-pdba})(\text{bipy})] \cdot 2\text{H}_2\text{O}\]ₙ (5). Synthesis of 5 was similar to 4 except using CoCl₂·6H₂O (47.6 mg, 0.20 mmol) instead of CuCl₂·2H₂O. Pink block-shaped crystals of 5 were isolated manually, washed with distilled water and dried (yield 48% based on H₂pdba). Calcd for C₂₉H₂₂CoN₃O₆: C, 61.27; H, 4.08; N, 7.39%. Found: C, 61.53; H, 4.10; N, 7.36%. FTIR (KBr, cm⁻¹): 3422 w, 3067 w, 1608 s, 1546 m, 1476 w, 1443 m, 1414 s, 1394 s, 1320 w, 1245 w, 1163 w, 1101 w, 1019 w, 911 w, 862 w, 821 w, 784 m, 771 w, 739 w, 714 w, 668 w, 627 w.

\[[\text{Co}_2(\mu_3\text{-pdba})(\mu\text{-Hbiim})](\text{Hbiim})]ₙ (6). A mixture of CoCl₂·6H₂O (47.6 mg, 0.20 mmol), H₂pdba (63.8 mg, 0.20 mmol), H₂biim (26.8 mg, 0.20 mmol), NaOH (16.0 mg, 0.40 mmol), and H₂O (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. Purple block-shaped crystals of 6 were obtained (yield 35% based on H₂pdba). Anal. Calcd for C₃₇H₂₆Co₂N₁₃O₄: C, 53.25; H, 3.14; N, 21.82. Found: C, 53.37; H, 3.17; N, 21.56. FTIR (KBr, cm⁻¹): 1637 m, 1620 w, 1587 w, 1551 w, 1517 w, 1411 s, 1328 s, 1217 w, 1147 m, 1085 w, 957 w, 940 w, 903 w, 850 w, 817 w, 780 m, 751 m, 697 w, 656 w.

\[[\text{M}(\mu_4\text{-pdba})(\text{py})]ₙ (M = \text{Co}, 7; \text{Ni}, 8). A mixture of CoCl₂·6H₂O or NiCl₂·6H₂O (0.20 mmol), H₂pdba (63.8 mg, 0.20 mmol), py (0.50 mL, 6.20 mmol), and H₂O (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. Pink (7) or green (8) block-shaped crystals of 7 and 8 were isolated manually, washed with distilled water and dried (yield 51% for 7; 54% for 8, based on H₂pdba). Anal. Calcd for C₂₄H₁₆CoN₂O₄ (7): C, 63.31; H, 3.54; N, 6.15. Found: C, 63.14; H, 3.53; N, 6.12%. FTIR (KBr, cm⁻¹): 1612 m, 1534 w, 1418 s, 1386 s, 1332 w, 1217 w, 1167 w, 1072 w, 1010 w, 903 w, 866 w, 812 w, 788 m, 755 w, 709 w, 693 w, 672 w, 631 w. Anal. Calcd for C₂₄H₁₆NiN₂O₄ (8): C, 63.34; H, 3.54; N, 6.16. Found: C, 63.21; H, 3.51; N, 6.19%. FTIR (KBr, cm⁻¹): 1612 s, 1583 m, 1558 w, 1534 m, 1427 s, 1386 s, 1332 w, 1216 w, 1167 w, 1072 w, 1014 w, 903 w, 866 m, 812 w, 788 m, 755 w, 709 w, 688 w, 627 w.
Figure S1. FTIR spectra of compounds 1–8.
Figure S2. PXRD patterns of compounds 1–8 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). Blue patterns are those after the water treatment experiment (the samples were kept in water at 50 °C for 12 h, then isolated and dried before PXRD measurements).

Figure S3. X-ray photoelectron spectroscopy (XPS) spectrum of 6. The ratio of Co$^{2+}$ and Co$^{3+}$ peak areas is 1.07:1 (by peak deconvolution).
Figure S4. Examples for integration of $^1$H NMR spectra for the determination of Knoevenagel condensation products. Reactions with different substrates (a)-(l). For details, see below the product yield calculations based on $^1$H NMR.
Product Yield Calculations based on $^1$H NMR (Figure S4)

(a): Conditions of Table 3, entry 6.

Product yield calculation in the Knoevenagel condensation reaction. The C(=O)$^1$H signal of benzaldehyde (substrate) appears at $\delta$ 10.02 ppm, while 2-benzylidemalononitrile (product) shows a characteristic signal at $\delta$ 7.79 ppm.

Total integration of both signals: unreacted benzaldehyde + 2-benzylidemalononitrile = 0 + 1.00 = 1.00.

Percentage of the unreacted substrate: 0/1.00 = 0%

Conversion of benzaldehyde = yield of 2-benzylidemalononitrile = 100 – 0 = 100%.

(b) Conditions of Table 4, entry 2.

Product yield calculation in the Knoevenagel condensation reaction. The C(=O)$^1$H signal of 2-nitrobenzaldehyde (substrate) appears at $\delta$ 10.40 ppm, while (2-nitrobenzylidene)malononitrile (product) shows a characteristic signal at $\delta$ 8.45 ppm.

Total integration of both signals: unreacted 2-nitrobenzaldehyde + (2-nitrobenzylidene)malononitrile = 0 + 1.00 = 1.00.

Percentage of the unreacted substrate: 0/1.00 = 0%

Conversion of 2-nitrobenzaldehyde = yield of (2-nitrobenzylidene)malononitrile = 100 – 0 = 100%.
(c) Conditions of Table 4, entry 3.

*Product yield calculation in the Knoevenagel condensation reaction.* The C(=O)H signal of 3-nitrobenzaldehyde (substrate) appears at δ 10.03 ppm, while (3-nitrobenzylidene)malononitrile (product) shows a characteristic signal at δ 7.89 ppm.

Total integration of both signals: unreacted 3-nitrobenzaldehyde + (3-nitrobenzylidene)malononitrile = 0 + 1.00 = 1.00.

Percentage of the unreacted substrate: 0/1.00 = 0%

Conversion of 3-nitrobenzaldehyde = yield of (3-nitrobenzylidene)malononitrile = 100 – 0 = 100%.

(d) Conditions of Table 4, entry 4.

*Product yield calculation in the Knoevenagel condensation reaction.* The C(=O)H signal of 4-nitrobenzaldehyde (substrate) appears at δ 10.15 ppm, while (4-nitrobenzylidene)malononitrile (product) shows a characteristic signal at δ 7.88 ppm.

Total integration of both signals: unreacted 4-nitrobenzaldehyde + (4-nitrobenzylidene)malononitrile = 0 + 1.00 = 1.00.

Percentage of the unreacted substrate: 0/1.00 = 0%

Conversion of 4-nitrobenzaldehyde = yield of (4-nitrobenzylidene)malononitrile = 100 – 0 = 100%.

(e) Conditions of Table 4, entry 5.
Product yield calculation in the Knoevenagel condensation reaction. The C (=O)H signal of 4-chlorobenzaldehyde (substrate) appears at $\delta$ 9.97 ppm, while (4-chlorobenzylidene)malononitrile (product) shows a characteristic signal at $\delta$ 7.73 ppm.

Total integration of both signals: unreacted 4-chlorobenzaldehyde + (4-chlorobenzylidene)malononitrile = 0 + 1.00 = 1.00.

Percentage of the unreacted substrate: 0/1.00 = 0%

Conversion of 4-chlorobenzaldehyde = yield of (4-chlorobenzylidene)malononitrile = 100−0 = 100%.

(f) Conditions of Table 4, entry 6.

Product yield calculation in the Knoevenagel condensation reaction. The C (=O)H signal of 4-bromobenzaldehyde (substrate) appears at $\delta$ 9.97 ppm, while (4-bromobenzylidene)malononitrile (product) shows a characteristic signal at $\delta$ 7.73 ppm.

Total integration of both signals: unreacted 4-bromobenzaldehyde + (4-bromobenzylidene)malononitrile = 0 + 1.00 = 1.00.

Percentage of the unreacted substrate: 0/1.00 = 0%

Conversion of 4-bromobenzaldehyde = yield of (4-bromobenzylidene)malononitrile = 100−0 = 100%

(g) Conditions of Table 4, entry 7.
Product yield calculation in the Knoevenagel condensation reaction. The –CH peak of 4-methylbenzaldehyde (substrate) appears at 9.96 ppm while that of (4-methylbenzylidene)malononitrile (product) can be seen at 7.73 ppm.

Total amount: unreacted substrate (4-methylbenzaldehyde) + formed product (4-methylbenzylidene)malononitrile = 1 + 64.54 = 65.54

Percentage of the unreacted substrate: 1/65.54 = 1.53%

Conversion of 4-methylbenzaldehyde = yield of (4-methylbenzylidene)malononitrile = 100−1.53 = 98.5%.

(h) Conditions of Table 4, entry 8.

Product yield calculation in the Knoevenagel condensation reaction. The –CH peak of 4-methoxybenzaldehyde (substrate) appears at 9.89 ppm while that of (4-methoxybenzylidene)malononitrile (product) can be seen at 7.66 ppm.

Total amount: unreacted substrate (4-methoxybenzaldehyde) + formed product (4-methoxybenzylidene)malononitrile = 1 + 3.84 = 4.84

Percentage of the unreacted substrate: 1/4.84 = 20.7%

Conversion of 4-methoxybenzaldehyde = yield of (4-methoxybenzylidene)malononitrile = 100−20.7 = 79.3%.

(i) Conditions of Table 4, entry 9.
Product yield calculation in the Knoevenagel condensation reaction. The –CH peak of 4-hydroxybenzaldehyde (substrate) appears at 9.87 ppm while that of (4-hydroxybenzylidene)malononitrile (product) can be seen at 7.64 ppm.

Total amount: unreacted substrate (4-hydroxybenzaldehyde) + formed product (4-hydroxybenzylidene)malononitrile = 1+0.47 = 1.47

Percentage of the unreacted substrate: 1/1.47 = 68.0%

Conversion of 4-hydroxybenzaldehyde = yield of (4-hydroxybenzylidene)malononitrile = 100−68.0 = 32.0%.

(j) Conditions of Table 4, entry 10. d$_6$-DMSO solvent used.

Product yield calculation in the Knoevenagel condensation reaction. The –CH peaks of cinnamaldehyde (substrate) appear at 9.67 and 9.69 ppm while that of 2-(3-phenyl-2-propen-1-ylidene)propanedinitrile (product) can be seen at 8.29 and 8.32 ppm.

Total amount: unreacted substrate (cinnamaldehyde) + formed product 2-(3-phenyl-2-propen-1-ylidene)propanedinitrile = 1 + 3.79 = 4.79

Percentage of the unreacted substrate: 1/4.79 = 20.9%

Conversion of cinnamaldehyde = yield of 2-(3-phenyl-2-propen-1-ylidene)propanedinitrile = 100−20.9 = 79.1%.

(k) Conditions of Table 5, entry 2.
Product yield calculation in the Knoevenagel condensation reaction. The –CH peak of 1-naphthaldehyde (substrate) appears at 10.40 ppm while that of 2-(naphthalen-1-ylmethylidene)propanedinitrile (product) can be seen at 8.67 ppm.

Total amount: unreacted substrate (1-naphthaldehyde) + formed product 2-(naphthalen-1-ylmethylidene)propanedinitrile = 1 + 41.05 = 42.05

Percentage of the unreacted substrate: 1/42.05 = 2.4%

Conversion of 1-naphthaldehyde = yield of 2-(naphthalen-1-ylmethylidene)propanedinitrile = 100 − 2.4 = 97.6%.

(l) Conditions of Table 5, entry 3.

Product yield calculation in the Knoevenagel condensation reaction. The –CH peak of 9-anthraldehyde (substrate) appears at 11.55 ppm while that of 2-(anthracen-9-ylmethylene)malononitrile (product) can be seen at 8.97 ppm.

Total amount: unreacted substrate (9-anthraldehyde) + formed product 2-(anthracen-9-ylmethylene)malononitrile = 1+5.10=6.10

Percentage of the unreacted substrate: 1/6.10 = 16.4%

Conversion of 9-anthraldehyde = yield of 2-(anthracen-9-ylmethylene)malononitrile = 100 − 16.4 = 83.6%.
**Figure S5.** Accumulation of 2-benzylidenemalononitrile vs. time in the Knoevenagel condensation of benzaldehyde with propanedinitrile catalyzed by 4 (dotted line refers to the reaction after removal of the catalyst after 20 min reaction time; see text for details). Reaction conditions are those of Table 3, entries 1–6.

**Figure S6.** Catalyst recycling experiments in the Knoevenagel condensation of benzaldehyde with propanedinitrile catalyzed by 4. Reaction conditions are those of Table 3, entry 6.
**Figure S7.** PXRD patterns for 4: simulated (red), before (black) and after (blue) catalysis.

**Scheme S1.** Plausible mechanism for the Knoevenagel condensation reaction catalyzed by 4.
Table S1. Selected Bond Lengths [Å] and Angles [°] for the Compounds 1–8.

|       | Bond Length/Angle                              | Value       |
|-------|-----------------------------------------------|-------------|
| 1     | Mn(1)-O(1)                                    | 2.1896(15)  |
|       | Mn(1)-O(1)                                    | 2.0815(14)  |
|       | O(2)-Mn(1)-O(2)                               | 143.69(9)   |
|       | O(2)-Mn(1)-O(1)                               | 86.57(6)    |
|       | N(2)-Co(2)-N(10)                              | 2.027(3)    |
|       | N(2)-Co(2)-N(5)                               | 2.139(4)    |
|       | O(2)-Co(1)-N(1)                               | 169.34(15)  |
|       | N(3)-Co(1)-N(2)                               | 76.82(15)   |
|       | O(1)-Co(1)-N(1)                               | 93.67(14)   |
|       | O(1)-Co(1)-O(2)                               | 94.75(16)   |
|       | O(3)-Co(1)-N(2)                               | 138.71(15)  |
|       | Ni(1)-O(1)                                    | 2.012(3)    |
|       | Ni(1)-N(1)                                    | 2.107(4)    |
|       | O(3i)-Ni(1)-O(1)                              | 97.37(17)   |
|       | O(1)-Ni(1)-N(2)                               | 91.17(17)   |
|       | N(1i)-Ni(1)-O(3)                              | 92.69(16)   |
|       | O(4i)-Ni(1)-N(2)                              | 83.97(15)   |
|       | Ni(1)-O(1)                                    | 98.38(15)   |
| 2     | Co(1)-O(1)                                    | 2.027(3)    |
|       | Co(1)-N(1)                                    | 2.139(4)    |
|       | N(1i)-Co(1)-N(3)                              | 169.34(15)  |
|       | N(3)-Co(1)-N(2)                               | 76.82(15)   |
|       | O(1)-Co(1)-N(1)                               | 93.67(14)   |
|       | O(1)-Co(1)-O(2)                               | 94.75(16)   |
|       | O(3)-Co(1)-N(2)                               | 138.71(15)  |
|       | Ni(1)-O(1)                                    | 2.012(3)    |
|       | Ni(1)-N(1)                                    | 2.107(4)    |
|       | O(3i)-Ni(1)-O(1)                              | 97.37(17)   |
|       | O(1)-Ni(1)-N(2)                               | 91.17(17)   |
|       | N(1i)-Ni(1)-O(3)                              | 92.69(16)   |
|       | O(4i)-Ni(1)-N(2)                              | 83.97(15)   |
|       | Ni(1)-O(1)                                    | 98.38(15)   |
| 3     | Cu(1)-O(2)                                    | 1.932(2)    |
|       | Cu(1)-N(4)                                    | 2.012(3)    |
|       | Cu(2)-O(3)                                    | 1.9181(18)  |
|       | O(2)-Cu(1)-O(7)                               | 98.46(10)   |
|       | N(3)-Cu(1)-O(7)                               | 166.04(12)  |
|       | O(3i)-Cu(2)-O(6)                              | 176.41(11)  |
|       | O(3i)-Cu(2)-N(1)                              | 92.78(9)    |
| 4     | Co(1)-O(2)                                    | 2.030(3)    |
|       | Co(1)-N(1)                                    | 2.134(3)    |
|       | N(3)-Co(1)-O(2)                               | 115.65(13)  |
|       | O(2i)-Co(1)-N(1)                              | 95.71(11)   |
|       | O(2i)-Co(1)-O(4)                              | 94.76(13)   |
|       | O(2i)-Co(1)-N(2)                              | 84.27(12)   |
|       | N(2)-Co(1)-O(4)                               | 91.73(11)   |
|       | N(1)-Co(1)-O(3)                               | 91.84(10)   |
| 5     | Co(1)-O(2)                                    | 2.028(4)    |
|       | Co(1)-N(1)                                    | 2.273(4)    |
|       | Co(2)-N(5)                                    | 1.939(5)    |
|       | Co(2)-N(10)                                   | 1.916(5)    |
|       | O(2)-Co(1)-O(4)                               | 124.40(18)  |
|       | O(2)-Co(1)-N(3)                               | 83.33(16)   |
|       | O(2)-Co(1)-N(12)                              | 88.64(16)   |
|       | N(1i)-Co(1)-N(12)                             | 167.45(17)  |
|       | N(2)-Co(2)-N(13)                              | 92.57(18)   |
| 6     | Co(1)-O(2)                                    | 2.028(4)    |
|       | Co(1)-N(1)                                    | 2.273(4)    |
|       | Co(2)-N(5)                                    | 1.939(5)    |
|       | Co(2)-N(10)                                   | 1.916(5)    |
|       | O(2)-Co(1)-O(4)                               | 124.40(18)  |
|       | O(2)-Co(1)-N(3)                               | 83.33(16)   |
|       | O(2)-Co(1)-N(12)                              | 88.64(16)   |
|       | N(1i)-Co(1)-N(12)                             | 167.45(17)  |
|       | N(2)-Co(2)-N(13)                              | 92.57(18)   |
| Complexes | D-H...A | d(D-H) | d(H...A) | d(D...A) | ∠DHA | Symmetry code |
|-----------|---------|--------|----------|----------|------|---------------|
| 1         | O(5)-H(1W)--O(1) | 0.861  | 2.202    | 2.689    | 115.65 | -x+2, y+1, -z+3/2 |
|           | O(5)-H(2W)--O(1) | 0.861  | 2.004    | 2.689    | 135.80 | x, y+1, z     |

| 4         | O(9)-H(1W)--O(8) | 0.850  | 2.209    | 2.825    | 129.22 | -x+1, -y+1/2, z+1/2 |
|           | O(9)-H(2W)--O(2) | 0.850  | 2.368    | 3.025    | 134.4  | -x+1, -y+1/2, z+1/2 |
|           | O(10)-H(3W)--O(1) | 0.850  | 2.026    | 2.811    | 153.14 | x+1, y+1, z    |
|           | O(10)-H(4W)--O(5) | 0.850  | 2.143    | 2.974    | 165.52 | x+1, y+1, z    |

| 6         | N(1)-H(1)--O(2) | 0.860  | 2.105    | 2.851    | 144.78 | -x+1, -y+1/2, z+1/2 |
|           | N(7)-H(2)--N(8) | 0.860  | 1.986    | 2.795    | 156.42 | -x, -y+1, -z+2  |
|           | N(11)-H(8)--O(3) | 0.860  | 2.188    | 2.816    | 129.66 | -x+1, y+1/2, z+1/2 |

Table S2. Hydrogen Bonds in Crystal Packing [Å, °] of 1, 4 and 6.

*aSymmetry transformations used to generate equivalent atoms: i, –y+1, z+1/2; ii, –x+2, –y+1, –z+1; iii, –x+2, y, –z+3/2 for 1; ix, –y+3/2, z+3/2; ii x, y, z+1 for 2; ix–1, –y+3/2, z–3/2; ii x, y, z+1 for 3; ix–x–2, +y+1/2, z+1/2; ii –x+2, –y+1, –z; iii –x+3, –y, –z+4 for 4; ix, y, z–1; ii x+1, –y+1/2, z+1/2 for 5; i –x+1, –y+1, –z; ii –x, –y+1/2, z+1/2; iii x, –y+3/2, z–1/2 for 6; i –x, –y+1, –z+3; ii x–1, y–1, z+2; iii x–1, y, z+1 for 7 and 8.
Table S3. Reaction Attempts for the Synthesis of CPs.

| No | Metal(II) precursor | Crystallization mediator (CM) | M^{2+}/H_{pdba}/CM/NaOH molar ratio | Result | Product formula (when available) |
|----|---------------------|-------------------------------|------------------------------------|--------|----------------------------------|
| 1  | CuCl_{2}·2H_{2}O    | -                             | 1/1/-/2                            | no crystallization | - |
| 2  | CoCl_{2}·6H_{2}O    | -                             | 1/1/-/2                            | no crystallization | - |
| 3  | NiCl_{2}·6H_{2}O    | -                             | 1/1/-/2                            | no crystallization | - |
| 4  | MnCl_{2}·4H_{2}O    | -                             | 1/1/-/2                            | monocrystals/X-ray structure | [Mn(\mu_4-pdba)(H_{2}O)]_{n} (1) |
| 5  | ZnCl_{2}            | -                             | 1/1/-/2                            | no crystallization | - |
| 6  | CdCl_{2}·H_{2}O     | -                             | 1/1/-/2                            | no crystallization | - |
| 7  | CuCl_{2}·2H_{2}O    | phen                          | 1/1/1/2                            | no crystallization | - |
| 8  | CoCl_{2}·6H_{2}O    | phen                          | 1/1/1/2                            | monocrystals/X-ray structure | \{[Co(\mu_3-pdba)(phen)]·2H_{2}O\}_{n} (2) |
| 9  | NiCl_{2}·6H_{2}O    | phen                          | 1/1/1/2                            | monocrystals/X-ray structure | \{[Ni(\mu_3-pdba)(phen)]·2H_{2}O\}_{n} (3) |
| 10 | MnCl_{2}·4H_{2}O    | phen                          | 1/1/1/2                            | no crystallization | - |
| 11 | ZnCl_{2}            | phen                          | 1/1/1/2                            | polycrystals/not suitable for SCXD | - |
| 12 | CdCl_{2}·H_{2}O     | phen                          | 1/1/1/2                            | no crystallization | - |
| 13 | CuCl_{2}·2H_{2}O    | 2,2′-bipy                      | 1/1/1/2                            | monocrystals/X-ray structure | \{[Cu(\mu_3-pdba)(bipy)]·2H_{2}O\}_{n} (4) |
| 14 | CoCl_{2}·6H_{2}O    | 2,2′-bipy                      | 1/1/1/2                            | monocrystals/X-ray structure | \{[Co(\mu_3-pdba)(bipy)]·2H_{2}O\}_{n} (5) |
| 15 | NiCl_{2}·6H_{2}O    | 2,2′-bipy                      | 1/1/1/2                            | polycrystals/not suitable for SCXD | - |
| 16 | MnCl_{2}·4H_{2}O    | 2,2′-bipy                      | 1/1/1/2                            | no crystallization | - |
| 17 | ZnCl_{2}            | 2,2′-bipy                      | 1/1/1/2                            | no crystallization | - |
| 18 | CdCl_{2}·H_{2}O     | 2,2′-bipy                      | 1/1/1/2                            | no crystallization | - |
| 19 | CuCl_{2}·2H_{2}O    | 4,4′-bipy                      | 1/1/1/2                            | no crystallization | - |
| 20 | CoCl_{2}·6H_{2}O    | 4,4′-bipy                      | 1/1/1/2                            | no crystallization | - |
| 21 | NiCl_{2}·6H_{2}O    | 4,4′-bipy                      | 1/1/1/2                            | no crystallization | - |
| 22 | MnCl_{2}·4H_{2}O    | 4,4′-bipy                      | 1/1/1/2                            | no crystallization | - |
| 23 | ZnCl_{2}            | 4,4′-bipy                      | 1/1/1/2                            | no crystallization | - |
| 24 | CdCl_{2}·H_{2}O     | 4,4′-bipy                      | 1/1/1/2                            | no crystallization | - |
| 25 | CuCl_{2}·2H_{2}O    | H_{2}biim                      | 1/1/1/2                            | no crystallization | - |
| 26 | CoCl_{2}·6H_{2}O    | H_{2}biim                      | 1/1/1/2                            | monocrystals/X-ray structure | \{[Co(\mu_3-pdba)(\mu_{H_{2}biim}})](H_{2}biim)]·(H_{2}biim)]_{n} (6) |
| 27 | NiCl_{2}·6H_{2}O    | H_{2}biim                      | 1/1/1/2                            | no crystallization | - |
| 28 | MnCl_{2}·4H_{2}O    | H_{2}biim                      | 1/1/1/2                            | no crystallization | - |
| 29 | ZnCl_{2}            | H_{2}biim                      | 1/1/1/2                            | no crystallization | - |
30 CdCl₂·H₂O  H₂biim  1/1/1/2  no crystallization  -
31 CuCl₂·2H₂O  py  1/1/31/  no crystallization  -
32 CoCl₂·6H₂O  py  1/1/31/  monocryts/X-ray structure  [Co(μ₄-pdba)(py)]ₙ (7)
33 NiCl₂·6H₂O  py  1/1/31/  monocryts/X-ray structure  [Ni(μ₄-pdba)(py)]ₙ (8)
34 MnCl₂·4H₂O  py  1/1/31/  no crystallization  -
35 ZnCl₂  py  1/1/31/  no crystallization  -
36 CdCl₂·H₂O  py  1/1/31/  no crystallization  -

*aHydrothermal synthesis: stainless steel reactor (Teflon-lined, 25 mL volume), water as solvent (10 mL), 160 °C, 3 days.

Table S4. Porosity and Gas Sorption Data for Compound 4.a

| Compound | Void volume (%) | Amount of adsorbed N₂ (cm³/g) | BET surface area (m²/g) |
|----------|----------------|-----------------|-----------------|
| 4        | 5.0            | 2.1             | 1.0             |

*aPrior to gas adsorption tests, the samples were activated to remove the guest water molecules (samples were heated under vacuum at 120 °C for 18 h). The sorption measurements were carried out on the activated samples and the N₂ adsorption/desorption isotherms were measured at 77 K.
Table S5. Comparison of Various Catalysts for the Knoevenagel Condensation Reaction between Benzaldehyde and Propanedinitrile.

| Entry | Catalyst | Catalyst (mol%) | Solvent | Time (h) | Temp. (°C) | Conversion (%) | Ref. |
|-------|----------|-----------------|---------|----------|------------|---------------|------|
| 1     | {[Cu₂(μ₃-pdba)₂(bipy)]·2H₂O}_n | 2 | MeOH | 1 | RT | >99 | This work |
| 2     | Zn₃(OH)(ATTCA)₂(H₂O)]·C₆H₆N H₂·4DMF·H₂O | 10 | DCM | 5 | RT | 94 | 77 |
| 3     | [Zn(L)₃(μ₂-OH)]_n | 4 | H₂O | 8 | 90 | 78 | 78 |
| 4     | [Zn₃(CA)(BIB)₂]·(NO₃) | 0.3 | – | 1 | 60 | 99 | 52 |
| 5     | {[Zn₅(μ₅-O)₈(μ₅-OH)₄(H₂O)₄(DCBA)₄]}·5DMF·3H₂O | 10 | DCM | 5 | RT | 89 | 5 |
| 6     | {[Ba₃Zn₄(TDP)₂(HCO₂)₂(OH₂)₂]}·7 DMF·4H₂O | 3 | Ethanol | 1 | 60 | 99 | 67 |
| 7     | {[Zn(L)(bpfp)]·H₂O}_n | 5 | DMF | 3 | 35 | 98 | 50 |
| 8     | [Zn(L)(H₂O)]_n·n(N-Methylformamide) | 3 | MeOH | 1.5 | 40 | 75 | 79 |
| 9     | [PbL₂]·2DMF·6H₂O | 3 | CH₃CN | 24 | RT | >99 | 80 |
| 10    | [Co₂(dtc)₄(tpxn)]·6H₂O | 2 | MeOH | 1 | 25-30 | 96 | 81 |
| 11    | [Zn(L)₃(NMeF)]_n·n(NMeF) | 3 | H₂O | 6 | 50 | >99 | 82 |
| 12    | {[Cd(Py₃TTz)(2-NH₂BDC)]·(DMF)·0.5(H₂O)}_n | 2 | – | 6 | 60 | 99.8 | 51 |
| 13    | [Zn₁₅(mbpz)₉(Hmbpz)₉(L-NO₂)₄(HL-NO₂)₂(μ₁-μ₁OH)]_n | 0.6 | – | 1 | 80 | >99 | 83 |

Linkers in coordination polymer catalysts: H₃ATTCA: 2-amino[1,1:3,1-terphenyl]-4,4,5-tricarboxylic acid; H₂L: 2-(hydroxymethyl)-1H-benzo[d]imidazole-5-carboxylic acid; H₃TCA: tricarboxytriphenyl amine, BIB: 1,3-bis(imidazol-1-ylmethyl)benzene; H₄DCBA: 4”,6”-diamino-5”,5”-bis(4-carboxyphenyl)-[1,1’:3’,1”’;3’,1”’-quaterphenyl]-4,4”’-dicarboxylic acid; H₆TDP: 2,4,6- tri(2,4-dicarboxyphenyl)pyridine; H₂L: methyl-3-hydroxy-5-carboxy-2-thiophenecarboxylate, bpfp:
bis(4-pyridylformyl)piperazine; L: 5-acetamidoisophthalic acid; HL: N-(4-carboxyphenyl)isonicotinamide 1-oxide; tpxn: N,N’-(1,4-phenylenebis(methylene))bis(1-(pyridin-2-yl)-N-(pyridin-2-ylmethyl)methanamine, H_2tdc: thiophene-2,5-dicarboxylic acid; H_2L1: 5-[(pyren-4-ylmethyl)amino]isophthalic acid; 2-NH_2-H_2BDC: 2-amino-1,4-benzenedicarboxylic acid, Py2TTz: 2,5-bis(4-pyridyl)thiazolo[5,4-d]thiazole; H_2mbpz: 3,3’,5,5’-Tetramethyl-4,4’-bi-1H-pyrazole, H_2L-NO_2: 2,2’-Dinitro-[1,1’-biphenyl]-4,4’-dicarboxylic acid.