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Hydrothermal Synthesis, Structures, and Photoluminescent Properties of Benzenepentacarboxylate Bridged Networks Incorporating Zinc(II)–Hydroxide Clusters or Zinc(II)–Carboxylate Layers

Jing Wang, Zhuojia Lin, Yong-Cong Ou, Nai-Liang Yang, Yue-Hua Zhang, and Ming-Liang Tong*

MOE Key Laboratory of Synthetic Bioinorganic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China

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The first coordination compounds of partially or wholly deprotonated benzenepentacarboxylic acid (H_5L) were synthesized in the presence or absence of auxiliary 2,2′-bipyridyl (2,2′-bpy) and 1,10-phenanthroline (phen) ligands, and their crystal structures and photoluminescent properties were characterized. Their formulas are $[Zn_6(\mu_3\text{-}OH)_2(L)_2(H_2O)_6]_n$ (**1**), $[Zn_5(\mu_3\text{-}OH)_2(HL)_2(2,2'\text{-bpy})_2]_n$ (**2**), $[Zn_2(HL)(phen)_2(H_2O)_2]_n$ (**3**), and $[Zn_5(L)_2(phen)_4(H_2O)_3]_n\cdot 2nH_2O$ (**4**). Both **1** and **2** are three-dimensional (3D) zinc(II)–hydroxide cluster based coordination frameworks. **1** contains distorted chairlike hexanuclear $Zn_6(\mu_3\text{-}OH)_2$ cluster units as secondary building blocks. Each $Zn_6(\mu_3\text{-}OH)_2$ unit connects six others through the three-connected nodes of L^{5-} ligands into a 3D rigid and condensed coordination network, whereas in **2**, each pentanuclear $Zn_5(\mu_3\text{-}OH)_2$ unit connects the other six ones through the three-connected $[HL]^{4-}$ nodes into a 3D network in the simple cubic packing mode. **3** has two-dimensional (2D) Zn(II)–carboxylate supramolecular layers constructed from a one-dimensional (1D) coordination chain structure by hydrogen bonds of the water and $\mu_5\text{-}[HL]^{4-}$ bridges, whereas **4** has 2D coordination layers composed of Zn(II) and $\mu_8\text{-}L^{5-}$ bridges. The adjacent coordination assemblies in **3** and **4** are further extended by hydrogen bonds and $\pi\cdots\pi$ interactions into 3D supramolecular architectures. **1**–**4** are photoluminescent active materials, and their photofluorescent properties are closely related to their intrinsic structure arrangements.

Introduction

The construction by design of metal−organic frameworks (MOFs) using various secondary building units (SBUs) connected through coordination bonds, supramolecular contacts (hydrogen bonding, $\pi\cdots\pi$ stacking, etc.), or their combination, has been an increasingly active research area. Considerable progress has been achieved in supramolecular and material chemistry.[1,2] In recent years, the design and controlled assembly of coordination polymers based on metal clusters and multifunctional bridging ligands are of great interest owing to their versatile intriguing architectures and topologies as well as potential applications in, for example, smart optoelectronics, magnetism, microporosity, and biomimetic materials.[3,4] In most cases, multinuclear metal cluster SBUs can direct the formation of novel geometry and topology of the architectures and help to retain the rigidity

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* To whom correspondence should be addressed. E-mail: tongml@mail.sysu.edu.cn.

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of the networks.[5] A number of carboxylate-bridged metal cluster SBUs have been utilized to build up extended coordination frameworks. Among these compounds, frameworks from multinuclear zinc cluster SBUs, including dinuclear (Zn_2),[6] trinuclear (Zn_3),[7] tetranuclear (Zn_4),[8a−d] pentanuclear (Zn_5),[8e,f] hexanuclear (Zn_6),[9] heptanuclear (Zn_7),[9c,10] and octanuclear clusters (Zn_8),[11] have particularly attracted great interest and have been investigated widely. Here we report the hydrothermal chemistry of zinc−benzenepentacarboxylate−hydroxide cluster based coordination polymers.

In the rational design and synthesis of metal−organic coordination compounds, several factors are always taken into consideration, such as the coordination nature of metal ions, the functionality, flexibility, and symmetry of organic ligands, and the template effect of structure-directing agents.[12] Aromatic polycarboxylate ligands such as 1,2,3-benzenetricarboxylic acid,[13] trimesic acid,[14] 1,2,4,5-benzenetetracarboxylic acid,[15] and mellitic acid[16] have been extensively employed in the preparation of various MOFs.[13] Nevertheless, 1,2,3,4,5-benzenepentacarboxylic acid (H_5L) has, to our knowledge, not been used in materials science to date, although similar to other benzenepolycarboxylic acids, it is expected to be a versatile ligand in the construction of functional MOFs. We have been particularly concerned in photoluminescent properties of coordination polymer solids in different coordination architectures and topologies. By extensive investigation and comparison of coordination polymers from various carboxylic acid ligands, we hope to delineate the influence of geometry and topology of coordination frameworks on photoluminescence and finally prepare and design materials with excellent photoactivity and stability. The unique five carboxylic groups of H_5L offer a variety of coordination/hydrogen-bonding modes and provide abundant structural motifs for the construction of multidimensional coordination polymers[13−16] while, learning from our recent study on metal mellitate coordination ploymers,[17] its relatively rigid structure is more useful to produce coordination polymers with active photoluminescent properties when reacted with d^{10} metals such as Zn(II) or Cd(II). Thus, it is interesting to study the hydrothermal and coordination chemistry of this novel ligand and explore the photoluminescence of the resulted coordination frameworks. In this work, two three-dimensional (3D) networks $[Zn_6(\mu_3\text{-}OH)_2(L)_2(H_2O)_6]_n$ (**1**) and $[Zn_5(\mu_3\text{-}OH)_2(HL)_2(2,2'\text{-bpy})_2]_n$ (**2**), one-dimensional (1D) chain $[Zn_2(HL)(phen)_2(H_2O)_2]_n$ (**3**), and two-dimensional (2D) sheet $[Zn_5(L)_2(phen)_4(H_2O)_3]_n\cdot 2nH_2O$ (**4**) were prepared under different hydrothermal conditions. Strong fluorescent emissions were found for all of the different coordination architectures.

Experimental Section

Materials and Physical Measurements. The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 4000−400 cm^{-1} on a Bio-Rad FTS-7 spectrometer. X-ray powder diffraction (XRPD) intensities for **1**−**4** were measured at 293 K on a Rigaku D/max-IIIA diffractometer (Cu Kα, λ

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Table 1. Crystal Data and Structure Refinements for **1**−**4**

	1	**2**	**3**	**4**
formula	$C_{11}H_8O_{14}Zn_3$	$C_{42}H_{22}N_4O_{22}Zn_5$	$C_{35}H_{22}N_4O_{12}Zn_2$	$C_{70}H_{44}N_8O_{25}Zn_5$
fw	560.28	1261.49	821.31	1723.98
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$C2/c$	$C2/c$	$C2/c$	$P\bar{1}$
a (Å)	19.643(2)	17.0298(14)	20.065(2)	12.4083(8)
b (Å)	10.3470(11)	13.9683(11)	7.9324(9)	16.1136(10)
c (Å)	13.4879(15)	19.3375(16)	19.605(2)	17.3138(11)
α (deg)	90.00	90.00	90.00	72.326(1)
β (deg)	98.476(2)	101.635(2)	94.863(2)	83.787(1)
γ (deg)	90.00	90.00	90.00	85.596(1)
vol (Å^3)	2711.5(5)	4505.4(6)	3109.3(6)	3275.5(4)
Z	8	4	4	2
D_c (g cm^{-3})	2.745	1.860	1.755	1.748
μ (mm^{-1})	5.360	2.716	1.622	1.899
reflns collected	4972	9459	5246	16539
unique reflns (R_{int})	2520 (0.0258)	4402 (0.0376)	2951 (0.0283)	11732 (0.0398)
params	281	334	253	988
S on F^2	1.011	1.031	1.047	1.066
R_1,^{a} wR_2^{b} ($I > 2\sigma(I)$)	0.0315, 0.0711	0.0476, 0.1173	0.0619, 0.1568	0.0726, 0.1489
R_1,^{a} wR_2^{b} (all data)	0.0407, 0.0763	0.0599, 0.1244	0.0756, 0.1658	0.1077, 0.1681

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

$= 1.54056$ Å), and the calculated patterns were generated with PowderCell. The crushed polycrystalline powder samples were prepared by crushing the crystals and scanned from 5° to 60° with a step of 0.1°/s. Thermal gravimetry (TG) of **1**−**4** were carried out with a NETZSCH TG209F3 thermal gravimetric analyzer heated from 20 to 600 °C with the rate of 10 °C/min. The emission/excitation spectra and the lifetime were measured on an Edinburgh FLS-920 spectrophotometer equipped with a continuous Xe-900 xenon lamp, an nF900 nanosecond flash lamp.

Hydrothermal Synthesis. All compounds were carried out by hydrothermal synthetic method.

$[Zn_6(\mu_3\text{-}OH)_2(L)_2(H_2O)_6]_n$ (1). A mixture of NaOH (0.080 g, 2.0 mmol) in H_2O (5.0 mL) and H_5L (0.077 g, 0.25 mmol) in H_2O (5.0 mL) was added to an aqueous solution (5.0 mL) of $Zn(NO_3)_2\cdot 6H_2O$ (0.297 g, 1.0 mmol) and stirred. The resultant solution was heated in a stainless steel reactor with Teflon liner at 175 °C for 90 h and then was cooled at a rate of ca. 5 °C·h^{-1} to give colorless needle-like crystals of **1** in pure phase (in ca. 40% yield based on H_5L), which were obtained, isolated by filtration, and washed with water. The sample was allowed to air-dry and was stable indefinitely in air. Anal. Calcd (Found) (%) $C_{11}H_8O_{14}Zn_3$: C, 23.58 (22.77); H, 1.44 (1.39). IR (4000−400 cm^{-1}): 3541m, 3441m, 1616vs, 1566vs, 1453s, 1359s, 1315m, 1199vw, 1156vs,1091vs, 1000vs, 902w, 836w, 785w, 730m, 647w, 560w, 503w.

$[Zn_5(\mu_3\text{-}OH)_2(HL)_2(2,2'\text{-}bpy)_2]_n$ (2). Similar to the preparation of **1**, the hydrothermal reaction of $Zn(NO_3)_2\cdot 6H_2O$ (0.297 g, 1.0 mmol), H_5L (0.077 g, 0.25 mmol), 2,2′-bpy (0.076 g, 0.50 mmol), NaOH (0.040 g, 1.0 mmol), and water (15 mL) in a molar ratio of 4:1:2:4:300 was performed at 175 °C for 60 h and then was cooled at a rate of ca. 5 °C·h^{-1} to give colorless block crystals of **2** in pure phase (in ca. 75% yield based on H_5L), which were obtained, isolated by filtration, and washed with water. The sample was allowed to air-dry and was stable indefinitely in air. Anal. Calcd (Found) (%) $C_{21}H_{11}N_2O_{11}Zn_{2.50}$: C, 39.99 (39.18); H, 1.76 (1.69); N, 4.44 (4.37). IR (4000−400 cm^{-1}): 3593s, 3425w, 1724vs, 1600s, 1560s, 1472s, 1463s, 1382s, 1348s, 1273vs, 1172w, 1146m, 1021w, 882s, 767vs, 731s, 682s, 630m, 601m, 550m, 471s.

$[Zn_2(HL)(phen)_2(H_2O)_2]_n$ (3). Similar to the synthesis of **1**, the hydrothermal reaction of $Zn(NO_3)_2\cdot 6H_2O$ (0.297 g, 1.0 mmol), H_5L (0.077 g, 0.25 mmol), phen (0.099 g, 0.50 mmol), NaOH (0.040 g, 1.0 mmol), and water (15 mL) was performed at 140 °C for 60 h and then was cooled at a rate of ca. 5 °C·h^{-1}. The resulting colorless block crystals were mechanically separated and then washed with water and absolute alcohol to give a ca. 60% yield of **3** (based on H_5L). The sample was allowed to air-dry and was stable indefinitely in air. Anal. Calcd (Found) (%) $C_{17.50}H_{11}N_2O_6Zn$: C, 51.18 (50.52); H, 2.70 (2.86); N, 6.82 (6.77). IR (400−4000 cm^{-1}): 3352w, 3062w, 1735vs, 1630m, 1580w, 1555w, 1519w,1461w, 1429w, 1391w, 1247s, 1183s, 1142m, 1103w, 1050w, 991w, 895m, 858s, 823s, 784m, 727vs, 680m, 645s, 606m, 531w, 460w.

$[Zn_5(L)_2(phen)_4(H_2O)_3]_n\cdot 2nH_2O$ (4). Similar to the synthesis of **1**, the hydrothermal reaction of $Zn(NO_3)_2\cdot 6H_2O$ (0.297 g, 1.0 mmol), H_5L (0.077 g, 0.25 mmol), phen (0.099 g, 0.50 mmol), NaOH (0.080 g, 2.0 mmol), and water (15 mL) was performed at 140 °C for 120 h and then was cooled at a rate of ca. 5 °C·h^{-1}. The resulting colorless block crystals were mechanically separated and then washed with water and absolute alcohol to give a ca. 40% yield of **4** (based on H_5L). The sample was allowed to air-dry and was stable indefinitely in air. Anal. Calcd (Found) (%) $C_{70}H_{44}N_8O_{25}Zn_5$: C, 48.76 (48.56); H, 2.57 (2.43); N, 6.50 (6.35). IR (400−4000 cm^{-1}): 3411s, 3068w, 1629vs, 1588vs, 1517m, 1454s, 1427s, 1351s, 1223w, 1146w, 1104w, 1051w, 902w, 852s, 779w, 727vs, 644w, 620w, 560w, 427w.

X-ray Crystallography. Diffraction intensities of **1**−**4** were collected on a Bruker Apex CCD area-detector diffractometer (Mo Kα, $\lambda = 0.71073$ Å). Absorption corrections were applied by using multiscan program SADABS.[18] The structures were solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package.[19] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C−H 0.93 Å); the aqua and carboxyl hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Crystal data as well as details of data collection and refinements for **1**−**4** are summarized in Table 1. Selected bond distances and bond angles are listed in Tables 2−5.

Results and Discussion

Synthesis. Hydrothermal synthesis is a straightforward and effective method for the preparation of metal hydroxide-

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Table 2. Bond Lengths (angstroms) and Angles (deg) for **1**[a]

Zn(1)−O(11)	2.066(3)	Zn(2)−O(4*d*)	2.036(3)
Zn(1)−O(2w)	2.076(3)	Zn(2)−O(2*d*)	2.335(3)
Zn(1)−O(6)	2.081(3)	Zn(2)−Zn(3)	3.1424(7)
Zn(1)−O(3*a*)	2.086(3)	Zn(3)−O(8*e*)	2.036(3)
Zn(1)−O(1w)	2.093(3)	Zn(3)−O(11)	2.057(3)
Zn(1)−O(1*b*)	2.137(3)	Zn(3)−O(10*c*)	2.062(3)
Zn(2)−O(9*c*)	1.956(3)	Zn(3)−O(5)	2.064(3)
Zn(2)−O(2*b*)	1.980(2)	Zn(3)−O(3w)	2.077(3)
Zn(2)−O(11)	2.013(3)		
O(11)−Zn(1)−O(2w)	93.99(11)	O(9*c*)−Zn(2)−O(2*d*)	86.49(10)
O(11)−Zn(1)−O(6)	95.21(10)	O(2*b*)−Zn(2)−O(2*d*)	76.67(10)
O(2w)−Zn(1)−O(6)	90.70(12)	O(11)−Zn(2)−O(2*d*)	162.80(11)
O(11)−Zn(1)−O(3*a*)	90.72(11)	O(4*d*)−Zn(2)−O(2*d*)	81.99(10)
O(2w)−Zn(1)−O(3*a*)	171.73(12)	O(9*c*)−Zn(2)−O(4*d*)	111.25(11)
O(6)−Zn(1)−O(3*a*)	82.09(11)	O(2*b*)−Zn(2)−O(4*d*)	125.79(11)
O(11)−Zn(1)−O(1w)	171.48(12)	O(11)−Zn(2)−O(4*d*)	82.26(11)
O(2w)−Zn(1)−O(1w)	86.84(12)	O(8*e*)−Zn(3)−O(11)	89.12(11)
O(6)−Zn(1)−O(1w)	93.25(12)	O(8*e*)−Zn(3)−O(10*c*)	100.04(11)
O(3a)−Zn(1)−O(1w)	89.51(11)	O(11)−Zn(3)−O(10*c*)	91.44(11)
O(11)−Zn(1)−O(1*b*)	88.28(10)	O(8*e*)−Zn(3)−O(5)	100.60(11)
O(2w)−Zn(1)−O(1*b*)	92.23(12)	O(11)−Zn(3)−O(5)	100.77(11)
O(6)−Zn(1)−O(1*b*)	175.28(10)	O(10*c*)−Zn(3)−O(5)	156.11(11)
O(3a)−Zn(1)−O(1*b*)	94.70(11)	O(8*e*)−Zn(3)−O(3w)	95.16(12)
O(1w)−Zn(1)−O(1*b*)	83.22(12)	O(11)−Zn(3)−O(3w)	172.71(12)
O(9*c*)−Zn(2)−O(2*b*)	116.36(12)	O(10*c*)−Zn(3)−O(3w)	82.01(12)
O(9*c*)−Zn(2)−O(11)	105.71(11)	O(5)−Zn(3)−O(3w)	84.27(12)
O(2*b*)−Zn(2)−O(11)	107.40(11)	Zn(2f)−O(2)−Zn(2d)	103.33(10)

[a] Symmetry codes: (*a*) $x + {}^{1}/_{2}, y + {}^{1}/_{2}, z$; (*b*) $-x - {}^{1}/_{2}, y + {}^{1}/_{2}, -z + {}^{1}/_{2}$; (*c*) $-x, y, -z + {}^{1}/_{2}$; (*d*) $x + {}^{1}/_{2}, -y + {}^{1}/_{2}, z + {}^{1}/_{2}$; (*e*) $x - {}^{1}/_{2}, -y + {}^{1}/_{2}, z - {}^{1}/_{2}$; (*f*) $-x - {}^{1}/_{2}, y - {}^{1}/_{2}, -z + {}^{1}/_{2}$.

Table 3. Bond Lengths (angstroms) and Angles (deg) for **2**[a]

Zn(1)−O(9*a*)	2.042(3)	Zn(2)−O(11)	1.984(3)
Zn(1)−O(9*b*)	2.042(3)	Zn(2)−O(8*b*)	2.009(3)
Zn(1)−O(2)	2.086(3)	Zn(3)−N(1)	2.203(4)
Zn(1)−O(2*c*)	2.086(3)	Zn(3)−N(2)	2.060(4)
Zn(1)−O(11)	2.158(3)	Zn(3)−O(11)	1.985(3)
Zn(1)−O(11*c*)	2.158(3)	Zn(3)−O(1)	1.995(3)
Zn(2)−O(10*a*)	1.942(3)	Zn(3)−O(7*b*)	2.013(3)
Zn(2)−O(6*d*)	1.949(3)		
O(9*a*)−Zn(1)−O(9*b*)	90.9(2)	O(6*d*)−Zn(2)−O(11)	125.66(14)
O(9*a*)−Zn(1)−O(2)	167.32(13)	O(10*a*)−Zn(2)−O(8*b*)	95.58(15)
O(9*b*)−Zn(1)−O(2)	89.45(13)	O(6*d*)−Zn(2)−O(8*b*)	100.89(14)
O(9*b*)−Zn(1)−O(2*c*)	167.32(13)	O(11)−Zn(2)−O(8*b*)	99.92(15)
O(2)−Zn(1)−O(2*c*)	92.98(19)	O(11)−Zn(3)−O(1)	110.23(13)
O(9*a*)−Zn(1)−O(11*c*)	86.44(13)	O(11)−Zn(3)−O(7*b*)	91.77(15)
O(2)−Zn(1)−O(11*c*)	80.92(13)	O(1)−Zn(3)−O(7*b*)	95.14(15)
O(9*a*)−Zn(1)−O(11)	96.16(13)	O(11)−Zn(3)−N(2)	145.81(17)
O(9*b*)−Zn(1)−O(11)	86.43(13)	O(1)−Zn(3)−N(2)	103.43(17)
O(2)−Zn(1)−O(11)	96.52(12)	O(7*b*)−Zn(3)−N(2)	91.06(16)
O(2*c*)−Zn(1)−O(11)	80.92(13)	O(11)−Zn(3)−N(1)	99.49(16)
O(11*c*)−Zn(1)−O(11)	176.32(19)	O(1)−Zn(3)−N(1)	85.77(17)
O(10*a*)−Zn(2)−O(6*d*)	109.06(15)	O(7*b*)−Zn(3)−N(1)	167.64(15)
O(10*a*)−Zn(2)−O(11)	118.08(14)	N(2)−Zn(3)−N(1)	76.77(17)

[a] Symmetry codes: (*a*) $-x + {}^{1}/_{2}, y + {}^{1}/_{2}, -z + {}^{1}/_{2}$; (*b*) $x + {}^{1}/_{2}, y + {}^{1}/_{2}, z$; (*c*) $x + {}^{1}/_{2}, y - {}^{1}/_{2}, z$; (*d*) $-x + {}^{1}/_{2}, -y - {}^{1}/_{2}, -z$.

Table 4. Bond Lengths (angstroms) and Angles (deg) for **3**[a]

Zn(1)−O(4*a*)	1.995(4)	Zn(1)−N(2)	2.117(5)
Zn(1)−O(1)	2.040(4)	Zn(1)−N(1)	2.132(4)
Zn(1)−O(1w)	2.043(4)	C(3)···O(3*f*)	3.340(8)
O(1w)···O(4*d*)	2.840(6)	C(11)···O(2*f*)	3.279(8)
O(1w)···O(2)	2.714(6)	C(12)···O(2*g*)	3.484(8)
O(5)···O(1*e*)	2.918(9)		
O(4*a*)−Zn(1)−O(1)	98.0(2)	O(1w)−Zn(1)−N(2)	148.56(19)
O(4*a*)−Zn(1)−O(1w)	95.81(17)	O(4*a*)−Zn(1)−N(1)	110.41(18)
O(1)−Zn(1)−O(1w)	88.18(17)	O(1)−Zn(1)−N(1)	151.4(2)
O(4*a*)−Zn(1)−N(2)	115.58(17)	O(1w)−Zn(1)−N(1)	92.53(18)
O(1)−Zn(1)−N(2)	86.09(19)	N(2)−Zn(1)−N(1)	78.50(18)
O(1w)−H(1wa)···O(4*d*)	160(6)	C(3)−H(3)···O(3*f*)	150.8
O(1w)−H(1wa)···O(2)	137(3)	C(11)−H(11)···O(2*f*)	144.0
O(5)−H(5O)···O(1*e*)	179.7	C(12)−H(12)···O(2g)	164.3

[a] Symmetry codes: (*a*) $x, y + 1, z$; (*d*) $-x, -y + 1, -z$; (*e*) $-x, y - 1, -z + {}^{1}/_{2}$; (*f*) $-x + {}^{1}/_{2}, -y + {}^{3}/_{2}, -z$; (*g*) $x + {}^{1}/_{2}, y + {}^{1}/_{2}, z$.

Table 5. Bond Lengths (angstroms) and Angles (deg) for **4**[a]

Zn(1)−O(17*a*)	1.955(5)	Zn(3)−N(4)	2.120(6)
Zn(1)−O(1)	1.972(5)	Zn(4)−O(19)	1.965(5)
Zn(1)−N(1)	2.051(6)	Zn(4)−O(9*c*)	2.035(5)
Zn(1)−O(1w)	2.119(5)	Zn(4)−O(3w)	2.084(4)
Zn(1)−N(2)	2.226(6)	Zn(4)−N(5)	2.097(6)
Zn(2)−O(5)	1.931(5)	Zn(4)−N(6)	2.202(6)
Zn(2)−O(3*b*)	1.950(5)	Zn(4)−O(10*c*)	2.452(6)
Zn(2)−O(12)	2.012(5)	Zn(5)−O(15)	1.997(5)
Zn(2)−O(2w)	2.050(4)	Zn(5)−O(14*d*)	2.026(6)
Zn(3)−O(7)	1.950(5)	Zn(5)−O(16*d*)	2.074(5)
Zn(3)−O(20)	2.000(5)	Zn(5)−N(7)	2.101(7)
Zn(3)−O(11)	2.041(5)	Zn(5)−N(8)	2.125(6)
Zn(3)−N(3)	2.097(6)		
O(17*a*)−Zn(1)−O(1)	116.8(2)	O(11)−Zn(3)−N(4)	88.4(3)
O(17*a*)−Zn(1)−N(1)	121.5(2)	N(3)−Zn(3)−N(4)	78.0(3)
O(1)−Zn(1)−N(1)	121.4(3)	O(19)−Zn(4)−N(5)	101.9(2)
O(17*a*)−Zn(1)−O(1w)	90.4(2)	O(9*c*)−Zn(4)−N(5)	107.2(2)
O(1)−Zn(1)−O(1w)	93.5(2)	O(3W)−Zn(4)−N(5)	97.4(3)
N(1)−Zn(1)−O(1w)	91.9(2)	O(19)−Zn(4)−N(6)	89.6(2)
O(17*a*)−Zn(1)−N(2)	97.4(2)	O(9*c*)−Zn(4)−N(6)	91.7(2)
O(1)−Zn(1)−N(2)	89.8(2)	O(3W)−Zn(4)−N(6)	171.6(2)
N(1)−Zn(1)−N(2)	77.6(3)	N(5)−Zn(4)−N(6)	77.4(3)
O(1W)−Zn(1)−N(2)	169.2(2)	O(19)−Zn(4)−O(10*c*)	92.5(2)
O(5)−Zn(2)−O(3*b*)	113.1(2)	O(9*c*)−Zn(4)−O(10*c*)	58.12(19)
O(5)−Zn(2)−O(12)	125.2(2)	O(3w)−Zn(4)−O(10*c*)	95.88(19)
O(3*b*)−Zn(2)−O(12)	104.3(2)	N(5)−Zn(4)−O(10*c*)	158.8(2)
O(5)−Zn(2)−O(2w)	118.6(3)	N(6)−Zn(4)−O(10*c*)	87.3(2)
O(3*b*)−Zn(2)−O(2w)	99.9(3)	O(15)−Zn(5)−O(14*d*)	104.8(2)
O(12)−Zn(2)−O(2w)	91.23(19)	O(15)−Zn(5)−O(16*d*)	95.25(19)
O(7)−Zn(3)−O(20)	106.7(2)	O(14d)−Zn(5)−O(16*d*)	91.3(2)
O(7)−Zn(3)−O(11)	95.0(2)	O(15)−Zn(5)−N(7)	98.8(2)
O(20)−Zn(3)−O(11)	89.9(2)	O(14*d*)−Zn(5)−N(7)	156.0(2)
O(7)−Zn(3)−N(3)	107.6(2)	O(16*d*)−Zn(5)−N(7)	91.0(2)
O(20)−Zn(3)−N(3)	91.2(2)	O(15)−Zn(5)−N(8)	112.0(2)
O(11)−Zn(3)−N(3)	156.0(2)	O(14*d*)−Zn(5)−N(8)	89.2(2)
O(7)−Zn(3)−N(4)	105.7(2)	O(16*d*) −Zn(5)−N(8)	151.7(2)
O(20)−Zn(3)−N(4)	147.7(2)	N(7)−Zn(5)−N(8)	77.8(3)

[a] Symmetry codes: (*a*) $x - 1, y + 1, z$; (*b*) $-x + 1, -y + 1, -z + 1$; (*c*) $-x + 1, -y + 1, -z$; (*d*) $-x + 2, -y, -z + 1$.

based coordination polymers. The synthesis parameters play an important role in the formation of fascinating new compounds. However, a detailed understanding of the role that these variables play in the synthesis of hybrid inorganic−organic systems is, to date, a challenging work in this field. Recently, systematic studies on the cobalt(II)−succinate system have been carried out to elucidate the role of four variables (temperature, pH, concentration, and reaction time).[20a,b] By judicious control of reaction conditions, we have even successfully achieved the hydrothermal transformation of a novel 3D coordination polymer with 1D $Co_3(OH)_2$ chains from a 2D double-layered coordination polymer.[20c] Another elegant example is that two novel isomeric 3D organic−inorganic hybrid metal hydroxide materials were rearranged from a precursor of 2D coordination layers $[Cd(\mu_2\text{-}H_2O)(H_2O)(2,4\text{-pyda})]$ (2,4-pyda = 2,4-pyridinedicarboxylate) by the controlled hydrothermal reactions.[20d] Herein, two 3D coordination polymers with Zn_6-

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(20) (a) Forster, P. M.; Stock, N.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2005**, *44*, 7608. (b) Forster, P. M.; Burbank, A. R.; Livage, C.; Férey, G.; Cheetham, A. K. *Chem. Commun.* **2004**, 368. (c) Tong, M. L.; Ohba, M.; Chang, H. C.; Kitagawa, S. *Chem. Commun.* **2004**, 418. (d) Tong, M. L.; Hu, S.; Wang, J.; Kitagawa, S.; Ng, S. W. *Cryst. Growth Des.* **2005**, *5*, 837.

Scheme 1. Summary of Hydrothermal Conditions in the Preparation of **1**−**4**

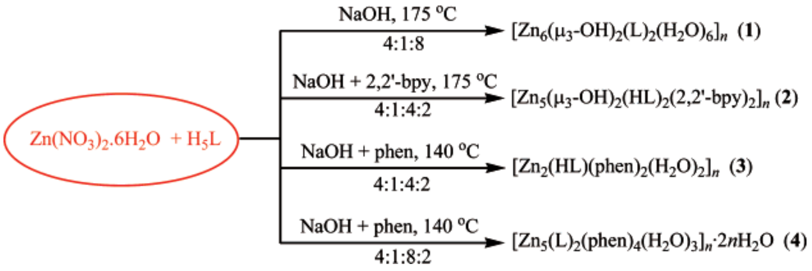
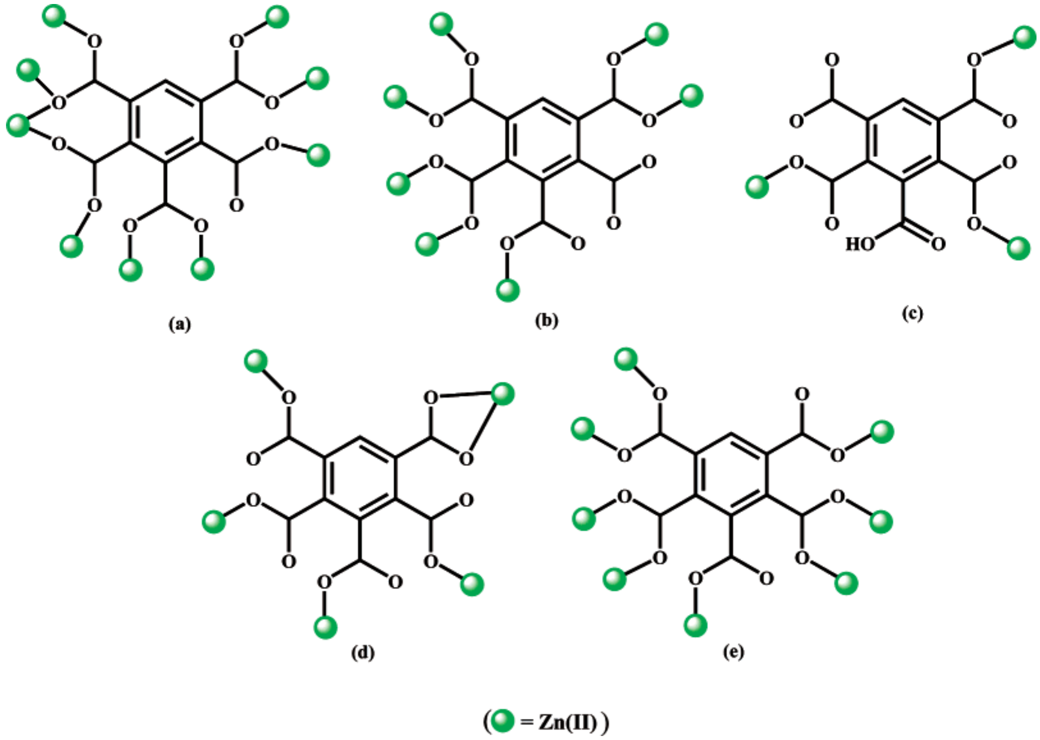


Chart 1. Coordination Modes of the $[HL]^{4-}$ and L^{5-} Ligands in **1** (a), **2** (b), **3** (c), and **4** (d and e)



(μ_3-OH)$_2$ and Zn_5(μ_3-OH)$_2$ clusters bridged by the organic ligands were obtained by finely tuning the pH value of reactant solutions to control the hydrolysis of metal ions and the deprotonation of the carboxylic groups. Moreover, the introduction of auxiliary N-donor chelating ligands has a subtle influence on both molecular formation and crystal packing. In comparison with 2,2′-bpy, phen is more likely to chelate zinc ions in such a system, which in turn terminates the coordination sites around the metal centers and results in low-dimensional coordination arrays, as shown in compounds **3** and **4**. In the meanwhile, the bulky aromatic rings on phen help to direct the spatial arrangement of the bridging groups and form extensive $\pi\cdots\pi$ interactions between coordination layers. The hydrothermal conditions employed in the preparation of **1**−**4**, including reacting time, temperature, pH value, and molar ratio of reactants,[21] are summarized in Scheme 1. Of the reaction parameters investigated, the H_5L/NaOH ratio and temperature proved to be the most important factors.

1,2,3,4,5-Benzenepentacarboxylic acid (H_5L) has great ability to construct coordination architectures with metal ions, adopting versatile coordination fashions from monodentate to chelating and bridging. Chart 1 shows the five coordination modes of $[HL]^{4-}$ and L^{5-} observed in this work. The IR spectra of these compounds show the characteristic bands of the $[HL]^{4-}$ or L^{5-} at 1630−1555 cm^{-1} for the asymmetric vibration and at 1454−1348 cm^{-1} for the symmetric vibration and the broad bands of water at 3215−3442 cm^{-1}. The absence of the absorption bands at 1730−1690 cm^{-1} in **1** and **4** indicates the H_5L ligand adopts the complete deprotonated L^{5-} form, whereas the presence of strong peaks at 1724 cm^{-1} for **2** and 1735 cm^{-1} for **3** suggests the H_5L ligand adopts the partly deprotonated $[HL]^{4-}$ form,[22] which is consistent with the X-ray structural analysis.

Crystal Structures. 1. Structure of $[Zn_6(\mu_3\text{-}OH)_2(L)_2(H_2O)_6]_n$ (1). Single-crystal X-ray diffraction study of **1** reveals an infinite 3D coordination polymer that crystallizes

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(21) (a) Zhang, X.-M.; Tong, M.-L.; Gong, M.-L.; Chen, X.-M. *Eur. J. Inorg. Chem.* **2003**, 138. (b) Forster, P. M.; Burbank, A. R.; Livage, C.; Férey, G.; Cheetham, A. K. *Chem. Commun.* **2004**, 368. (c) Forster, P. M.; Stock, N.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2005**, *44*, 7608. (d) Cheetham, A. K.; Rao, C. N. R.; Feller, R. K. *Chem. Commun.* **2006**, 4780.

(22) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Wiley: New York, 1958.

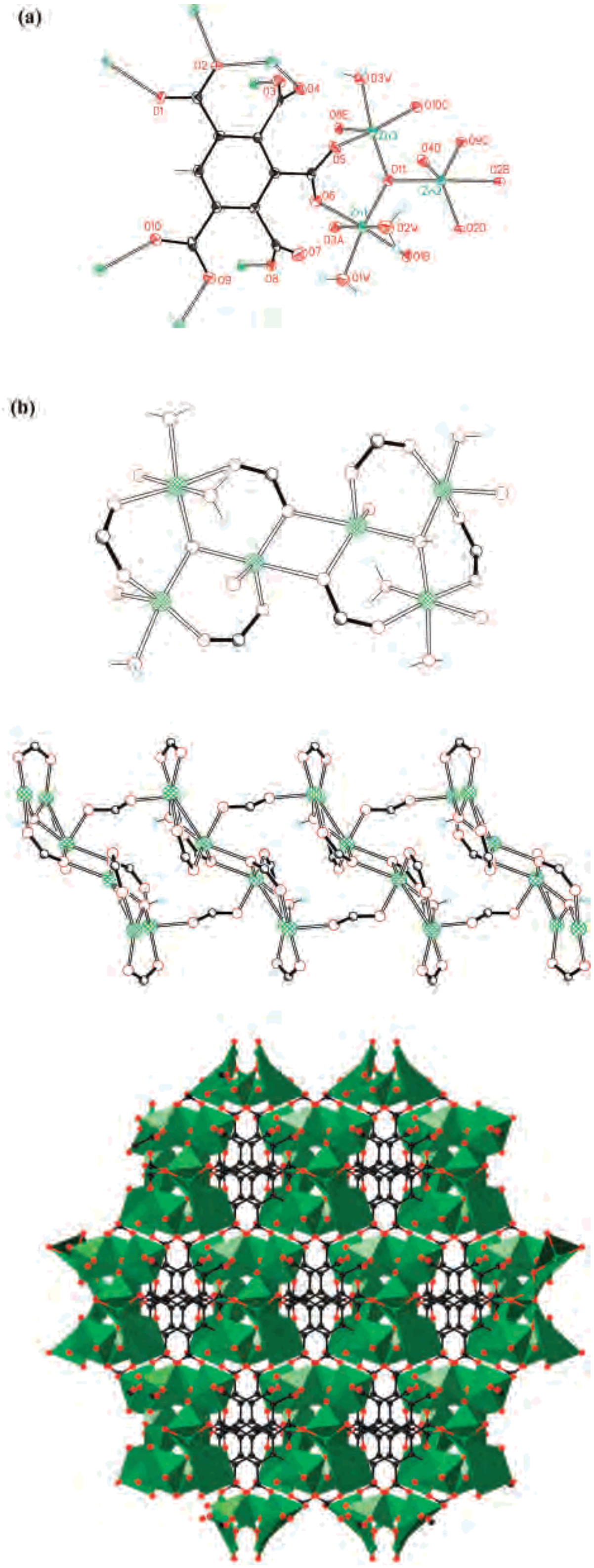

Figure 1. (a) Perspective views of coordination environments of the Zn atoms and the coordination mode of the L^{5-} ligand in **1**. (b) View of the $Zn_6(OH)_2(COO)_2$ SBU in **1**. (c) View of the arrangement of the $Zn_6(OH)_2(COO)_2$ SBU along the *b*-axis in **1** (some carbon and hydrogen atoms are omitted for clarity). (d) View of the 3D network connectivity along the *c*-axis in **1**.

in space group $C2/c$. The asymmetric unit contains three zinc atoms, one μ_3 hydroxyl group, three water molecules, and one deprotonated L^{5-} ligand (Figure 1a). Zn1 adopts a slightly distorted octahedral geometry, coordinated by a μ_3-OH^- group (Zn−O = 2.066(3) Å), three carboxylate oxygen atoms from three different L^{5-} ligands, and two water molecules (Zn−O = 2.076(3)−2.137(3) Å, O−Zn−O = 82.09(11)−171.73(12)°). Zn2 adopts a slightly distorted trigonal bipyramidal geometry, surrounded by a μ_3-OH group (Zn−O = 2.013(3) Å) and four carboxylate oxygen atoms from three different L^{5-} ligands (Zn−O = 1.956(3)−2.335(3) Å, O−Zn−O = 82.26(11)−125.79(11)°). Zn3 also adopts a distorted trigonal bipyramidal geometry, coordinated by a μ_3-OH^- group (Zn−O = 2.057(3) Å), a water molecule, and three different L^{5-} ligands (Zn−O = 2.036(3)−2.077(3) Å, O−Zn−O = 82.01(12)−172.71(12)°). The carboxylate groups of L^{5-} have diverse coordination modes, including monodentate, bridging, and μ_3-η^1:η^2, to link nine zinc atoms (Chart 1a). The bridging carboxylate groups from three distinctive ligands bind three zinc atoms into a 12-membered ring with the μ_3-OH^- at the center and, thus, form a trinuclear basic building unit (Figure 1b). The μ_3-OH^- group is displaced 0.69 Å out of the plane of three Zn atoms in the $Zn_3(\mu_3\text{-OH})$ core. The distance of three zinc atoms among each other are 3.371 Å for Zn1···Zn2, 3.537 Å for Zn1···Zn3, and the shortest 3.1424(7) Å for Zn2···Zn3. The different separations among the zinc atoms lie on the various binding modes of the carboxylate groups, compared to the trinuclear-clustered 3D framework $Zn_3(BDC)_3\cdot 6CH_3OH$ (BDC = 1,4-benzenedicarboxylate) in which the three zinc centers are arranged in line with an inversion center on Zn1.[7a] Two μ_3-η^1:η^2 carboxylate groups from two trinuclear zinc building blocks bridge the $Zn_3(\mu_3\text{-OH})$ cores in pairs and form a $Zn_6(\mu_3\text{-OH})_2(\mu_2\text{-COO})_2$ SBU in a chairlike conformation (Figure 1c). Each SBU connects the other six ones through the three-connected L^{5-} bridges into a 3D coordination network (Figure 1d).

2. Structure of $[Zn_5(\mu_3\text{-OH})_2(HL)_2(2,2'\text{-bpy})_2]_n$ (2). Compound **2** contains three distinctive zinc atoms, one μ_3-hydroxyl group, one 2,2′-bpy, and one monoprotonated $[HL]^{4-}$ ligand. The partly deprotonation of carboxylic groups revealed by X-ray structural analysis is in agreement with the IR spectrum where a strong characteristic absorption peak at 1724 cm^{-1} for a carboxylic group was observed.[21] The framework structure of **2** is constructed from pentanuclear cluster $Zn_5(\mu_3\text{-OH})_2$ SBUs, which is composed of two tetrahedral zinc atoms (Zn2), two heavily distorted square pyramidal zinc centers (Zn3), and one octahedral zinc atom (Zn1) on the 2-fold rotation axis connected with two μ_3-OH groups (Zn1−O =2.159(3) Å, Zn2−O = 1.984(3) Å, and Zn3−O = 1.984(3) Å). The tetrahedral coordination geometry of Zn2 is completed by three carboxylate oxygen atoms from three different $[HL]^{4-}$ ligands (Zn−O = 1.942(3)−2.008(3) Å, O−Zn−O = 95.58(15)−125.66(14)°), whereas the square pyramidal coordination of the Zn3 is completed by the chelation of 2,2′-bpy (Zn−N = 2.060(4) and 2.203(4) Å, N−Zn−N = 76.77(17)°) and two carboxylate oxygen atoms from two $[HL]^{4-}$ ligands (Zn−O = 1.995(3) and 2.013(3) Å, O−Zn−O = 91.77(15)−110.23(13)°, O−Zn−N = 85.77(17)−167.64(15)°). Zn1 lies in the center of the cluster, and its octahedral coordination environment is

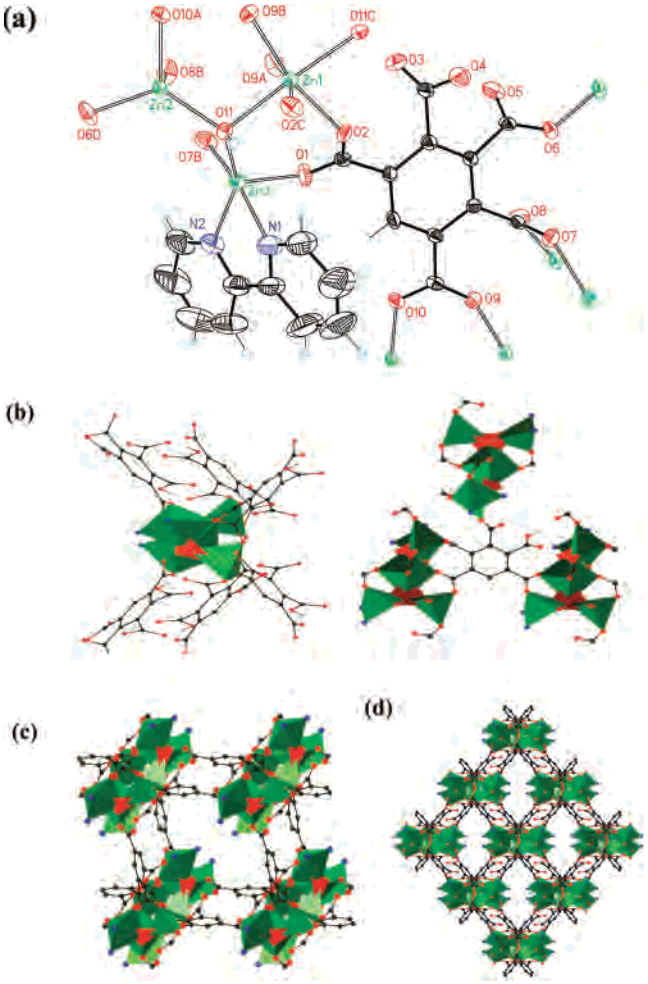

Figure 2. (a) Perspective views of coordination environments of the Zn atoms and the coordination mode of the $[HL]^{4-}$ ligand in **2**. (b) View of the six-connected pentanuclear unit surrounded by six $[HL]^{4-}$ ligands and the three-connected node of the $[HL]^{4-}$ ligand surrounded by three pentanuclear clusters in **2**. (c) Views of the $[Zn_5(OH)_2]_8(HL)_{12}$ cubic unit. (d) View of the 3D network connectivity along *c*-axis in **2** (the carbon and hydrogen atoms of the 2,2′-bpy ligands are omitted for clarity).

completed by four $[HL]^{4-}$ ligands (Zn−O = 2.042(3) and 2.086(3) Å, O−Zn−O = 80.92(13)−167.32(13)°) and two μ_3-OH. The $[HL]^{4-}$ ligand connects seven Zn(II) atoms in the monodentate and bridging coordination modes (Chart 1b). As shown in Figure 2b, each $Zn_5(\mu_3\text{-}OH)_2$ links six other SBUs as a distorted octahedral node while the $[HL]^{4-}$ ligand connects to three pentanuclear zinc clusters. The SBUs and the acid ligands are arranged in such a way that eight zinc clusters are in the apex of the cubic $[Zn_5(\mu_3\text{-}OH)_2]_8(HL)_{12}$ packing unit and linked by twelve $[HL]^{4-}$ ligands (Figure 2c). The packing units share corners with one another to form a 3D coordination framework (Figure 2d), compared to the great work of a novel, three-dimensional, noninterpenetrating MOF with an intersecting channel system $[Zn_7O_2(pda)_5(H_2O)_2]\cdot 5DMF\cdot 4EtOH\cdot 6H_2O$ (H_2pda = *p*-phenylenediacrylic acid, DMF = *N*,*N*-dimethylformamide, EtOH = ethanol)[10] by constructing heptanuclear zinc carboxylate SBUs.

3. Structure of $[Zn_2(HL)(phen)_2(H_2O)_2]_n$ (3). X-ray crystallography shows that the structure of **3** consists of infinite 1D linear chains along the *b*-axis where each zinc ion is coordinated to two oxygen atoms from $[HL]^{4-}$ ligands,

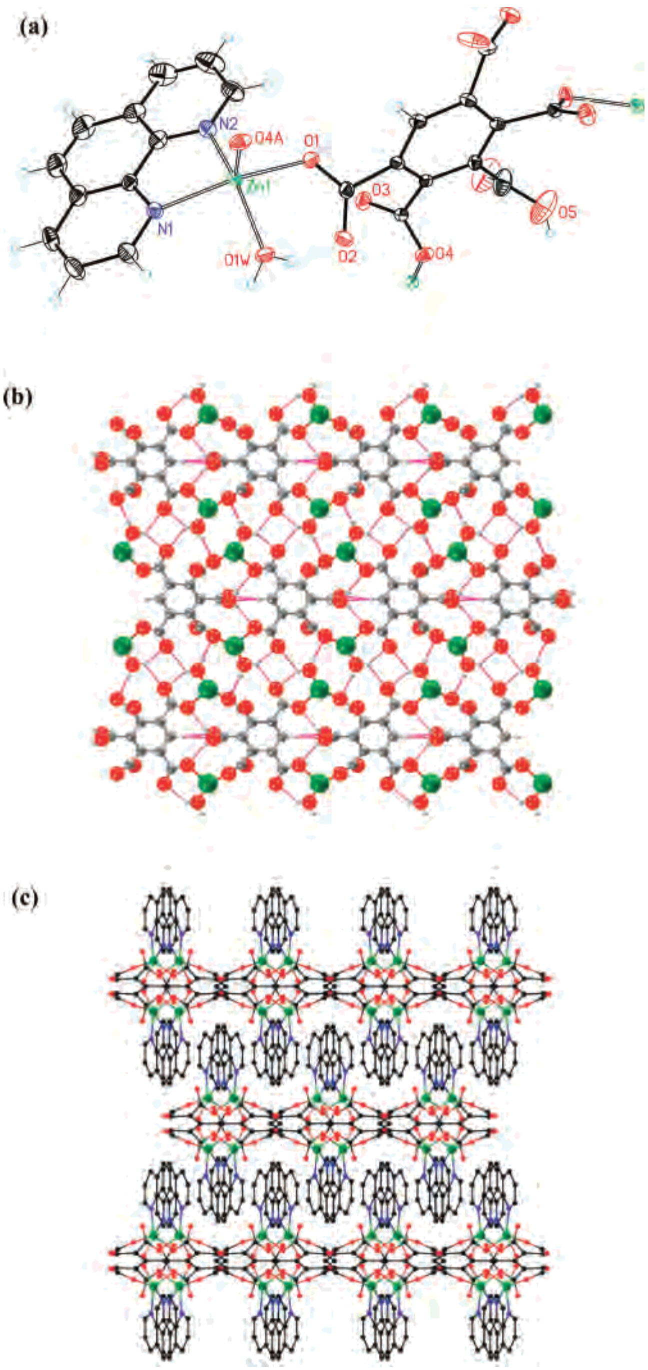

Figure 3. (a) Perspective views of coordination environments of the Zn atoms and the coordination mode of the $[HL]^{4-}$ ligand in **3**. (b) View of the Zn−carboxylate layer connected from 1D chains by hydrogen bonds in **3**. (c) View of the 3D supramolecular network constructed from 1D coordination chains by hydrogen bonds and $\pi\cdots\pi$ stacking interaction along the *c*-axis in **3**.

two nitrogen atoms from one phen ligand, and an aqua molecule in a slightly distorted trigonal bipyramidal geometry (Figure 3a) with O_3N_2 donor set (Zn−O = 1.997(4)−2.045(4) Å, Zn−N = 2.116(5) and 2.132(4) Å, O/N−Zn−O/N = 78.44(18)−148.69(19)°). The $[HL]^{4-}$ ligands within one Zn−carboxylate chain are aligned in the same direction along the *b*-axis with the carboxylate groups on the 1-, 2- and 4-, 5-positions linking four zinc atoms on both sides of the coordination band (Chart 1c). These infinite chains connect to each other via hydrogen bonds between the coordinated water molecules and the carboxylate groups (O1w···O4*a* = 2.835 Å, O1w−H1wa···O4*a* = 162.04°, O1w···O2 = 2.716 Å, O1w−H1wb···O2 = 152.70°, O1w···O2*a* = 2.922 Å, O1w−H1wb···O2*a* = 116.69°).[23] Adjacent chains are arranged in the opposite directions and form a 2D hydrogen-bonded sheet (Figure 3b). Furthermore, the stacked 2D sheets are held together via $\pi\cdots\pi$ interactions between phen into a 3D supramolecular network (Figure 3c). The shortest distance between the two parallel phen planes is ~3.7 Å, which is within the common range for $\pi\cdots\pi$ interactions between two aryl rings.[24]

4. Structure of $[Zn_5(L)_2(phen)_4(H_2O)_3]_n\cdot 2nH_2O$ (4). X-ray crystallography shows that the structure of **4** consists of infinite 2D coordination layers in the crystallographic *ab*-plane, which are further connected into a 3D supramolecular framework via rich hydrogen-bond and $\pi\cdots\pi$ interactions. In comparison to **3**, the structure of compound **4** is more complicated since all the carboxylic groups of H_5L are deprotonated under more basic synthesis condition and have more diverse binding modes (Chart 1, d and e). The basic unit cell contains five Zn(II) atoms in different coordination environments, two L^{5-} ligands, four phen ligands, three coordinated aqua molecules, and two disordered guest water molecules (Figure 4a). Zn1 adopts a slightly distorted trigonal bipyramidal geometry, coordinated by two carboxylate oxygen atoms from different L^{5-} ligands, one oxygen atoms of an aqua molecule (Zn−O = 1.955(5)−2.119(5) Å, O−Zn−O = 90.4(2)−116.8(2)°), and two nitrogen atoms of the phen ligand (Zn−N = 2.051(6) and 2.226(6) Å, O/N−Zn−O/N = 77.6(3)−169.2(2)°). Zn2 adopts a tetragonal geometry, coordinated by three carboxylate oxygen atoms from three different L^{5-} ligands and an aqua molecule (Zn−O = 1.931(5)−2.050(4) Å, O−Zn−O = 91.23(19)−125.2(2)°). Zn3 adopts a distorted square pyramidal geometry, coordinated by three carboxylate oxygen atoms of two different L^{5-} ligands (Zn−O = 1.950(5)−2.041(5) Å, O−Zn−O = 89.9(2)−106.7(2)°) and two nitrogen atoms of the phen ligand (Zn−N = 2.097(6) and 2.120(6) Å, O/N−Zn−O/N = 78.0(3)−156.0(2)°). Zn4 adopts a distorted octahedral geometry, coordinated by three carboxylate oxygen atoms from three different L^{5-} ligands, an aqua molecule (Zn−O = 1.965(5)−2.452(6) Å, O−Zn−O = 58.12(19)−95.88(19)°), and one phen ligand (Zn−N = 2.097(6) and 2.202(6) Å, O/N−Zn−O/N = 77.4(3)−171.6(2)°). Zn5 also adopts a slightly distorted trigonal dipyramidal geometry, coordinated by three carboxylate oxygen atoms from different L^{5-} ligands (Zn−O = 1.997(5)−2.074(5) Å, O−Zn−O = 90.4(2)−116.8(2)°) and two nitrogen atoms of the phen ligand (Zn−N = 2.101(7) and 2.125(6) Å, O/N−Zn−O/N = 77.8(3)−156.0(2)°). There are two kinds of the L^{5-} ligand in the molar ratio of 1:1: one connects five Zn(II) atoms via the monodentate and chelating fashions (Chart 1d), whereas the other connects eight metal centers via the monodentate and bridging modes (Chart 1e). The versatile carboxylate groups connect the zinc atoms into a delicate 2D girding layer in the *ab*-plane (Figure 4b). The 2D sheets further extend into a 3D framework via the $\pi\cdots\pi$ interactions between the phen units arranging above and below the sheets (Figure 4c). Steric hindrance renders the phen rings stacking in two directions, one of which has the distance of 3.5 Å along the *b*-axis and the other 3.8 Å along the *c*-axis.[15b,25] Moreover, rich hydrogen-bond inter-and intralayers between the water molecules and the carboxylate groups (O1w···O2 = 2.851 Å, O1w−H1wa···O2 = 121.9°, O1w···O14*a* =

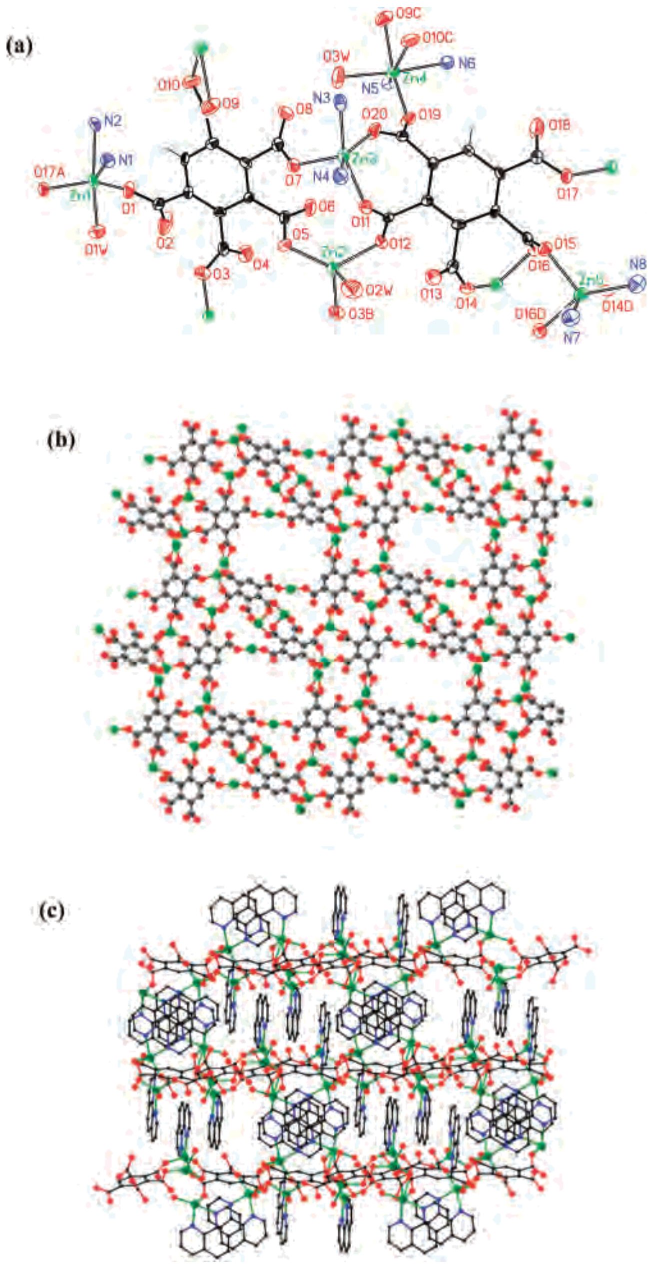

Figure 4. (a) Perspective views of coordination environments of the Zn atoms and the coordination mode of the L^{5-} ligand in **4**. (b) View of the Zn−carboxylate layer in **4**. (c) View of the 3D network constructed of 2D coordination layers by $\pi\cdots\pi$ stacking interaction along the *c*-axis in **4**.

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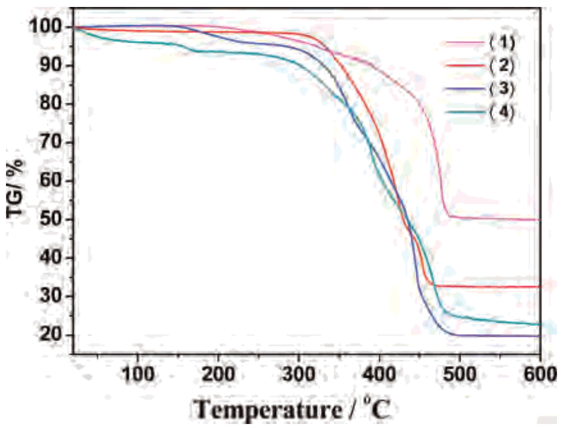

Figure 5. Thermal gravimetric analyses (TGA) curves of **1**, **2**, **3**, and **4**.

2.880 Å, O1w−H1wB⋯O14*a* = 130.7°, O2w⋯O13 = 2.848 Å, O2w−H2wa⋯O13 = 127.6°, O2W⋯O4*a* = 2.969 Å, O2w−H2wb⋯O4*a* = 179.8°, O3w⋯O8 = 2.794 Å, O3w−H3wb⋯O8 = 125.6°) further strengthen the stacking of the superarchitecture.

Thermogravimetric Analyses. In order to examine the thermal stabilities of the four compounds, we carried out TG analyses (Figure 5). Phase purity of the bulk material of **1**−**4** was confirmed by comparison of its powder diffraction (XRPD) pattern with that calculated from the single-crystal study (Supporting Information, Figure S1). Samples of the compounds were heated to 600 °C under an atmospheric environment. The TGA curve of **1** shows that the first weight loss of 9.5% appeared between 200 and 385 °C corresponds to the loss of the three coordinated water molecules (calculated, 9.6%) of one unit cell, and then the network was decomposed quickly resulting in the residue ZnO. Compound **2** is much more stable even up to 300 °C. With the weight loss 25.2% of two 2,2′-bpy (calculated, 24.7%) molecules after 395 °C, the 3D framework was gradually decomposed and finally generated the residue ZnO (calculated, 32.3%; found, 32.5%) at 468 °C. For **3**, the first weight loss of 4.2% between 150 and 240 °C corresponds to the loss of the two coordinated water molecules (calculated, 4.4%), and the second weight loss of 47.4% began 290 and 431 °C corresponding to the loss of two phen molecules. Since 431 °C, the structure was then decomposed, and finally produced the residue ZnO (calculated, 19.8%; found, 19.7%) at 500 °C. Comparably, compound **4** is less stable with the first weight loss of two lattice water molecules 2.5% (calculated, 2.1%) before 50 °C, and the three coordinated water molecules were gradually removed up to 160 °C (calculated, 3.1%; found, 3.3%). After a platform in the range of 166−278 °C with no weight loss, the four coordinated phen molecules began to be removed and were totally lost up to 420 °C (calculated, 45.9%; found, 45.8%), and then the structure was decomposed to the residue ZnO at 510 °C.

Fluorescent Properties. The fluorescent properties of the as-synthesized compounds were studied in the solid state at room temperature (Figure 6). All of the four compounds exhibit strong fluorescence at room temperature. The emission of the free H_5L at about 363 nm (Supporting Information, Figure S2) is attributed to a $\pi^* \rightarrow$ n transition in the solid state, similar to those of the reported free benzenecarboxylic acids.[26] Comparably, the emission of **1** observed at 439 nm (Figure 6a, λ_{ex} = 345 nm) might be attributable to the ligand-to-metal charge transfer (LMCT).[8b,27] With the chelation of the 2,2′-bpy ligand and the rigid $[Zn_5(OH)_2]$ clusters, the emission of **2** was observed at about 405 nm (Figure 6b, λ_{ex} = 356 nm), which may be ascribed to the cooperative effect of the intraligand emission and the LMCT.[29] Moreover, the lifetime of **1** (τ = 2.29 ns, Supporting Information, Figure S3) is also longer than that of **2** (τ = 1.60 ns), which may be due to its more condensed and rigid framework with stronger interactions of wholly deprotonated L^{5-} to zinc atoms in **1** (Chart 1, a and b), resulting in less vibrations of the skeleton and less radiationless decay

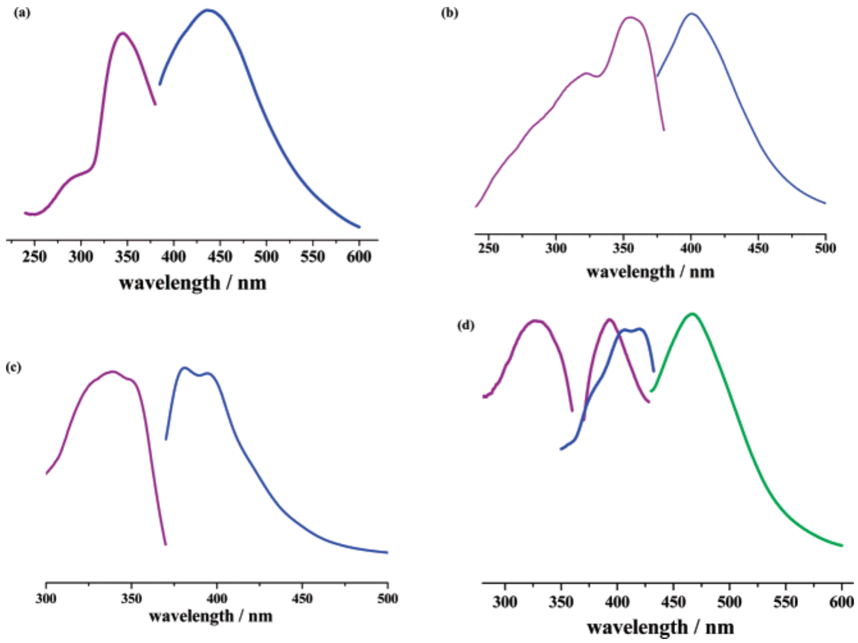

Figure 6. Emission and excitation spectra of **1** (a), **2**(b), **3**(c), and **4** (d).

of the energy.[30] For compounds **3** and **4** (Figure 6d), the H_5L ligands in monoprotonated $[HL]^{4-}$ or wholly deprotonated L^{5-} form show very little contribution to the fluorescent emission since the fluorescent emission $\pi^* \rightarrow n$ transition is very weak compared with the $\pi^* \rightarrow \pi$ transition of phen. Therefore, the emissions of **3** at 390 nm ($\lambda_{ex} = 338$ nm) and **4** at 392 nm ($\lambda_{ex} = 325$ nm) may be assigned to intraligand charge transfer of coordinated phen ligands.[31] Interestingly, another emission at about 460 nm ($\lambda_{ex} = 400$ nm) can be observed in compound **4**, which can tentatively be assigned to the LMCT for its more complicated 2D Zn–carboxylate layer and $\pi \cdots \pi$ interactions.[28]

Conclusions

In this study, four new coordination polymers with different architectures have been synthesized and characterized using a novel ligand benzenepentacarboxylic acid (H_5L) in the presence of different N-heterocycles as auxiliary ligands by controlling the conditions of hydrothermal systems. It is for the first time that H_5L was introduced to construct coordination polymers. Compounds **1** and **2** are 3D coordination frameworks constructed from $Zn_6(\mu_3\text{-}OH)_2$ and $Zn_5(\mu_3\text{-}OH)_2$ clusters as the secondary building units, whereas compounds **3** and **4** are 3D supramolecular frameworks constructed from 1D coordination chains and 2D coordination sheets extended by hydrogen bonds and $\pi \cdots \pi$ interactions, respectively. This study not only demonstrates that the nature of ligands and the geometric requirements of metal atoms play an important role in the crystal packing of MOFs but also illustrates that the hydrogen bonds and $\pi \cdots \pi$ interactions have great influence on the formation of the supramolecular architectures. Furthermore, all of the reported coordination polymers can be excited directly and emit strong fluorescence at room temperature, which makes them excellent candidates for blue fluorescent materials.

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Supporting Information Available: X-ray crystallographic files of **1**–**4** (CIF), simulated and experimental XRPD data, and the luminescence decay of **1**–**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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