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Tuning the Framework Topologies of Co^{II}-Doped Zn^{II}−Tetrazole-benzoate Coordination Polymers by Ligand Modifications: Structures and Spectral Studies

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In our continuing efforts to explore the effects of ligand modifications on the structures and properties of their metal complexes, we studied the in situ [2 + 3] cycloaddition reactions of benzonitrile, o-phthalodinitrile, 3-cyanobenzoic acid, 4-cyanobenzoic acid with NaN_3 in the presence of Zn^{II} and/or Co^{II} salts under hydrothermal conditions, and obtained four new Co^{II}-doped Zn^{II}-tetrazole-benzoate coordination polymers with the formula of $[Co_xZn_{1-x}(\mathbf{L}^m)_y]_n$ [5-phenyl-1*H*-tetrazole (H$\mathbf{L}^1$) for **1**, 2-(1*H*-tetrazol-5-yl)benzoic acid ($H_2\mathbf{L}^2$) for **2**, 3-(1*H*-tetrazol-5-yl)benzoic acid ($H_2\mathbf{L}^3$) for **3**, and 4-(1*H*-tetrazol-5-yl)benzoic acid ($H_2\mathbf{L}^4$) for **4**]. The structure of **1** shows a classical diamondoid net, while **2** and **3**, take 2D layer structure with $(4.6^2)(4.6.4.6)$ topology and 3D $SrAl_2$ topology, respectively. The structure of **4** exhibits a four-connected 3D network with rare non-diamondoid 6^6 topology. The coordination modes of the center metal and the ligands in the four complexes are almost the same, being tetrahedral or four-connected, but their topologies are quite different. Thus, the four structurally related ligands allow analysis of the effects of the disposition of a second functional carboxylate group on an aromatic ring and the twist angles of the carboxylate and tetrazoyl out of the plane of the aromatic ring on the overall structural topology of their complexes. Interestingly, the Co^{II} ions were doped into the Zn^{II} complexes, as confirmed by their macroscopical colors, inductively coupled plasma (ICP) analysis and UV−visible spectra. In addition, the photoluminescence of the four complexes in the solid state at room temperature was briefly studied.

Introduction

Coordination polymers with interesting structures and/or peculiar properties, such as ion-exchange, adsorption, catalysis, magnetism, and luminescence, have been the focus of intense study in recent years.[1] Structural design of coordination frameworks is still very active, but designed synthesis of expected functional framework structures is still not easy, and there still remains a great challenge to truly understand the factors that affect their formation.[2] It is known that the structures of such complexes can often be adjusted by the intelligent selection of organic ligands with suitable shape, functionality, flexibility, and symmetry, and the coordination geometry of the metal ions, the reaction conditions, and so on,[3] and much attention has been focusing on tuning the frameworks through rational selection of structurally related ligands, such as the metal complexes with flexible dithioether and disulfoxide ligands, urocanic acid taumers ligands, and benzenedicarboxylate ligands and so on.[4]

Azole heterocycles and carboxylate groups have good coordination ability and diverse coordination modes, and the ligands bearing both carboxylate and *N*-heterocyclic groups

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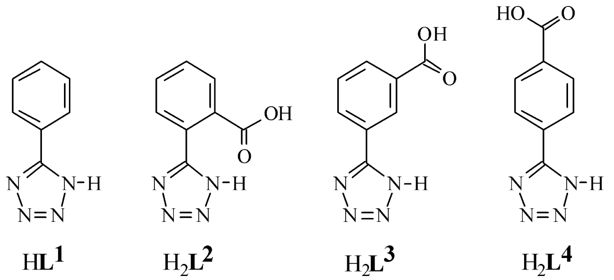
have been well used in constructing coordination frameworks.[4b,5] Polycarboxylates, such as benzenedicarboxylic acids, have been extensively employed to construct functional metal-organic frameworks with high porosity and new topology.[6] As the analogue of carboxylic acid group, tetrazole has attracted much attention because its four nitrogen electron-donating atoms allows it to serve as either a multidentate ligand or a bridging building block in supramolecular assemblies.[7] However, ligands based on tetrazole-benzoate as building blocks for constructing coordination complexes have been less studied,[8] and such ditopic ligands may become a type of building block to construct coordination polymers with novel topologies and properties.

Chart 1. Four Structurally Related Ligands H**L**^{1}-H$_2$**L**^{4}



In this paper, we use a series of structurally related ligands (Chart 1), which contain both -COOH (carboxyl) and -CN$_4$H (1*H*-tetrazolyl) groups, to construct coordination polymers with new topologies and multidimensional frameworks. Such ligands bear several particular characteristics when bonding to metal centers: (i) both the carboxyl and tetrazole groups manifest versatile coordination modes in different conditions, and they may act as linkers to connect metal ions into higher dimensional structures; (ii) the structural geometries of the ligands themselves are also multiform. The dihedral angles of the carboxylate and tetrazoyl out of the plane of the aromatic ring are flexible and adaptable to meet the requirements for constructing coordination frameworks with diverse frameworks; (iii) the relative positions of the two kinds of functional groups may affect the structural topology of their complexes. Scheme 1 represents the coordination modes of the ligands found in our work. Notably, each tetrazolate ring is attached to two metal ions via its N1 and N4 atoms, in an "opposite-on" coordination mode,[7g] and each carboxyl is attached to two metal ions via two O atoms, in a *syn-anti* bridging mode.

In fact, since Sharpless et al. reported the synthesis of a variety of tetrazoles through [2 + 3] cycloaddition reactions of nitriles and azide in the present of zinc salt as Lewis acid,[9] this synthetic approach has been extended by various metal ions such as Zn^{II}, Cd^{II}, Cu^{I}/Cu^{II}, Fe^{II}, and Ag^{I} in the construction of coordination frameworks.[7a,8d,10] On the other hand, most studied coordination polymers are unimetallic, and studies on bimetallic coordination polymers are still rare and usually involve either two different metals in different or similar oxidation states or the same metal in two different oxidation states.[11] Incorporating a second type of metal ion into the crystal lattice of a coordination polymer is theoretically and practically feasible; more important, the solid solution exhibits new properties such as indices of refraction

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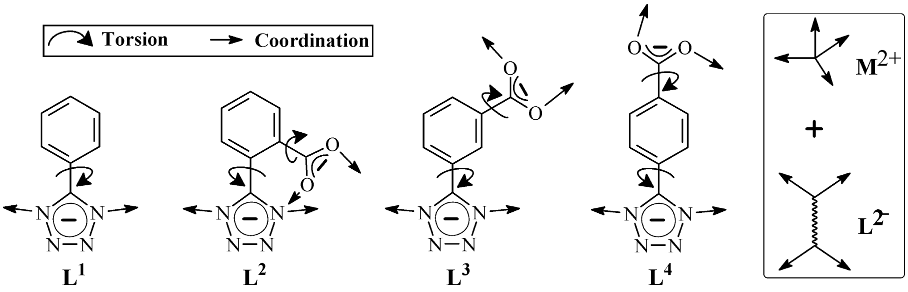
Scheme 1. Coordination Modes of Ligands in **1**−**4**



and color that can be precisely and reliably fine-tuned.[11a,12] Herein, we report the in situ hydrothermal reactions of benzonitrile, *o*-phthalodinitrile, 3-cyanobenzoic acid, 4-cyanobenzoic acid with $ZnCl_2$ in the presence of NaN_3 and Co^{II} to obtain four Co^{II}-doped Zn^{II}-tetrazolate complexes (Supporting Information, Figure S1). By the ligand modifications, the framework topologies change from classical diamondoid (**dia**) net (**1**), to 2D layer with $(4.6^2)(4.6.4.6)$ net (**2**), $SrAl_2$ (**sra**) (**3**) and rare non-diamond 6^6 topological framework (**4**). The photoluminescence of the four complexes in the solid state at room temperature were also studied.

Experimental Section

Materials and General Methods. All reagents and solvents for synthesis were purchased from commercial sources and used as received. Pure Zn^{II} complexes of $\mathbf{1^p}$, $\mathbf{3^p}$, and $\mathbf{4^p}$ were synthesized according to the literature methods.[7a,8c,g]

Caution! *Azide and tetrazolate compounds are potentially explosive. Only a small amount of material should be prepared and handled with care.*

Elemental analyses (C, H, and N) were performed on a Perkin-Elemer 240C analyzer and IR spectra were measured on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. Solid state UV−vis spectra were recorded at room temperature on a computer-controlled Jasco V-550 Spectrometer (JASCO Corp.) in the wavelength range of 200−800 nm. Emission spectra in solid state at room temperature were taken on a Cary Eclips fluorescence spectrophotometer. Inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300 DV spectrometer. The thermogravimetric analysis (TGA) was done on a standard TG-DTA analyzer under air atmosphere at a heating rate of 10 °C/min for all measurements. The X-ray powder diffraction (XRPD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury program available free of charge via the Internet at http://www.iucr.org.

Synthesis of $[Co_{0.03}Zn_{0.97}(L^1)_2]_n$ (1). A mixture of $ZnCl_2$ (0.40 mmol), $CoCl_2\cdot 6H_2O$ (0.40 mmol), NaN_3 (0.60 mmol), benzonitrile (2.45 mmol), and H_2O (10 mL) were placed in a Teflon-lined stainless container. The mixture was heated at 110 °C for 2 days, and then it was cooled to room temperature. Pink crystals of **1** were obtained. Yield: about 30% based on Zn. ICP analysis of **1** gave the contents of Zn and Co as 15.72 and 0.43 wt %, respectively, indicating a Zn/Co ratio of about 0.97:0.03. Anal. Calcd for $C_{14}H_{10}N_8Co_{0.03}Zn_{0.97}$: C, 47.30; H, 2.84; N, 31.52. Found: C, 47.14; H, 2.67; N, 31.32. IR (KBr, cm^{-1}): 3438(m), 3062(m), 1523(m), 1456(s), 1081(m), 782(m), 731(s).

Synthesis of $[CoZn(L^2)_2\cdot(H_2O)_2]_n$ (2). A mixture of $ZnCl_2$ (0.30 mmol), $CoCl_2\cdot 6H_2O$ (0.40 mmol), NaN_3 (0.40 mmol), *o*-phthalodinitrile (0.20 mmol), and H_2O (10 mL) were placed in a Teflon-lined stainless container, then heated to 160 at 3.8 $°C\cdot h^{-1}$ and kept the temperature for 2 days, then cooled to 60 at 2.8 $°C\cdot h^{-1}$. Rosiness crystals of **2** were obtained in about 30% yield based on Zn. ICP analysis of **2** gave the contents of Zn and Co as 11.42 and 8.69 wt %, respectively, indicating a Zn/Co ratio of 1:1. Anal. Calcd for $C_{16}H_{12}N_8O_6CoZn$: C, 35.81; H, 2.25; N, 20.88. Found: C, 35.68; H, 2.50; N, 20.81. IR (KBr, cm^{-1}): 3390(m), 1581(s), 1469(w), 1411(s), 877(w), 752(m).

Synthesis of $[Co_{0.04}Zn_{0.96}(L^3)]_n$ (3). A mixture of $ZnCl_2$ (0.20 mmol), $CoCl_2\cdot 6H_2O$ (0.20 mmol), NaN_3 (0.30 mmol), 3-cyanobenzoic acid (0.10 mmol), and H_2O (10 mL) were mixed in a Teflon-lined stainless container, then heated to 148 at 9.2 $°C\cdot h^{-1}$ and kept at the temperature for one and a half days, finally cooled to 60 at 3.7 $°C\cdot h^{-1}$. Purple crystals of **3** were obtained in about 20% yield based on Zn. ICP analysis of **3** gave the contents of Zn and Co as 18.81 and 0.79 wt %, respectively, indicating a Zn/Co ratio of about 0.96:0.04. Anal. Calcd for $C_8H_4N_4O_2Co_{0.04}Zn_{0.96}$: C, 37.94; H, 1.59; N, 22.12. Found: C, 37.65; H, 1.68; N, 21.79. IR (KBr, cm^{-1}): 3432(w), 1610(w), 1541(s), 1425(s), 831(w), 740(m).

Synthesis of $[Co_{0.04}Zn_{0.96}(L^4)]_n$ (4). A mixture of $ZnCl_2$ (0.30 mmol), $CoCl_2\cdot 6H_2O$ (0.17 mmol), NaN_3 (0.26 mmol), 4-cyanobenzoic acid (0.20 mmol), and H_2O (10 mL) were placed in a Teflon-lined stainless container, then heated to 160 at 14.5 $°C\cdot h^{-1}$ and kept the temperature for 2 days, finally cooled to 60 at 2.8 $°C\cdot h^{-1}$. Purple crystals of **4** were obtained in about 30% yield based on Zn. ICP analysis of **4** gave the contents of Zn and Co as 18.77 and 0.62 wt %, respectively, indicating a Zn/Co ratio of about 0.96: 0.04. Anal. Calcd for $C_8H_4N_4O_2Co_{0.04}Zn_{0.96}$: C, 37.94; H, 1.59; N, 22.12. Found: C, 37.44; H, 1.70; N, 22.17. IR (KBr, cm^{-1}): 3432(w), 1583(m), 1521(s), 1425(s), 1282(m), 868(m), 756(m).

X-ray Data Collection and Structure Determinations. X-ray single-crystal diffraction data for complexes **1**−**4** were collected on a Rigaku RAXIS-RAPID diffractometer with Mo-Kα radiation (λ = 0.71073 Å). All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL.[13] Metal atoms in each complex were located from the *E*-maps, and other non-hydrogen atoms were located in successive difference Fourier

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Table 1. Summary of Crystallographic Data for Complexes **1**−**4**

complex	**1**	**2**	**3**	**4**
formula	$C_{14}H_{10}Co_{0.03}Zn_{0.97}N_8$	$C_{16}H_{12}CoZnN_8O_6$	$C_8H_4Co_{0.04}Zn_{0.96}N_4O_2$	$C_8H_4Co_{0.04}Zn_{0.96}N_4O_2$
Fw	355.48	536.64	253.26	253.26
color	pink	roseate	purple	purple
crystal system	tetragonal	monoclinic	monoclinic	monoclinic
space group	$I\bar{4}2d$	$C2/c$	$P2_1/c$	Pc
a/Å	14.258(2)	19.645(4)	4.9001(10)	4.8280(10)
b/Å	14.258(2)	7.1372(14)	17.030(3)	8.2319(16)
c/Å	28.416(6)	14.884(3)	10.470(2)	10.598(2)
β/deg	90	114.42(3)	97.83(3)	96.09(3)
V/Å^3	5776.7(16)	1900.1(7)	865.6(3)	418.83(15)
D_c/Mg·m^{-3}	1.635	1.876	1.943	2.008
Z	16	4	4	2
T/K	293(2)	293(2)	293(2)	293(2)
$R1$ [$I > 2\sigma(I)$]	0.0292	0.0243	0.0232	0.0237
$wR2$ (all data)	0.0825	0.0657	0.0571	0.0448
Flack parameters	0.0(2)			0.04(1)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1**−**4**[a]

		1	
Zn(1)−N(1)	2.007(3)	Zn(2)−N(4)	2.004(3)
Zn(1)−N(5)	2.017(3)	Zn(3)−N(8)	1.994(3)
N(1)−Zn(1)−N(1A)	115.2(1)	N(4)−Zn(2)−N(4C)	115.8(2)
N(1)−Zn(1)−N(5)	108.2(1)	N(5)−Zn(1)−N(5A)	114.3(1)
N(1)−Zn(1)−N(5A)	105.6(1)	N(8E)-Zn(3)−N(8)	104.9(2)
N(4)−Zn(2)−N(4B)	106.41(7)	N(8F)-Zn(3)−N(8)	111.79(8)
		2	
Zn(1)−O(1)	2.003(1)	Co(1)−N(1)	2.083(2)
Zn(1)−N(4B)	2.009(2)	Co(1)−O(1W)	2.154(2)
Co(1)−O(2)	2.062(1)		
O(1)−Zn(1)−N(4B)	106.13(6)	O(2)−Co(1)−O(1W)	92.76(6)
O(1)−Zn(1)−N(4C)	124.76(6)	O(2)−Co(1)−O(1WD)	87.24(6)
O(1A)−Zn(1)−O(1)	96.89(8)	N(1)−Co(1)−O(1W)	90.19(6)
O(2)−Co(1)−N(1)	85.64(6)	N(1)−Co(1)−O(1WD)	89.81(6)
O(2)−Co(1)−N(1D)	94.36(6)	N(4B)−Zn(1)−N(4C)	100.54(9)
		3	
Zn(1)−O(1A)	1.940(1)	Zn(1)−N(1)	1.975(2)
Zn(1)−O(2B)	1.966(1)	Zn(1)−N(4C)	1.984(2)
O(1A)−Zn(1)−O(2B)	108.31(6)	O(2B)−Zn(1)−N(1)	104.39(7)
O(1A)−Zn(1)−N(1)	114.02(7)	O(2B)−Zn(1)−N(4C)	103.84(7)
O(1A)−Zn(1)−N(4C)	108.03(7)	N(1)−Zn(1)−N(4C)	117.36(7)
		4	
Zn(1)−O(1B)	1.971(2)	Zn(1)−N(1)	1.997(3)
Zn(1)−O(2A)	1.953(2)	Zn(1)−N(4C)	1.976(3)
O(1B)−Zn(1)−N(1)	103.8(1)	O(2A)−Zn(1)−N(1)	107.4(1)
O(1B)−Zn(1)−N(4C)	103.8(1)	O(2A)−Zn(1)−N(4C)	114.4(1)
O(2A)−Zn(1)−O(1B)	108.6(1)	N(4C)−Zn(1)−N(1)	117.9(1)

[a] Symmetry codes: for **1**, A $x, -y + 3/2, -z + 5/4$; B $y - 1/2, -x + 3/2, -z + 3/2$; C $-x + 1, -y + 2, z$; E $-x, -y + 1, z$; F $-y + 1/2, x + 1/2, -z + 3/2$; for **2**, A $-x + 1, y, -z + 1/2$; B $-x + 1, y - 1, -z + 1/2$; C $x, y - 1, z$; D $-x + 1, -y + 1, -z + 1$; for **3**, A $-x, -y + 1, -z + 2$; B $-x + 1, -y + 1, -z + 2$; C $x, -y + 3/2, z + 1/2$; for **4**, A $x - 1, y - 1, z$; B $x, y - 1, z$; C $x, -y + 2, z - 1/2$.

syntheses and refined with anisotropic thermal parameters on F^2. The hydrogen atoms of the ligand were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. H atoms of water were added by the difference Fourier maps and refined with constrained. Crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengthes and angles are listed in Table 2.

Results and Discussion

Synthesis and General Characterization. In situ hydrothermal reaction of divalent Zn^{II} and/or Co^{II} with a series of bifunctional ligands afforded the four complexes as single crystals. When the reactions were conducted in the absence of Zn^{II} salt, we just got precipitations. However, when Zn^{II} salt was introduced into the reaction system, Co^{II}-doped Zn^{II} complexes were afforded, and the colors of the four complexes are purple or roseate. ICP analysis indicated the existence of Co^{II} in the target complexes. To the best of our knowledge, there are very few examples of Co^{II}-tetrazlate coordination polymers,[14] and the formation mechanism is still unclear. It is worth noting that the 2-(1*H*-tetrazol-5-yl)benzoic acid ($H_2\mathbf{L}^2$) ligand in complex **2** is generated through the [2 + 3] cycloaddition and hydrolyzation reactions from the *o*-phthalodinitrile precursor, with one of the two cyano-groups changed to tetrazole and another to carboxyl.

When we tried to increase or decrease the Co(II)/Zn(II) ratio, we got complexes with almost the same Co^{II} contents. This occurrence may suggest that Zn(II) is preferentially included during the synthesis of the mixed-metal system. When we tried to dope other metal ions [we tried Mn(II), Ni(II), Cu(II), Cd(II)], unfortunately, we only obtained precipitates and no single crystals were afforded for structure analysis in our efforts. Indeed, the mixed-metal system is very complicated, and the mechanism is still unclear. Further studies are still under way in our laboratory.

To examine the thermal stability of the obtained coordination polymers, thermogravimetric analyses (TGA) experiments were carried out (Supporting Information, Figure S2). All the four complexes exhibit high thermal stability. It is worth noting that coordination polymers are usually unstable at above 300 °C, only some examples are reported to be stable at higher temperatures.[15] The IR spectra of **1**−**4** were consistent with their structures. The absence of the peaks of a cyano group in the 2200 cm^{-1} region, indicating the cyano group is no longer existing

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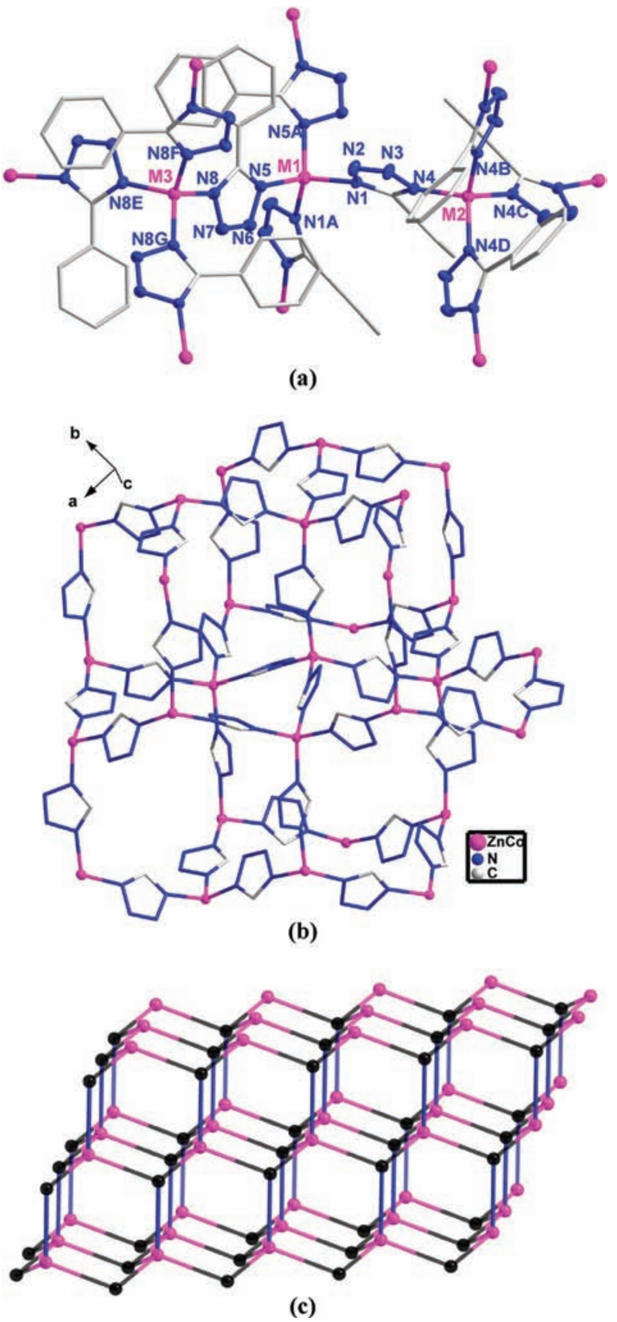

Figure 1. View of (a) the structure of **1**, M represents Zn/Co in the same lattice (H atoms omitted for clarity); (b) the 3D structure of **1**; (c) schematic representation of **dia** net in **1** (spheres represent M, and the long lines represent $\mathbf{L}^1$).

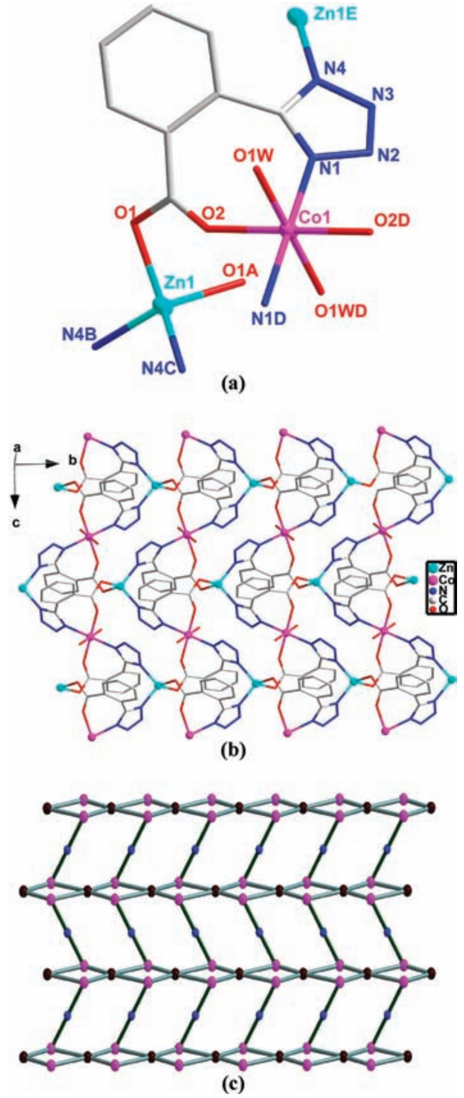

Figure 2. View of (a) the structure of **2** (H atoms omitted for clarity); (b) the 2D structure of **2**; (c) 2D layer with $(4.6^2)(4.6.4.6)$ topology in **2** (brown spheres, Zn; blue spheres, Co; pink spheres, $\mathbf{L}^2$).

in the product, and the emergence of a peak at 1400−1500 cm^{-1} indicate the formation of the tetrazole group, in good accord with previous reports.[7] For complexes **2**−**4** the difference between $\upsilon_{as}(COO)$ and $\upsilon_{sym}(COO)$ stretching frequencies is near 170 cm^{-1}, suggesting a bridging coordination mode of the carboxylate group.

Structure Description. Complex 1. 1 is isostructural to the reported 5-phenyl-1*H*-tetrazole derivative ($C_{14}H_{10}N_8Zn$).[7a] There exist three crystallographically independent M centers, the local coordination geometry around the M center can be described as a slightly distorted tetrahedron (Figure 1a). The M−N bond distances [1.994(3)−2.017(3) Å] are in the reported normal range. Each M center coordinates to four nitrogen atoms of four different $\mathbf{L}^1$ and is connected to four adjacent metal centers through the $\mathbf{L}^1$ bridges (1 and 4-position N) to result in a three-dimensional network with a diamondoid topological structure (Figure 1b). The M−M separations are 6.163 and 6.170 Å. When the bridging tetrazole groups treated as connecting points, the M center has a tetrahedral geometry with the M−M−M angles ranging from 109.35 to 109.71°. These angles deviate slightly from 109.45° expected for an idealized diamond network.

Complex 2. 2 crystallizes in the monoclinic space group *C2/c* and the asymmetrical unit contains half of Co^{II} and Zn^{II} ions, one $\mathbf{L}^2$ ligand and one coordinated water (Figure 2a). Each ligand coordinates to two Zn^{II} ions and one Co^{II} ion: it acts as a quadridentate ligand by utilizing its one N atom from the tetrazole ring and one O atom from the carboxylate group to chelate one Co^{II} ion and bridging two Zn^{II} ions via *syn-anti* bridging carboxylate O atoms (Zn1−O1 = 2.003(1) Å; Co1−O2 = 2.062(1) Å) and tetrazole N atoms through the 1 and 4-position (Co1−N1 = 2.083(2) Å; Zn1A−N4 = 2.009(2) Å), resulting in a 2D layer. The Zn^{II}

ion is tetrahedrally coordinated to two N atoms and two O atoms of four distinct **L**^{2} ligands. The angles around the Zn^{II} atom range from 96.89(8) to 124.76(6)°, to give a highly distorted tetrahedral geometry. The Co^{II} ion is located at a crystallographic inversion center and coordinated by two N atoms and two O atoms from two **L**^{2} ligands in the equatorial plane and two O atoms from two water molecules, in slightly distorted elongated octahedron geometry (Figure 2b). In addition, there are abundant intramolecular O−H···O/N hydrogen-bonding between the O1F and N3G atoms of the **L**^{2} ligands and the coordinated water (Supporting Information, Table S1 and Figure S4a). Meantime, the adjacent tetrazole rings are approximately parallel to each other with the center-center distance of about 3.445 Å, the average interplanar separation of 3.399 Å, and the dihedral angle of 0.02° indicating the presence of intramolecular face-to-face $\pi\cdots\pi$ stacking (Supporting Information, Figure S4b). Topologically, Zn^{II} ions can act as a bridge, Co^{II} ions as 4-connecting nodes, and the ligands act as 3-connecting nodes to form a $(4.6^2)(4.6.4.6)$ net (Figure 2c).

Complex 3. 3 is isostructural to the reported 3-(1*H*-tetrazol-5-yl)benzoic acid derivative ($C_8H_4N_4O_2Zn$).[8c] **3** crystallizes in the monoclinic space group, $P2_1/c$. The crystallographically asymmetric unit contains one M ion and one **L**^{3} ligand (Figure 3a). To better understand the structures and how the topology is a prototype for frameworks, it would be helpful to explore the connection mode of the metal centers and organic ligands. Each ligand coordinates to four metal ions: two via the *syn-anti* bridging carboxylate O atoms (M−O1 = 1.940(1) Å; M−O2 = 1.966(1) Å), two via the bridging tetrazole N atoms through the 1 and 4-position (M−N1 = 1.975(2) Å; M−N4 = 1.984(2) Å). In turn, the M center is tetrahedral and coordinates to four different ligands, two via N atoms and two via O atoms. The structure can also be seen as zigzag chains of the metal centers extending along the *c*-direction through bridging tetrazole groups, each chain is linked by the **L**^{3} ligands to afford a 2D sheet (Supporting Information, Figure S5). The 2D sheet is extended through the bridging carboxylate groups along the *a*-direction; then a overall 3D network is formed (Figure 3b) in which both the metal and the ligand act as 4-connecting nodes with distorted tetrahedral geometry. The O/N−M−O/N angles range from 103.84(7) to 117.36(7)°. The network topology (Figure 3c) is that of $SrAl_2$ (**sra**, Schläfli symbol $4^2.6^3.8$).

Complex 4. 4 crystallizes in the monoclinic space group *Pc*. The asymmetric unit of **4** contains one M center and one unique **L**^{4} ligand (Figure 4a). The M center is tetrahedral and coordinates to four different ligands, two via 1,4-N atoms (M−N1 = 1.997(3) Å; M−N4 = 1.976(3) Å), and two via *syn-anti* O atoms (M−O1 = 1.971(2) Å; M−O2 = 1.953(2) Å). Each ligand in turn coordinates to four M atoms; the ligand is not planar and thus the coordinated M atoms are arranged in a highly distorted tetrahedral fashion about the ligand, giving a 3D coordination network (Figure 4b). The O/N−M−O/N angles range from 103.8(1) to 117.9(1)°. From a topological point of view, the structure of **4** contains two types of 4-connecting nodes (M and **L**^{4}). The overall network topology can thus be described in terms of corrugated 2D (6,3) hexagonal sheets (Supporting Information, Figure S6a), which are bridged to give the overall 3D network with the Schläfli symbol 6^6 $(6.6_2.6.6_2.6.6_2)$ (Figure 4c). Interestingly, this is the same short Schläfli symbol as that of diamond, Lonsdaleite, and a number of other 4-connected nets,[2a] which are nonetheless topologically different. The relationship to this net to Lonsdaleite is shown in Figure 4d. In **4**, there are five six-membered circuits with a chair form and one distorted non-chair six-membered form (Supporting Information, Figure S6b).[16]

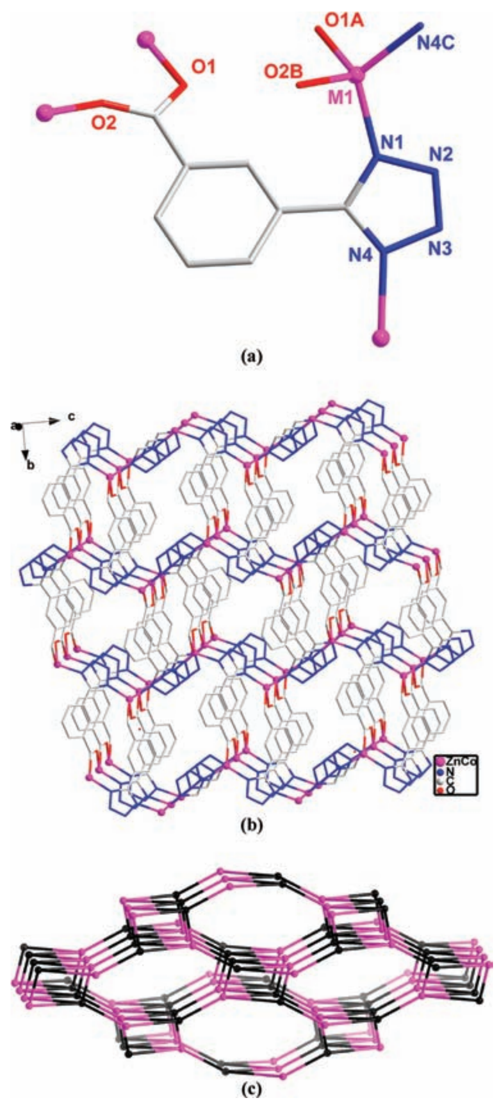

Figure 3. View of (a) the structure of **3**, M represents Zn/Co in the same lattice (H atoms omitted for clarity); (b) the 3D structure of **3**; (c) the overall 4-connected 3D $SrAl_2$ (**sra**) topology of **3** (pink spheres, M; black spheres, **L**^{3}).

It is worth noting that the ligands take the same coordination modes but the complexes have different structural

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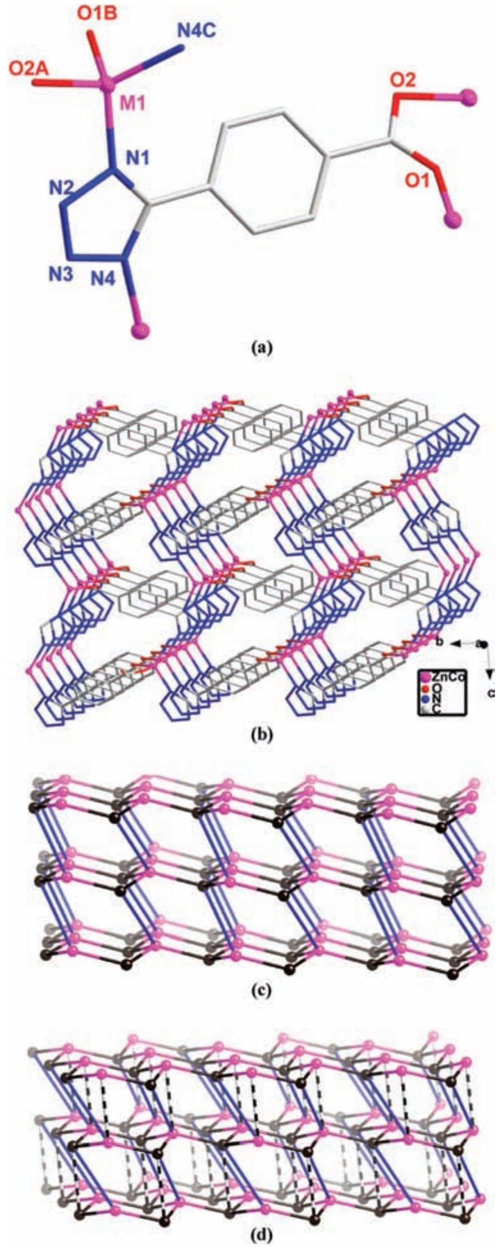

Figure 4. View of (a) the structure of **4**, M represents Zn/Co in the same lattice (H atoms omitted for clarity); (b) the 3D structure of **4**; (c) the overall 3D structure, to emphasize the hexagonal sheet substructure, the intersheet bonds shown in blue (pink spheres: M; black spheres: **L**^{4}); (d) the relationship of this net to Lonsdaleite: by incorporating the dashed links and omitting the blue links, the Lonsdaleite is generated.

topologies. In complex **1**, the metal center can be seen as a tetrahedral node, most commonly, linked by ditopic linkers (**L**^{1}) forming a diamond net. Comparing the topological structures of complexes **3** and **4**, the ligands can serve as tetrahedral building-units, connecting the metal ions leading to the formation of different structural topologies, which may be attributed to the twist angles of the carboxyl and tetrazoyle out of the plane of the aromatic ring and the different dispositions of the two functional groups (i.e., the values of dispersion angles being 120 and 180°, respectively, in the selected ligands) as shown in Scheme 1 and Supporting Information, Scheme S1. All of them can be seen as the undulated hexagonal sheets extended by the bridging ligands; as a result, the differences in the stacking mode and interlayer connection of the 2D sheets generate distinct 3D nets.

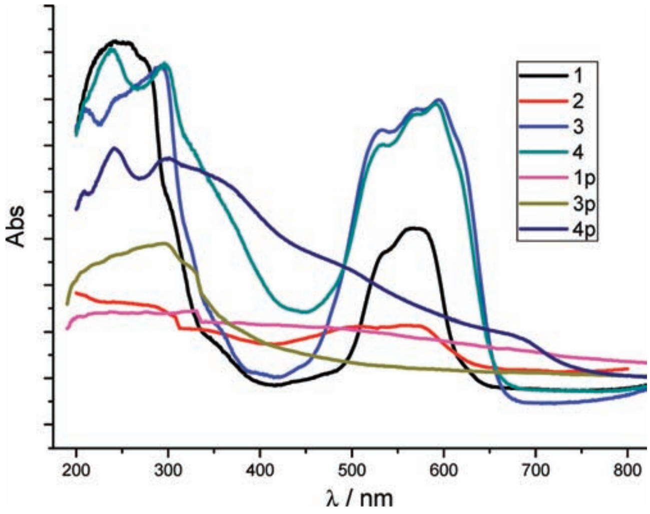

Figure 5. Solid UV−visible spectra of **1**−**4**, **1**^{p}, **3**^{p}, and **4**^{p}.

UV−Visible and Photoluminescent Spectra. Electronic spectra of phase-pure microcrystal samples of **1**−**4**, **1**^{p} and **3**^{p} are shown in Figure 5. Complex **2** shows two broad absorption bands: one centered at 210 nm (ligands n-π^*); the second at 480 nm [$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$] with a shoulder at 560 nm [$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$], the bands are typical high spin hexa-coordinated octahedral Co^{II} species,[12e,17] being well in accord with the coordination environment of Co atoms in **2**. As expected, the spectra features of **1**, **3**, and **4** are similar to each other, and thus indicate that the low spin tetrahedral coordination geometry around Co^{II} is the same: a multiple absorption at 520 nm [$^4A_2 \rightarrow {}^4T_2$] and 560 nm [$^4A_2 \rightarrow {}^4T_1$]; the absence of the multiple absorption of **1**^{p}, **3**^{p}, and **4**^{p} also clearly confirmed the successful Co^{II}-doping in our complexes.[12e,17] Photoluminescent measurements of the four complexes were carried out in the solid state at room temperature (Supporting Information, Figure S7). Complexes **1**−**4** display fluorescent emissions at 389, 395, 397, 387 nm in the solid state, respectively, which may be assigned to intraligand n-π^* or π-π^* transitions.

In summary, this work reports four new Co^{II}-doped Zn^{II}-tetrazole-benzoate coordination polymers with a series structurally related tetrazole-benzoic acid ligands by in situ hydrothermal synthesis. The tuning of structural frameworks were achieved through ligand modifications in these complexes. This series of structurally related ligands allow us to systematically investigate the effect of the disposition of two functional groups of an aromatic ring of ligands on the structures of the resulting coordination polymers. Further investigations on mixed metal systems are still under way in our laboratory.

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Supporting Information Available: Hydrogen bond parameters (Table S1) and detailed crystallographic information files in CIF format. Photos of the crystals of **1**−**4** showing the presence of Co^{II} in the crystals (Figure S1). TGA plots for all complexes (Figure S2). XPRD patterns for **1**−**4** (Figure S3). Additional figures (Figures S4−S6). Emission spectra of **1**−**4** in the solid state (Figure S7). The twisting modes of the carboxyl and tetrazoyl out-of-plane of the aromatic rings (Scheme S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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