Electronic Supplementary Information (ESI)

Metal-organic architectures designed from triphenyl-pentacarboxylate linker: hydrothermal assembly, structural multiplicity, and catalytic Knoevenagel condensation

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Electronic Supplementary Information (ESI) contains:

Synthesis and analytical data for 1–8

Synthesis of [Cu_2(μ-H_3ddba)$_2$(phen)$_2$] (1). A mixture of $CuCl_2·2H_2O$ (17.1 mg, 0.10 mmol), H_5ddba (45.0 mg, 0.10 mmol), NaOH (8 mg, 0.20 mmol), phen (20.0 mg, 0.1 mmol), and H_2O (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 **1** were isolated manually, washed with distilled water and dried (yield: 65% based on H_5ddba). Anal. Calcd for $C_{70}H_{40}Cu_2N_4O_{20}$: C, 60.74; H, 2.91; N, 4.05. Found: C, 60.41; H, 2.90; N, 4.07%. IR (KBr, cm^{-1}): 1721 m, 1686 s, 1638 s, 1568 m, 1520 w, 1493 w, 1428 s, 1371 w, 1344 m, 1256 m, 1212 w, 1156 w, 1125 w, 1098 w, 914 w, 875 w, 844 w, 804 w, 765 w, 712 w, 681 w, 642 w.

Synthesis of {[Cd_2(μ$_4$-Hddba)(phen)$_2$(H_2O)$_2$]·2H_2O}$_n$ (2). A mixture of $CdCl_2·H_2O$ (40.2 mg, 0.20 mmol), H_5ddba (45.0 mg, 0.10 mmol), phen (40.0 mg, 0.20 mmol), NaOH (16 mg, 0.40 mmol), and H_2O (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}. Colourless block-shaped crystals of **2** were isolated manually, washed with distilled water and dried (yield: 56% based on H_5ddba). Anal. Calcd for $C_{47}H_{34}Cd_2N_4O_{14}$: C, 51.15; H, 3.11; N, 5.08. Found: C, 51.34; H, 3.13; N, 5.06%. IR (KBr, cm^{-1}): 3460 w, 3066 w, 1704 w, 1598 s, 1546 s, 1511 w, 1428 m, 1371 s, 1287 w, 1209 w, 1142 w, 1103 w, 1046 w, 927 w, 853 m, 814 w, 778 w, 725 m, 703 w, 686 w, 637 w.

Synthesis of [Ni_4(μ$_3$-Hddba)$_2$(2,2′-bipy)$_6$(H_2O)]·6H_2O (3). A mixture of $NiCl_2·6H_2O$ (47.5 mg, 0.20 mmol), H_5ddba (45.0 mg, 0.10 mmol), 2,2′-bipy (31.2 mg, 0.20 mmol), NaOH (16 mg, 0.40 mmol), and H_2O (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 block-shaped crystals of **3** were isolated manually, washed with distilled water and dried (yield: 42% based on H_5ddba). Anal. Calcd for $C_{106}H_{84}Ni_4N_{12}O_{27}$: C, 58.06; H, 3.86; N, 7.67. Found: C, 58.03; H, 3.88; N, 7.64%. IR (KBr, cm^{-1}): 3421 m, 3066 w, 1701 w, 1625 s, 1603 s, 1577 s, 1528 m, 1489 w, 1476 w, 1445 s, 1410 s, 1371 m, 1314 w, 1252 w, 1160 w, 1103 w, 1054 w, 1024 w, 931 w, 905 w, 848 w, 818 w, 760 m, 733 w, 703 w, 654 w.

Synthesis of [Mn_4(μ_3-Hddba)$_2$(2,2′-bipy)$_6$(H_2O)]·$6H_2O$ (4). Synthesis of **4** was similar to **3** except using $MnCl_2 \cdot 4H_2O$ (39.6 mg, 0.20 mmol) instead of $NiCl_2 \cdot 6H_2O$. Yellow block-shaped crystals of **4** were isolated manually, washed with distilled water and dried (yield: 38% based on H_5ddba). Calcd for $C_{106}H_{82}Mn_4N_{12}O_{27}$: C 51.12, H 1.79, N 4.97%. Found: C 51.27, H 1.80, N 4.95%. IR (KBr, cm^{-1}): 3402 w, 3021 w, 1695 w, 1608 s, 1553 s, 1485 w, 1425 w, 1386 s, 1341 w, 1298 w, 1262 w, 1226 w, 1202 w, 1155 w, 1067 w, 1008 w, 976 w, 908 w, 856 w, 844 w, 804 m, 737 w, 717 w, 669 w, 650 w.

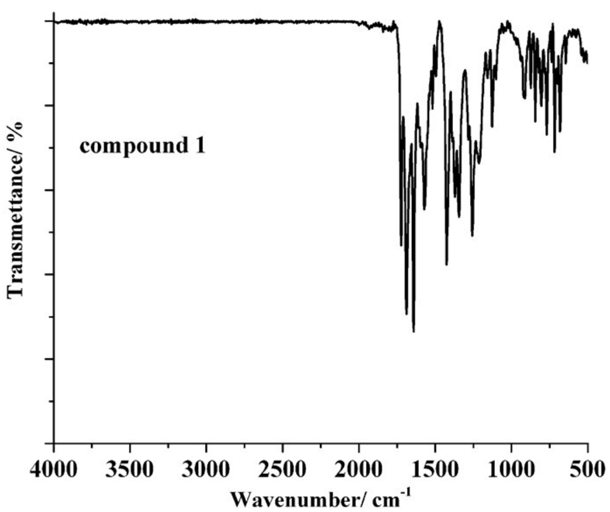
Synthesis of {[Co_2(μ_5-Hddba)(4,4′-bipy)$_{1.5}$(H_2O)]·H_2O}$_n$ (5). A mixture of $CoCl_2 \cdot 6H_2O$ (47.4 mg, 0.20 mmol), H_5ddba (45.0 mg, 0.10 mmol), 4,4′-bipy (31.2 mg, 0.20 mmol), NaOH (16.0 mg, 0.40 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL 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 block-shaped crystals of **5** were obtained (yield: 45% based on H_5ddba). Anal. Calcd for $C_{38}H_{26}Co_2N_3O_{12}$: C, 54.69; H, 3.14; N, 5.04. Found: C, 54.77; H, 3.16; N, 5.06. IR (KBr, cm^{-1}): 3610 w, 3460 w, 3061 w, 1717 w, 1608 s, 1572 m, 1533 m, 1485 w, 1450 w, 1384 s, 1322 w, 1265 w, 1213 m, 1164 w, 1129 w, 1098 w, 1063 w, 1046 w, 901 w, 848 w, 814 m, 795 w, 764 w, 730 w, 681 w, 637 w.

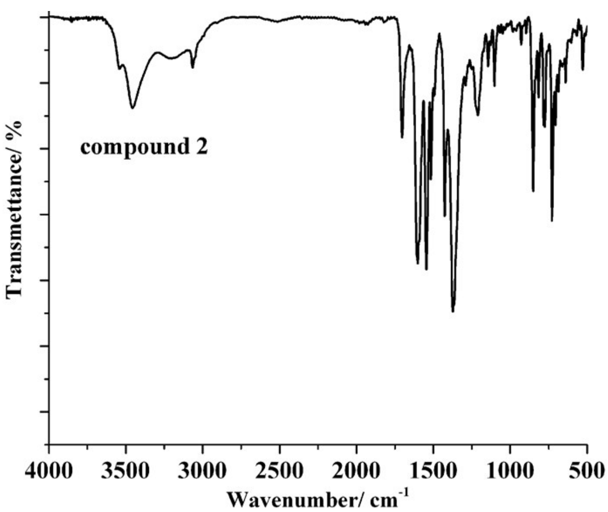
Synthesis of {[Zn_2(μ_5-Hddba)(4,4′-bipy)$_{1.5}$]·4,4′-bipy·$2H_2O$}$_n$ (6). Synthesis of **6** was similar to **5** except using $ZnCl_2$ (27.3 mg, 0.20 mmol) instead of $CoCl_2 \cdot 6H_2O$. Colourless block-shaped crystals of **6** were isolated manually, washed with distilled water and dried (yield: 40% based on H_5ddba). Calcd for $C_{48}H_{34}Zn_2N_5O_{12}$: C 57.44, H 3.41, N 6.98%. Found: C 57.28, H 3.39, N 7.01%. IR (KBr, cm^{-1}): 3583 w, 3399 w, 3070 w, 1718 w, 1638 s, 1595 s, 1537 m, 1493 w, 1397 s, 1235 w, 1195 w, 1120 w, 1072 w, 1050 w, 993 w, 936 w, 840 w, 809 m, 782 m, 730 w, 695 w, 672 w, 642 w.

Synthesis of [Mn_2(μ_6-Hddba)(H_2biim)(H_2O)]$_n$ (7). A mixture of $MnCl_2 \cdot 4H_2O$ (39.6 mg, 0.20 mmol), H_5ddba (45.0 mg, 0.10 mmol), H_2biim (26.8 mg, 0.20 mmol), NaOH (16 mg, 0.40 mmol), and

H_2O (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 **7** were isolated manually, washed with distilled water and dried (yield: 53% based on H_5ddba). Anal. Calcd for $C_{29}H_{18}Mn_2N_4O_{11}$: C, 49.17; H, 2.56; N, 7.91. Found: C, 49.38; H, 2.57; N, 7.87%. IR (KBr, cm^{-1}): 3462 w, 3128 w, 1700 m, 1620 s, 1581 s, 1537 s, 1429 m, 1397 s, 1358 s, 1310 m, 1278 w, 1223 m, 1167 w, 1099 w, 996 w, 916 w, 856 w, 804 m, 757 m, 741 w, 686 w, 649 w.

Synthesis of {[Cd_2(μ_7-ddba)(Hbpa)]·$5H_2O$}$_n$ (8). A mixture of $CdCl_2 \cdot H_2O$ (40.2 mg, 0.20 mmol), H_5ddba (45.0 mg, 0.10 mmol), bpa (34.2 mg, 0.20 mmol), NaOH (20.0 mg, 0.50 mmol), and H_2O (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}. Colourless block-shaped crystals of **8** were isolated manually, washed with distilled water and dried (yield: 57% based on H_5ddba). Anal. Calcd for $C_{33}H_{29}Cd_2N_3O_{15}$: C, 42.51; H, 3.13; N, 4.51. Found: C, 42.43; H, 3.14; N, 4.53%. IR (KBr, cm^{-1}): 3431 m, 3251 w, 3064 w, 1643 m, 1604 s, 1576 w, 1520 s, 1433 s, 1397 s, 1362 m, 1313 w, 1218 w, 1198 w, 1131 w, 1099 w, 1059 w, 1016 m, 912 w, 832 w, 780 m, 769 m, 741 w, 697 w, 661 w.





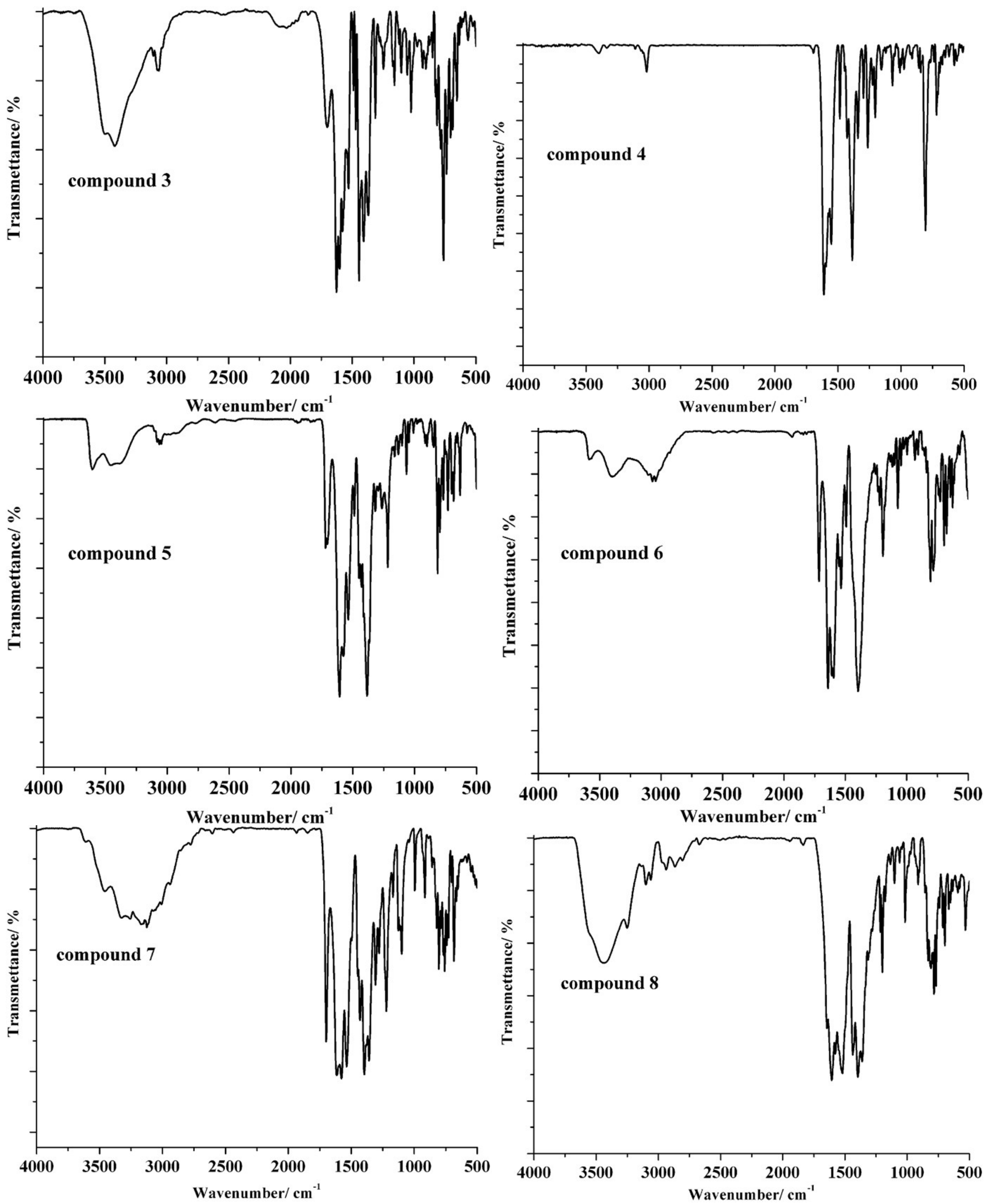


Fig. S1. FTIR spectra of compounds **1**–**8**.

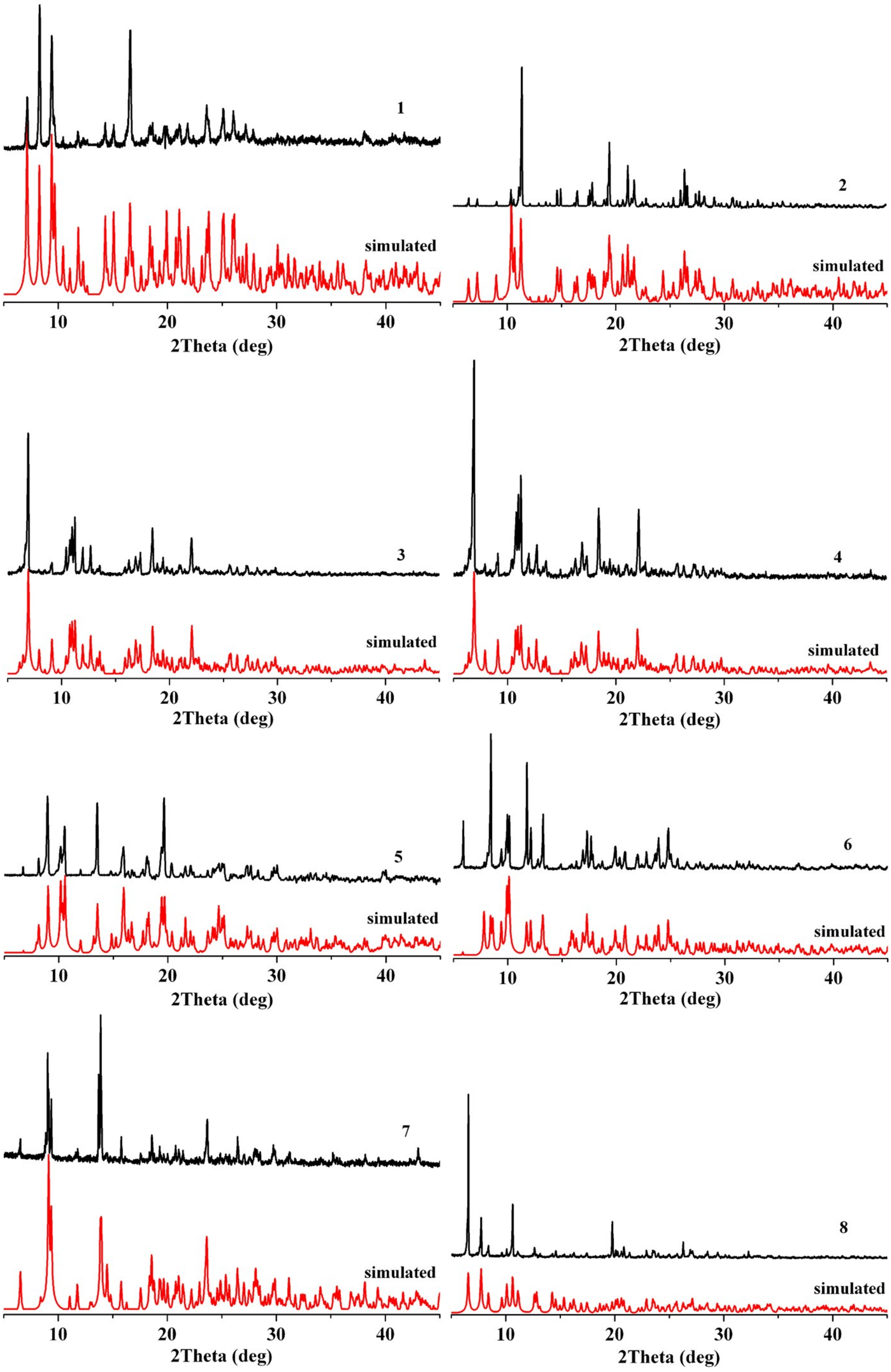

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Fig. S2. PXRD patterns of compounds **1–8** at room temperature.

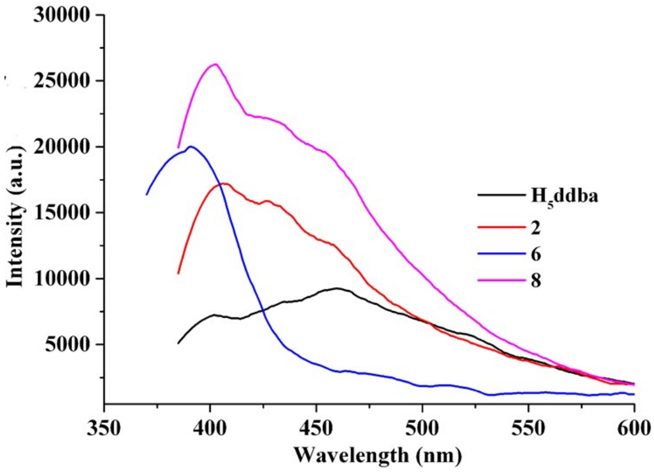

Fig. S3. Solid-state emission spectra of H_5ddba and compounds **2**, **6**, and **8** at room temperature (λ_{ex} = 360 nm) with emission maxima at 460, 407, 390, and 403 nm, respectively.

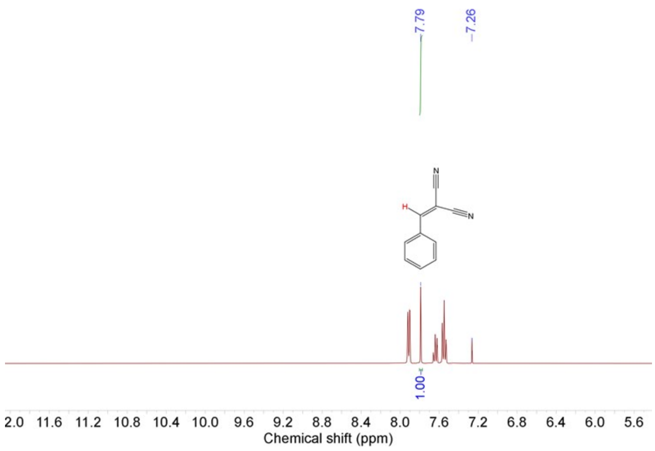

Fig. S4. Example of the integration in the ^{1}H NMR spectrum of the reaction mixture for the determination of the Knoevenagel condensation product (conditions of Table 3, Entry 6).

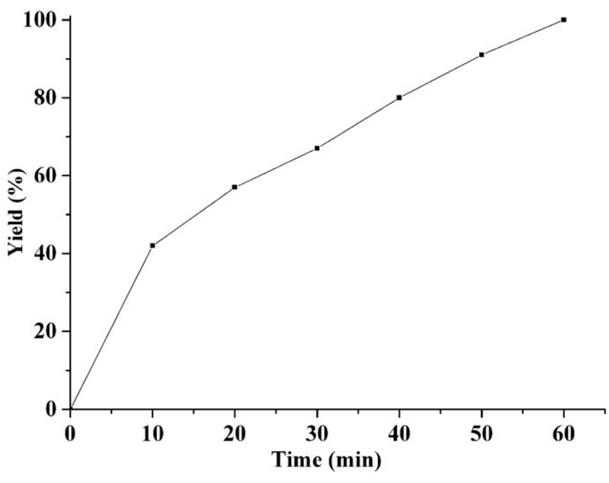

Fig. S5. Accumulation of 2-benzylidenemalononitrile vs. time in the Knoevenagel condensation of benzaldehyde with malononitrile catalysed by **1**. Reaction conditions are those of Table 3, entries 1−6.

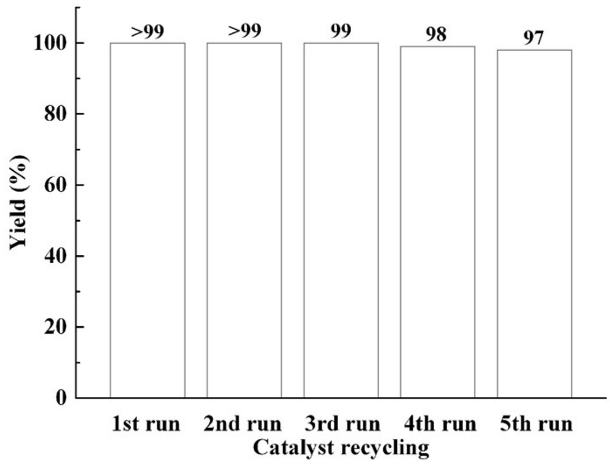

Fig. S6. Catalyst recycling experiments in the Knoevenagel condensation of benzaldehyde with malononitrile catalysed by **1**. Reaction conditions are those of Table 3, entry 6.

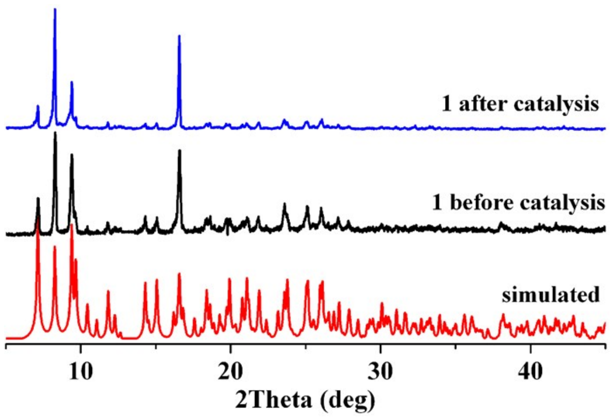

Fig. S7. PXRD patterns for **1**: simulated (red), before (black) and after (blue) catalysis.

Table S1. Selected bond lengths [Å] and angles [°] for the compounds **1–8**[a].

1					
Cu(1)-O(1)	1.973(3)	Cu(1)-O(1)i	2.497(3)	Cu(1)-O(7)	1.922(3)
Cu(1)-N(1)	2.019(4)	Cu(1)-N(2)	2.024(3)		
O(7)-Cu(1)-O(1)	91.08(12)	O(7)-Cu(1)-N(1)	94.27(14)	O(1)-Cu(1)-N(1)	174.27(13)
O(7)-Cu(1)-N(2)	172.05(13)	O(1)-Cu(1)-N(2)	93.29(13)	N(1)-Cu(1)-N(2)	81.63(14)
O(1)-Cu(1)-O(1)i	74.63(10)	O(7)-Cu(1)-O(1)i	86.95(14)	N(1)-Cu(1)-O(1)i	107.66(15)
N(2)-Cu(1)-O(1)i	87.79(11)				
2					
Cd(1)-O(1)	2.317(6)	Cd(1)-O(2)	2.553(7)	Cd(1)-O(4)i	2.258(6)
Cd(1)-O(11)	2.300(7)	Cd(1)-N(1)	2.340(9)	Cd(1)-N(2)	2.336(8)
Cd(2)-O(7)	2.469(6)	Cd(2)-O(8)	2.332(6)	Cd(2)-O(10)ii	2.258(7)
Cd(2)-O(12)	2.323(6)	Cd(2)-N(3)	2.291(9)	Cd(2)-N(4)	2.351(9)
O(4)i-Cd(1)-O(11)	97.3(2)	O(4)i-Cd(1)-O(1)	85.6(2)	O(1)-Cd(1)-O(11)	93.2(3)
O(4)i-Cd(1)-N(2)	132.9(2)	O(11)-Cd(1)-N(2)	93.2(3)	O(1)-Cd(1)-N(2)	139.5(2)
O(4)I-Cd(1)-N(1)	89.8(3)	O(11)-Cd(1)-N(1)	164.0(3)	O(1)-Cd(1)-N(1)	101.7(3)
N(1)-Cd(1)-N(2)	71.6(3)	O(2)-Cd(1)-O(4)i	134.6(2)	O(11)-Cd(1)-O(2)	101.7(3)
O(1)-Cd(1)-O(2)	52.8(2)	O(2)-Cd(1)-N(2)	86.8(2)	N(1)-Cd(1)-O(2)	83.1(3)

N(3)-Cd(2)-O(10)ii	128.6(3)	O(10)ii-Cd(2)-O(12)	96.6(3)	O(12)-Cd(2)-N(3)	94.3(3)
O(10)ii-Cd(2)-O(8)	83.8(2)	O(8)-Cd(2)-N(3)	143.9(3)	O(12)-Cd(2)-O(8)	97.4(2)
O(10)ii-Cd(2)-N(4)	92.5(3)	N(3)-Cd(2)-N(4)	71.4(4)	O(12)-Cd(2)-N(4)	165.7(3)
O(8)-Cd(2)-N(4)	94.6(3)	O(10)ii-Cd(2)-O(7)	136.7(2)	O(7)-Cd(2)-N(3)	91.7(3)
O(12)-Cd(2)-O(7)	95.1(3)	O(7)-Cd(2)-O(8)	53.4(2)	O(7)-Cd(2)-N(4)	85.6(3)
3					
Ni(1)-O(1)i	2.0142(17)	Ni(1)-O(2)	2.0449(17)	Ni(1)-O(7)	2.0370(17)
Ni(1)-O(11)	2.0897(13)	Ni(1)-N(1)	2.081(2)	Ni(1)-N(2)	2.113(2)
Ni(2)-O(9)	2.0829(17)	Ni(2)-O(10)	2.1716(19)	Ni(2)-N(3)	2.059(2)
Ni(2)-N(4)	2.044(2)	Ni(2)-N(5)	2.047(3)	Ni(2)-N(6)	2.069(2)
O(1)i-Ni(1)-O(7)	179.54(8)	O(1)i-Ni(1)-O(2)	90.75(7)	O(7)-Ni(1)-O(2)	88.93(7)
O(1)i-Ni(1)-N(1)	94.39(8)	O(7)-Ni(1)-N(1)	85.27(8)	O(2)-Ni(1)-N(1)	89.39(9)
O(1)i-Ni(1)-O(11)	89.41(6)	O(11)-Ni(1)-O(7)	90.94(6)	O(11)-Ni(1)-O(2)	93.77(7)
O(11)-Ni(1)-N(1)	175.02(8)	O(1)i-Ni(1)-N(2)	92.00(8)	O(7)-Ni(1)-N(2)	88.24(9)
O(2)-Ni(1)-N(2)	167.58(9)	N(2)-Ni(1)-N(1)	78.32(10)	O(11)-Ni(1)-N(2)	98.36(9)
N(4)-Ni(2)-N(5)	96.18(11)	N(4)-Ni(2)-N(3)	79.51(10)	N(3)-Ni(2)-N(5)	101.86(10)
N(4)-Ni(2)-N(6)	100.23(10)	N(6)-Ni(2)-N(5)	79.42(10)	N(3)-Ni(2)-N(6)	178.71(10)
N(4)-Ni(2)-O(9)	166.42(10)	N(5)-Ni(2)-O(9)	96.76(9)	N(3)-Ni(2)-O(9)	93.80(8)
N(6)-Ni(2)-O(9)	86.19(8)	N(4)-Ni(2)-O(10)	105.35(9)	N(5)-Ni(2)-O(10)	157.81(8)
N(3)-Ni(2)-O(10)	87.49(9)	N(6)-Ni(2)-O(10)	91.37(8)	O(9)-Ni(2)-O(10)	62.25(7)
4					
Mn(1)-O(1)i	2.034(3)	Mn(1)-O(2)	2.016(3)	Mn(1)-O(7)i	2.039(3)
Mn(1)-O(11)	2.098(3)	Mn(1)-N(1)	2.095(5)	Mn(1)-N(2)	2.072(5)
Mn(2)-O(9)	2.176(4)	Mn(2)-O(10)	2.097(4)	Mn(2)-N(3)	2.052(4)
Mn(2)-N(4)	2.062(4)	Mn(2)-N(5)	2.042(5)	Mn(2)-N(6)	2.058(4)
O(2)-Mn(1)-O(1)i	90.89(14)	O(7)-Mn (1)-O(2)	179.68(14)	O(1)i-Mn (1)-O(7)i	88.94(14)
O(2)-Mn(1)-N(2)	94.17(16)	N(2)-Mn(1)-O(1)i	89.34(17)	N(2)-Mn(1)-O(7)i	86.10(16)
O(2)-Mn(1)-N(1)	92.09(17)	O(1)i-Mn(1)-N(1)	166.96(19)	O(7)i-Mn(1)-N(1)	88.12(17)
N(2)-Mn (1)-N(1)	77.8(2)	O(2)-Mn (1)-O(11)	89.43(12)	O(1)i-Mn (1)-O(11)	93.85(13)
O(7)i-Mn (1)-O(11)	90.31(12)	O(11)-Mn (1)-N(2)	175.16(17)	O(11)-Mn (1)-N(1)	98.87(18)
N(5)-Mn (2)-N(3)	101.17(19)	N(5)-Mn (2)-N(6)	79.8(2)	N(3)-Mn (2)-N(6)	178.9(2)
N(5)-Mn (2)-N(4)	96.0(2)	N(3)-Mn (2)-N(4)	79.36(19)	N(6)-Mn (2)-N(4)	100.09(19)
O(10)-Mn (2)-N(5)	96.59(17)	O(10)-Mn (2)-N(3)	94.09(17)	O(10)-Mn (2)-N(6)	86.27(16)
O(10)-Mn (2)-N(4)	166.69(19)	O(9)-Mn (2)-N(5)	158.08(17)	O(9)-Mn (2)-N(3)	87.41(16)
O(9)-Mn (2)-N(6)	91.87(17)	N(4)-Mn (2)-O(9)	105.40(17)	O(10)-Mn (2)-O(9)	62.43(13)
5					
Co(1)-O(1)	2.079(4)	Co(1)-O(5)i	2.097(4)	Co(1)-O(6)ii	2.083(5)
Co(1)-O(11)	2.203(6)	Co(1)-N(2)	2.157(6)	Co(1)-N(3)iii	2.158(5)
Co(2)-O(3)	2.131(5)	Co(2)-O(4)iv	2.034(6)	Co(2)-O(7)	2.007(5)
Co(2)-O(8)iv	2.034(5)	Co(2)-N(1)	2.035(6)		
O(1)-Co(1)-O(6)ii	92.30(19)	O(1)-Co(1)-O(5)i	166.83(19)	O(6)ii-Co(1)-O(5)i	98.09(19)
O(1)-Co(1)-N(2)	87.5(2)	O(6)ii-Co(1)-N(2)	86.6(2)	O(5)i-Co(1)-N(2)	85.10(19)
O(1)-Co(1)-N(3)iii	94.68(19)	O(6)ii-Co(1)-N(3)iii	91.7(2)	O(5)i-Co(1)-N(3)iii	93.09(19)
N(2)-Co(1)-N(3)iii	177.3(2)	O(1)-Co(1)-O(11)	87.5(2)	O(11)-Co(1)-O(6)ii	179.7(2)
O(11)-Co(1)-O(5)i	82.2(2)	O(11)-Co(1)-N(2)	93.6(2)	O(11)-Co(1)-N(3)iii	88.1(2)
O(7)-Co(2)-N(1)	95.5(2)	O(7)-Co(2)-O(8)iv	165.57(19)	O(8)iv-Co(2)-N(1)	96.7(2)
O(7)-Co(2)-O(4)iv	96.2(2)	N(1)-Co(2)-O(4)iv	101.1(2)	O(4)iv-Co(2)-O(8)iv	88.9(2)
O(7)-Co(2)-O(3)	87.2(2)	N(1)-Co(2)-O(3)	93.3(2)	O(3)-Co(2)-O(8)iv	84.5(2)
O(3)-Co(2)-O(4)iv	164.8(2)				
6					

Zn(1)-O(1)	1.967(3)	Zn(1)-O(2)ii	1.964(3)	Zn(1)-O(9)i	2.080(4)
Zn(1)-O(10)i	2.269(4)	Zn(1)-N(1)	2.062(4)	Zn(2)-O(3)	2.025(3)
Zn(2)-O(4)iii	2.036(3)	Zn(2)-O(7)	2.079(3)	Zn(2)-O(8)iii	2.023(3)
Zn(2)-N(2)	2.041(3)				
O(1)-Zn(1)-O(2)ii	116.87(14)	O(1)-Zn(1)-N(1)	99.73(13)	N(1)-Zn(1)-O(2)ii	95.56(14)
O(1)-Zn(1)-O(9)i	106.07(15)	O(9)i-Zn(1)-O(2)ii	98.26(14)	N(1)-Zn(1)-O(9)i	140.93(16)
O(1)-Zn(1)-O(10)i	96.05(14)	O(2)ii-Zn(1)-O(10)i	145.10(14)	N(1)-Zn(1)-O(10)i	89.56(15)
O(9)i-Zn(1)-O(10)i	59.31(13)	O(3)-Zn(2)-O(8)iii	90.01(15)	O(4)iii-Zn(2)-O(8)iii	89.19(15)
O(3)-Zn(2)-O(4)iii	157.84(13)	N(2)-Zn(2)-O(8)iii	108.72(15)	N(2)-Zn(2)-O(3)	99.31(15)
N(2)-Zn(2)-O(4)iii	101.91(15)	O(7)-Zn(2)-O(8)iii	157.58(13)	O(7)-Zn(2)-O(3)	86.15(14)
O(7)-Zn(2)-O(4)iii	86.19(14)	O(7)-Zn(2)-N(2)	93.70(14)		
7					
Mn(1)-O(1)	2.109(3)	Mn(1)-O(4)i	2.163(3)	Mn(1)-O(5)ii	2.405(3)
Mn(1)-O(8)i	2.135(2)	Mn(1)-N(1)	2.223(3)	Mn(1)-N(4)	2.261(3)
Mn(2)-O(2)iii	2.121(2)	Mn(2)-O(3)iv	2.276(3)	Mn(2)-O(4)iv	2.449(3)
Mn(2)-O(5)	2.101(2)	Mn(2)-O(7)iv	2.201(2)	Mn(2)-O(11)	2.127(3)
O(1)-Mn(1)-O(8)i	85.81(10)	O(1)-Mn(1)-O(4)i	91.24(11)	O(4)i-Mn(1)-O(8)i	93.51(11)
O(1)-Mn(1)-N(1)	104.37(11)	O(8)i-Mn(1)-N(1)	157.88(12)	O(4)i-Mn(1)-N(1)	105.65(12)
O(1)-Mn(1)-N(1)	100.09(12)	O(8)i-Mn(1)-N(4)	83.70(12)	O(4)i-Mn(1)-N(4)	168.07(12)
N(1)-Mn(1)-N(4)	75.28(13)	O(5)ii-Mn(1)-O(1)	166.03(10)	O(8)i-Mn(1)-O(5)ii	88.21(9)
O(4)i-Mn(1)-O(5)ii	76.52(9)	N(1)-Mn(1)-O(5)ii	85.68(10)	N(4)-Mn(1)-O(5)ii	91.77(11)
O(2)iii-Mn(2)-O(5)	101.40(10)	O(5)-Mn(2)-O(11)	118.16(13)	O(2)iii-Mn(2)-O(11)	90.07(10)
O(7)iv-Mn(2)-O(5)	101.62(10)	O(2)iii-Mn(2)-O(7)iv	156.93(10)	O(11)-Mn(2)-O(7)iv	80.35(11)
O(5)-Mn(2)-O(3)iv	131.53(10)	O(2)iii-Mn(2)-O(3)iv	83.77(10)	O(11)-Mn(2)-O(3)iv	109.92(13)
O(7)iv-Mn(2)-O(3)iv	79.94(10)	O(5)-Mn(2)-O(4)iv	76.67(9)	O(2)iii-Mn(2)-O(4)iv	88.71(9)
O(11)-Mn(2)-O(4)iv	165.04(13)	O(7)iv-Mn(2)-O(4)iv	95.18(9)	O(3)iv-Mn(2)-O(4)iv	55.13(9)
8					
Cd(1)-O(1)	2.3124(17)	Cd(1)-O(2)i	2.3153(16)	Cd(1)-O(5)ii	2.3996(17)
Cd(1)-O(6)ii	2.3012(18)	Cd(1)-O(7)	2.2097(17)	Cd(1)-O(8)i	2.2082(18)
Cd(2)-O(2)iii	2.3329(17)	Cd(2)-O(3)	2.299(2)	Cd(2)-O(4)	2.3962(19)
Cd(2)-O(9)iv	2.490(2)	Cd(2)-O(10)iv	2.2816(19)	Cd(2)-N(1)	2.336(2)
O(7) -Cd(1)-O(8)i	151.11(7)	O(8)i-Cd(1)-O(6)ii	90.61(7)	O(7)-Cd(1)-O(6)ii	116.57(7)
O(1)-Cd(1)-O(8)i	89.58(7)	O(7)-Cd(1)-O(1)	83.49(7)	O(6)ii-Cd(1)-O(1)	85.32(7)
O(8)i-Cd(1)-O(2)i	83.64(7)	O(7)-Cd(1)-O(2)i	89.42(7)	O(6)ii-Cd(1)-O(2)i	121.80(6)
O(2)i-Cd(1)-O(1)	151.96(6)	O(8)i-Cd(1)-O(5)ii	117.68(7)	O(7)-Cd(1)-O(5)ii	87.55(7)
O(6)ii-Cd(1)-O(5)ii	55.58(6)	O(5)ii-Cd(1)-O(1)	129.88(6)	O(5)ii-Cd(1)-O(2)i	76.56(6)
O(3)-Cd(2)-O(10)iv	132.02(8)	O(2)iii-Cd(2)-O(10)iv	100.55(7)	O(3)-Cd(2)-O(2)iii	98.85(7)
N(1)-Cd(2)-O(10)iv	85.78(8)	O(3)-Cd(2)-N(1)	137.72(7)	N(1)-Cd(2)-O(2)iii	89.76(7)
O(4)-Cd(2)-O(10)iv	140.46(8)	O(3)-Cd(2)-O(4)	55.18(7)	O(4)-Cd(2)-O(2)iii	117.49(7)
O(2)iii-Cd(2)-O(9)iv	84.10(7)	O(9)iv-Cd(2)-O(10)iv	54.26(7)	O(3)-Cd(2)-O(9)iv	89.08(8)
N(1)-Cd(2)-O(10)	148.83(7)	N(1)-Cd(2)-O(9)iv	104.51(8)	O(9)iv-Cd(2)-O(4)	91.80(8)

[a]Symmetry transformations used to generate equivalent atoms: i –*x*+2, –*y*+1, –*z*+1 for **1**; i *x*–1, *y*, *z*; ii *x*+1, *y*, *z* for **2**; i –*x*+1, *y*, –*z*+3/2 for **3**; #1 –*x*+2, *y*, –*z*+1/2 for **4**; i *x*, *y*–1, *z*+1; ii –*x*+1, –*y*, –*z*; iii *x*–1, *y*, *z*; iv –*x*+2, –*y*, –*z* for **5;** i –*x*+1, –*y*+1, –*z*+2; ii –*x*+1, –*y*+1, –*z*+3; iii –*x*+1, –*y*+2, –*z*+2 for **6**; i –*x*+1, –*y*+1, –*z*+1; ii *x*–1/2, –*y*+1/2, *z*–1/2; iii *x*+1/2, *y*–1/2, *z*; iv –*x*+3/2, *y*–1/2, –*z*+3/2 for **7**; i –*x*, –*y*, –*z*+1; ii –*x*+1, –*y*+1, –*z*+1; iii –*x*, –*y*, –*z*; iv *x*, *y*+1, *z*–1 for **8**.

Table S2. Hydrogen Bonds in Crystal Packing [Å, °] of **1**, **2**, **4–6**, and **8**.

Complexes	D-H…A	*d*(D-H)	*d*(H…A)	*d*(D…A)	∠DHA	Symmetry code
1	O(4)-H(4)···O(5)	0.822	2.298	2.978	140.45	*x*+1/2, -*y*+3/2, *z*-1/2
	O(6)-H(1)···O(2)	0.820	1.811	2.630	176.18	-*x*+1, -*y*+1, -*z*+1
	O(9)-H(9)···O(10)	0.823	1.850	2.660	167.86	-*x*+2, -*y*+1, -*z*+2
2	O(5)-H(5)···O(14)	0.820	1.648	2.465	173.59	
	O(11)-H(1W)···O(8)	0.850	2.039	2.889	179.06	*x*-1/2, -*y*+1/2, *z*-1/2
	O(11)-H(2W)···O(10)	0.850	1.906	2.756	179.64	*x*+1/2, -*y*+1/2, *z*-1/2
	O(12)-H(3W)···O(1)	0.850	2.026	2.877	179.56	*x*+1/2, -*y*+1/2, *z*+1/2
	O(12)-H(4W)···O(4)	0.850	1.878	2.729	179.68	*x*-1/2, -*y*+1/2, *z*+1/2
	O(13)-H(5W)···O(6)	0.850	2.103	2.953	179.35	*x*-1/2, -*y*+1/2, *z*+1/2
	O(13)-H(6W)···O(9)	0.850	1.818	2.668	179.04	
	O(14)-H(7W)···O(13)	0.847	1.767	2.559	154.79	-*x*+3/2, *y*+1/2, -*z*+1/2
	O(14)-H(8W)···O(7)	0.850	1.861	2.710	177.89	-*x*+3/2, *y*+1/2, -*z*+1/2
3	O(4)-H(4)···O(5)	0.841	1.628	2.463	170.96	*x*, -*y*, *z*-1/2
	O(11)-H(1W)···O(8)	0.853	1.716	2.546	163.55	
	O(12)-H(3W)···O(6)	0.850	2.097	2.947	179.34	-*x*+1/2, -*y*+1/2, -*z*+1
	O(12)-H(4W)···O(6)	0.850	1.988	2.838	179.09	*x*, *y*, *z*-1
4	O(3)-H(3)···O(6)	0.820	1.654	2.453	164.37	*x*, -*y*+2, *z*-1/2
	O(11)-H(1W) ···O(8)	0.850	1.699	2.549	179.35	-*x*+2, *y*, -*z*+1/2
	O(11)-H(2W) ···O(8)	0.850	1.699	2.549	179.35	
	O(12)-H(3W) ···O(5)	0.850	2.018	2.868	179.21	
	O(12)-H(4W) ···O(8)	0.850	2.125	2.975	178.60	-*x*+3/2, -*y*+3/2, -*z*+1
5	O(10)-H(10)···O(12)	0.820	1.884	2.659	157.14	-*x*+2, -*y*+1, -*z*
	O(11)-H(2W)···O(2)	0.850	1.799	2.648	178.64	
	O(12)-H(3W)···O(5)	0.850	2.121	2.971	179.60	-*x*+1, -*y*+1, -*z*
	O(12)-H(4W)···O(11)	0.732	2.261	2.990	173.26	-*x*+1, -*y*, -*z*+1
6	O(6)-H(6)···O(10)	0.820	1.850	2.613	154.39	*x*+1, *y*, *z*
	O(11)-H(1W)···O(12)	0.850	1.898	2.725	164.02	*x*+1, *y*, *z*
	O(11)-H(2W)···O(12)	0.850	2.221	2.820	127.46	-*x*+1, -*y*+1, -*z*+1
	O(12)-H(3W)···O(1)	0.850	2.194	3.044	179.42	-*x*+1, -*y*+1, -*z*+2
	O(12)-H(4W)···O(9)	0.850	2.464	3.314	179.8	-*x*+1, -*y*+1, -*z*+1
7	N(2)-H(1)···O(7)	0.868	2.030	2.846	157.93	*x*-1/2, -*y*+1/2, *z*-1/2
	N(3)-H(2)···O(3)	0.860	2.076	2.850	149.36	*x*-1/2, -*y*+1/2, *z*-1/2
	O(10)-H(45)···O(6)	0.820	1.894	2.683	161.22	*x*+1/2, *y*+1/2, *z*
	O(11)-H(1W)···O(1)	0.837	2.195	2.808	130.11	*x*+1/2, *y*-1/2, *z*
	O(11)-H(2W)···O(9)	0.836	1.971	2.726	149.92	*x*-1/2, *y*-1/2, *z*
8	N(3)-H(2)···O(5)	0.893	1.938	2.799	161.30	-*x*, -*y*+1, -*z*

Table S3. Knoevenagel condensation of Aliphatic Aldehydes with Malononitrile.[a]

Entry	Aldehyde substrate	Product yield, %[b]
1	Cyclopropyl formaldehyde	>99
2	Acetaldehyde	>99
3	Propanal	>99
4	N-butyl aldehyde	>99
5	Amyl aldehyde	>99

[a]Conditions: fatty aldehyde substrate (0.5 mmol), malononitrile (1.0 mmol), catalyst **1** (2.0 mol.%), H_2O solvent (1.0 mL), temperature (25 °C). [b]Yield based on ^1H NMR analysis: [moles of product per mol of aldehyde substrate]×100%.

Table S4. Comparison among various catalysts for the Knoevenagel condensation reaction between malononitrile and benzaldehyde.

Entry	Catalyst	Catalyst (mol%)	Solvent	Time (h)	Temp. (°C)	Product yield (%)	Ref.
1	$[Cu_2(\mu\text{-}H_3ddba)_2(phen)_2]$	2	H_2O	1	RT[a]	>99	This work
2	$Zn_3(OH)(ATTCA)_2(H_2O)]\cdot C_2H_6NH_2\cdot 4DMF\cdot H_2O$	10	DCM	5	RT	94	72
3	$[Zn_3(L)_2(\mu_2\text{-}OH)_2]_n$	4	H_2O	8	90	78	73
4	$[Zn_2(TCA)(BIB)_{2.5}]\cdot(NO_3)$	0.3	–	1	60	99	74
5	$\{[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(OH)_4(H_2O)_4(DCBA)_2]\cdot 5DMF\cdot 3H_2O\}$	10	DCM	5	RT	89	5
6	$\{[Ba_3Zn_4(TDP)_2(HCO_2)_2(OH_2)_2]\cdot 7DMF\cdot 4H_2O\}_n$	3	Ethanol	1	60	99	75
7	$\{[Zn(L)(bpfp)](H_2O)_3\}_n$	5	DMF	3	35	98	57
8	$[[Zn(L)(H_2O)_2]n\cdot n$(N-methylformamide)	3	MeOH	1.5	40	75	76
9	$[PbL_2]\cdot 2DMF\cdot 6H_2O$	3	CH_3CN	24	RT	>99	77

[a]RT, room temperature.

Table S5. Knoevenagel condensation of substituted benzaldehydes with malononitrile catalyzed by **3** and **4**.[a]

Entry	Aldehyde substrate	Product yield, %[b]	
		3	**4**
1	*p*-Nitrobenzaldehyde	>99	>99
2	*o*-Nitrobenzaldehyde	>99	>99
3	*m*-Nitrobenzaldehyde	>99	>99
4	Benzaldehyde	99	99
5	*p*-Chlorobenzaldehyde	>99	>99
6	*p*-Methylbenzaldehyde	99	97
7	*p*-Methoxybenzaldehyde	80	79
8	*p*-Hydroxybenzaldehyde	56	58
9	Cinnamaldehyde	98	94
10	Cyclopropyl formaldehyde	>99	99
11	Acetaldehyde	>99	>99
12	Propanal	>99	>99
13	N-butyl aldehyde	>99	99
14	Amyl aldehyde	>99	99

[a]Conditions: aldehyde (0.5 mmol), malononitrile (1.0 mmol), catalyst **3** or **4** (2.0 mol.%), H_2O (1.0 mL), 25 °C. [b]Yield on the basis of ^1H NMR analysis: [moles of product per mol of aldehyde substrate]×100%.