Supplementary Material (ESI) for CrystEngComm

# A series of coordination polymers based on a multidentate N-donor ligand and different polycarboxylate anions: syntheses, structures and photoluminescent properties

**Wei-Qiu Kan, Jin Yang*, Ying-Ying Liu and Jian-Fang Ma***

*Key Lab of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China*

* Correspondence authors

E-mail: yangjinnenu@yahoo.com.cn (J. Yang)

E-mail: jianfangma@yahoo.com.cn (J.-F. Ma)

Fax: +86-431-85098620 (J.-F. Ma)

**Table S1.** Selected bond distances and angles for compound **1**.

| | | | |
|---|---|---|---|
| Cd(1)-N(1)#1 | 2.319(4) | Cd(1)-O(1) | 2.325(4) |
| Cd(1)-O(2W) | 2.354(5) | Cd(1)-O(3)#2 | 2.368(4) |
| Cd(1)-N(8) | 2.389(5) | Cd(1)-O(4)#2 | 2.487(4) |
| Cd(1)-O(2) | 2.492(4) | | |
| N(1)#1-Cd(1)-O(1) | 139.83(15) | N(1)#1-Cd(1)-O(2W) | 78.28(18) |
| O(1)-Cd(1)-O(2W) | 101.71(18) | N(1)#1-Cd(1)-O(3)#2 | 139.31(15) |
| O(1)-Cd(1)-O(3)#2 | 80.77(14) | O(2W)-Cd(1)-O(3)#2 | 93.12(16) |
| N(1)#1-Cd(1)-N(8) | 90.12(16) | O(1)-Cd(1)-N(8) | 94.53(16) |
| O(2W)-Cd(1)-N(8) | 163.72(19) | O(3)#2-Cd(1)-N(8) | 88.25(15) |
| N(1)#1-Cd(1)-O(4)#2 | 86.18(14) | O(1)-Cd(1)-O(4)#2 | 133.82(13) |
| O(4)#2-Cd(1)-O(2) | 165.10(15) | O(2W)-Cd(1)-O(4)#2 | 89.49(17) |
| O(3)#2-Cd(1)-O(4)#2 | 53.73(13) | N(8)-Cd(1)-O(4)#2 | 78.25(16) |
| N(1)#1-Cd(1)-O(2) | 86.66(15) | O(1)-Cd(1)-O(2) | 53.67(13) |
| O(2W)-Cd(1)-O(2) | 101.82(19) | O(3)#2-Cd(1)-O(2) | 133.91(14) |
| N(8)-Cd(1)-O(2) | 88.72(17) | | |

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x + 1/2, y - 1/2, z; $^{\#2}$ x - 1/2, -y + 1/2, -z + 1.

**Table S2.** Selected bond distances and angles for compound **2**.

| | | | |
|---|---|---|---|
| Cd(1)-O(1) | 2.220(2) | Cd(1)-N(8) | 2.263(3) |
| Cd(1)-O(4)#1 | 2.299(3) | Cd(1)-N(1)#2 | 2.357(3) |
| Cd(1)-O(3)#1 | 2.415(2) | Cd(1)-O(1)#3 | 2.529(3) |
| O(1)-Cd(1)-N(8) | 112.65(11) | O(1)-Cd(1)-O(4)#1 | 90.72(9) |
| N(8)-Cd(1)-O(4)#1 | 149.78(10) | O(1)-Cd(1)-N(1)#2 | 113.00(10) |
| N(8)-Cd(1)-N(1)#2 | 90.65(12) | O(4)#1-Cd(1)-N(1)#2 | 97.72(10) |

| | | | |
|---|---|---|---|
| O(1)-Cd(1)-O(3)#1 | 145.59(10) | N(8)-Cd(1)-O(3)#1 | 97.72(10) |
| O(4)#1-Cd(1)-O(3)#1 | 55.50(9) | N(1)#2-Cd(1)-O(3)#1 | 81.17(11) |
| O(1)-Cd(1)-O(1)#3 | 78.73(9) | N(8)-Cd(1)-O(1)#3 | 80.72(10) |
| O(4)#1-Cd(1)-O(1)#3 | 85.71(10) | N(1)#2-Cd(1)-O(1)#3 | 167.62(9) |
| O(3)#1-Cd(1)-O(1)#3 | 91.14(9) | | |

Symmetry transformations used to generate equivalent atoms: [#1] x-1, y, z; [#2] -x -1/2, y + 1/2, -z + 1/2; [#3] -x, -y, -z + 1.

**Table S3.** Selected bond distances and angles for compound **3**.

| | | | |
|---|---|---|---|
| Cd(1)-O(4)#1 | 2.233(2) | Cd(1)-N(8) | 2.267(3) |
| Cd(1)-O(2) | 2.285(2) | Cd(1)-N(1)#2 | 2.402(2) |
| Cd(1)-O(1) | 2.479(2) | Cd(1)-O(4)#3 | 2.480(2) |
| O(4)#1-Cd(1)-N(8) | 115.39(9) | O(4)#1-Cd(1)-O(2) | 135.26(8) |
| N(8)-Cd(1)-O(2) | 103.18(9) | O(4)#1-Cd(1)-N(1)#2 | 109.08(8) |
| N(8)-Cd(1)-N(1)#2 | 99.61(9) | O(2)-Cd(1)-N(1)#2 | 84.64(8) |
| O(4)#1-Cd(1)-O(1) | 82.58(7) | N(8)-Cd(1)-O(1) | 156.89(8) |
| O(2)-Cd(1)-O(1) | 55.08(7) | N(1)#2-Cd(1)-O(1) | 86.94(8) |
| O(4)#1-Cd(1)-O(4)#3 | 74.94(7) | N(8)-Cd(1)-O(4)#3 | 90.35(8) |
| O(2)-Cd(1)-O(4)#3 | 83.38(7) | N(1)#2-Cd(1)-O(4)#3 | 165.90(8) |
| O(1)-Cd(1)-O(4)#3 | 80.12(7) | | |

Symmetry transformations used to generate equivalent atoms: [#1] x+1, y-1, z; [#2] -x, -y, -z+1; [#3] -x - 1, -y + 1, -z + 2.

**Table S4.** Selected bond distances and angles for compound **4**.

| | | | |
|---|---|---|---|
| Cd(1)-O(1) | 2.310(3) | Cd(1)-O(1W) | 2.330(3) |
| Cd(1)-N(1) | 2.317(3) | Cd(2)-O(11)#2 | 2.180(3) |
| Cd(2)-O(7) | 2.346(3) | Cd(2)-O(5) | 2.374(2) |

| | | | |
|---|---|---|---|
| Cd(2)-O(3)#3 | 2.417(3) | Cd(2)-O(6) | 2.437(3) |
| Cd(2)-O(8) | 2.466(2) | Cd(2)-O(4)#3 | 2.613(3) |
| Cd(3)-O(9) | 2.225(3) | Cd(3)-O(2)#3 | 2.274(3) |
| Cd(3)-N(8)#4 | 2.280(3) | Cd(3)-N(5)#5 | 2.308(3) |
| Cd(3)-O(8) | 2.342(2) | Cd(3)-O(4)#3 | 2.370(2) |
| Na(1)-O(3W)#3 | 2.300(2) | | |
| Na(1)-O(12)#2 | 2.311(3) | Na(1)-O(5)#3 | 2.445(3) |
| Na(1)-O(3)#3 | 2.492(3) | Na(1)-O(5) | 2.508(3) |
| Na(1)-O(4) | 2.556(3) | O(1)-Cd(1)-O(1W)#1 | 92.23(10) |
| O(1)-Cd(1)-O(1W) | 87.77(10) | O(1)-Cd(1)-N(1)#1 | 90.90(11) |
| O(1W)-Cd(1)-N(1)#1 | 90.86(12) | O(1)-Cd(1)-N(1) | 89.10(11) |
| O(1W)-Cd(1)-N(1) | 89.14(12) | O(11)#2-Cd(2)-O(7) | 116.29(10) |
| O(11)#2-Cd(2)-O(5) | 115.38(9) | O(7)-Cd(2)-O(5) | 103.12(9) |
| O(11)#2-Cd(2)-O(3)#3 | 88.83(9) | O(7)-Cd(2)-O(3)#3 | 144.37(9) |
| O(5)-Cd(2)-O(3)#3 | 86.27(8) | O(11)#2-Cd(2)-O(6) | 84.73(10) |
| O(7)-Cd(2)-O(6) | 79.01(9) | O(5)-Cd(2)-O(6) | 54.14(8) |
| O(3)#3-Cd(2)-O(6) | 130.93(8) | O(11)#2-Cd(2)-O(8) | 104.20(9) |
| O(7)-Cd(2)-O(8) | 54.07(9) | O(5)-Cd(2)-O(8) | 140.35(8) |
| O(3)#3-Cd(2)-O(8) | 97.16(8) | O(6)-Cd(2)-O(8) | 131.58(8) |
| O(11)#2-Cd(2)-O(4)#3 | 138.75(9) | O(7)-Cd(2)-O(4)#3 | 95.65(9) |
| O(5)-Cd(2)-O(4)#3 | 78.66(8) | O(3)#3-Cd(2)-O(4)#3 | 52.01(8) |
| O(6)-Cd(2)-O(4)#3 | 128.82(9) | O(8)-Cd(2)-O(4)#3 | 72.97(8) |
| O(9)-Cd(3)-O(2)#3 | 161.06(11) | O(9)-Cd(3)-N(8)#4 | 88.45(12) |
| O(2)#3-Cd(3)-N(8)#4 | 104.38(12) | O(9)-Cd(3)-N(5)#5 | 102.61(12) |

| | | | |
|---|---|---|---|
| O(2)#3-Cd(3)-N(5)#5 | 88.58(11) | N(8)#4-Cd(3)-N(5)#5 | 101.63(12) |
| O(9)-Cd(3)-O(8) | 85.69(10) | O(2)#3-Cd(3)-O(8) | 78.50(9) |
| N(8)#4-Cd(3)-O(8) | 165.47(11) | N(5)#5-Cd(3)-O(8) | 92.62(10) |
| O(9)-Cd(3)-O(4)#3 | 83.66(10) | O(2)#3-Cd(3)-O(4)#3 | 83.33(9) |
| N(8)#4-Cd(3)-O(4)#3 | 86.36(11) | N(5)#5-Cd(3)-O(4)#3 | 169.85(11) |
| O(8)-Cd(3)-O(4)#3 | 79.79(9) | O(3W)#3-Na(1)-O(12)#2 | 113.4(6) |
| O(3W)#3-Na(1)-O(5)#3 | 83.4(6) | O(12)#2-Na(1)-O(5)#3 | 151.61(11) |
| O(3W)#3-Na(1)-O(3)#3 | 97.7(6) | O(12)#2-Na(1)-O(3)#3 | 79.50(10) |
| O(5)#3-Na(1)-O(3)#3 | 75.54(9) | O(3W)#3-Na(1)-O(5) | 165.6(6) |
| O(12)#2-Na(1)-O(5) | 80.73(10) | O(5)#3-Na(1)-O(5) | 82.56(10) |
| O(3)#3-Na(1)-O(5) | 81.85(9) | O(3W)#3-Na(1)-O(4) | 101.9(6) |
| O(12)#2-Na(1)-O(4) | 117.30(11) | O(5)#3-Na(1)-O(4) | 78.51(9) |
| O(7W)#3-Na(1)-O(5) | 154.6(4) | O(7W)#3-Na(1)-O(4) | 95.8(4) |
| O(3)#3-Na(1)-O(4) | 145.21(11) | O(5)-Na(1)-O(4) | 72.10(9) |

Symmetry transformations used to generate equivalent atoms: [#1] -x, -y - 1, -z + 1; [#2] -x + 2, -y, -z + 1; [#3] -x + 1, -y, -z + 1; [#4] -x, -y, -z; [#5] -x + 1, -y, -z.

**Table S5.** Selected bond distances and angles for compound **5**.

| | | | |
|---|---|---|---|
| Cd(1)-O(1) | 2.218(4) | Cd(1)-O(4)#1 | 2.217(4) |
| Cd(1)-O(5)#2 | 2.306(4) | Cd(1)-O(6)#2 | 2.426(5) |
| Cd(1)-N(1) | 2.449(5) | Cd(1)-O(3W) | 2.471(9) |
| Cd(2)-O(3) | 2.283(4) | Cd(2)-O(1W) | 2.290(5) |
| Cd(2)-O(2) | 2.305(4) | Cd(2)-N(6)#4 | 2.31(8) |
| O(1)-Cd(1)-O(4)#1 | 108.64(19) | O(1)-Cd(1)-O(5)#2 | 146.49(16) |
| O(4)#1-Cd(1)-O(5)#2 | 99.34(16) | O(1)-Cd(1)-O(6)#2 | 92.24(17) |

| | | | |
|---|---|---|---|
| O(4)#1-Cd(1)-O(6)#2 | 150.25(16) | O(5)#2-Cd(1)-O(6)#2 | 55.31(14) |
| O(1)-Cd(1)-N(1) | 85.74(17) | O(4)#1-Cd(1)-N(1) | 77.06(17) |
| O(5)#2-Cd(1)-N(1) | 82.87(17) | O(6)#2-Cd(1)-N(1) | 83.84(18) |
| O(1)-Cd(1)-O(3W) | 108.5(2) | O(4)#1-Cd(1)-O(3W) | 110.0(2) |
| O(5)#2-Cd(1)-O(3W) | 77.6(2) | O(6)#2-Cd(1)-O(3W) | 81.7(2) |
| N(1)-Cd(1)-O(3W) | 160.0(2) | O(3)-Cd(2)-O(3)#3 | 80.3(2) |
| O(3)-Cd(2)-O(1W) | 89.06(16) | O(3)-Cd(2)-O(2)#3 | 160.55(16) |
| O(3)-Cd(2)-O(2) | 82.00(17) | O(1W)-Cd(2)-O(2) | 82.74(12) |
| O(2)#3-Cd(2)-O(2) | 114.2(2) | O(3)-Cd(2)-N(6)#4 | 96.4(18) |
| O(2)-Cd(2)-N(6)#4 | 93.4(15) | O(1W)-Cd(2)-N(6)#4 | 172.9(16) |

Symmetry transformations used to generate equivalent atoms: [#1] x-1/2, y, -z + 3/2; [#2] x-1, y, z; [#3] x, -y + 1/2, z; [#4] -x + 3/2, -y + 1, z - 1/2.

**Table S6.** Selected bond distances and angles for compound **6**.

| | | | |
|---|---|---|---|
| Zn(1)-O(1) | 1.960(2) | Zn(1)-O(4)#1 | 1.964(2) |
| Zn(1)-N(8) | 2.027(2) | Zn(1)-N(1)#2 | 2.102(2) |
| O(1)-Zn(1)-O(4)#1 | 101.09(8) | O(1)-Zn(1)-N(8) | 111.38(9) |
| O(4)#1-Zn(1)-N(8) | 128.23(9) | O(1)-Zn(1)-N(1)#2 | 116.15(9) |
| O(4)#1-Zn(1)-N(1)#2 | 103.93(9) | N(8)-Zn(1)-N(1)#2 | 96.71(9) |

Symmetry transformations used to generate equivalent atoms: [#1] x-1, y, z; [#2] -x + 1/2, y + 1/2, -z + 1/2.

**Table S7.** Selected bond distances and angles for compound **7**.

| | | | |
|---|---|---|---|
| Zn(1)-O(5) | 1.937(2) | Zn(1)-O(1) | 1.974(2) |
| Zn(1)-O(3)#1 | 2.060(2) | Zn(1)-N(1) | 2.073(3) |
| Zn(1)-O(4)#1 | 2.334(2) | Zn(2)-O(6) | 2.026(2) |
| Zn(2)-O(2) | 2.071(2) | Zn(2)-O(4)#1 | 2.133(2) |

| | | | |
|---|---|---|---|
| O(5)-Zn(1)-O(1) | 129.52(10) | O(5)-Zn(1)-O(3)#1 | 125.34(10) |
| O(1)-Zn(1)-O(3)#1 | 101.46(10) | O(5)-Zn(1)-N(1) | 98.16(10) |
| O(1)-Zn(1)-N(1) | 95.88(10) | O(3)#1-Zn(1)-N(1) | 94.22(10) |
| O(5)-Zn(1)-O(4)#1 | 97.70(9) | O(1)-Zn(1)-O(4)#1 | 90.90(9) |
| O(3)#1-Zn(1)-O(4)#1 | 58.55(8) | N(1)-Zn(1)-O(4)#1 | 152.76(9) |
| O(6)-Zn(2)-O(2) | 91.78(9) | O(6)#2-Zn(2)-O(2) | 88.22(9) |
| O(6)-Zn(2)-O(4)#1 | 91.64(9) | O(2)-Zn(2)-O(4)#1 | 89.66(9) |
| O(6)-Zn(2)-O(4)#3 | 88.36(9) | O(2)-Zn(2)-O(4)#3 | 90.35(9) |

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ x, -y, z - 1/2; $^{\#2}$ -x + 1/2, -y - 1/2, -z + 1; $^{\#3}$ -x + 1/2, y - 1/2, -z + 3/2.

**Table S8.** Selected bond distances and angles for compound **8**.

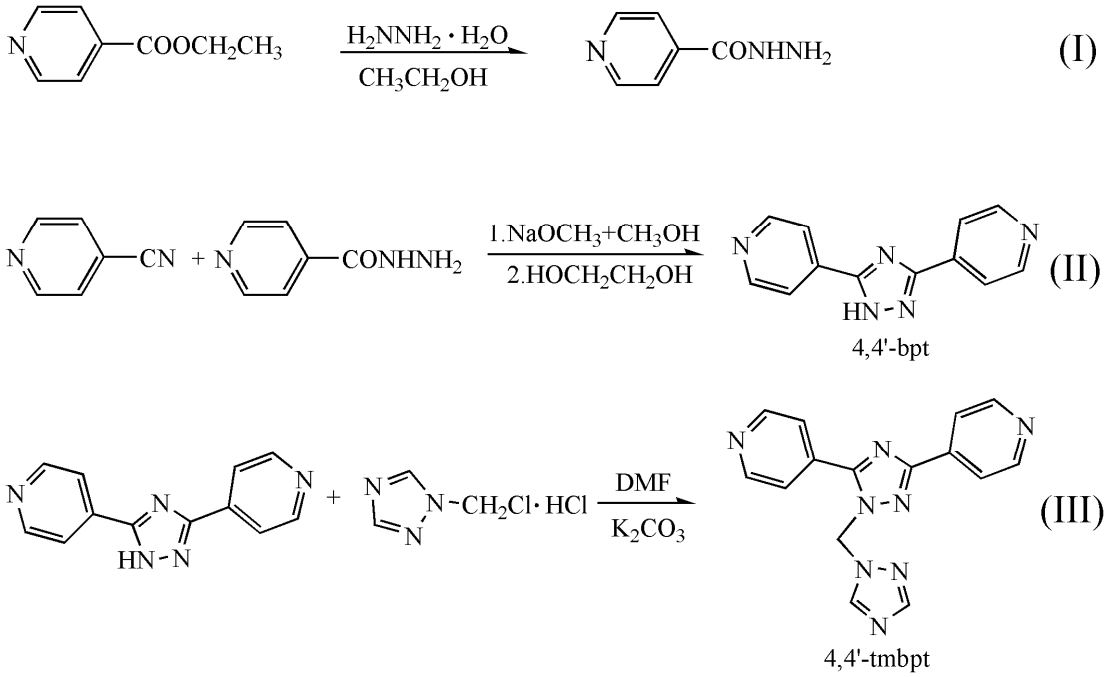
| | | | |
|---|---|---|---|
| Zn(1)-O(6)#1 | 1.988(6) | Zn(1)-O(3)#2 | 2.008(6) |
| Zn(1)-O(2) | 2.101(6) | Zn(1)-N(1) | 2.134(7) |
| Zn(1)-O(3W) | 2.234(11) | Zn(1)-O(1) | 2.288(8) |
| Zn(2)-O(4) | 2.068(5) | Zn(2)-N(6)#4 | 2.121(11) |
| Zn(2)-O(5) | 2.116(5) | Zn(2)-O(1W) | 2.181(6) |
| O(6)#1-Zn(1)-O(3)#2 | 106.9(3) | O(6)#1-Zn(1)-O(2) | 153.2(3) |
| O(3)#2-Zn(1)-O(2) | 98.5(3) | O(6)#1-Zn(1)-N(1) | 96.8(2) |
| O(3)#2-Zn(1)-N(1) | 84.3(3) | O(2)-Zn(1)-N(1) | 93.8(3) |
| O(6)#1-Zn(1)-O(3W) | 89.1(2) | O(3)#2-Zn(1)-O(3W) | 100.9(2) |
| O(2)-Zn(1)-O(3W) | 77.9(3) | N(1)-Zn(1)-O(3W) | 170.7(2) |
| O(6)#1-Zn(1)-O(1) | 96.2(2) | O(3)#2-Zn(1)-O(1) | 156.4(2) |
| O(2)-Zn(1)-O(1) | 59.5(3) | N(1)-Zn(1)-O(1) | 88.3(3) |
| O(3W)-Zn(1)-O(1) | 83.9(3) | O(4)#3-Zn(2)-O(4) | 82.4(3) |
| O(4)-Zn(2)-N(6)#5 | 100.1(6) | O(4)-Zn(2)-N(6)#4 | 100.1(6) |

| | | | |
|---|---|---|---|
| N(6)#4-Zn(2)-N(6)#5 | 7.0(19) | O(4)#3-Zn(2)-O(5) | 167.2(3) |
| O(4)-Zn(2)-O(5) | 88.7(2) | N(6)#4-Zn(2)-O(5) | 89.9(6) |
| N(6)#5-Zn(2)-O(5) | 95.8(6) | O(5)-Zn(2)-O(5)#3 | 98.5(3) |
| O(4)-Zn(2)-O(1W) | 89.5(3) | N(6)#4-Zn(2)-O(1W) | 169.9(4) |
| O(5)-Zn(2)-O(1W) | 81.0(3) | | |

Symmetry transformations used to generate equivalent atoms: [#1] x + 1, y, z; [#2] x + 1/2, -y + 1/2, z; [#3] x, y, -z + 1/2; [#4] -x + 3/2, y - 1/2, -z; [#5] -x + 3/2, y - 1/2, z + 1/2.

## Experimental

**Syntheses.** The synthetic protocol of the 4,4'-tmbpt ligand is shown in Scheme S1.




Scheme S1. Preparation of the 4,4'-tmbpt ligand.

**Synthesis of 4-pyridylhydrazide.** Ethyl isonicotinate (15.1 g, 0.1 mol) was dissolved in 15 mL ethanol, and hydrazine monohydrate (5 g, 0.1 mol) was added drop-wise with stirring. The solution was then kept at -4 °C for 12 h, and crystalline 4-pyridylhydrazide was formed. The solid 4-pyrazylhydrazide was filtered off and

air-dried. Yield 12.4 g, 86.6%.

**Synthesis of 3,5-bis(pyridin-4-yl)-1H-1,2,4-triazole (4,4'-bpt).** 4-cyanopyridine (10.4 g, 0.1 mol) was dissolved in 30 mL methanol with sodium methoxide (5.4 g, 0.1 mol), and the mixture was heated under reflux for 3 h. 4-Pyridylhydrazide (13.8 g, 0.1 mol) was added to the solution and heated for 15 min. The solution was cooled to room temperature and the precipitate formed (yellow) was filtered off and air-dried for 2 h. The solid obtained was heated under reflux for 1 h in ethylene glycol to yield 4,4'-bpt. Yield 15.2 g, 68.2%.

**Synthesis of 4,4'-tmbpt.** 4,4'-bpt (6.69 g, 0.03 mol), $K_2CO_3$ (16.65 g, 0.12 mol), 1-(chloromethyl)-1,2,4-triazole hydrochloride salt (9.24 g, 0.06 mol) and N,N'-dimethylfomamide (50 mL) was heated at 90 °C for 12 h. After cooling to room temperature, the mixture was poured into 300 mL water and extracted with chloroform. The solution was dried with $Na_2SO_4$ anhydrous and filtered. Then the solvent was removed. Colorless crystals of the 4,4'-tmbpt ligands were obtained. Yield: 2.2 g, 24.2%.

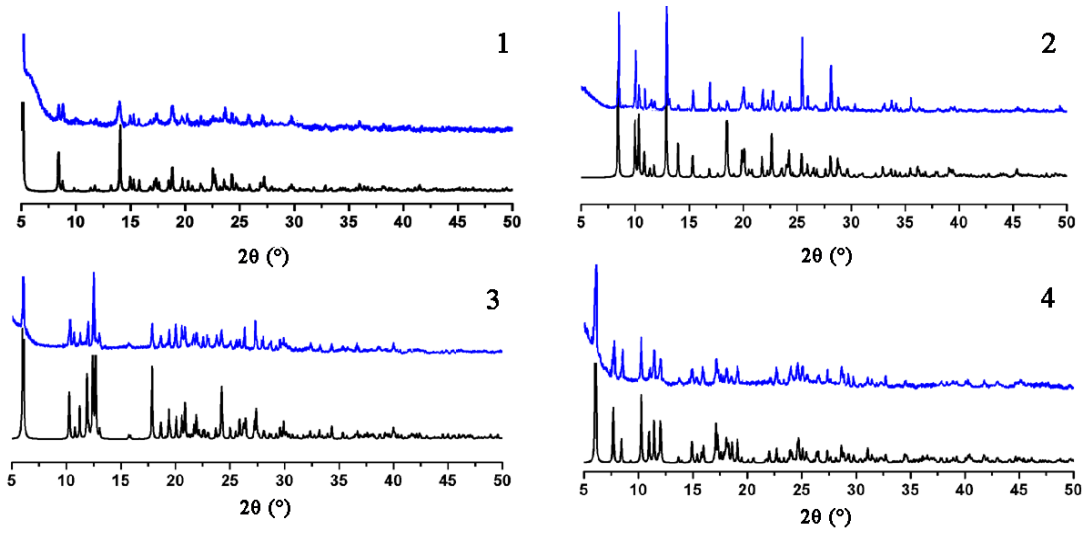



**Fig. S1** The simulated (black) and experimental (blue) PXRD patterns for compounds **1-4**.

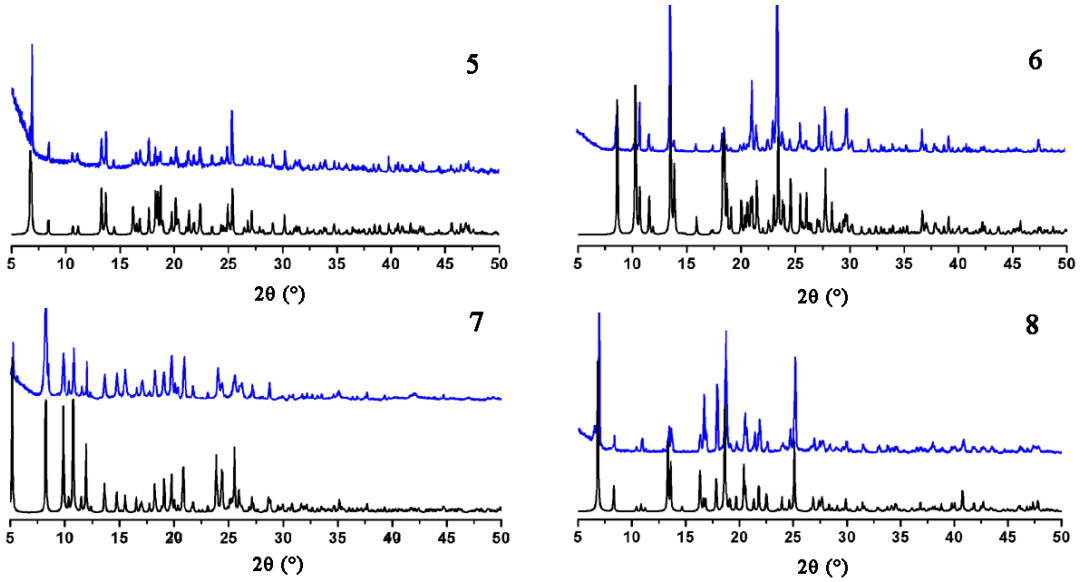



**Fig. S2** The simulated (black) and experimental (blue) PXRD patterns for compounds **5**-**8**.