Hydrothermal Synthesis of Five New Coordination Polymers Based on Benzophenone-2,4'-dicarboxylic Acid and N-Donor Spacers

Jiakun Xu,^[a,b] Xiaochun Sun,^[c] Yuhua Fan,^[b] Caifeng Bi,^{*[b]} and Mi Sun^{*[a]}

Keywords: Coordination polymer; Dicarboxylic acid; Nickel; Zinc; Crystal structure

Abstract. Five new coordination polymers, namely, $[Ni_2(L)_2(4,4'-bipy)_3]\cdot H_2O]_n$ (1), $[Ni_2(L)_2(O) (bpp)_2]_n$ (2), $[Zn(L)(bib)_{0.5}]_n$ (3), $[Zn(L)(PyBIm)]_n$ (4), and $[Zn_3(L)_2(OH)(im)]_n$ (5) $[H_2L = benzophenone-2,4'-dicarboxylic acid, 4,4'-bipy = 4,4'-bipyridine, bpp = 1,3-bis(4-pyridyl)propane, PyBIm = 2-(4-pyridyl)benzimidazole, and im = imidazole] were synthesized under hydrothermal conditions. Structure determination revealed that compound 1 is a 3D network and exhibits a 4-connected metal-organic framework with (4².6³.8) topology, whereas$

Introduction

During the past decades, the design and synthesis of metalligand coordination have attracted great interest due to their potential application in the fields of gas storage, molecular magnetism and luminescence.^[1–14] Great efforts have been devoted to the design of suitable organic ligands to construct new coordination polymers. Among the reported studies, coordination polymers with organic ligands that contain carboxylic groups are of special interest because the carboxylate ligands are able to adopt various coordination modes (such as monodentately, chelating, bis-monodentately and/or bridging), which results in a large diversity of the structures.^[15–20]

Bisphenyldicarboxylic acids such as 2,2'-bisphenyl dicarboxylic acid, 2,4'-bisphenyldicarboxylic acid, 3,3'-bisphenyldicarboxylic acid, 3,4'-bisphenyldicarboxylic acid, and 4,4'-bisphenyldicarboxylic acid, which are able to act as rigid multicarboxylate ligands, have been extensively investigated for their metal-ligand coordination.^[21–27] In contrast, semirigid dicarboxylate ligands with two benzene rings bridged by a nonmetallic atom (C, N, O, S) have been reported less often.^[28–31] Herein we present the syntheses and crystal structures of five coordination polymers with nickel(II) and zinc(II) ions based on benzophenone-2,4'-carboxylate and N-donor ligands.

* Dr. M. Sun, Dr. C. Bi

- E-Mail: hhsunmi@yeah.net
- [a] Yellow Sea Fisheries Research Institute Chinese Academy of Fishery Sciences Qingdao, 266071, P. R. China
- [b] Key Laboratory of Marine Chemistry Theory and Technology Ministry of Education Ocean University of China Qingdao, 266100, P. R. China
- [c] National Oceanographic Center Qingdao, 266071, P. R. China

compounds 2, 3, 4, and 5 are two-dimensional layer structures. In compounds 2–4, dinuclear metal clusters are formed through carboxylic groups. In compound 5, trinuclear metal clusters are formed through μ_3 -OH and carboxylic groups. The carboxylic groups exhibit three coordination modes in compounds 1–5: monodentately, bidentate-chelating, and *bis*-monodentately. Furthermore, the luminescent properties for compounds 3, 4, and 5 were investigated.

Results and Discussion

Description of Crystal Structures

$\{[Ni_2(L)_2(4,4'-bipy)_3)] \cdot H_2O\}_n$ (1)

The fundamental building unit of compound **1** contains one nickel(II) ion, two L ligands and three 4,4'-bipy ligands. The central Ni^{II} ion is coordinated by three oxygen atoms from two L ligands and three nitrogen atoms form three 4,4'-bipy ligands in an octahedral arrangement. The Ni–O and Ni–N bond lengths are in the range of 1.990(4)–2.178(3) Å and 2.076–2.115(4) Å, respectively. Each L anion adopts two coordination modes: monodentately and bidentately-chelating, which lead to form a 24-membered ring (Figure 1b). The 24-membered bimetal rings are further connected by 4,4'-bipy to form a three-dimensional structure. The separation of Ni–Ni in the ring is 8.748 Å. Topological analysis reveals compound **1** is a 4-connected net with ($4^2.6^3.8$) topology if the nickel ion is treated as a 4-connected node (Figure 1c).

$[Ni_2(L)_2(O)(bpp)_2]_n$ (2)

Crystallographic analysis reveals that compound $[Ni_2(L)_2(O)(bpp)_2]_n$ (2) crystallizes in the monoclinic group *C2/c*. The coordination environment around the Ni^{II} atom of compound 2 is represented in Figure 2a. One bridging oxygen atom and one bridging carboxylic group from L ligand connect two Ni^{II} ions into a dimeric structure, in which the Ni–Ni distance is 3.542 Å, and the angle of Ni–O–Ni is 116.49(9)°. The central nickel(II) atom is six-coordinate in a distorted octahedral arrangement. The equatorial positions are occupied by one carboxylic oxygen atom [Ni(1)–O(5) = 2.0124(16) Å], one oxygen atom [Ni(1)–O(5) = 2.0825(11) Å] and two nitrogen atoms from two bpp ligands [Ni(1)–N(1) = 2.0878(18) Å and Ni(1)–





Figure 1. (a) Coordination environment of the Ni^{II} ion in 1. Hydrogen atoms and free water molecules are omitted for clarity. (b) 24-Membered bimetal rings formed in 1. (c) Schematic description of the 4-connected 3D polymer with $(4^2.6^{3}.8)$ topology.

N(2) = 2.1062(18) Å], the axial positions are occupied by two carboxylic oxygen atoms [Ni(1)–O(1) = 2.0811(15) Å and Ni(1)–O(4) = 2.0637(15) Å]. Each ligand L adopts monodentate and *bis*-monodentate coordination modes, which lead to one-dimensional zigzag chains (Figure 2b). The 1D chains are bridged together by ligands to generate a 2D (4,4) layer framework (Figure 2c)

$[Zn(L)(bib)_{0.5}]_n$ (3)

Single-crystal X-ray reveals that complex 3 crystallizes in the triclinic space group $P\overline{1}$. In the asymmetry unit, exists an independent Zn^{II} ion, which is coordinated by four oxygen



Figure 2. (a) Coordination environment of the Ni^{II} ion in **2**. Hydrogen atoms are omitted for clarity. (b) View of the 1D chain formed by the dinuclear units in **2**. (c) 2D layer structure formed through bbp ligands.

atoms from four L ligands [Zn(1)-O(1) = 2.0585(18), Zn(1)-O(2) = 2.0477(17), Zn(1)-O(4) = 2.0515(18) and Zn(1)-O(5) = 2.0360(19) Å] and one nitrogen atom <math>[Zn(1)-N(1) = 2.0193(18) Å] from the bbi ligand to give a pentahedral arrangement (Figure 3a). Each L ligand adopts a *bis*-monodentate coordination mode, which leads to the formation of 1D strand that can be described as double zigzag chains. It is interesting to note that four μ_4 -carboxylic groups bridge the dinuclear central Zn^{II} atoms in syn-syn coordination, which lead to a paddle wheel secondary building units (SBUs). The Zn–Zn separation in the SBUs is 3.094 Å (Figure 3b). The 1D zigzag chains are further connected by bib ligands to form a 2D layer structure (Figure 3c).

$[Zn(L)(PyBIm)]_n$ (4)

Complex 4 crystallizes in the monoclinic space group $P2_1/c$. The zinc(II) ion holds the ZnO₄N pentahedral arrangement. The five atoms coordinated to the Zn^{II} ion come from one nitrogen atom of PyBIm ligand [Zn(1)–N(1) = 2.0143(17) Å] and four carboxylic oxygen atoms from three L ligands (Fig-





Figure 3. (a) Coordination environment of the Zn^{II} ion in 3. Hydrogen atoms are omitted for clarity. (b) 1D chain structure of 3. (c) 2D (4,4) layer structure of 3.

ure 4a). The ligand L acts as in a μ_3 -mode (μ_2 - η^1 : η^1 and μ_1 - η^1 : η^1) with one carboxylic group bridging two Zn^{II} atoms through a *bis*-monodentate mode and the other carboxylic group bridging the Zn^{II} atom in a bidentate chelating mode. The ligands L link the inorganic Zn^{II} nodes to form a 2D layer structure. The PyBIm ligand displays a monodentate coordination mode hanging on the both sides to the 2D layer (Figure 4b).

$[Zn_3(L)_2(\mu_3-OH)(im)]_n$ (5)

X-ray diffraction structure analysis reveals compound **5** crystallizes in the triclinic space group $P\bar{1}$ with three crystallographically independent zinc ions. The three zinc(II) atoms Zn1, Zn2, and Zn3 form a trinuclear unit through μ_3 -OH [Zn(1)–O(1) = 2.0201(13), Zn(2)–O(1) = 2.0610(13), and Zn(3)–O(1) = 1.9824(13) Å]. The atoms Zn1 and Zn3 are both coordinated by three oxygen atoms and one nitrogen atom [Zn(1)–N(2) = 1.9523(15) Å and Zn(3)–N(1) = 1.9537(15) Å] forming a distorted ZnO₃N tetrahedral arrangement. The central Zn2 atom adopts a distorted pentahedral ZnO₄N coordination. The Zn–O_{carboxylate} distances are in the range of

Figure 4. (a) Coordination environment of the Zn^{II} ion in 4. Hydrogen atoms are omitted for clarity. (b) The 2D layer structure of 4.

1.9486(13)–2.0829(12) Å, all of them are within the normal range as reported in other literature.^[30,31] The trinuclear clusters Zn₃ (μ_3 -OH) can be considered as the secondary building units (SBUs) for construction of the metal-organic architecture of compound **5**. From a topological viewpoint, the neighboring SBUs can be viewed 6-connected node with the Schläfli symbol of (3⁶.4⁶.5³) shown in Figure 5b.

Photoluminescent Properties

The solid-state fluorescent properties of H₂L and compounds **3–5** at room temperature are shown in Figure 6. The ligand H₂L exhibits a broad weak fluorescent emission centered at 394 nm with an excitation maximum at 280 nm. Compounds **3**, **4**, and **5** display a fluorescent emission at around 445 nm (λ_{ex} = 400 nm), 499 nm (λ_{ex} = 427 nm), and 485 nm (λ_{ex} = 412 nm), respectively. The free ligands bib and PyBIm display fluorescent emission bands at ca. 465 nm (λ_{ex} = 280 nm) and 492 nm (λ_{ex} = 370 nm), respectively.^[34–36] The much more enhanced fluorescent intensities of compound **3**, **4**, and **5** could be attributed to the increased rigidity of the ligand after coordination to the zinc(II) ions compared to that of the free ligands, which





Figure 5. (a) Coordination environment of the Zn^{II} ion in 5. Hydrogen atoms are omitted for clarity. (b) Schematic description of the 6-connected framework with $(3^6.4^6.5^3)$ topology.

effectively reduced the loss of energy.^[37-39] The shifts of emission bands occurring in complexes 3, 4, and 5 are probably due to the cooperative effects of intraligand emission and the ligand-to-metal charge transfer (LMCT).[30-42]



Figure 6. Solid-state emission spectra of H₂L and compounds 3-5 at room temperature.

Conclusions

Five metal-organic polymers were synthesized and characterized based on benzophenone-2,4'-carboxylate and N-donor ligands, which formed different frameworks. Furthermore, the solid state luminescent spectra demonstrated that complexes 3–5 could serve as good candidates for optical materials.

Experimental Section

Materials and Physical Measurements: All reagents and solvents employed were commercially available and were used as received without further purification. Elemental analysis was carried out with a Carlo Erba 1106 full-automatic trace organic elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer as a dry KBr pellet in the 400-4000 cm⁻¹ range. Solid-state fluorescence spectra were recorded with a F-4600 equipped with a xenon lamp and a quartz carrier at room temperature.

Synthesis of $[Ni_2(L)_2(4,4'-bipy)_3)] \cdot H_2O]_n$ (1): Compound 1 was prepared by hydrothermal reaction. A mixture of NiCl₂·6H₂O (0.119 g. 0.5 mmol), H₂L (0.135 g, 0.5 mmol), 4.4'-bipy(0.156 g, 0.5 mmol), NaOH (0.04 g, 1 mmol) and distilled water (15 mL) was heated to 160 °C for 96 h in a 25 mL stainless steel reactor with a Teflon liner, followed by slow cooling to room temperature. Yield 56% for 1 (based on Ni). Elemental analysis for C600H42Ni2N6O11: calcd. C 63.19; H 3.71; N 10.29%; found: C,63.12; H,3.70; N, 10.22%. IR (KBr): v = 3414 b, 3066 m, 1633 s, 1564 s, 1442 s, 1400 s, 1233 w, 1160 m, 862 m, 740 m, 664 w, 582 m cm⁻¹.

 $[Ni_2(L)_2(O)(bpp)_2]_n$ (2): The preparation of 2 was similar to that of 1 except that bpp (0.099g. 0.5 mmol) was used in place of 4,4'-bipy. Green crystals of 2 were collected in 42% (based on Ni). Elemental analysis for C₅₆H₄₄Ni₂N₄O₁₁: calcd. C 63.07; H 4.16; N 5.25 %; found: C 63.12; H 4.18; N 5.22%. **IR** (KBr): $\tilde{v} = 1624$ s, 1466 s, 1411 s, 1365 w, 1037 m, 996 m, 872 m, 764 m, 661 w, 581 m, 516 m cm⁻¹.

[Zn(L)(bib)_{0.5}]_n (3): A mixture of H₂L (0.135 g, 0.5 mmol), Zn(OAc)₂. 2H₂O (0.108 g, 0.5 mmol), bib (0.109 g, 0.5 mmol), NaOH (0.04 g, 1 mmol), and distilled water (15 mL) was heated to 160 °C for 96 h in a 25 mL stainless steel reactor with a Teflon liner, followed by slow cooling to room temperature. Colorless crystals of compound 3 were obtained in 53% yield (based on Zn). Elemental analysis for C21H17ZnN2O5: calcd. C 56.96; H 3.87; N 6.33%; found: C 56.93; H 3.84; N 6.32%. **IR** (KBr): $\tilde{v} = 1617$ s, 1455 s, 1388m, 1227 m, 1164 m, 1015 m, 948 w, 894 m, 814 m, 627 m, 557 m, 462 m cm⁻¹.

 $[Zn(L)(PyBIm)]_n$ (4): The preparation of compound 4 was similar to that of compound 3 except that PyBIm (0.098 g. 0.5 mmol) was used in place of bib. Colorless crystals of 4 were collected in 42% (based on Zn). Elemental analysis for C₂₇H₁₇ZnN₃O₅: calcd. C 61.32; H 3.24; N 7.95%; found: C 61.30; H 3.24; N 7.94%. IR (KBr): $\tilde{v} = 1609$ s, 1533 s, 1394 s, 1310 w, 1241 m, 1103 m,1016 m, 943 m, 834 m, 716 m, 694 w, 553 m cm⁻¹.

 $[Zn_3(L)_2(\mu_3-OH)(im)]_n$ (5): The preparation of compound 5 was similar to that of compound 3 except that im (0.068 g. 0.5 mmol) was used in place of bib. Colorless crystals of 5 were collected in 40% (based on Zn). Elemental analysis for $C_{33}H_{19}N_2O_{11}Zn_3{:}$ calcd. C 48.59; H 2.35; N 3.43%; found: C 48.56; H 2.34; N 3.45%. IR (KBr): $\tilde{v} = 1631$ s, 1470 s, 1402 s, 1344 m, 1257 m, 1075 m, 925 m, 874 w, 738 m cm⁻¹.

X-ray Crystallography: Diffraction intensity data of the single crystal of the five compounds were collected with a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) by using a ω -scan mode. Empirical absorption correction was applied using the SADABS programs.^[43] All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHEXL 97.^[44] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations, and their positions and



Table 1. Crystallographic data and structure refinement summary for complexes 1-5.

	1	2	3	4	5
Empirical formula	C ₆₀ H ₄₂ N ₆ Ni ₂ O ₁₁	C ₅₆ H ₄₄ Ni ₂ N ₄ O ₁₁	C ₂₁ H ₁₇ ZnN ₂ O ₅	C ₂₇ H ₁₇ ZnN ₃ O ₅	C ₃₃ H ₁₉ Zn ₃ N ₂ O ₁₁
Formula weight	1140.42	1066.37	442.74	528.81	815.61
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	C2/c	C2/c	P1	$P2_1/c$	<i>P</i> 1
Unit cell dimensions	a = 15.303(3) Å	a = 21.887(10) Å	a = 9.6099(7) Å	a = 11.505(7)Å	a = 10.949(6) Å
	b = 33.873 Å	b = 9.997(5) Å	b = 9.8590(7) Å	b = 9.076(6) Å	b = 12.293(7) Å
	c = 10.825(2) Å	c = 23.855(11) Å	c = 11.2613(8) Å $a = 90.9650(10)^{\circ}$	c = 24.058(14) Å	c = 12.519(7) Å $a = 76.987(7)^{\circ}$
	$\beta = 104.483^\circ$	$\beta=101.547(5)^\circ$	$\beta = 106.9690 (10)^{\circ}$ $\gamma = 108.6200 (10)^{\circ}$	$\beta=115.839(13)^\circ$	$\beta = 73.293(6)^{\circ}$ $\gamma = 80.099(7)^{\circ}$
Volume /Å ³	5433(2)	5114(3)	959.92(12)	2261.0(17)	1562.02(15)
Z	4	4	2	4	2
Calculated density / mg·m ⁻³	1.394	1.385	1.532	1.554	1.734
Independent reflections	2760	4699	3558	4324	6121
$[I > 2\sigma(I)]$					
F(000)	2352	2208	454	1080	818
θ range for data collection	1.20–27.45	1.74–27.48	1.90–27.49	1.88–27.48	2.19–27.53
Limiting indices	$-19 \le h \le 19$	$-18 \le h \le 28$	$-10 \le h \le 12$	$-14 \le h \le 13$	$-14 \le h \le 14$
e	$-28 \le k \le 43$	$-12 \leq k \leq 12$	$-12 \le k \le 10$	$-11 \leq k \leq 11$	$-15 \le k \le 12$
	$-13 \le l \le 13$	$-30 \le l \le 30$	$-12 \le l \le 14$	$-27 \le l \le 31$	$-13 \le l \le 16$
Goodness-of-fit on F^2	1.069	1.021	1.026	1.003	1.017
$R_{1}^{(a)} w R_{2}^{(b)} [I \ge 2\sigma(I)]$	$R_1 = 0.0595$	$R_1 = 0.0346$	$R_1 = 0.0359$	$R_1 = 0.0299$	$R_1 = 0.0234$
$R_1, R_2 [1 > 20(1)]$	$wR_2 = 0.1070$	$wR_2 = 0.0890$	$wR_2 = 0.0834$	$wR_2 = 0.0748$	$wR_2 = 0.0624$
$R_{a}^{a} w R_{b}^{b}$ (all data)	$R_1 = 0.1133$	$R_1 = 0.0459$	$R_1 = 0.0455$	$R_1 = 0.0381$	$R_1 = 0.0276$
n_1 , m_2 (an uata)	$w_{R} = 0.1165$	$m_1 = 0.0457$	$m_1 = 0.0433$ $m_2 = 0.0876$	$w_{R} = 0.0785$	$w_{R_{1}}^{R} = 0.0270$
Largest diff peak and	$WR_2 = 0.1105$	$wR_2 = 0.0933$	$wR_2 = 0.0070$	0.352 and 0.218	$WR_2 = 0.0044$
hole /e·Å ^{-3}	0.404 alla -0.421	0.500 allu-0.234	0.402 and -0.219	0.332anu -0.318	0.300 and-0.421

a) $R = \Sigma(||F_0| - |F_c||) / \Sigma |F_0|$. b) $wR = [\Sigma w (|F_0|^2 - |F_c|^2)^2 / \Sigma w (F_0^2)]^{1/2}$.

thermal parameters were fixed during the structure refinement. The crystallographic data and experimental details of structural analyses for coordination polymers are summarized in Table 1. Selected bond and angle parameters are listed in Table 2. The carbon atoms (C26, C27, C29, and C30) in the 4,4'-bipy ligand in compound **1** are disordered.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-822057, -822058, -822059, -822060, and -822061 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http:// www.ccdc.cam.ac.uk).

Acknowledgement

We thank the support of this work by National Natural Science Foundation of China (20971115 and 21071134), National High Technology Research and Development Program of China (No. 2011AA090703), the International Scientific and Technological Cooperation Projects of China (No. 2011DFB30250) and the Special Funds for the Basic R & D Program in the Central Non-profit Research Institutes (No. 20603022012018).

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Table 2. Selected bond lengths /Å and angles /° for complexes 1–5.

1			
Ni(1)-O(2)	1.990(4)	$Ni(1)-O(4)^{ii}$	2.112(3)
Ni(1) - N(1)	2.076(3)	Ni(1) - N(3)	2.115(4)
$Ni(1) - N(2)^{i}$	2.098(3)	$Ni(1) - O(5)^{ii}$	2.178(3)
O(2)-Ni(1)-N(1)	104.61(15)	O(2) - Ni(1) - N(3)	88.16(15)
$O(2)-Ni(1)-N(2)^{i}$	91.34(14)	N(1)-Ni(1)-N(3)	94.24(13)
$N(1)-Ni(1)-N(2)^{i}$	92.43(12)	$N(2)^{i} - Ni(1) - N(3)$	173.22(13)
$O(2)-Ni(1)-O(4)^{ii}$	96 23(13)	$O(4)^{ii} - Ni(1) - N(3)$	86 31(12)
$N(1)-Ni(1)-O(4)^{ii}$	159 16(15)	$O(2) - Ni(1) - O(5)^{ii}$	157.84(12)
$N(2)^{i} - Ni(1) - O(4)^{ii}$	87.03(12)	$N(1)-Ni(1)-O(5)^{ii}$	97 55(14)
	01.03(12)		77.00(11)
<u></u>			
Ni(1)–O(5)	2.0120(15)	Ni(1)-N(1)	2.0876(17)
$Ni(1) - O(4)^{i}$	2.0636(14)	$Ni(1)-N(2)^{iii}$	2.1059(16)
$Ni(1)-O(1)^{ii}$	2.0808(14)	$O(4) - Ni(1)^{i}$	2.0636(14)
Ni(1)–O(6)	2.0822(10)		
$O(5)-Ni(1)-O(4)^{i}$	89.30(7)	O(5)–Ni(1)–N(1)	177.55(6)
O(5)–Ni(1)–O(1) ⁱⁱ	88.17(7)	$O(4)^{i} - Ni(1) - N(1)$	92.23(6)
$O(4)^{i}-Ni(1)-O(1)^{ii}$	174.86(6)	$O(1)^{ii}-Ni(1)-N(1)$	90.14(6)
O(5)-Ni(1)-O(6)	91.77(6)	O(6)-Ni(1)-N(1)	90.01(6)
O(4) ⁱ -Ni(1)-O(6)	94.65(5)	O(5)–Ni(1)–N(2) ⁱⁱⁱ	87.40(7)
$O(1)^{ii}-Ni(1)-O(6)$	89.90(5)	$O(4)^{i} - Ni(1) - N(2)^{iii}$	88.25(6)
O(1) ⁱⁱ –Ni(1)–N(2) ⁱⁱⁱ	87.16(6)	N(1)-Ni(1)-N(2) ⁱⁱⁱ	90.74(7)
O(6)–Ni(1)–N(2) ⁱⁱⁱ	176.97(5)		
3			
$\overline{Zn(1)-N(1)}$	2.0193(18)	$Zn(1)-O(4)^{iii}$	2.0515(18)
$Zn(1) - O(5)^i$	2.0360(19)	Zn(1)-O(1)	2.0585(18)
$ZN(1) - O(2)^{ii}$	2.0477(17)		
$N(1)-Zn(1)-O(5)^{i}$	104.97(8)	$O(2)^{ii}$ -Zn(1)-O(4) ⁱⁱⁱ	87.87(8)
$N(1)-Zn(1)-O(2)^{ii}$	101.32(8)	N(1)-Zn(1)-O(1)	102.92(8)
$O(5)^{i}$ -Zn(1)-O(2) ⁱⁱ	89.80(9)	$O(5)^{i} - Zn(1) - O(1)$	85.00(9)
$N(1)-Zn(1)-O(4)^{iii}$	99.79(8)	$O(2)^{ii}-Zn(1)-O(1)$	155.74(8)
$O(5)^{i}$ -Zn(1)-O(4) ⁱⁱⁱ	155.11(7)	$O(4)^{iii}$ -Zn(1)-O(1)	87.02(8)
4			
$\overline{Zn(1)-O(1)}$	1.9294(14)	$Zn(1)-O(4)^{ii}$	2.0009(16)
$Zn(1) - O(5)^{i}$	1.9551(13)	Zn(1)-N(1)	2.0131(17)
$O(1)-Zn(1)-O(5)^{i}$	116.69(6)	O(1)-Zn(1)-N(1)	118.34(7)
$O(1)-Zn(1)-O(4)^{ii}$	94.30(6)	$O(5)^{i} - Zn(1) - N(1)$	110.08(6)
$O(5)^{i}$ -Zn(1)-O(4) ⁱⁱ	114.17(6)	$O(4)^{ii}$ –Zn(1)–N(1)	101.15(7)
5			
Zn(1)–O(2)	1.9486(13)	$Zn(2)-O(6)^{ii}$	1.9742(13)
$Zn(1) - N(2)^{i}$	1.9523(15)	$Zn(2) - O(1)1^{iii}$	2.0163(12)
$Zn(1) - O(5)^{ii}$	2.0201(14)	Zn(2) - O(1)	2.0610(13)
Zn(1) - O(1)	2.0201(13)	Zn(2) - O(3)	2.0656(13)
Zn(2) - O(7)	2.0829(12)	Zn(3) - O(8)	1.9560(14)
Zn(3) - N(1)	1.9537(15)	Zn(3) - O(1)	1.9824(13)
$Zn(3) = O(1)0^{iv}$	1.9561(14)		
$O(2) - Zn(1) - N(2)^{i}$	107.22(6)	$O(6)^{ii}$ -Zn(2)-O(1)1 ⁱⁱⁱ	112.87(6)
$O(2)-Zn(1)-O(5)^{ii}$	103.91(6)	$O(6)^{ii}-Zn(2)-O(1)$	98.00(5)
$N(2)^{i}-Zn(1)-O(5)^{ii}$	103.10(6)	$O(1)1^{iii}$ -Zn(2)-O(1)	149.12(6)
O(2) - Zn(1) - O(1)	109 40(5)	$O(6)^{ii} - Zn(2) - O(3)$	103.97(6)
$N(2)^{i} - Zn(1) - O(1)$	135 44(6)	$O(1)1^{iii}$ -Zn(2)-O(3)	80 47(5)
$O(5)^{ii}$ -Zn(1)-O(1)	91.92(6)	O(1) - Zn(2) - O(3)	93.17(5)
$O(6)^{ii} - Zn(2) - O(7)$	103 42(6)	$N(1) = 7n(3) = O(1)0^{iv}$	102 25(6)
$O(1)1^{iii} - Zn(2) - O(7)$	78 74(5)	N(1) - Zn(3) - O(1)O N(1) - Zn(3) - O(8)	111 59(6)
O(1) - 7n(2) - O(7)	93 95(5)	$\Omega(1)0^{iv} - 7n(3) - \Omega(8)$	104 35(7)
O(3) - Zn(2) - O(7)	150 40(5)	N(1) - Zn(3) - O(0)	114 96(6)
$O(1)0^{iv} - Zn(3) - O(1)$	117 97(6)	O(8) - Zn(3) - O(1)	105.35(5)
	*****		100.00(0)

Symmetry code for compounds: (1): (i) x+1/2, -y+1/2, z+1/2; (ii) -x+1, y, -z+3/2. (2) (i) -x+1, y, -z+1/2; (ii) x, y+1, z; (iii) -x+1/2, -y+1/2, -z+1/2; (i) x, y+1, z; (iii) -x, -y+2, -z+2; (iii) -x, -y+1, -z+2. (4) (i) x+1, -y+3/2, z+1/2; (ii) -x, y-1/2, -z+3/2. (5) (ii) -x+1, -y, -z; (iii) -x+1, -y, -z+1; (iv) x-1, y, z.



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Received: January 8, 2012 Published Online: ■ J. Xu, X. Sun, Y. Fan, C. Bi, * M. Sun* 1-8

Hydrothermal Synthesis of Five New Coordination Polymers Based on Benzophenone-2,4'-dicarboxylic Acid and N-Donor Spacers

