Electronic Supplementary Information (ESI)

Coordination polymers from unexplored biphenyl-tricarboxylate linker: hydrothermal synthesis, structural traits and catalytic cyanosilylation

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Electronic Supplementary Information (ESI) contains:

Synthesis and analytical data for 3–9

Synthesis of [M_2(μ-Hbta)$_2$(4,4′-bipy)$_2$(H_2O)$_2$]·2H_2O (M = Zn (3), Cd (4)). A mixture of $ZnCl_2$ or $CdCl_2 \cdot H_2O$ (0.20 mmol), H_3bta (57.2 mg, 0.20 mmol), 4,4′-bipy (31.2 mg, 0.2 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}. Colourless block-shaped crystals were isolated manually, washed with distilled water and dried to give compound **3** or **4**. Yield: 60% for **3**; 55% for **4** (based on H_3bta). Anal. Calcd for $C_{50}H_{40}Zn_2N_4O_{16}$ (**3**): C, 55.42; H, 3.72; N, 5.17. Found: C, 55.61; H, 3.73; N, 5.14%. IR for **3** (KBr, cm^{-1}): 3468 w, 3053 w, 1705 w, 1606 s, 1568 s, 1436 m, 1413 m, 1368 s, 1304 m, 1281 m, 1239 w, 1207 w, 1165 w, 1130 w, 1092 w, 1071 w, 1007 w, 924 w, 887 w, 814 s, 769 s, 701 w, 668 w, 632 w. Anal. Calcd for $C_{50}H_{40}Cd_2N_4O_{16}$ (**4**): C, 50.99; H, 3.42; N, 4.76. Found: C, 50.77; H, 3.40; N, 4.79%. IR for **4** (KBr, cm^{-1}): 3437 w, 3176 w, 1705 w, 1606 s, 1550 s, 1413 m, 1394 m, 1377 m, 1304 m, 1280 m, 1239 w, 1221 w, 1130 w, 1092 w, 1071 w, 1007 w, 924 w, 887 w, 809 m, 760 m, 696 w, 668 w, 634 w.

Synthesis of {[Cd_2(μ_4-bta)(μ-Cl)(phen)$_2$]·2H_2O}$_n$ (5). A mixture of $CdCl_2 \cdot H_2O$ (60.3 mg, 0.3 mmol), H_3bta (57.2 mg, 0.2 mmol), phen (60.0 mg, 0.3 mmol), NaOH (24.0 mg, 0.6 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 were isolated manually, washed with distilled water and dried to give compound **5**. Yield: 50% (based on H_3bta). Anal. Calcd for $C_{39}H_{27}Cd_2ClN_4O_8$: C, 49.84; H, 2.90; N, 5.96. Found: C, 50.05; H, 2.91; N, 5.93%. IR (KBr, cm^{-1}): 3566 w, 3067 w, 1578 s, 1536 s, 1495 m, 1431 s, 1382 s, 1253 w, 1216 w, 1165 w, 1144 w, 1102 w, 1085 w, 988 w, 924 w, 842 m, 818 w, 760 m, 727 s, 701 w, 672 w, 641 w.

Synthesis of {[Zn_2(μ_3-bta)(2,2′-bipy)$_2$(H_2O)$_3$][Zn(μ-bta)(2,2′-bipy)(H_2O)]·3H_2O}$_n$ (6). A mixture of $ZnCl_2$ (40.9 mg, 0.30 mmol), H_3bta (57.2 mg, 0.20 mmol), 2,2′-bipy (46.8 mg, 0.30 mmol), NaOH

(24.0 mg, 0.60 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 were isolated manually, washed with distilled water and dried to produce compound **6**. Yield: 46% (based on H_3bta). Anal. Calcd for $C_{60}H_{52}Zn_3N_6O_{19}$: C, 53.09; H, 3.86; N, 6.19. Found: C, 53.41; H, 3.83; N, 6.27%. IR (KBr, cm^{-1}): 3395 m, 3110 w, 1599 s, 1554 s, 1476 m, 1435 m, 1365 s, 1254 w, 11163 w, 1097 w, 1065 w, 1019 w, 978 w, 954 w, 916 w, 883 w, 851 w, 821 w, 768 m, 731 w, 698 w, 652 w.

Synthesis of {[Cd_3(μ$_4$-bta)$_2$(2,2′-bipy)$_3$]·4H_2O}$_n$ (7). A mixture of $CdCl_2·H_2O$ (60.3 mg, 0.30 mmol), H_3bta (57.2 mg, 0.20 mmol), 2,2′-bipy (46.8 mg, 0.30 mmol), NaOH (24.0 mg, 0.60 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 were isolated manually, washed with distilled water and dried to give compound **7**. Yield 53% (based on H_3bta). Anal. Calcd for $C_{60}H_{46}Cd_3N_6O_{16}$: C, 49.90; H, 3.21; N, 5.82. Found: C, 50.07; H, 3.19; N, 5.86%. IR (KBr, cm^{-1}): 3395 w, 3071 w, 1592 s, 1545 m, 1476 w, 1441 m, 1368 s, 1312 w, 1276 w, 1248 w, 1158 w, 1097 w, 1057 w, 1015 m, 929 w, 878 w, 814 w, 774 s, 731 w, 695 w, 667 w, 644 w.

Synthesis of {[Zn_3(μ$_3$-bta)$_2$(H_2biim)$_2$(μ-H_2biim)(H_2O)$_2$]·2H_2O}$_n$ (8). A mixture of $ZnCl_2$ (40.9 mg, 0.30 mmol), H_3bta (57.2 mg, 0.20 mmol), H_2biim (40.2 mg, 0.30 mmol), NaOH (24.0 mg, 0.60 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 were isolated manually, washed with distilled water and dried to furnish compound **8**. Yield: 45% (based on H_3bta). Anal. Calcd for $C_{48}H_{40}Zn_3N_{12}O_{16}$: C, 46.60; H, 3.26; N, 13.59. Found: C, 46.78; H, 3.23; N, 13.64%. IR (KBr, cm^{-1}): 3580 w, 3094 w, 1607 m, 1546 s, 1426 m, 1368 m, 1332 s, 1246 w, 1180 w, 1110 w, 1044 w, 990 w, 945 w, 924 w, 879 w, 830 w, 772 m, 710 w, 685 w, 603 w.

Synthesis of {[Zn_3(μ$_6$-bta)$_2$(py)$_2$]}$_n$ (9). A mixture of $ZnCl_2$ (40.9 mg, 0.3 mmol), H_3bta (57.2 mg, 0.20 mmol), py (0.5 mL, 6.30 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 were isolated manually, washed with distilled water and dried to give compound **9**. Yield: 55% (based on H_3bta). Anal. Calcd for $C_{40}H_{24}Zn_3N_2O_{12}$: C, 52.17; H, 2.63; N, 3.04. Found: C, 51.95; H, 2.64; N, 3.01%. IR (KBr, cm^{-1}): 1613 s, 1568 w, 1486 w, 1455 w, 1399 m, 1377 s, 1344 s, 1267 w, 1248 w, 1226 w, 1158 w, 1130 w, 1102 w, 1075 w, 1047 w, 1015 w, 970 w, 910 w, 872 w, 833 w, 791 w, 760 m, 701 w, 668 w, 641 w.

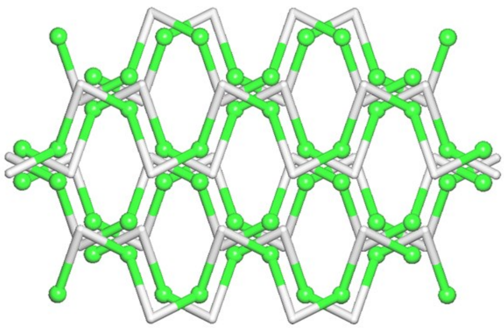


Fig. S1. Topological view of a crystal packing 3D arrangement of eight metal-organic chains in **2**; view along the *c* axis; Ni centers (green balls); centroids of μ-Hbta^{2-} linkers (gray).

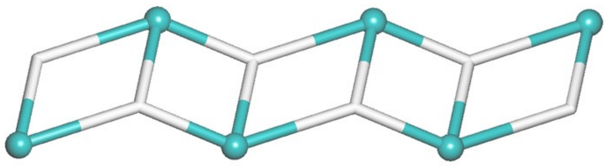


Fig. S2. Topological representation of a further simplified double chain with the SP 1-periodic net (4,4)(0,2) topology in **5**; view along the *b* axis; centroids of Cd_2(μ-Cl) nodes (turquoise balls), centroids of μ_3-bta^{3-} nodes (gray).

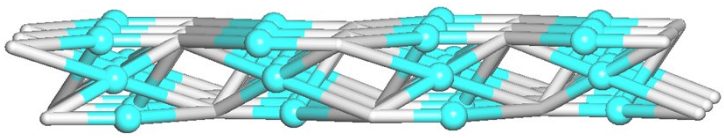
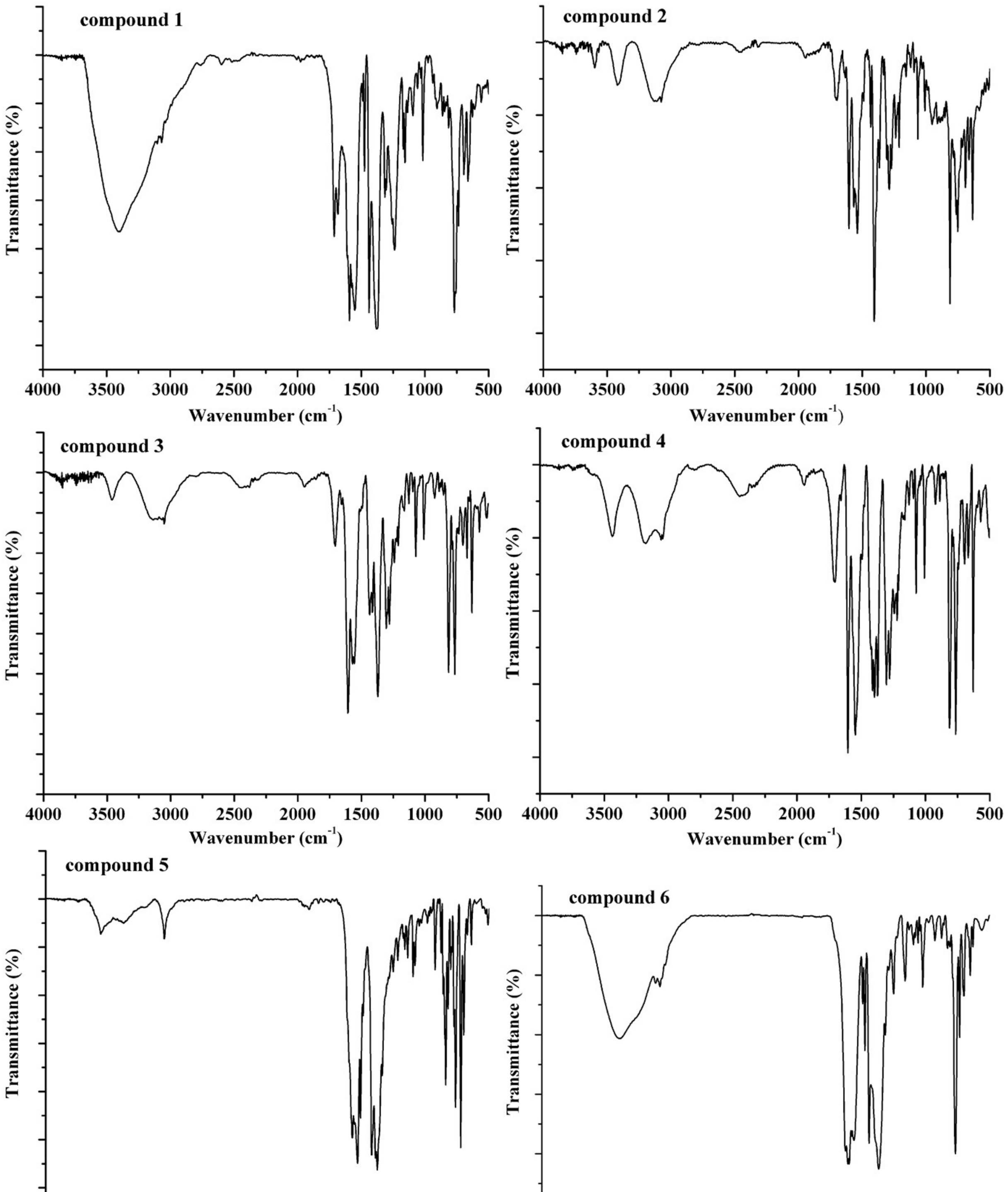


Fig. S3. Topological representation of a trinodal 3,6,6-connected metal-organic layer in **9** with the unique topology and point symbol of $(4^3)_2(4^8.6^4.8^3)_2(4^8.6^6.8)$; side view along the *b* axis; 3-connected Zn1 and 6-connected Zn2 nodes (cyan balls), centroids of 6-connected μ_5-bta^{3-} blocks (gray).


compound 1
compound 2
compound 3
compound 4
compound 5
compound 6
Transmittance (%)
Wavenumber (cm-1)
4000 3500 3000 2500 2000 1500 1000 500

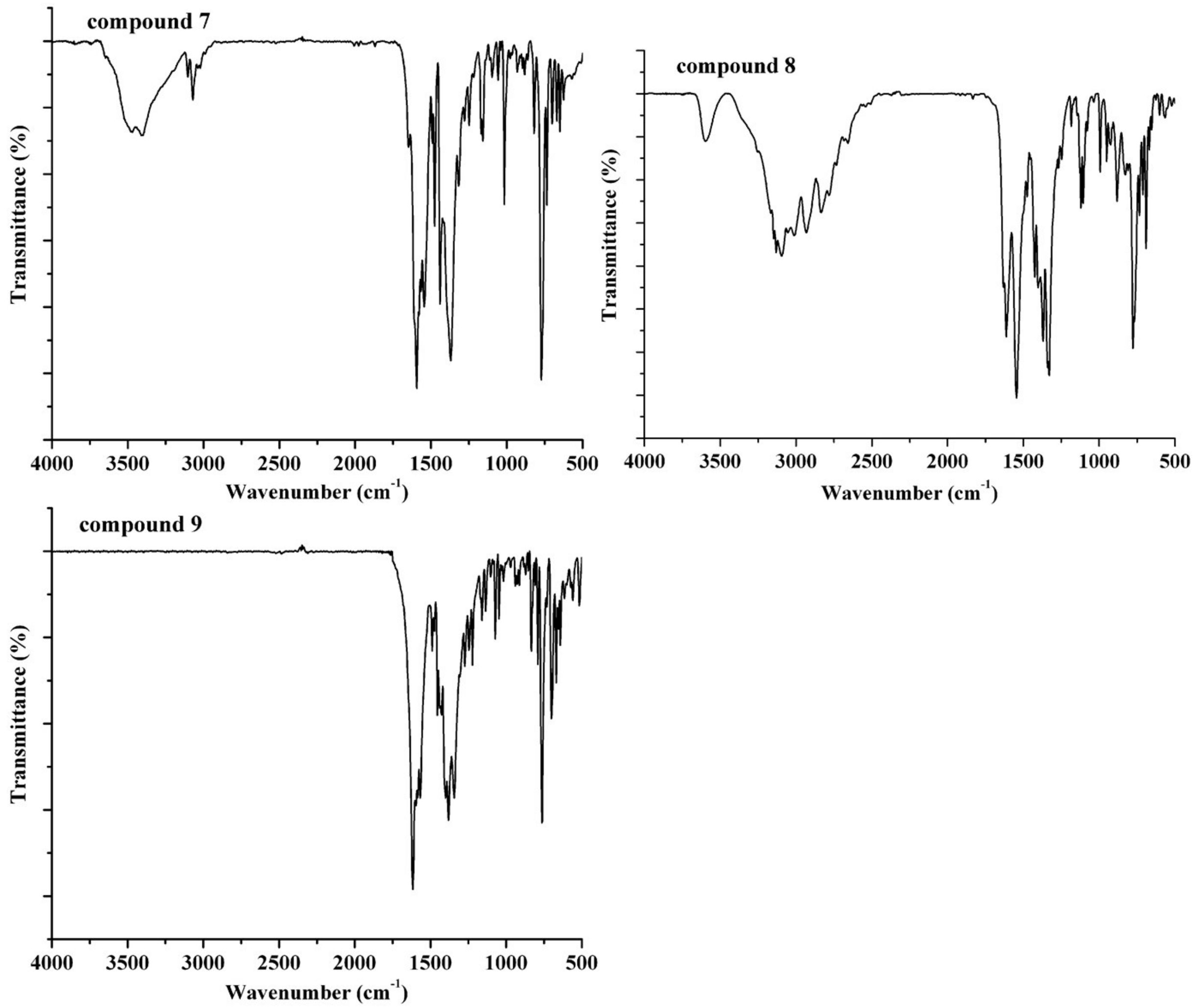
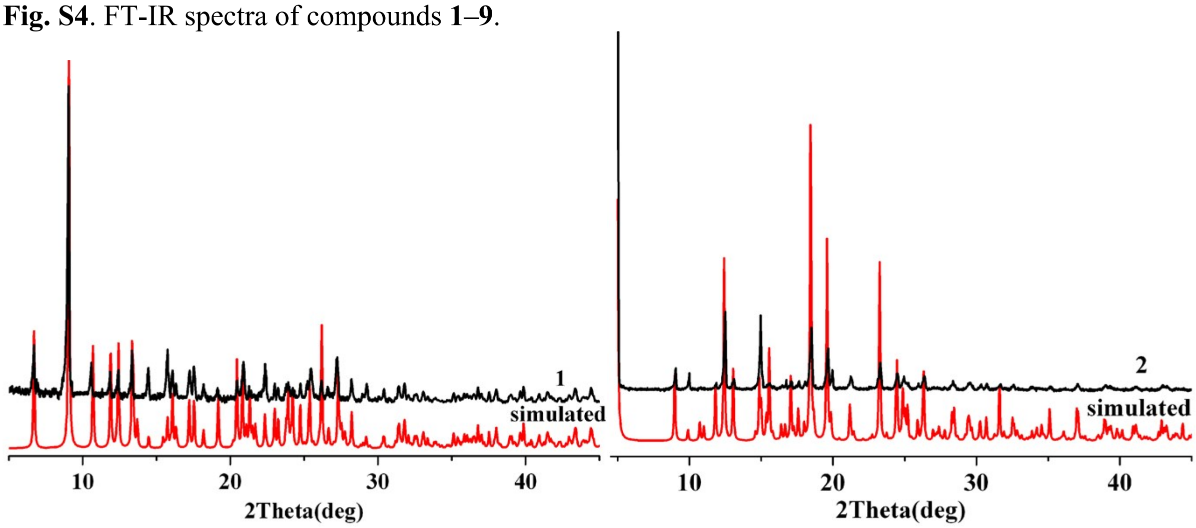
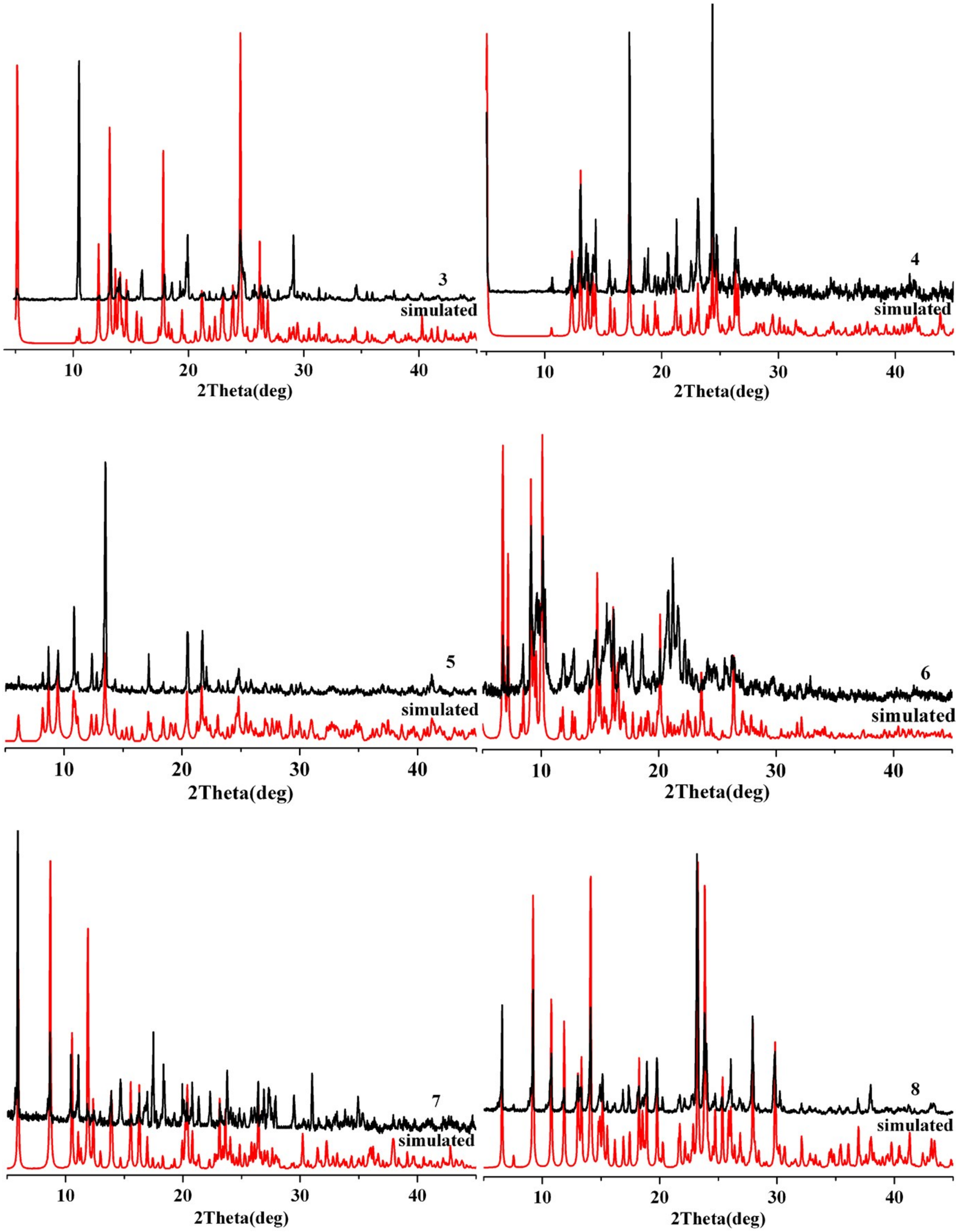


Fig. S4. FT-IR spectra of compounds **1**–**9**.




3
simulated
10
20
30
40
2Theta(deg)
4
simulated
10
20
30
40
2Theta(deg)
5
simulated
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30
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2Theta(deg)
6
simulated
10
20
30
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8
simulated
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20
30
40
2Theta(deg)

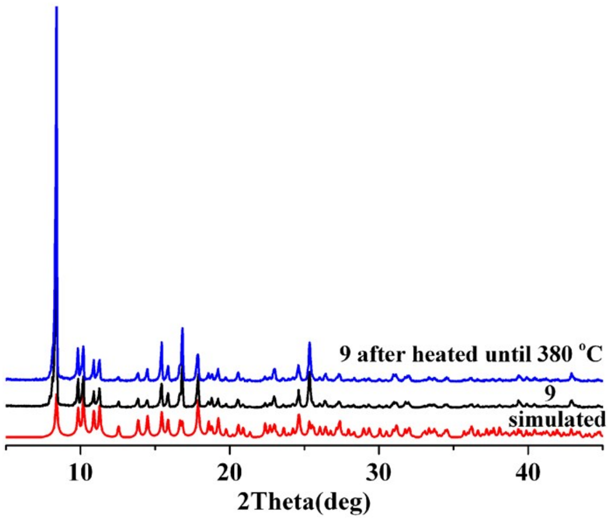

Fig. S5. PXRD patterns of compounds **1**–**9** at room temperature. Black paterns correspond to the experimental data obtained using the as-synthesized bulk samples. Red patterns were simulated from the single crystal X-ray data. For **9**, an additional experimental pattern (blue) is shown for a sample after being heated until 380 °C.

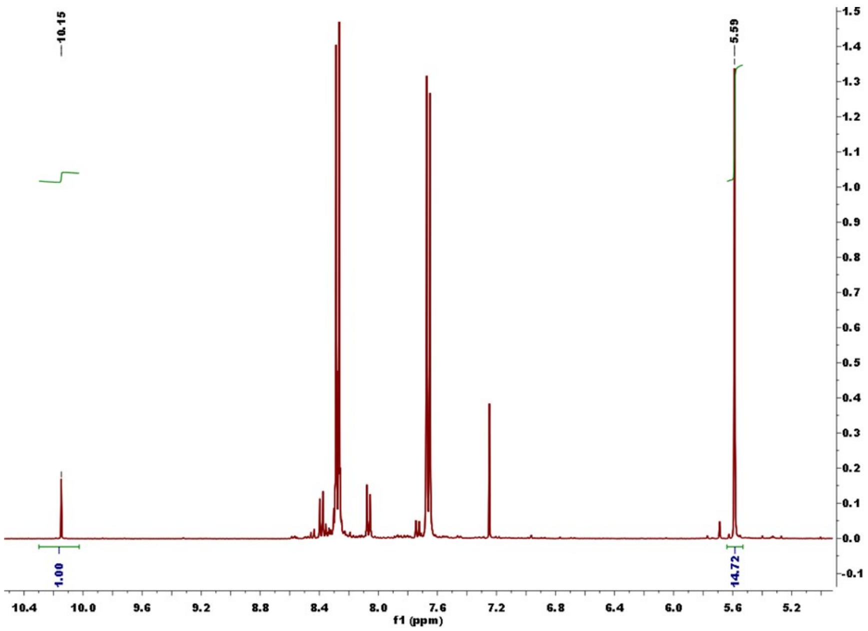

Fig. S6. Example of the integration in the ^{1}H NMR spectrum for determining product yield in Zn-catalyzed cyanosilylation of 4-nitrobenzaldehyde. Reaction conditions are those of Table 3 (entry 7).

Product yield calculation based on ^{1}H NMR data

The –CH peak of 4-nitrobenzaldehyde (reactant) appears at 10.15 ppm and the 2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile (product) appears at 5.59 ppm.

Total amount in the reaction mixture: unreacted 4-nitrobenzaldehyde + 2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile = 1+14.72 = 15.72

Percentage of the unreacted benzaldehyde: 100/15.72 = 6.36%

Conversion of 4-nitrobenzaldehyde = yield of 2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile = 100-6.36 = 93.6%.

The accurateness of this procedure was confirmed by repeating a number of the [1]H NMR analyses in the presence of internal standard (1,2-dimethoxyethane) which was added to the $CDCl_3$ solution. These experiments gave the same product yields similar to those obtained by the above method.

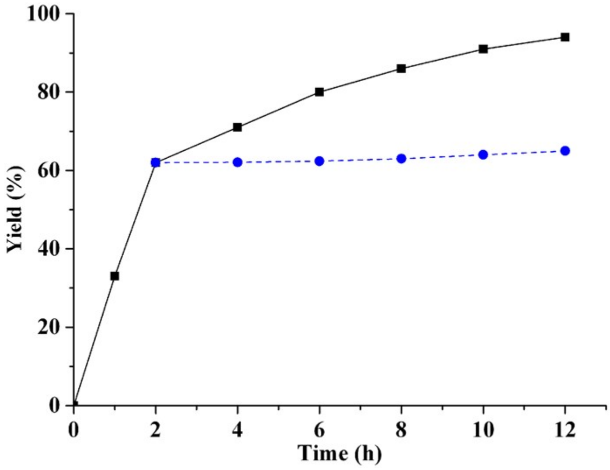

Fig. S7. Accumulation of 2-(4-nitrophenyl)-2-[(trimethylsilyl)oxy]acetonitrile vs. time in the cyanosilylation of 4-nitrobenzaldehyde with TMSCN catalysed by **3** (dotted line concerns removal of the catalyst after 2 h of the reaction: see text). Reaction conditions are those of Table 3 (entries 1−7).

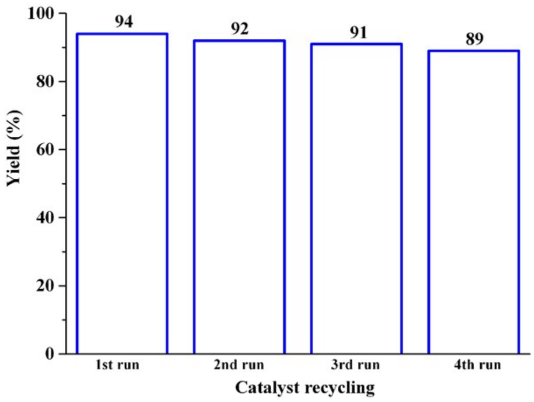

Fig. S8. Catalyst recycling experiments in the cyanosilylation of 4-nitrobenzaldehyde with TMSCN and catalyst **3**.

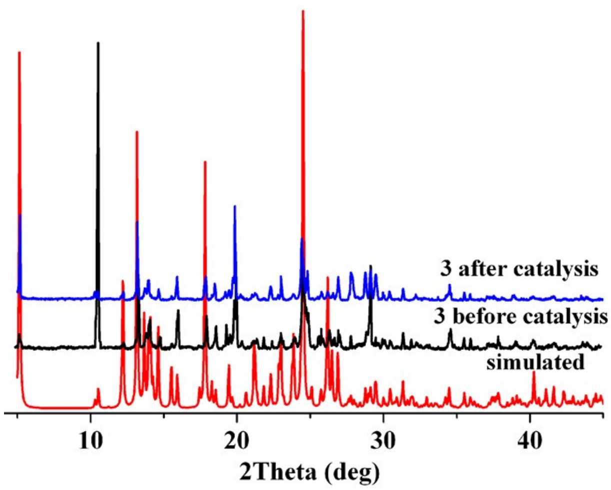

Fig. S9. PXRD patterns for **3**: simulated (red), before (blue) and after (black) catalysis.

Table S1. Selected bond lengths [Å] and angles [°] for the compounds **1–9**[a].

1					
Cd(1)-O(1)	2.320(4)	Cd(1)-O(2)	2.505(4)	Cd(1)-O(4)#1	2.197(3)
Cd(1)-O(7)	2.284(4)	Cd(1)-N(1)	2.303(4)	Cd(1)-N(2)	2.322(4)
O(7)-Cd(1)-O(4)#1	95.92(13)	O(4)#1-Cd(1)-N(1)	153.74(15)	N(1)-Cd(1)-O(7)	85.49(15)
O(1)-Cd(1)-O(4)#1	92.19(13)	O(7)-Cd(1)-O(1)	84.14(14)	O(1)-Cd(1)-N(1)	114.00(14)
O(4)#1-Cd(1)-N(2)	90.65(14)	O(7)-Cd(1)-N(2)	136.43(15)	N(1)-Cd(1)-N(2)	71.17(15)
O(1)-Cd(1)-N(2)	138.71(14)	O(4)#1-Cd(1)-O(2)	97.55(13)	O(7)-Cd(1)-O(2)	135.89(13)
O(2)-Cd(1)-N(1)	99.54(13)	O(2)-Cd(1)-O(1)	53.60(12)	N(2)-Cd(1)-O(2)	85.20(13)
2					
Ni(1)-O(1)	2.049(3)	Ni(1)-O(3)#1	2.032(3)	Ni(1)-O(7)	2.072(3)
Ni(1)-O(8)	2.123(3)	Ni(1)-O(9)	2.086(3)	Ni(1)-N(1)	2.079(4)
O(3)#1-Ni(1)-O(1)	95.28(14)	O(3)#1-Ni(1)-O(7)	91.65(13)	O(1)-Ni(1)-O(7)	92.53(13)
O(3)#1-Ni(1)-N(1)	88.65(16)	O(1)-Ni(1)-N(1)	90.20(15)	O(7)-Ni(1)-N(1)	177.21(15)
O(3)#1-Ni(1)-O(9)	177.14(14)	O(1)-Ni(1)-O(9)	87.49(14)	O(7)-Ni(1)-O(9)	87.48(13)
N(1)-Ni(1)-O(9)	92.08(15)	O(8)-Ni(1)-O(3)#1	89.52(14)	O(1)-Ni(1)-O(8)	175.04(14)
O(8)-Ni(1)-O(7)	86.06(12)	N(1)-Ni(1)-O(8)	91.18(14)	O(8)-Ni(1)-O(9)	87.70(13)
3					
Zn(1)-O(1)	2.126(4)	Zn(1)-O(2)	2.288(4)	Zn(1)-O(5)	2.044(3)
Zn(1)-O(6)	2.383(3)	Zn(1)-O(7)	1.992(4)	Zn(1)-N(1)	2.117(4)
O(7)-Zn(1)-O(5)	104.86(15)	O(7)-Zn(1)-N(1)	96.50(15)	O(5)-Zn(1)-N(1)	96.40(14)
O(7)-Zn(1)-O(1)	94.73(15)	O(5)-Zn(1)-O(1)	152.06(14)	O(1)-Zn(1)-N(1)	101.02(15)
O(7)-Zn(1)-O(2)	153.74(14)	O(2)-Zn(1)-O(5)	99.70(13)	O(2)-Zn(1)-N(1)	89.78(14)
O(1)-Zn(1)-O(2)	59.02(14)	O(6)-Zn(1)-O(7)	90.87(14)	O(5)-Zn(1)-O(6)	58.56(12)
N(1)-Zn(1)-O(6)	154.96(14)	O(1)-Zn(1)-O(6)	102.18(13)	O(2)-Zn(1)-O(6)	94.11(13)
4					
Cd(1)-O(1)	2.376(4)	Cd(1)-O(2)	2.329(4)	Cd(1)-O(5)	2.349(4)
Cd(1)-O(6)	2.344(4)	Cd(1)-O(7)	2.206(4)	Cd(1)-N(1)	2.322(4)
O(7)-Cd(1)-N(1)	98.50(15)	O(7)-Cd(1)-O(2)	148.35(14)	O(2)-Cd(1)-N(1)	87.67(15)
O(7)-Cd(1)-O(6)	90.50(15)	N(1)-Cd(1)-O(6)	146.65(15)	O(6)-Cd(1)-O(2)	101.29(14)
O(5)-Cd(1)-O(7)	105.26(15)	N(1)-Cd(1)-O(5)	90.99(14)	O(2)-Cd(1)-O(5)	105.65(14)
O(6)-Cd(1)-O(5)	55.68(12)	O(7)-Cd(1)-O(1)	92.91(14)	N(1)-Cd(1)-O(1)	95.86(16)
O(1)-Cd(1)-O(2)	55.49(13)	O(6)-Cd(1)-O(1)	115.78(14)	O(5)-Cd(1)-O(1)	159.43(14)
5					
Cd(1)-O(1)	2.234(4)	Cd(1)-O(3)#1	2.550(4)	Cd(1)-O(4)#1	2.285(4)
Cd(1)-Cl(1)	2.5420(17)	Cd(1)-N(1)	2.327(4)	Cd(1)-N(2)	2.339(5)
Cd(2)-O(2)	2.288(4)	Cd(2)-O(5)#2	2.394(4)	Cd(2)-O(6)#2	2.344(4)
Cd(2)-Cl(1)	2.4854(17)	Cd(2)-N(3)	2.347(5)	Cd(2)-N(4)	2.322(5)
O(1)-Cd(1)-O(4)#1	89.18(15)	O(1)-Cd(1)-N(1)	173.93(15)	O(4)#1-Cd(1)-N(1)	96.79(15)
O(1)-Cd(1)-N(2)	104.06(16)	N(2)-Cd(1)-O(4)#1	144.52(14)	N(1)-Cd(1)-N(2)	71.63(16)
O(1)-Cd(1)-Cl(1)	88.12(12)	O(4)#1-Cd(1)-Cl(1)	93.61(11)	N(1)-Cd(1)-Cl(1)	90.36(12)
N(2)-Cd(1)-Cl(1)	119.19(11)	O(3)#1-Cd(1)-O(1)	84.70(14)	O(4)#1-Cd(1)-O(3)#1	53.99(13)
N(1)-Cd(1)-O(3)#1	99.71(15)	N(2)-Cd(1)-O(3)#1	94.00(14)	O(3)#1-Cd(1)-Cl(1)	146.79(10)
O(2)-Cd(2)-N(4)	83.74(14)	O(2)-Cd(2)-O(6)#2	86.35(15)	N(4)-Cd(2)-O(6)#2	101.40(16)
O(2)-Cd(2)-N(3)	134.20(15)	N(4)-Cd(2)-N(3)	71.22(16)	N(3)-Cd(2)-O(6)#2	135.03(16)
O(2)-Cd(2)-O(5)#2	140.36(14)	N(4)-Cd(2)-O(5)#2	109.90(15)	O(6)#2-Cd(2)-O(5)#2	54.98(14)
N(3)-Cd(2)-O(5)#2	85.03(16)	O(2)-Cd(2)-Cl(1)	86.52(11)	N(4)-Cd(2)-Cl(1)	138.26(12)
O(6)-Cd(2)-Cl(1)	118.38(12)	N(3)-Cd(2)-Cl(1)	87.64(12)	O(5)#2-Cd(2)-Cl(1)	103.34(11)
6					
Zn(1)-O(1)	2.012(5)	Zn(1)-O(6)#1	2.099(5)	Zn(1)-O(13)	2.117(5)

Zn(1)-N(1)	2.100(5)	Zn(1)-N(2)	2.155(6)	Zn(2)-O(4)	1.980(4)
Zn(2)-O(14)	2.131(6)	Zn(2)-O(15)	2.065(5)	Zn(2)-N(3)	2.160(7)
Zn(2)-N(4)	2.103(7)	Zn(3)-O(7)	2.275(5)	Zn(3)-O(8)	2.235(5)
Zn(3)-O(12)#2	2.006(5)	Zn(3)-O(16)	2.122(5)	Zn(3)-N(5)	2.147(5)
Zn(3)-N(6)	2.160(6)				
O(6)#1-Zn(1)-O(1)	139.8(2)	O(1)-Zn(1)-N(1)	122.8(2)	O(6)#1-Zn(1)-N(1)	97.3(2)
O(1)-Zn(1)-O(13)	90.2(2)	O(13)-Zn(1)-O(6)#1	89.4(2)	N(1)-Zn(1)-O(13)	92.7(2)
N(2)-Zn(1)-O(1)	96.2(2)	N(2)-Zn(1)-O(6)#1	90.5(2)	N(1)-Zn(1)-N(2)	77.6(2)
N(2)-Zn(1)-O(13)	170.2(2)	O(4)-Zn(2)-O(15)	99.7(2)	O(4)-Zn(2)-N(4)	117.3(2)
O(15)-Zn(2)-N(4)	94.6(3)	O(14)-Zn(2)-O(4)	106.7(2)	O(14)-Zn(2)-O(15)	85.4(2)
O(14)-Zn(2)-N(4)	135.2(2)	O(4)-Zn(2)-N(3)	98.1(2)	O(15)-Zn(2)-N(3)	162.1(2)
N(4)-Zn(2)-N(3)	78.2(3)	O(14)-Zn(2)-N(3)	88.3(3)	O(16)-Zn(3)-O(12)#2	89.1(2)
N(5)-Zn(3)-O(12)#2	117.4(2)	O(16)-Zn(3)-N(5)	92.5(2)	N(6)-Zn(3)-O(12)#2	96.9(2)
O(16)-Zn(3)-N(6)	168.7(2)	N(6)-Zn(3)-N(5)	76.3(2)	O(12)#2-Zn(3)-O(8)	145.4 (2)
O(16)-Zn(3)-O(8)	89.9 (2)	N(5)-Zn(3)-O(8)	97.3(2)	N(6)-Zn(3)-O(8)	90.6(2)
O(12)#2-Zn(3)-O(7)	88.3(2)	O(16)-Zn(3)-O(7)	102.3(2)	N(5)-Zn(3)-O(7)	150.7(2)
N(6)-Zn(3)-O(7)	87.5(2)	O(8)-Zn(3)-O(7)	58.1(2)		
7					
Cd(1)-O(1)	2.226(4)	Cd(1)-O(2)#1	2.328(4)	Cd(1)-O(3)#2	2.616(4)
Cd(1)-O(4)#2	2.300(4)	Cd(1)-O(4)#3	2.804(4)	Cd(1)-N(1)	2.344(5)
Cd(1)-N(2)	2.359(5)	Cd(2)-O(5)	2.429(5)	Cd(2)-O(5)#4	2.429(5)
Cd(2)-O(6)	2.289(4)	Cd(2)-O(6)#4	2.289(4)	Cd(2)-N(3)	2.259(6)
Cd(2)-N(3)#4	2.259(6)				
O(4)#2-Cd(1)-O(1)	135.12(17)	O(2)#1-Cd(1)-O(1)	82.93(15)	O(2)#1-Cd(1)-O(4)#2	78.78(14)
O(1)-Cd(1)-N(1)	87.01(16)	O(4)#2-Cd(1)-N(1)	129.51(17)	O(2)#1-Cd(1)-N(1)	144.09(17)
O(1)-Cd(1)-N(2)	113.97(17)	O(4)#2-Cd(1)-N(2)	104.04(18)	O(2)#1-Cd(1)-N(2)	83.04(17)
N(1)-Cd(1)-N(2)	69.82(18)	O(3)#2-Cd(1)-O(1)	140.81(14)	O(3)#2-Cd(1)-O(4)#2	52.94(14)
O(3)#2-Cd(1)-O(2)#1	129.42(14)	O(3)#2-Cd(1)-N(1)	77.02(16)	O(3)#2-Cd(1)-N(2)	93.88(17)
O(4)#3-Cd(1)-O(1)	73.67(15)	O(4)#3-Cd(1)-O(2)#1	110.58(15)	O(4)#3-Cd(1)-O(4)#2	75.09(14)
O(4)#3-Cd(1)-O(3)#2	74.00(15)	O(4)#3-Cd(1)-N(1)	99.36(16)	O(4)#3-Cd(1)-N(2)	165.60(15)
N(3)#4-Cd(2)-N(3)	72.4(3)	O(6)-Cd(2)-N(3)#4	140.4(2)	O(6)-Cd(2)-N(3)	112.27(19)
O(6)#4-Cd(2)-O(6)	89.1(2)	O(5)#4-Cd(2)-N(3)#4	131.1(2)	O(5)#4-Cd(2)-N(3)	91.3(2)
O(5)#4-Cd(2)-O(6)	88.49(18)	O(5)#4-Cd(2)-O(6)#4	55.01(17)	O(5)#4-Cd(2)-O(5)	130.2(2)
8					
Zn(1)-O(2)	2.432(3)	Zn(1)-O(2)#1	2.432(3)	Zn(1)-N(1)	2.136(3)
Zn(1)-N(1)#1	2.136(3)	Zn(1)-N(4)	2.083(3)	Zn(1)-N(4)#1	2.083(3)
Zn(2)-O(3)#2	1.958(3)	Zn(2)-O(5)	2.286(4)	Zn(2)-O(6)	2.044(3)
Zn(2)-O(7)	2.009(3)	Zn(2)-N(5)	2.071(3)		
N(1)-Zn(1)-N(4)	79.84(13)	N(1)-Zn(1)-N(4)#1	100.16(13)	O(2)-Zn(1)-N(4)	87.24(12)
O(2)-Zn(1)-N(4)#1	92.76(12)	O(2)-Zn(1)-N(1)	83.66(13)	O(2)-Zn(1)-N(1)#1	96.34(13)
O(2)#1-Zn(1)-N(4)	92.75(12)	O(3)#2-Zn(2)-O(7)	97.33(13)	O(3)#2-Zn(2)-O(6)	152.30(14)
O(7)-Zn(2)-O(6)	96.60(14)	O(3)#2-Zn(2)-N(5)	103.86(13)	O(7)-Zn(2)-N(5)	104.29(14)
O(6)-Zn(2)-N(5)	95.71(14)	O(3)#2-Zn(2)-O(5)	96.52(13)	O(7)-Zn(2)-O(5)	146.60(14)
O(6)-Zn(2)-O(5)	59.95(14)	N(5)-Zn(1)-O(5)	101.64(15)		
9					
Zn(1)-O(1)	1.980(4)	Zn(1)-O(3)#1	2.062(4)	Zn(1)-O(4)#1	2.379(4)
Zn(1)-O(6)#2	1.929(4)	Zn(1)-N(1)	2.024(5)	Zn(2)-O(2)	2.027(4)
Zn(2)-O(2)#3	2.027(4)	Zn(2)-O(3)#1	2.146(4)	Zn(2)-O(3)#4	2.146(4)
Zn(2)-O(5)#2	2.142(4)	Zn(2)-O(5)#5	2.142(4)		
O(1)-Zn(1)-O(6)#2	107.19(17)	O(6)#2-Zn(1)-N(1)	114.3(2)	N(1)-Zn(1)-O(1)	94.89(18)

O(6)#2-Zn(1)-O(3)#1	111.67(18)	O(1)-Zn(1)-O(3)#1	101.02(16)	N(1)-Zn(1)-O(3)#1	123.67(19)
O(6)#2-Zn(1)-O(4)#1	90.55(18)	O(4)#1-Zn(1)-O(1)	157.59(17)	N(1)-Zn(1)-O(4)#1	89.93(19)
O(3)#1-Zn(1)-O(4)#1	58.75(15)	O(2)#3-Zn(2)-O(5)#2	84.32(17)	O(2)#3-Zn(2)-O(5)#5	95.68(17)
O(2)#3-Zn(2)-O(3)#4	91.07(15)	O(2)-Zn(2)-O(3)#4	88.93(14)	O(5)#2-Zn(2)-O(3)#4	88.79(16)
O(5)#5-Zn(2)-O(3)#4	91.21(16)				

[a] Symmetry transformations used to generate equivalent atoms: #1 x–1, y, z for **1** ; #1 –x+3/2, y+1/2, z for **2**; #1 –x, –y+1, –z; #2 –x+1, –y+1, –z for **5**; #1 x, y–1, z; #2 x, y+1, z for **6**; #1 –x, y, –z+1/2; #2 –x, y–1, –z+1/2; #3 x, y–1, z; #4 –x+1, y, –z+1/2 for **7**; #1 –x+1, –y+1, –z+2; #2 x+1, y+1, z for **8**; #1 x, –y+2, z+1/2; #2 –x+2, –y+1, –z+2; #3 –x+2, –y+2, –z+2; #4 –x+2, y, –z+3/2; #5 x, y+1, z for **9**.

Table S2. Hydrogen bonds in crystal packing [Å, °] of **1**–**9**.

Complexes	D-H…A	*d*(D-H)	*d*(H…A)	*d*(D…A)	∠DHA	Symmetry code
1	O(6)-H(6)···O(2)	0.820	1.810	2.600	161.36	x+1, y-1, z
	O(7)-H(1W)···O(8)	0.850	1.942	2.792	179.09	-x+1, -y+1, -z
	O(7)-H(2W)···O(10)	0.850	2.052	2.902	179.17	-x, -y+1, -z
	O(8)-H(3W)···O(5)	0.850	2.116	2.966	179.36	
	O(8)-H(4W)···O(9)	0.770	2.108	2.861	165.92	x+1, y, z
	O(9)-H(5W)···O(1)	0.850	2.004	2.854	179.13	
	O(9)-H(6W)···O(10)	0.850	1.923	2.773	179.75	
	O(10)-H(7W)···O(3)	0.850	1.884	2.734	179.14	
	O(10)-H(8W)···O(8)	0.850	1.977	2.827	178.81	-x+1, -y+1, -z
2	O(5)-H(5)···N(2)	0.820	1.808	2.620	170.06	-x+1, -y+1, -z+1
	O(7)-H(1W)···O(2)	0.849	2.077	2.822	146.09	
	O(7)-H(2W)···O(4)	0.820	1.876	2.629	152.17	-x+3/2, y+1/2, z
	O(8)-H(3W)···O(4)	0.820	1.877	2.662	160.03	x, y+1, z
	O(8)-H(4W)···O(10)	0.754	1.974	2.726	175.00	
	O(9)-H(5W)···O(8)	0.848	1.995	2.810	160.72	-x+1, y, -z+3/2
	O(9)-H(6W)···O(2)	0.820	2.363	2.912	125.05	
	O(10)-H(7W)···O(2)	0.845	1.976	2.796	163.68	x+1/2, y+1/2, -z+3/2
3	O(3)-H(1)···N(2)	0.820	2.040	2.839	164.65	-x+1, -y+1, -z+1
	O(7)-H(1W)···O(8)	0.847	1.828	2.615	153.83	
	O(7)-H(2W)···O(5)	0.820	1.900	2.710	169.25	x+1, y+1, z
	O(8)-H(3W)···O(6)	0.861	2.083	2.816	142.74	x+1, y, z
	O(8)-H(4W)···O(2)	0.849	1.968	2.817	177.93	x+1, y, z
4	O(3)-H(1)···N(2)	0.820	2.087	2.877	161.59	-x+1, -y+2, -z+1
	O(7)-H(1W)···O(5)	0.850	1.836	2.686	179.44	x+1, y+1, z
	O(7)-H(2W)···O(8)	0.850	1.763	2.613	179.70	
	O(8)-H(3W)···O(2)	0.850	1.936	2.786	179.41	x+1, y, z
	O(8)-H(4W)···O(6)	0.850	1.993	2.842	179.35	x+1, y, z
5	O(7)-H(1W)···O(6)	0.850	2.236	3.086	178.99	-x+1, y-1/2, -z+1/2
	O(7)-H(2W)···O(5)	0.850	2.063	2.912	177.69	x, y, z+1
	O(8)-H(3W)···O(3)	0.850	1.988	2.838	178.71	x, y, z+1
	O(8)-H(4W)···O(7)	0.850	2.336	3.185	176.99	-x+1, y+1/2, -z+3/2

6	O(13)-H(2W)···O(10)	0.820	1.947	2.700	152.23	-*x*+1, -*y*, -*z*+1
	O(15)-H(5W)···O(9)	0.820	1.852	2.667	172.71	
	O(16)-H(7W)···O(3)	0.820	1.998	2.695	142.54	-*x*+2, -*y*+1, -*z*+1
7	O(7)-H(1W)···O(6)	0.850	1.889	2.739	179.21	
	O(7)-H(2W)···O(4)	0.850	2.172	3.022	179.30	*x*, *y*-1, *z*
	O(8)-H(3W)···O(7)	0.850	1.958	2.808	178.88	-*x*+1, *y*, -*z*+1/2
	O(8)-H(4W)···O(5)	0.850	2.097	2.947	179.33	
8	O(7)-H(1W)···O(8)	0.871	1.860	2.652	150.32	
	O(7)-H(2W)···O(1)	0.871	1.782	2.647	172.11	*x*, *y*+1, *z*
	O(8)-H(4W)···O(4)	0.850	1.890	2.733	171.11	*x*, *y*+1, *z*

Table S3. Emission wavelengths (nm) for **1–9**, and H_3bta.[a]

Compound	**H_3bta**	**1**	**2**	**3**	**4**
λ_{em}	463	406	461	381	446
Compound	**5**	**6**	**7**	**8**	**9**
λ_{em}	406	426	411	374	385

[a] λ_{ex} = 371 nm for H_3bta, λ_{ex} = 360 nm for **1–9**.

Table S4. Comparison of various catalysts for the cyanosilylation of 4-nitrobenzaldehyde with trimethylsilyl cyanide in CH_2Cl_2 at RT.

Entry	Catalyst	Catalyst mol%	Time (h)	Conversion (%)	Reference
1	$[Zn_2(\mu\text{-Hbta})_2(4,4'\text{-bipy})_2(H_2O)_2]\cdot 2H_2O$	3	12	96	This work
2	$[Zn(L)(dmf)_2]$	5	10	95	50
3	$[Zn_2(L)(NO_3)_2\text{-}(4,4'\text{-bipyridine})_2]_n\cdot n(DMF)$	2	10	85	50
4	$[Cu(L)(H_2O)_2]_n\cdot 2n(H_2O)$	2	10	79	50
5	$[Cu_3(OH)_2(L)_2]_n\cdot n(H_2O)$	2	10	65	50
6	$[Zn_2(\mu\text{-Hdcna})_2(bipy)_2(H_2O)_4]\cdot 6H_2O$	3	12	75	52
7	$[Zn(\mu_3\text{-Hdcna})(H_2biim)]_n$	3	12	60	52
8	$[Zn(\mu\text{-Hdcna})(phen)]_n$	3	12	55	52
9	Z_1M_1-110A	2	14	55	53
10	$(Me_2NH_2)[Ni_3(L)_2(\mu_3\text{-OH})(H_2O)]_2\cdot DMF$	2	24	96	54