# Electronic Supplementary Information

# A series of Zn(II) and Cd(II) coordination polymers based on flexible bis-[(pyridyl)-benzimidazole] ligand and different carboxylates: syntheses, structures, and photoluminescent properties

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**Table S1**. Selected bond distances (Å) and angles (°) for compounds **1**-**8**.

| | | | |
|---|---|---|---|
| **1** | | | |
| Zn(1)-O(1) | 1.9089(18) | Zn(1)-O(3)$^{\#1}$ | 1.9364(19) |
| Zn(1)-N(1) | 2.036(2) | Zn(1)-N(3)$^{\#2}$ | 2.093(2) |
| O(1)-Zn(1)-O(3)$^{\#1}$ | 105.65(9) | O(1)-Zn(1)-N(1) | 122.60(9) |
| O(3)$^{\#1}$-Zn(1)-N(1) | 100.19(9) | O(1)-Zn(1)-N(3)$^{\#2}$ | 112.55(9) |
| O(3)$^{\#1}$-Zn(1)-N(3)$^{\#2}$ | 117.04(9) | N(1)-Zn(1)-N(3)$^{\#2}$ | 98.93(9) |
| **2** | | | |
| Zn(1)-O(1) | 1.927(2) | Zn(1)-O(4)$^{\#1}$ | 1.9316(19) |
| Zn(1)-N(1) | 2.015(2) | Zn(1)-N(3)$^{\#2}$ | 2.086(3) |
| O(1)-Zn(1)-O(4)$^{\#1}$ | 103.58(9) | O(1)-Zn(1)-N(1) | 126.16(9) |
| O(4)$^{\#1}$-Zn(1)-N(1) | 99.61(9) | O(1)-Zn(1)-N(3)$^{\#2}$ | 106.85(9) |
| O(4)$^{\#1}$-Zn(1)-N(3)$^{\#2}$ | 119.09(10) | N(1)-Zn(1)-N(3)$^{\#2}$ | 102.79(10) |
| **3** | | | |
| Zn(1)-O(5)$^{\#1}$ | 1.940(3) | Zn(1)-O(1) | 1.958(3) |
| Zn(1)-O(3) | 1.982(3) | Zn(1)-N(1) | 2.001(4) |
| Zn(2)-O(2) | 2.035(3) | Zn(2)-O(6)$^{\#1}$ | 2.054(3) |
| Zn(2)-O(3) | 2.193(3) | | |
| O(5)$^{\#1}$-Zn(1)-O(1) | 111.97(15) | O(5)$^{\#1}$-Zn(1)-O(3) | 112.03(13) |
| O(1)-Zn(1)-O(3) | 99.57(14) | O(5)$^{\#1}$-Zn(1)-N(1) | 109.09(16) |
| O(1)-Zn(1)-N(1) | 102.95(15) | O(3)-Zn(1)-N(1) | 120.38(15) |
| O(2)-Zn(2)-O(6)$^{\#3}$ | 84.78(13) | O(2)-Zn(2)-O(6)$^{\#1}$ | 95.22(13) |
| O(2)-Zn(2)-O(3)$^{\#2}$ | 89.64(12) | O(6)$^{\#1}$-Zn(2)-O(3)$^{\#2}$ | 89.84(12) |
| O(2)-Zn(2)-O(3) | 90.36(12) | O(6)$^{\#1}$-Zn(2)-O(3) | 90.16(12) |
| **4** | | | |
| Zn(1)-O(6)$^{\#1}$ | 1.902(3) | Zn(1)-O(2)$^{\#2}$ | 1.932(3) |
| Zn(1)-O(1) | 1.978(3) | Zn(1)-N(1) | 2.040(3) |
| Zn(2)-O(3) | 1.942(3) | Zn(2)-O(3)$^{\#3}$ | 1.942(3) |
| Zn(2)-O(1W) | 2.021(5) | Zn(2)-N(3)$^{\#4}$ | 2.235(4) |
| Zn(2)-N(3)$^{\#5}$ | 2.235(4) | | |
| O(6)$^{\#1}$-Zn(1)-O(2)$^{\#2}$ | 128.26(17) | O(6)$^{\#1}$-Zn(1)-O(1) | 100.41(16) |
| O(2)$^{\#2}$-Zn(1)-O(1) | 114.17(15) | O(6)$^{\#1}$-Zn(1)-N(1) | 104.90(15) |
| O(2)$^{\#2}$-Zn(1)-N(1) | 100.13(13) | O(1)-Zn(1)-N(1) | 107.42(15) |
| O(3)-Zn(2)-O(3)$^{\#3}$ | 154.9(2) | O(3)-Zn(2)-O(1W) | 102.53(12) |
| O(3)$^{\#3}$-Zn(2)-O(1W) | 102.53(12) | O(3)-Zn(2)-N(3)$^{\#4}$ | 87.53(16) |
| O(3)$^{\#3}$-Zn(2)-N(3)$^{\#4}$ | 90.79(16) | O(1W)-Zn(2)-N(3)$^{\#4}$ | 93.88(11) |
| O(3)-Zn(2)-N(3)$^{\#5}$ | 90.79(16) | O(3)$^{\#3}$-Zn(2)-N(3)$^{\#5}$ | 87.53(16) |

| | | | |
|---|---|---|---|
| O(1W)-Zn(2)-N(3)$^{\#5}$ | 93.88(11) | N(3)$^{\#4}$-Zn(2)-N(3)$^{\#5}$ | 172.2(2) |

**5**

| | | | |
|---|---|---|---|
| Cd(1)-N(1) | 2.318(3) | Cd(1)-O(2) | 2.341(3) |
| Cd(1)-N(3)$^{\#1}$ | 2.373(3) | Cd(1)-O(4)$^{\#2}$ | 2.393(3) |
| Cd(1)-O(1W) | 2.439(3) | Cd(1)-O(3)$^{\#2}$ | 2.447(3) |
| Cd(1)-O(1) | 2.568(3) | | |
| N(1)-Cd(1)-O(2) | 101.13(10) | N(1)-Cd(1)-N(3)$^{\#1}$ | 94.92(10) |
| O(2)-Cd(1)-N(3)$^{\#1}$ | 131.89(12) | N(1)-Cd(1)-O(4)$^{\#2}$ | 104.07(11) |
| O(2)-Cd(1)-O(4)$^{\#2}$ | 133.41(10) | N(3)$^{\#1}$-Cd(1)-O(4)$^{\#2}$ | 84.06(11) |
| N(1)-Cd(1)-O(1W) | 171.42(13) | O(2)-Cd(1)-O(1W) | 81.32(10) |
| N(3)$^{\#1}$-Cd(1)-O(1W) | 77.56(11) | O(4)$^{\#2}$-Cd(1)-O(1W) | 79.49(12) |
| N(1)-Cd(1)-O(3)$^{\#2}$ | 101.09(10) | O(2)-Cd(1)-O(3)$^{\#2}$ | 83.77(10) |
| N(3)$^{\#1}$-Cd(1)-O(3)$^{\#2}$ | 136.93(11) | O(4)$^{\#2}$-Cd(1)-O(3)$^{\#2}$ | 53.39(9) |
| O(1W)-Cd(1)-O(3)$^{\#2}$ | 87.31(11) | | |

**6**

| | | | |
|---|---|---|---|
| Cd(1)-O(1) | 2.209(3) | Cd(1)-O(3)$^{\#1}$ | 2.329(4) |
| Cd(1)-N(1) | 2.334(4) | Cd(1)-N(2)$^{\#2}$ | 2.349(4) |
| Cd(1)-O(4)$^{\#1}$ | 2.486(4) | Cd(1)-O(3)$^{\#3}$ | 2.586(4) |
| O(1)-Cd(1)-O(3)$^{\#1}$ | 120.27(13) | O(1)-Cd(1)-N(1) | 136.38(13) |
| O(3)$^{\#1}$-Cd(1)-N(1) | 91.71(13) | O(1)-Cd(1)-N(2)$^{\#2}$ | 110.20(13) |
| O(3)$^{\#1}$-Cd(1)-N(2)$^{\#2}$ | 102.90(13) | N(1)-Cd(1)-N(2)$^{\#2}$ | 87.85(13) |
| O(1)-Cd(1)-O(4)$^{\#1}$ | 80.93(13) | O(3)$^{\#1}$-Cd(1)-O(4)$^{\#1}$ | 53.91(12) |
| N(1)-Cd(1)-O(4)$^{\#1}$ | 141.69(12) | N(2)$^{\#2}$-Cd(1)-O(4)$^{\#1}$ | 84.77(14) |
| O(1)-Cd(1)-O(3)$^{\#3}$ | 74.55(13) | O(3)$^{\#1}$-Cd(1)-O(3)$^{\#3}$ | 81.55(12) |
| N(1)-Cd(1)-O(3)$^{\#3}$ | 82.70(12) | N(2)$^{\#2}$-Cd(1)-O(3)$^{\#3}$ | 169.70(12) |
| O(4)$^{\#1}$-Cd(1)-O(3)$^{\#3}$ | 105.21(12) | | |

**7**

| | | | |
|---|---|---|---|
| Cd(1)-O(2) | 2.217(2) | Cd(1)-O(3)$^{\#1}$ | 2.290(2) |
| Cd(1)-N(1) | 2.340(2) | Cd(1)-N(2)$^{\#2}$ | 2.444(2) |
| Cd(1)-O(4)$^{\#1}$ | 2.463(2) | Cd(1)-O(1)$^{\#3}$ | 2.465(2) |
| O(2)-Cd(1)-O(3)$^{\#1}$ | 96.31(9) | O(2)-Cd(1)-N(1) | 124.17(9) |
| O(3)$^{\#1}$-Cd(1)-N(1) | 138.90(9) | O(2)-Cd(1)-N(2)$^{\#2}$ | 89.28(9) |
| O(3)$^{\#1}$-Cd(1)-N(2)$^{\#2}$ | 96.35(9) | N(1)-Cd(1)-N(2)$^{\#2}$ | 91.41(8) |
| O(2)-Cd(1)-O(4)$^{\#1}$ | 150.15(8) | O(3)$^{\#1}$-Cd(1)-O(4)$^{\#1}$ | 54.71(8) |
| N(1)-Cd(1)-O(4)$^{\#1}$ | 85.58(8) | N(2)$^{\#2}$-Cd(1)-O(4)$^{\#1}$ | 87.38(9) |
| O(2)-Cd(1)-O(1)$^{\#3}$ | 90.84(8) | O(3)$^{\#1}$-Cd(1)-O(1)$^{\#3}$ | 81.22(8) |
| N(1)-Cd(1)-O(1)$^{\#3}$ | 90.53(8) | N(2)$^{\#2}$-Cd(1)-O(1)$^{\#3}$ | 177.56(8) |

| | | | |
|---|---|---|---|
| O(4)$^{\#1}$-Cd(1)-O(1)$^{\#3}$ | 91.30(8) | | |
| **8** | | | |
| Cd(1)-O(1) | 2.207(7) | Cd(1)-N(1) | 2.283(9) |
| Cd(1)-N(3)$^{\#1}$ | 2.335(7) | Cd(1)-O(3)$^{\#2}$ | 2.377(8) |
| Cd(1)-O(4')$^{\#2}$ | 2.388(18) | Cd(1)-O(4)$^{\#2}$ | 2.399(16) |
| Cd(1)-O(1') | 2.45(3) | Cd(1)-O(3')$^{\#2}$ | 2.45(3) |
| Cd(1)-O(2) | 2.460(7) | Cd(1)-O(2') | 2.46(4) |
| O(1)-Cd(1)-N(1) | 136.4(4) | O(1)-Cd(1)-N(3)$^{\#1}$ | 97.7(4) |
| N(1)-Cd(1)-N(3)$^{\#1}$ | 104.6(2) | O(1)-Cd(1)-O(3)$^{\#2}$ | 96.3(4) |
| N(1)-Cd(1)-O(3)$^{\#2}$ | 93.9(3) | N(3)$^{\#1}$-Cd(1)-O(3)$^{\#2}$ | 134.8(4) |
| O(1)-Cd(1)-O(4')$^{\#2}$ | 93.5(6) | N(1)-Cd(1)-O(4')$^{\#2}$ | 124.3(5) |
| N(3)$^{\#1}$-Cd(1)-O(4')$^{\#2}$ | 86.8(5) | O(3)$^{\#2}$-Cd(1)-O(4')$^{\#2}$ | 49.5(6) |
| O(1)-Cd(1)-O(4)$^{\#2}$ | 112.3(5) | N(1)-Cd(1)-O(4)$^{\#2}$ | 107.6(5) |
| N(3)$^{\#1}$-Cd(1)-O(4)$^{\#2}$ | 82.2(5) | O(3)$^{\#2}$-Cd(1)-O(4)$^{\#2}$ | 52.7(5) |
| O(4')$^{\#2}$-Cd(1)-O(4)$^{\#2}$ | 18.9(5) | N(1)-Cd(1)-O(1') | 106.9(7) |
| N(3)$^{\#1}$-Cd(1)-O(1') | 123.9(7) | O(3)$^{\#2}$-Cd(1)-O(1') | 87.7(7) |
| O(4)$^{\#2}$-Cd(1)-O(1') | 128.2(8) | O(1)-Cd(1)-O(3')$^{\#2}$ | 120.1(8) |
| N(1)-Cd(1)-O(3')$^{\#2}$ | 80.1(7) | N(3)$^{\#1}$-Cd(1)-O(3')$^{\#2}$ | 119.4(7) |
| O(3)$^{\#2}$-Cd(1)-O(3')$^{\#2}$ | 24.5(7) | O(4')$^{\#2}$-Cd(1)-O(3')$^{\#2}$ | 48.8(4) |
| O(4)$^{\#2}$-Cd(1)-O(3')$^{\#2}$ | 41.7(8) | O(1')-Cd(1)-O(3')$^{\#2}$ | 111.0(10) |
| O(1)-Cd(1)-O(2) | 51.7(3) | N(1)-Cd(1)-O(2) | 92.1(4) |
| N(3)$^{\#1}$-Cd(1)-O(2) | 87.3(4) | O(3)$^{\#2}$-Cd(1)-O(2) | 133.6(5) |
| O(4')$^{\#2}$-Cd(1)-O(2) | 143.4(6) | O(4)$^{\#2}$-Cd(1)-O(2) | 159.5(6) |
| O(1')-Cd(1)-O(2) | 46.8(7) | O(3')$^{\#2}$-Cd(1)-O(2) | 153.3(8) |
| O(1)-Cd(1)-O(2') | 41.1(15) | N(1)-Cd(1)-O(2') | 110.9(13) |
| N(3)$^{\#1}$-Cd(1)-O(2') | 74.3(11) | O(3)$^{\#2}$-Cd(1)-O(2') | 136.2(14) |
| O(4')$^{\#2}$-Cd(1)-O(2') | 124.5(13) | O(4)$^{\#2}$-Cd(1)-O(2') | 138.7(11) |
| O(1')-Cd(1)-O(2') | 51.4(14) | O(3')$^{\#2}$-Cd(1)-O(2') | 160.7(17) |

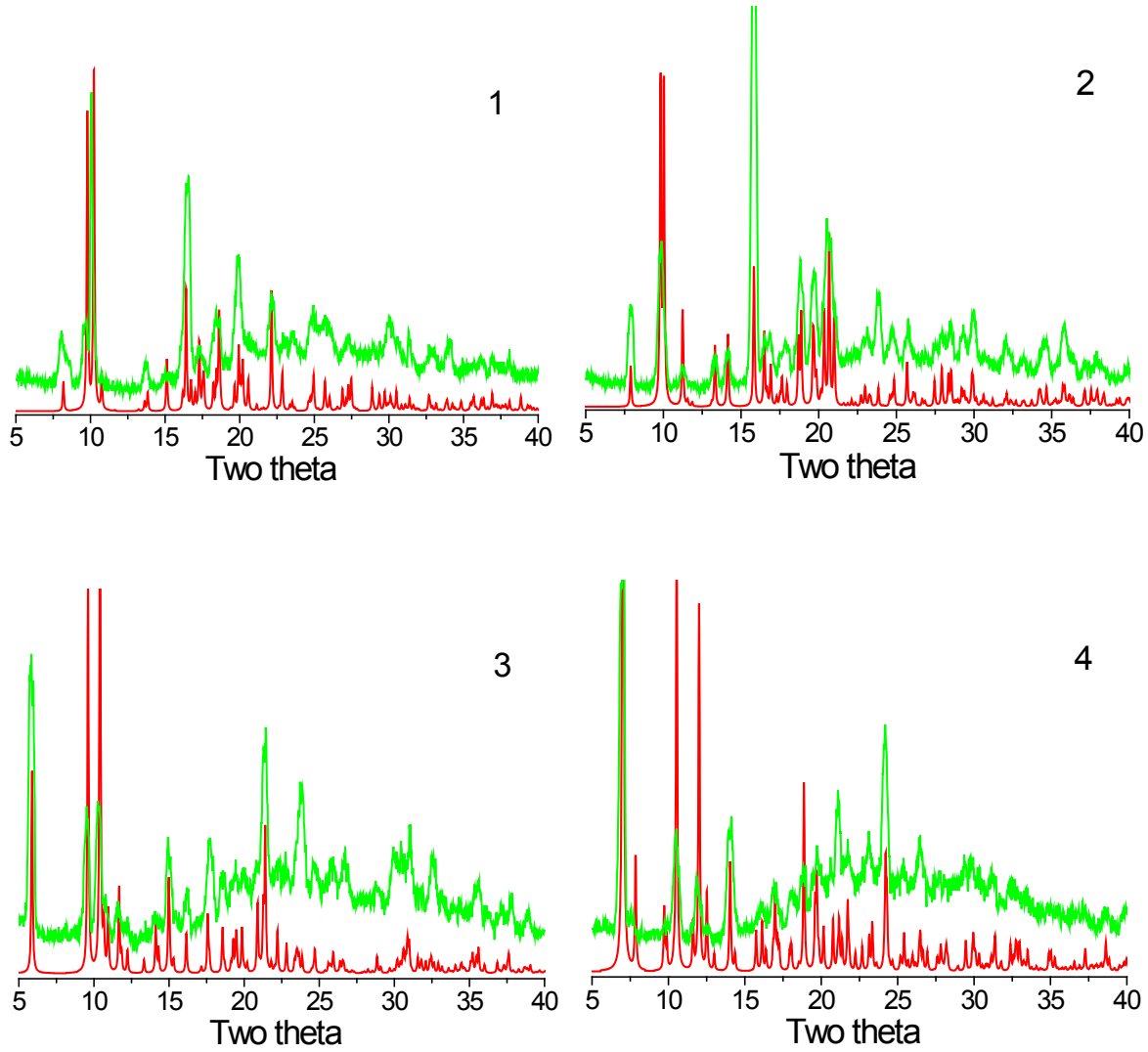
Symmetry codes for **1**: $^{\#1}$ x+1/2, -y+1/2, z+1/2; $^{\#2}$ -x+1, -y, -z+1. For **2**: $^{\#1}$ x, -y+1/2, z-1/2; $^{\#2}$ -x+1, -y, -z. For **3**: $^{\#1}$ x, -y-1/2, z+1/2; $^{\#2}$ -x+1, -y, -z+2; $^{\#3}$ -x+1, y+1/2, -z+3/2. For **4**: $^{\#1}$ -x, y, -z+1/2; $^{\#2}$ -x, -y+1, -z; $^{\#3}$ -x+1/2, -y+2, z; $^{\#4}$ -x, y+1, -z+1/2; $^{\#5}$ x+1/2, -y+1, -z+1/2. For **5**: $^{\#1}$ -x+1, -y+1, -z+1; $^{\#2}$ -x+1, -y+1, -z. For **6**: $^{\#1}$ x, y+1, z; $^{\#2}$ -x+1, -y+1, -z+2; $^{\#3}$ -x+2, -y, -z+2. For **7**: $^{\#1}$ -x, y+1/2, -z+1/2; $^{\#2}$ -x+1, -y, -z; $^{\#3}$ -x, -y, -z. For **8**: $^{\#1}$ -x+1/2, -y+1/2, -z; $^{\#2}$ -x+3/2, -y+1/2, -z.

**Table S2**. Hydrogen-bonding parameters for **2-5** (in Å and deg)

| D-H···A | d(D-H) | d(D···A) | ∠(D-H···A) |
|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| **2** | | | | |
| N(4)-H(4B)...O(2)$^{\#3}$ | 0.844(10) | 2.004(16) | 2.776(3) | 152(2) |
| **3** | | | | |
| O(1W)-H(1A)...O(2W) | 0.762(18) | 2.26(3) | 2.916(13) | 145(3) |
| O(2W)-H(2A)...O(1W) | 0.86(2) | 2.59(4) | 2.916(13) | 104(3) |
| **4** | | | | |
| O(1W)-H(1A)...O(2W) | 0.869(10) | 2.12(4) | 2.703(7) | 124(4) |
| **5** | | | | |
| O(1W)-H(1B)...O(2)$^{\#2}$ | 0.860(19) | 2.16(4) | 2.844(5) | 136(5) |
| O(1W)-H(1A)...O(3) | 0.863(19) | 1.95(3) | 2.706(5) | 146(5) |

Symmetry codes for **2:** $^{\#3}$ -x, y+1/2, -z+1/2. **For 5**: $^{\#2}$ -x+1, -y+1, -z.



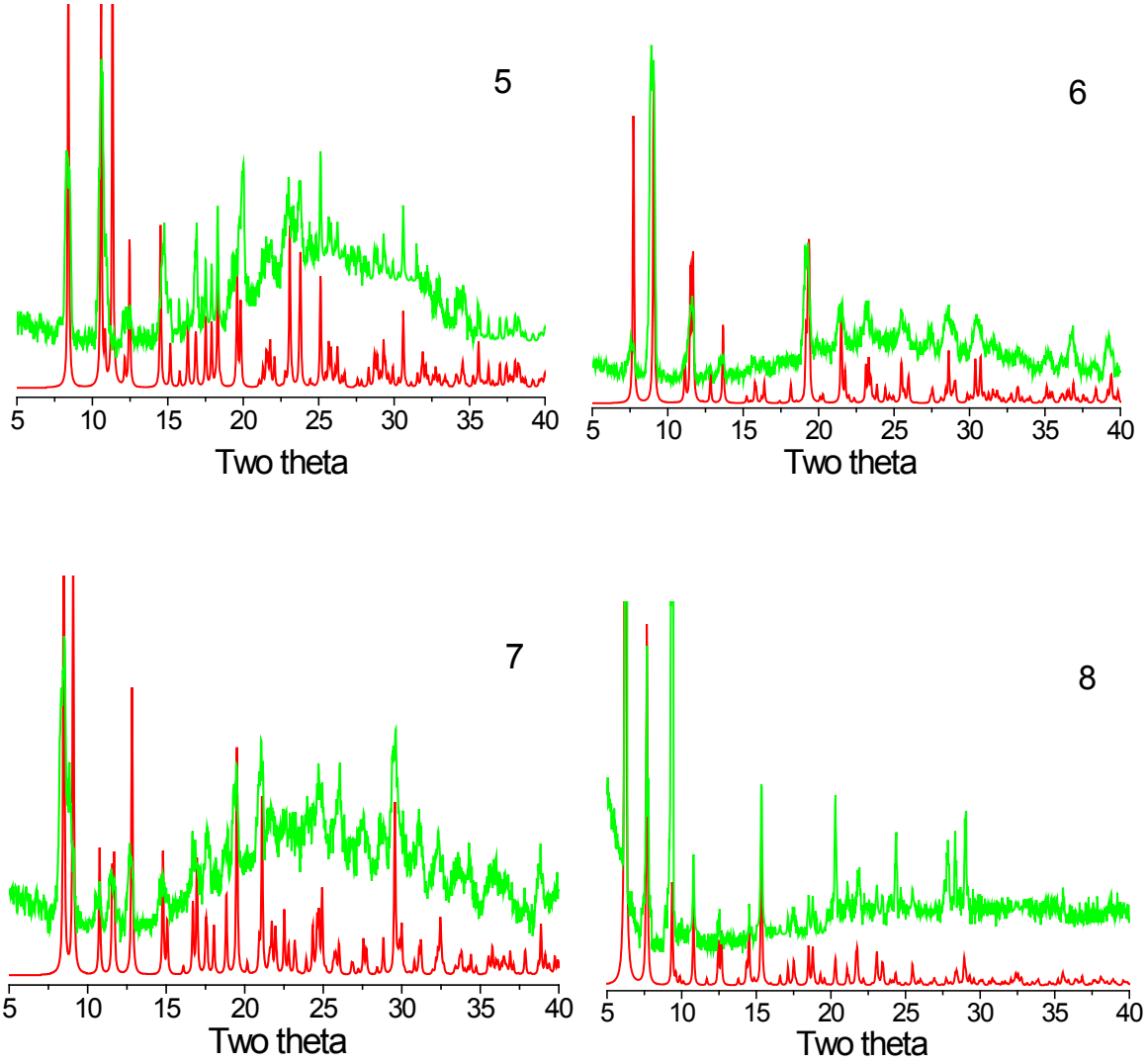
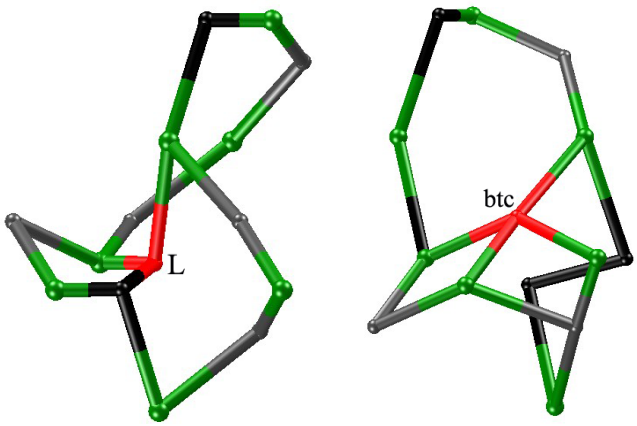



**Fig. S1** The simulated (green) and experimental (red) XRPD patterns for the compounds **1-8** (the diffraction peaks of both simulated and experimental patterns match well in relevant positions, indicating that the phase purities of compounds **1-8** are good).



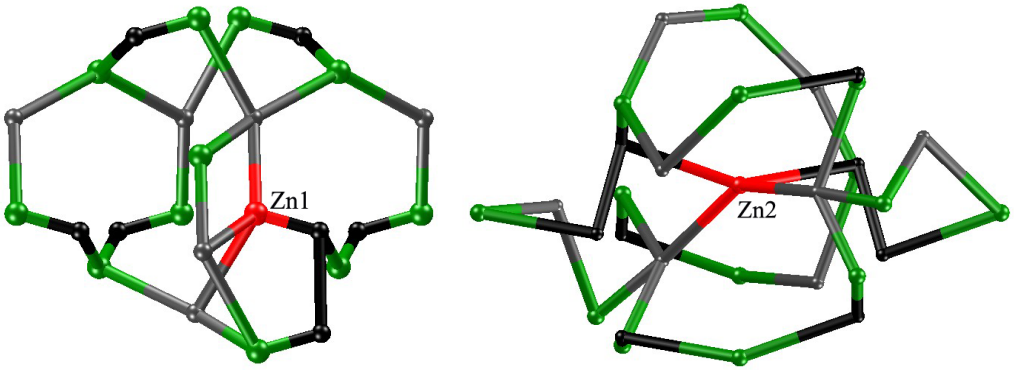



**Fig. S2**. View of the 3- and 4-connected nodes of **4**.

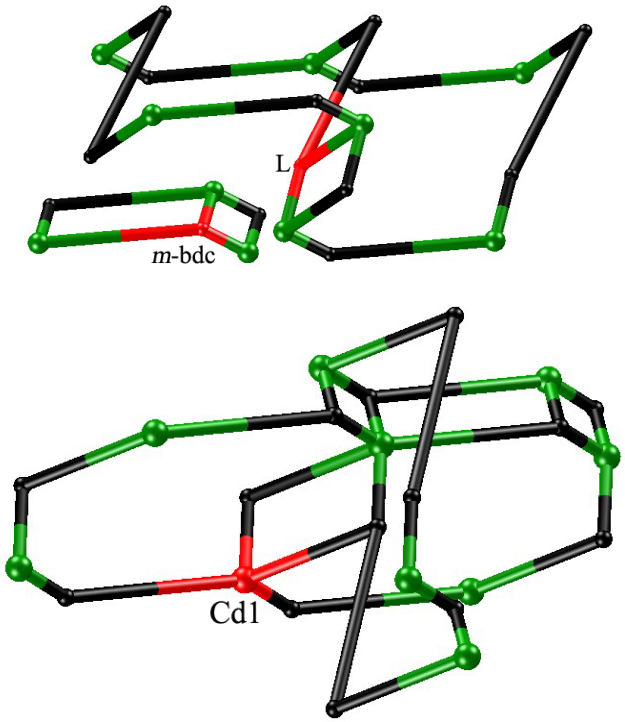
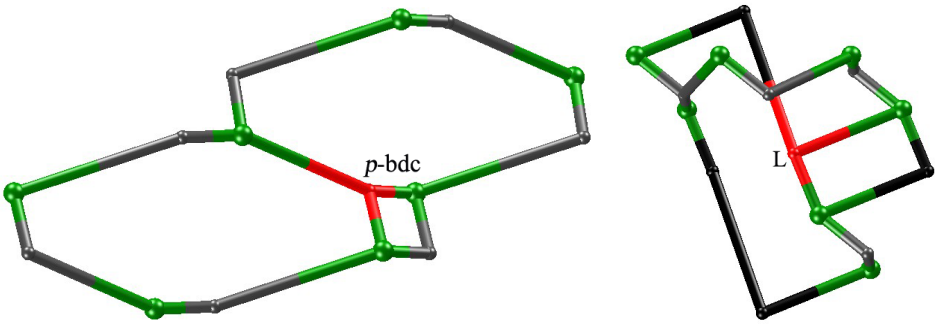



**Fig. S3**. View of the 3- and 4-connected nodes of **6**.



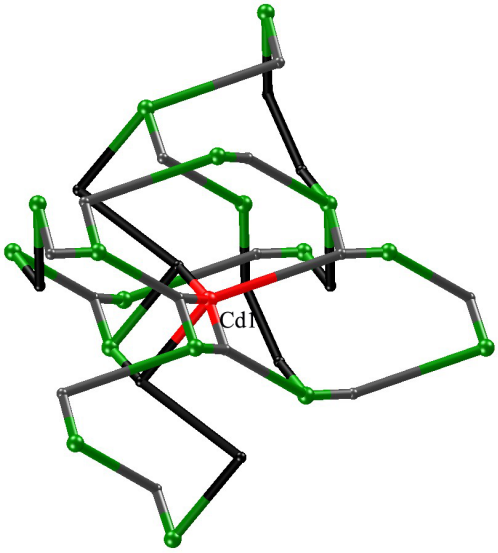



**Fig. S4**. View of the 3- and 5-connected nodes of **7**.

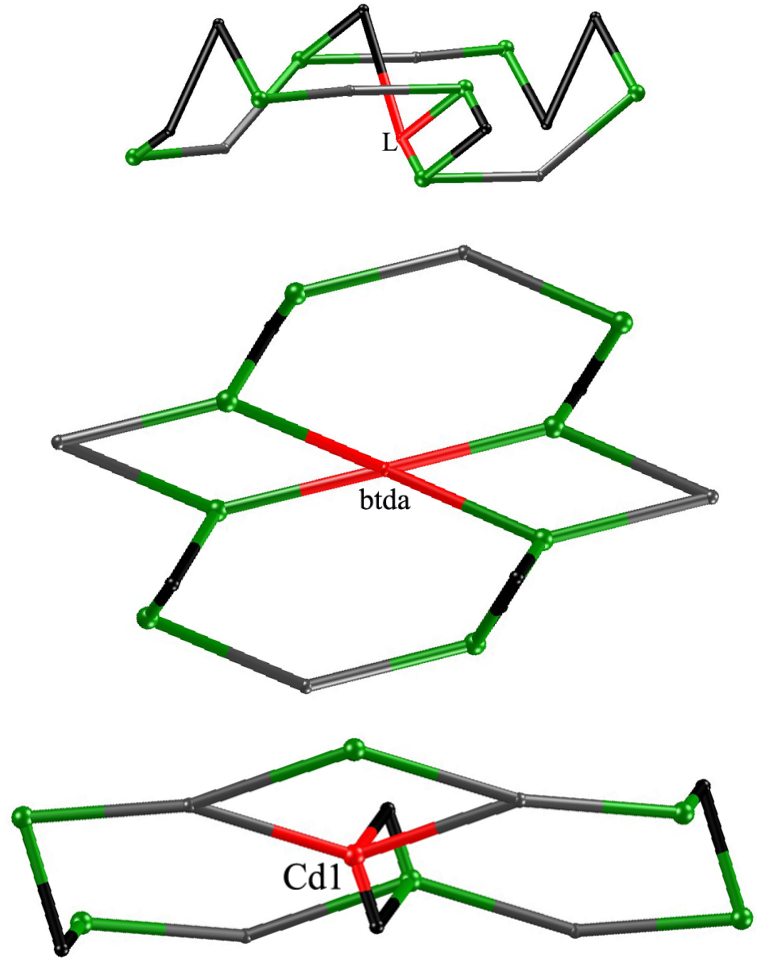



**Fig. S5**. View of the 3- and 4-connected nodes of **8**.

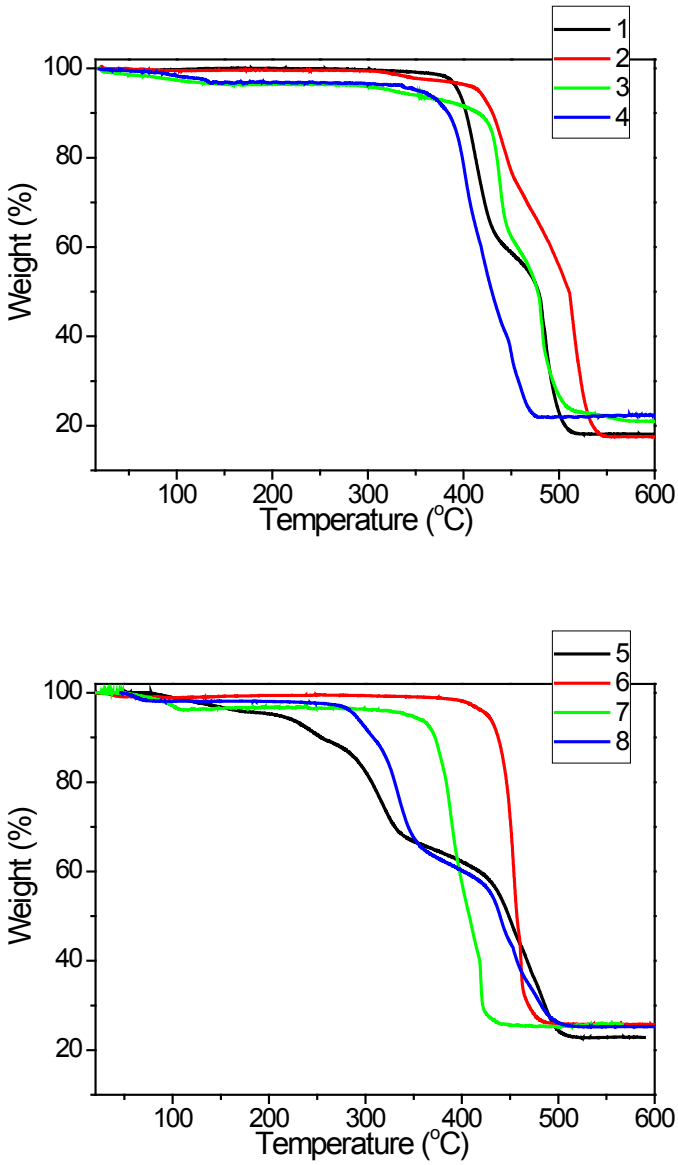
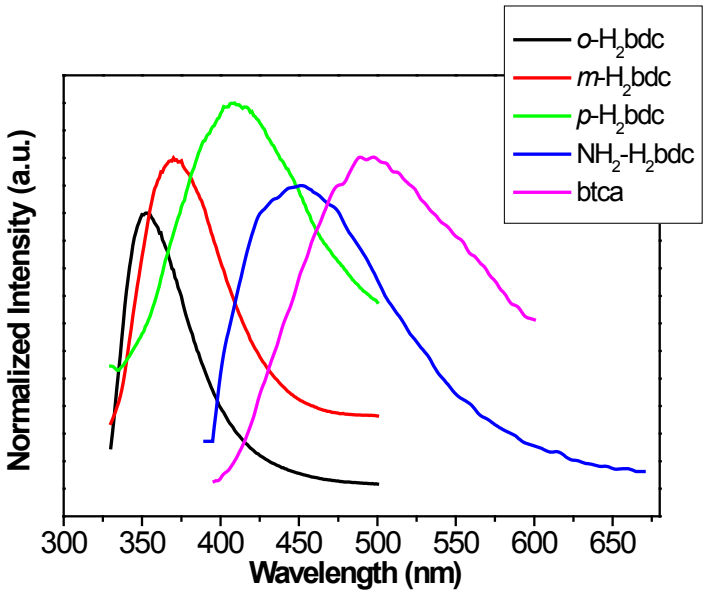
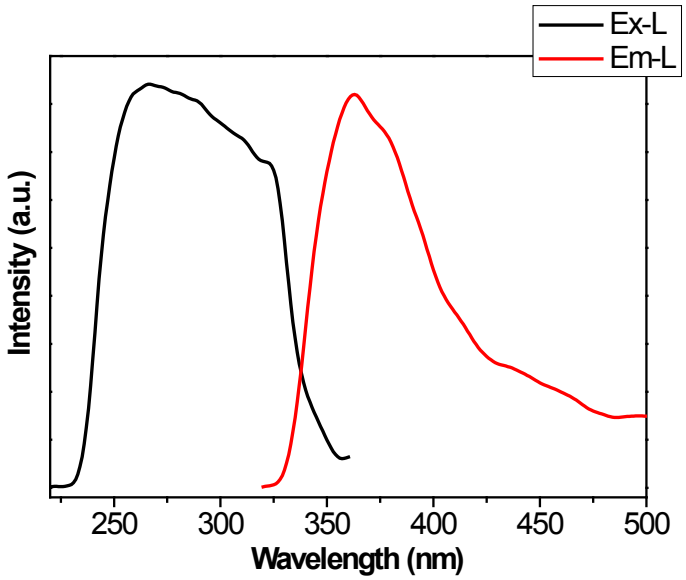



**Fig. S6**. TGA curves of compounds **1-8**.




(a)




(b)

**Fig. S7**. (a) Solid-state emission spectra of free *o*-$H_2$bdc, *m*-$H_2$bdc, *p*-$H_2$bdc, $H_4$btec ligands at room temperature. (b) The excitation and emission spectra of L ligand at room temperature.