Tuning the Structure of Metal Phosphonate Using Uncoordinating Methyl group: Syntheses, Structures and Properties of a Series of Metal Diphosphonates

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Table S1. Selected angles of compounds **1**-**8**.

1			
O(2)#1-Mn(1)-O(2)#2	179.03(10)	O(1)#3-Mn(1)-O(1W)	88.19(10)
O(2)#1-Mn(1)-O(1)#3	93.21(7)	O(1)-Mn(1)-O(1W)	172.85(9)
O(2)#2-Mn(1)-O(1)#3	87.43(7)	O(2)#1-Mn(1)-O(1W)#3	92.24(9)
O(2)#1-Mn(1)-O(1)	87.43(7)	O(2)#2-Mn(1)-O(1W)#3	87.06(9)
O(2)#2-Mn(1)-O(1)	93.21(7)	O(1)#3-Mn(1)-O(1W)#3	172.85(9)
O(1)#3-Mn(1)-O(1)	96.67(11)	O(1)-Mn(1)-O(1W)#3	88.19(10)
O(2)#1-Mn(1)-O(1W)	87.06(9)	O(1W)-Mn(1)-O(1W)#3	87.47(16)
O(2)#2-Mn(1)-O(1W)	92.24(9)		
2			
O(1W)-Co(1)-O(2W)	88.49(9)	O(6W)-Co(1)-O(3W)	87.33(9)
O(1W)-Co(1)-O(6W)	177.74(8)	O(4W)-Co(1)-O(3W)	172.55(8)
O(2W)-Co(1)-O(6W)	92.82(9)	O(1W)-Co(1)-O(5W)	92.27(9)
O(1W)-Co(1)-O(4W)	93.78(9)	O(2W)-Co(1)-O(5W)	175.97(9)
O(2W)-Co(1)-O(4W)	87.22(9)	O(6W)-Co(1)-O(5W)	86.30(9)
O(6W)-Co(1)-O(4W)	88.12(9)	O(4W)-Co(1)-O(5W)	96.67(8)
O(1W)-Co(1)-O(3W)	90.90(9)	O(3W)-Co(1)-O(5W)	88.92(8)
O(2W)-Co(1)-O(3W)	87.11(9)		
3			
O(1W)-Co(1)-O(1W)#1	180.0	O(3W)#1-Co(1)-O(2W)	90.44(15)
O(1W)-Co(1)-O(3W)#1	89.07(15)	O(3W)-Co(1)-O(2W)	89.56(15)
O(1W)#1-Co(1)-O(3W)#1	90.93(15)	O(1W)-Co(1)-O(2W)#1	91.03(17)
O(1W)-Co(1)-O(3W)	90.93(15)	O(1W)#1-Co(1)-O(2W)#1	88.97(17)
O(1W)#1-Co(1)-O(3W)	89.07(15)	O(3W)#1-Co(1)-O(2W)#1	89.49(15)
O(3W)#1-Co(1)-O(3W)	180.0	O(3W)-Co(1)-O(2W)#1	90.51(15)
O(1W)-Co(1)-O(2W)	88.97(17)	O(2W)-Co(1)-O(2W)#1	180.0
O(1W)#1-Co(1)-O(2W)	91.03(17)		
4			
O(1W)-Ni(1)-O(2W)	87.40(10)	O(6W)-Ni(1)-O(3W)	87.39(9)
O(1W)-Ni(1)-O(6W)	177.92(10)	O(4W)-Ni(1)-O(3W)	173.21(9)
O(2W)-Ni(1)-O(6W)	93.06(10)	O(1W)-Ni(1)-O(5W)	92.69(10)
O(1W)-Ni(1)-O(4W)	92.99(10)	O(2W)-Ni(1)-O(5W)	176.98(10)
O(2W)-Ni(1)-O(4W)	86.96(10)	O(6W)-Ni(1)-O(5W)	86.74(9)
O(6W)-Ni(1)-O(4W)	89.06(9)	O(4W)-Ni(1)-O(5W)	96.05(9)

O(1W)-Ni(1)-O(3W)	90.61(9)	O(3W)-Ni(1)-O(5W)	89.53(9)
O(2W)-Ni(1)-O(3W)	87.45(10)		
5			
O(2)-Cu(1)-O(2)#1	180.0	O(2)-Cu(1)-O(3)#3	87.99(11)
O(2)-Cu(1)-O(3)#2	92.01(11)	O(2)#1-Cu(1)-O(3)#3	92.01(11)
O(2)#1-Cu(1)-O(3)#2	87.99(11)	O(3)#2-Cu(1)-O(3)#3	180.0
6			
O(3W)-Zn(1)-O(3W)#1	180.0	O(1W)-Zn(1)-O(2W)	88.76(12)
O(3W)-Zn(1)-O(1W)	90.90(11)	O(1W)#1-Zn(1)-O(2W)	91.24(12)
O(3W)#1-Zn(1)-O(1W)	89.10(11)	O(3W)-Zn(1)-O(2W)#1	89.94(11)
O(3W)-Zn(1)-O(1W)#1	89.10(11)	O(3W)#1-Zn(1)-O(2W)#1	90.06(11)
O(3W)#1-Zn(1)-O(1W)#1	90.90(11)	O(1W)-Zn(1)-O(2W)#1	91.24(12)
O(1W)-Zn(1)-O(1W)#1	180.0	O(1W)#1-Zn(1)-O(2W)#1	88.76(13)
O(3W)-Zn(1)-O(2W)	89.94(11)	O(2W)-Zn(1)-O(2W)#1	180.0
O(3W)#1-Zn(1)-O(2W)	90.06(11)		
7			
O(1)-Zn(1)-O(1)#1	130.28(11)	O(1)-Zn(1)-O(1W)	105.88(7)
O(1)-Zn(1)-O(2W)	102.19(7)	O(1)#1-Zn(1)-O(1W)	105.88(7)
O(1)#1-Zn(1)-O(2W)	102.19(7)	O(2W)-Zn(1)-O(1W)	109.24(15)
8			
O(3)#1-Cd(1)-O(3)	179.14(14)	O(2)#2-Cd(1)-O(1W)	84.98(13)
O(3)#1-Cd(1)-O(2)#2	94.49(11)	O(2)#3-Cd(1)-O(1W)	167.80(13)
O(3)-Cd(1)-O(2)#2	86.06(10)	O(3)#1-Cd(1)-O(1W)#1	96.52(13)
O(3)#1-Cd(1)-O(2)#3	86.06(11)	O(3)-Cd(1)-O(1W)#1	82.87(13)
O(3)-Cd(1)-O(2)#3	94.49(11)	O(2)#2-Cd(1)-O(1W)#1	167.80(13)
O(2)#2-Cd(1)-O(2)#3	101.03(16)	O(2)#3-Cd(1)-O(1W)#1	84.98(13)
O(3)#1-Cd(1)-O(1W)	82.87(13)	O(1W)-Cd(1)-O(1W)#1	91.2(2)
O(3)-Cd(1)-O(1W)	96.52(13)		

Symmetry transformations used to generate equivalent atoms: For **1**: #1 x, -y, z-1/2; #2 -x+1, -y, -z+2; #3 -x+1, y, -z+3/2; #4 -x+3/2, -y+1/2, -z+2. For **3** and **6**: #1 -x+1,-y+1,-z. For 5: #1 -x+2, -y+2, -z; #2 -x+1, -y+2, -z; #3 x+1, y, z. For **7**: #1 x, -y+3/2, z For **8**: #1 -x+1,y,-z+1/2; #2 x,-y,z-1/2; #3 -x+1,-y,-z+1.

Table S2 Some O-H···O interactions found for compounds **1**-**8**.

D-H	H···A	D···A	<(DHA)	
1				
0.82	1.83	2.638(2)	168.2	O3-H3A···O1_$1
2				
0.82	1.89	2.674(3)	158.8	O2-H2A···O6_$1
0.85	1.82	2.667(3)	176.4	O1W-H2W···O5_$3
0.85	1.99	2.832(3)	168.5	O2W-H3W···O3W_$4
0.85	2.00	2.748(3)	146.0	O2W-H4W···O4W_$5
0.85	1.94	2.787(3)	171.4	O3W-H6W···O8W_$6

0.85	1.86	2.704(3)	177.0	O3W-H5W···O7W
0.85	1.98	2.681(3)	139.4	O4W-H7W···O3
0.85	1.86	2.707(3)	171.6	O6W-H11W···O3_$5
0.85	1.96	2.806(3)	174.7	O6W-H12W···O7W_$2
0.85	1.96	2.811(3)	175.9	O7W-H14W···O6_$3
0.85	1.94	2.787(3)	177.4	O8W-H15W···O3_$7
3				
0.82	1.66	2.445(5)	160.7	O1-H1A···O4_$1
0.82	1.74	2.545(5)	166.0	O2-H2A···O6_$2
0.82	1.76	2.578(5)	177.6	O5-H5A···O3_$3
0.85	1.87	2.701(7)	165.1	O1W-H1W···O4W
0.85	1.99	2.823(7)	167.7	O1W-H1W···O4W_$4
0.85	2.00	2.815(5)	161.6	O2W-H3W···O4_$5
0.85	1.98	2.785(5)	158.9	O3W-H5W···O6_$1
4				
0.82	1.89	2.668(3)	159.0	O2-H2A···O6_$1
0.85	1.82	2.672(3)	177.4	O1W-H2W···O5_$3
0.85	2.00	2.844(3)	169.5	O2W-H3W···O3W_$4
0.85	2.00	2.755(3)	146.7	O2W-H4W···O4W_$5
0.85	1.93	2.778(3)	171.7	O3W-H6W···O8W_$6
0.85	1.86	2.710(3)	176.3	O3W-H5W···O7W
0.85	1.98	2.680(3)	139.1	O4W-H7W···O3
0.85	1.85	2.696(3)	172.6	O6W-H11W···O3_$5
0.85	1.96	2.807(3)	175.5	O6W-H12W···O7W_$2
0.85	1.96	2.804(3)	175.3	O7W-H14W···O6_$3
0.85	1.93	2.782(3)	177.5	O8W-H15W···O3_$7
6				
0.82	1.66	2.449(3)	160.9	O1-H1A···O4_$1
0.82	1.75	2.555(3)	166.2	O2-H2A···O6_$2
0.82	1.77	2.588(3)	177.5	O5-H5A···O3_$3
0.85	1.87	2.703(5)	165.8	O1W-H1W···O4W
0.85	1.98	2.816(5)	167.3	O1W-H1W···O4W_$4
0.85	2.00	2.815(4)	161.7	O2W-H3W···O4_$5
0.85	1.98	2.794(3)	159.3	O3W-H5W···O6_$1
7				
0.82	1.79	2.545(2)	153.1	O2-H2A···O3_$1
0.85	1.85	2.696(2)	176.3	O1W-H1W···O3_$2
0.85	1.88	2.724(2)	173.6	O2W-H3W···O2_$3
8				
0.82	1.84	2.654(4)	169.3	O1-H1A···O2_$1

Operators for generating equivalent atoms: **1**: $1x, -y+1, z+1/2. **2** and **4**: $1 x, y-1, z; $2 x-1, y, z; $3 x+1, y, z; $4 –x+2, -y+1, -z; $5 –x+1, -y+1, -z; $6 –x+1, -y+2, -z; $7 x, y+1, z. **3** and **6**: $1 –x+2, -y+2, -z; $2 –x+2, y-1/2, -z+1/2; $3 –x+2, y+1/2, -z+1/2;

$4 –x+1, y-1/2, -z-1/2; $5 –x+2, -y+1, -z. **5**: $1 x-1, y, z; $2 –x+2, -y+1, -z; $3 x+1, y-1, z. 7: $1 x, -y, z-1/2; $2 –x+1, y, -z+1/2. **7**: $1 x-1/2, y, -z-1/2; $2 x+1/2, y, -z-1/2; $3 x+1/2, y, -z+1/2. **8**: $1 x, -y, z-1/2; $2 -x+1, y, -z+1/2; $3 x, -y+1, z-1/2.

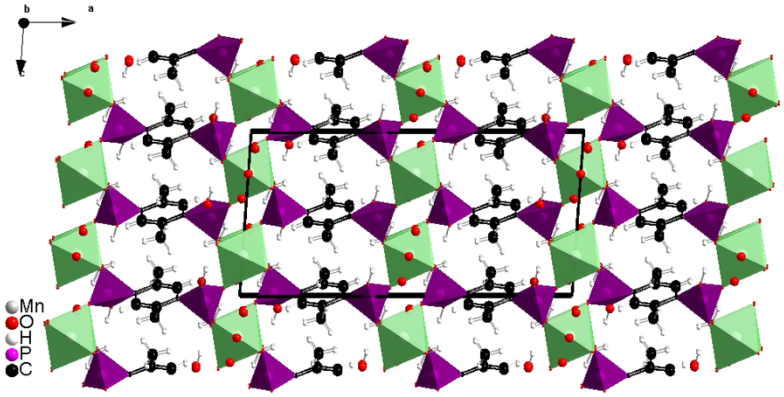

Figure S1. Three-dimensional packing diagram of compound **1** viewing along *b*-direction. The CPO_3 tetrahedrons and MnO_6 octahedrons are shaded in pink and green respectively. O-H···O interactions are shown as dash lines.

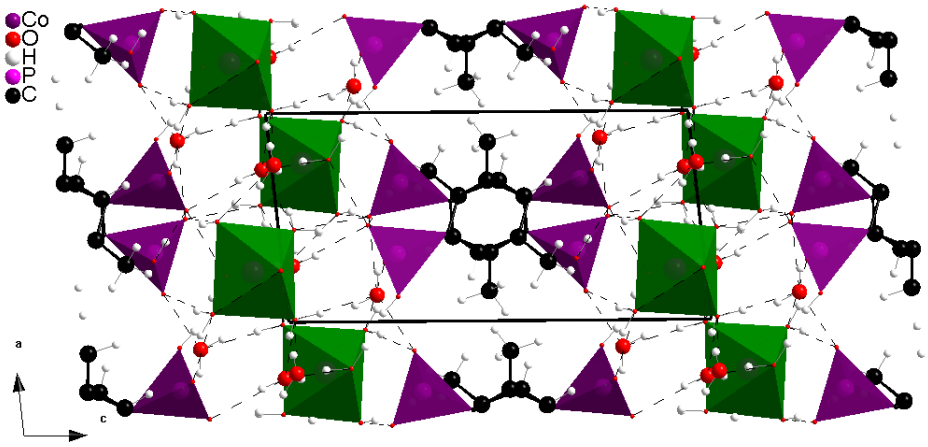

Figure S2. Three-dimensional packing diagram of compound **2** viewing along *b*-direction. The CPO_3 tetrahedrons and CoO_6 octahedrons are shaded in pink and green respectively. O-H···O interactions are shown as dash lines.

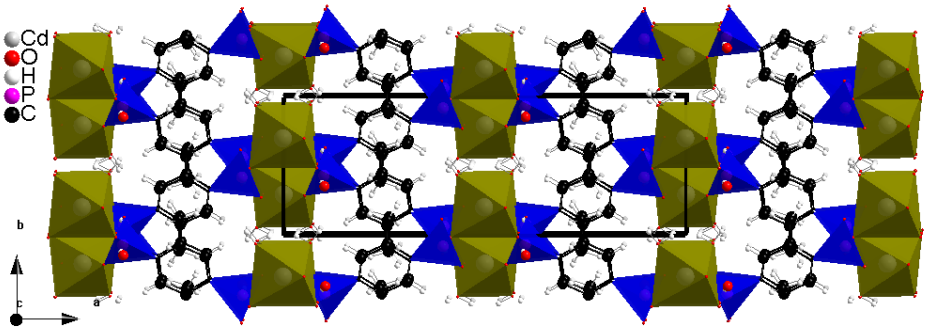

Figure S3. Three-dimensional packing diagram of compound **7** viewing along *c*-direction. The CPO_3 tetrahedrons and CdO_6 octahedrons are shaded in pink and green respectively.

Table S3. Comparison of the structures reported in this paper and those from literature synthesis condition used for 1,4-phenylendiphosphonic acid.

	Synthesis conditions		product	structure
Co	Literature method	$Co(en)_3Cl_3$ (0.3 mmol, 0.12 g), H_4L (0.3 mmol, 0.0798 g), 8 ml H_2O, pH=3-4, 140 °C, 54 h	Blue green powder and pink plate crystals	Unknown phases (see Figure S11)
	This paper	H_4L (0.0665 g), $Co(ac)_2{\cdot}4H_2O$ (0.0623 g), 3 mL H_2O, 160 °C, 3 days	Pink block crystals	Compound **2**
		H_4L (0.0665 g), $CoCl_2{\cdot}6H_2O$ (0.0595 g), 3 mL H_2O, 160 °C, 3 days	Pink block crystals	Compound **3**
Ni	Literature method	$NiSO_4{\cdot}6H_2O$ (0.2 mmol, 0.0525 g), H_4L (0.2 mmol, 0.0532 g), 8 ml H_2O, pH=3-4, 140 °C, 54 h	Clear solution	---
		$NiSO_4{\cdot}6H_2O$ (0.2 mmol, 0.0525 g), H_4L (0.2 mmol, 0.0532 g), 2 ml H_2O, pH=3-4, 140 °C, 54 h	Small green block crystals	Same to that of compound **4** (see Figure S12)
	This paper	H_4L (0.0665 g, 0.25 mmol), $NiSO_4{\cdot}H_2O$ (0.1586 g, 0.25 mmol), 10 mL H_2O, 160 °C, 3 days	Green block crystals	Compound **4**
Zn	Literature method	$ZnCl_2$ (1 mmol, 0.136 g), H_4L (0.5 mmol, 0.1331 g), 60 °C, 7 days	Small colorless crystals	Compound **7**
	This paper	H_4L (0.0665 g), $ZnCl_2$ (0.0623 g), 3 mL H_2O, 160 °C, 3 days		Compound **6**

Cu	Literature method	$CuSO_4 \cdot 5H_2O$ (1 mmol, 0.2497 g), H_4L (0.25 mmol, 0.0665 g), 60 °C 1 day	Blue plate crystals	Same to that of compound **5** (see Figure S13)
	This paper	H_4L (0.0887 g, 0.3333 mmol), $CuSO_4 \cdot 5H_2O$ (0.1665 g, 0.6666 mmol), and 10 mL H_2O, 160 °C, 3 days	Blue plate crystals	Compound 5

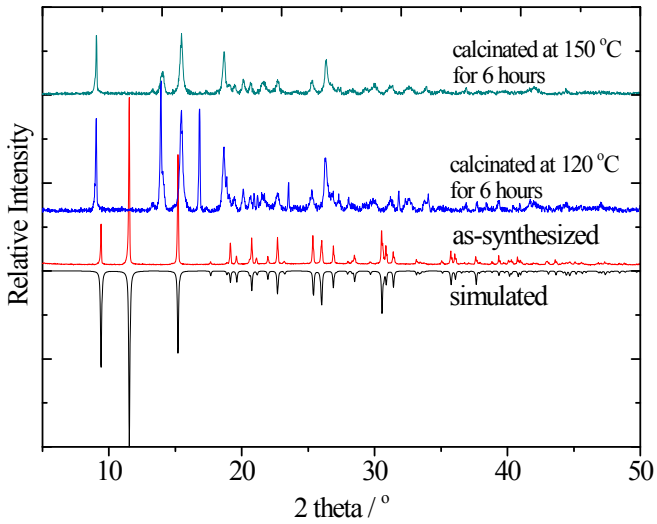

Figure S4. Comparison of simulated and experimental XRD pattern of compound **1**.

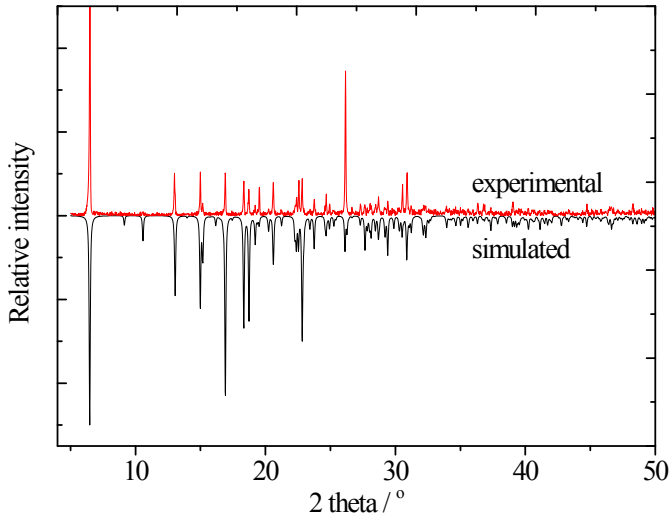

Figure S5. Comparison of simulated and experimental XRD pattern of compound **2**.

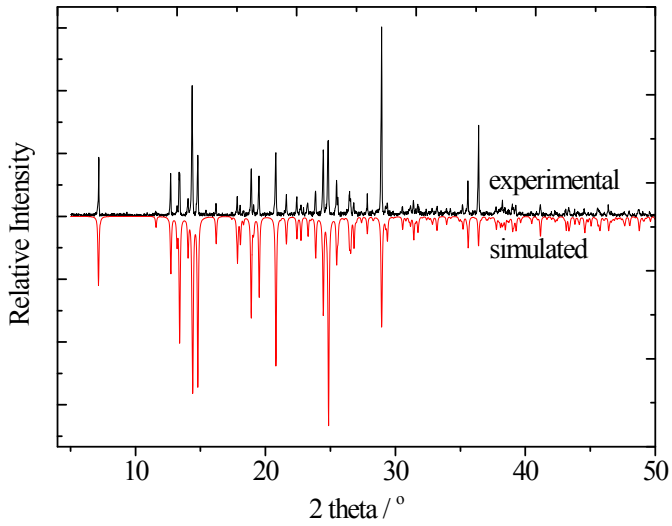

Figure S6. Comparison of simulated and experimental XRD pattern of compound **3**.

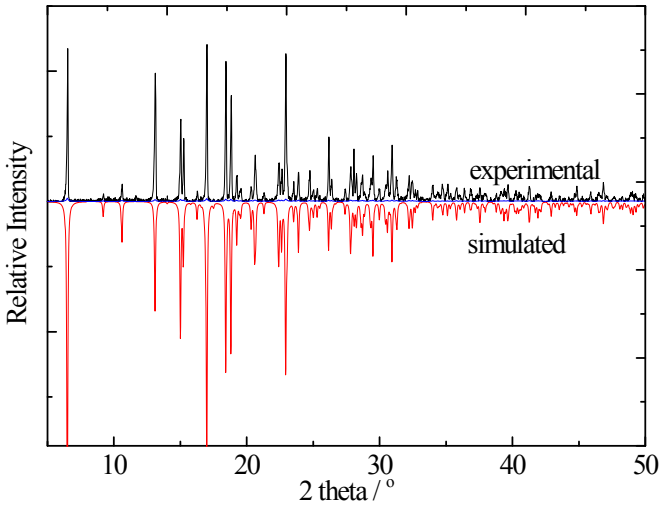

Figure S7. Comparison of simulated and experimental XRD pattern of compound **4**.

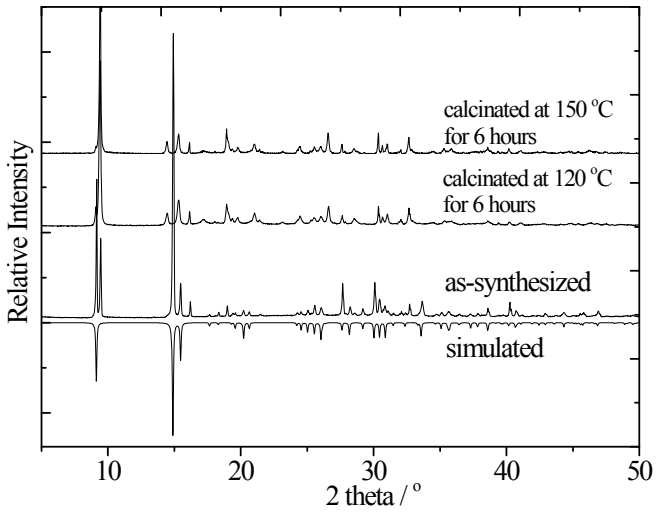

Figure S8. Comparison of simulated and experimental XRD pattern of compound **5**.

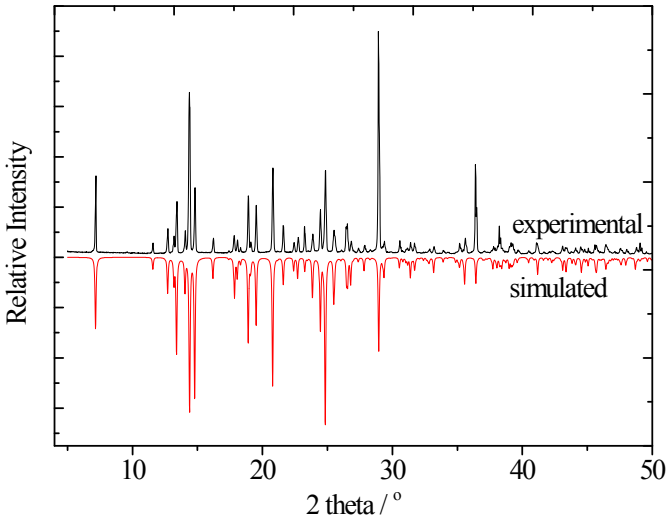

Figure S9. Comparison of simulated and experimental XRD pattern of compound **6**.

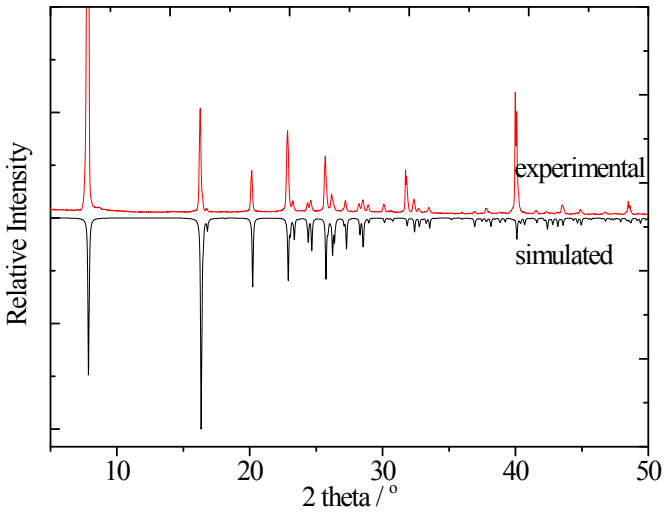

Figure S10. Comparison of simulated and experimental XRD pattern of compound **7**.

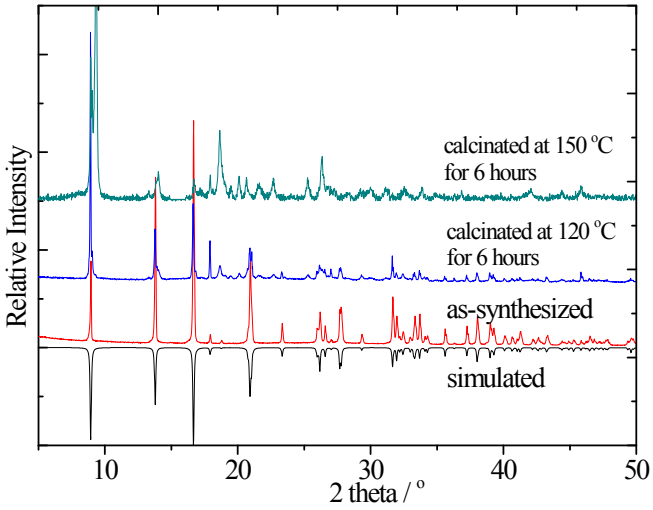

Figure S10. Comparison of simulated and experimental XRD pattern of compound **8**.

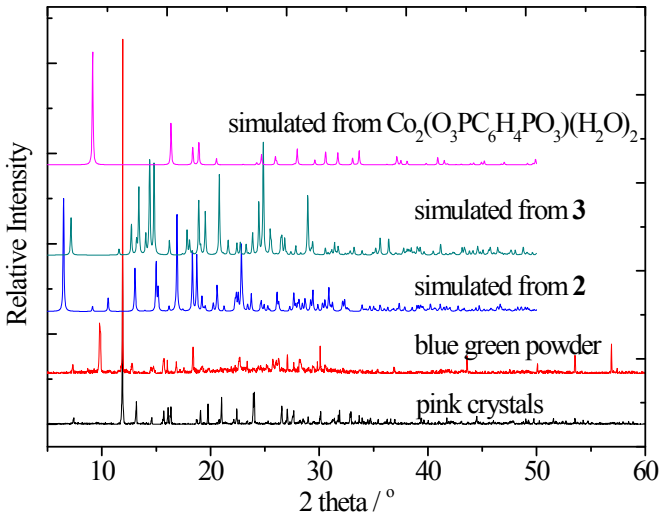

Figure S11. Comparison of the XRD pattern of the products synthesized from $Co(en)_3Cl_3$ and H4L and those from simulated compounds **2** and **3** and simulated from $Co_2(O_3PC_6H_4PO_3)(H_2O)_2$ reported in the literature (D.-K. Cao, S. Gao, L.-M. Zheng, *J. Solid State Chem.*, 2004, **177**, 2311-2315.).

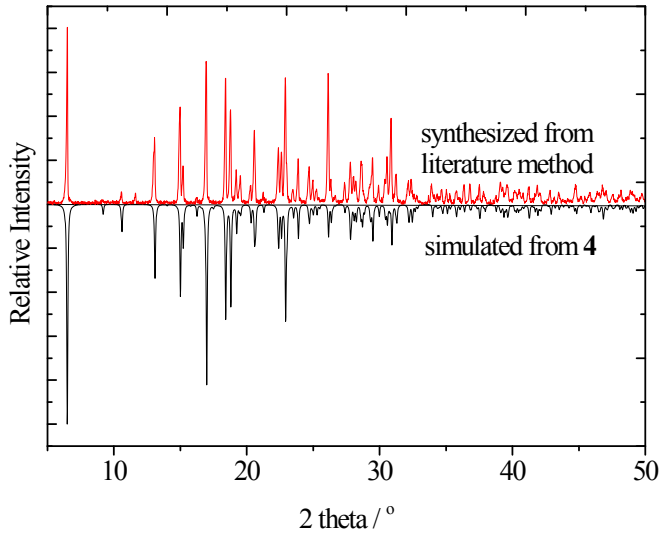

Figure S12. Comparison of the simulated and experimental XRD pattern of the product synthesized from $NiSO_4 \cdot 6H_2O$ and H_4L using literature method.

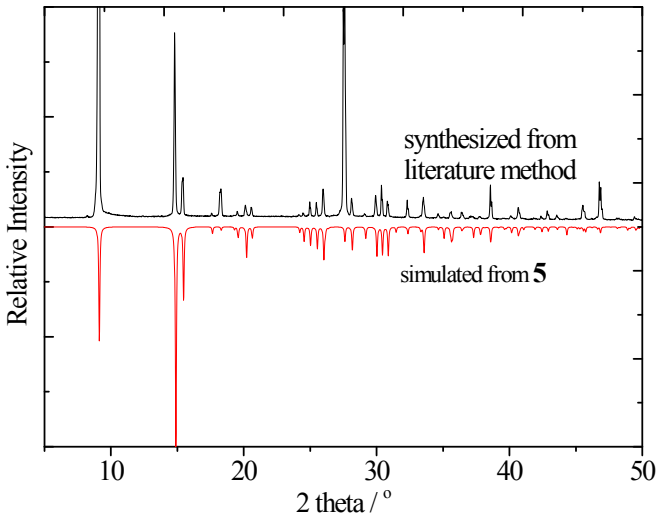

Figure S13. Comparison of the simulated and experimental XRD pattern of the product synthesized from $CuSO_4 \cdot 5H_2O$ and H4L using literature method.