Effect of pH/Auxiliary Ligand on the Structures of Coordination Compounds Based on a Novel Ligand 2,6-Bis(pyrazin-2-yl)pyridine-4-carboxylate Postprint

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Abstract

Four new coordination compounds, [Zn(bppc)2(H2O)2]·3H2O (1), [Zn2(bppc)2(m-bdc)(H2O)4]·7H2O (2), [Zn(bppc)2(H2O)2]n·n(m-Hbdc)·n(H2O) (3), [Zn2(bppc)(btc)(H2O)3]n·5nH2O (4) (Hbppc = 2,6-bis(pyrazin-2-yl)pyridine-4-carboxylate, H2(m-bdc) = 1,3-benzenedicarboxylic acid, H3btc = 1,3,5-benzene-tricarboxylic acid), have been hydrothermally synthesized and structurally characterized. Compound 1 shows a mononuclear structure and 2 shows a dinuclear structure. Compound 3 is a one-dimensional chain structure, which is extended into a 3D supramolecular network by intermolecular hydrogen interactions. In 4, a 1D loop-like chain is connected by (btc)3- anions to generate a 2D layer structure. The structure differences of 1–4 show that the pH and aromatic acid as auxiliary ligand have important influence on the final structures.[1] Additionally, the luminescent properties of 1–4 have been investigated with fluorescent spectra in the solid state, and 1–4 display a strong fluorescent emission at room temperature and have potential applications as fluorescent-emitting materials.

Full Text

Preamble

Effect of pH/Auxiliary Ligand on the Structures of Coordination Compounds Based on a Novel Ligand 2,6-Bis(pyrazin-2-yl)pyridine-4-carboxylate

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Abstract

Four coordination compounds, [Zn(bppc) (H O)] · 3H O (1), [Zn (bppc) (m-bdc)(H O)] · 7H O (2), [Zn(bppc) (H O)] · n(m-Hbdc) · n(H O) (3), and [Zn (bppc)(btc)(H O)] · 5nH O (4) (Hbppc = 2,6-bis(pyrazin-2-yl)pyridine-4-carboxylate, H (m-bdc) = 1,3-benzenedicarboxylic acid, H btc = 1,3,5-benzenetricarboxylic acid), have been hydrothermally synthesized and structurally characterized. Compound 1 exhibits a mononuclear structure, while 2 displays a dinuclear structure. Compound 3 features a one-dimensional chain structure that extends into a 3D supramolecular network through intermolecular hydrogen bonding interactions. In 4, 1D loop-like chains are connected by (btc)^{3} anions to generate a 2D layer structure. The structural differences among 1–4 demonstrate that both pH and aromatic acid auxiliary ligands exert important influences on the final architectures. Additionally, the luminescent properties of 1–4 were investigated using solid-state fluorescence spectroscopy. All four compounds display strong fluorescent emission at room temperature, indicating their potential applications as fluorescent-emitting materials.

Keywords: crystal structure; hydrothermal synthesis; coordination polymer; luminescence

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1. Introduction

Over the past two decades, increasing research attention has been devoted to constructing various coordination compounds, driven not only by their diverse applications as functional materials in fields such as luminescence, chemical and biological sensing, separation, magnetism, catalysis, gas adsorption, ion exchange, and chirality [1-9], but also by their intriguing architectures and fascinating topologies [10]. Among these, zero-dimensional (0D) multinuclear complexes, one-dimensional (1D) helical and zigzag chains, two-dimensional (2D) grids, three-dimensional (3D) porous structures, and interpenetrating networks have been reported [11]. Although numerous metal coordination frameworks with beautiful topologies and interesting properties have been synthesized, controlling structures with desired properties remains a significant challenge, as many factors influence the outcome, including solvent system selection, reaction temperature, time, pH, organic ligand choice, metal ion type, metal-to-ligand ratio, counterion, and other parameters [12-15]. An effective and facile approach to address this challenge is the appropriate selection of well-designed organic bridging ligands containing modifiable backbones and connectivity information, combined with metal centers having various coordination preferences.

Our research group focuses on ternary compounds constructed from rigid N-donor ligands (polypyridine pyrazine), O-donor ligands (polycarboxylate), and transition metal ions. 2,6-Bis(pyrazin-2-yl)pyridine-4-carboxylic acid (Hbppc, Chart 1) represents a rigid planar ligand that has not been previously reported in the chemical literature. This ligand possesses several notable structural features. First, it contains five nitrogen atoms and two oxygen atoms from one pyridyl, two pyrazinyl, and one carboxyl group, enabling it to function as either a chelating or bridging ligand. Second, the carboxyl and N-heterocyclic groups can act as both hydrogen-bond acceptors and donors, depending on their protonation state, which facilitates the construction of supramolecular architectures. Additionally, the extended conjugated system can readily form – interactions that significantly influence supramolecular framework construction. Consequently, Hbppc serves as an excellent candidate for building metal-organic supramolecular architectures.

Beyond coordination bonding, other noncovalent interactions such as hydrogen bonds [16] and · · · interactions [17] also profoundly affect coordination polymer structures, potentially linking multinuclear discrete subunits or low-dimensional entities into high-dimensional supramolecular networks to enhance overall structural stability. In this work, by employing the Hbppc ligand and varying pH and/or using auxiliary ligands, we prepared a series of coordination polymers: [Zn(bppc) (H O)] · 3H O (1), [Zn (bppc) (m-bdc)(H O)] · 7H O (2), [Zn(bppc)(H O)] · n(m-Hbdc) · n(H O) (3), and [Zn (bppc)(btc)(H O)] · 5nH O (4) under hydrothermal conditions. Furthermore, their luminescent properties and thermal stability were investigated.

2. Experimental

2.1 Materials and General Methods

The Hbppc ligand was prepared according to a literature method with some modifications [18]. All other chemicals and reagents were purchased commercially and used without further purification. Elemental analyses (C, H, N) were performed using a Vario EL III elemental analyzer. Infrared spectra were recorded on a Bruker EQUINOX55 spectrometer as KBr pellets in the 4000–400 cm ^{1} range. Fluorescence spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Thermogravimetric analyses (TGA) were conducted using a Universal V2.6 DTA system at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.2 Synthesis of Hbppc

A mixture of 2-furaldehyde (1.92 g, 2 mmol), acetylpyrazine (4.88 g, 4 mmol), and crushed NaOH powder (1.60 g, 40.0 mmol) was dissolved in ethanol (100 mL) and stirred at 60 °C for 24 h, resulting in a red solution. After cooling to room temperature, the mixture was filtered and dried in vacuo to yield 2.0 g of 4-furan-2-yl-2,6-diphenyl-pyridine. Subsequently, KMnO (3.21 g, 26.7 mmol) and water (100 mL) were added, the pH was adjusted to 9 with NaOH, and the solution was stirred at 80 °C for 1 h. After cooling to room temperature, the mixture was filtered, followed by pH adjustment to 5 with HCl. The resulting mauve precipitate was filtered, recrystallized from methanol, and dried in vacuo to afford 2.41 g (32.4% yield) of Hbppc as colorless needle crystals. Anal. Calcd. (%) for C H N O : C, 168.15; H, 9.07; N, 70.04; O, 32.00. Found (%): C, 168.09; H, 8.98; N, 70.01; O, 31.89. IR (KBr, cm ^{1}): 3414(s), 2474(w), 1898(w), 1617(s), 1524(w), 1467(w), 1370(m), 1252(m), 1164(w), 1108(m), 1081(w), 856(m), 776(m), 750(w), 679(w), 617(w), 484(w).

2.3 Synthesis of [Zn(bppc) (H O)] · 3H O (1)

A mixture of Hbppc (27.9 mg, 0.1 mmol) and ZnCl (27.3 mg, 0.2 mmol) in deionized water (10 mL) was stirred while adjusting the pH to 5.5 with 0.2 mol/L NaOH. After stirring for 30 min, the mixture was sealed in a 25 mL Teflon-lined stainless-steel vessel and heated to 160 °C for 96 h. The reaction system was then cooled to room temperature over 48 h, yielding colorless block crystals of 1 in approximately 50% yield based on Zn. The crystals were collected by filtration and washed with deionized water. Anal. Calcd. for C H N O Zn (701.88): C, 47.91; H, 2.3; N, 19.96%. Found: C, 47.93; H, 2.5; N, 19.95%. IR (KBr, cm ^{1}): 3385(s), 1621(s), 1560(m), 1468(w), 1431(w), 1377(s), 1321(s), 1233(w), 1166(m), 1136(w), 1108(w), 1034(m), 916(w), 857(w), 824(w), 791(w), 767(w), 699(w), 621(w), 495(w).

2.4 Synthesis of [Zn (bppc) (m-bdc)(H O)] · 7H O (2)

A mixture of Hbppc (27.9 mg, 0.1 mmol), ZnCl (27.3 mg, 0.2 mmol), and H (m-bdc) (16.6 mg, 0.1 mmol) in deionized water (10 mL) was stirred, and the pH was adjusted to 5.5 with 0.2 mol/L NaOH. After stirring for 30 min, the reaction mixture was sealed in a Teflon-lined stainless-steel vessel and heated to 160 °C for 96 h. The system was then cooled to room temperature over 48 h, affording colorless sheet crystals of 2 in approximately 50% yield based on Zn, which were collected by filtration and washed with deionized water. Anal. Calcd. for C H N O Zn (1049.55): C, 41.20; H, 4.03; N, 13.35%. Found: C, 41.21; H, 4.025; N, 13.31%. IR (KBr, cm ^{1}): 3415(m), 1615(s), 1562(m), 1456(m), 1403(m), 1375(vs), 1331(m), 1168(m), 1089(w), 1038(m), 861(w), 792(w), 745(w), 711(w), 683(w), 463(w).

2.5 Synthesis of [Zn(bppc) (H O)] · n(m-Hbdc) · n(H O) (3)

Compound 3 was synthesized similarly to 2, except the pH was adjusted to 6.5. Yellow block crystals were obtained in approximately 50% yield based on Zn. Anal. Calcd. for C H N O Zn (562.79): C, 46.95; H, 3.4; N, 12.44%. Found: C, 46.94; H, 3.5; N, 12.43%. IR (KBr, cm ^{1}): 3421(m), 1609(s), 1458(w), 1375(s), 1170(m), 1036(m), 916(w), 860(w), 793(w), 743(m), 714(m), 683(w), 528(w), 462(w).

2.6 Synthesis of [Zn (bppc)(btc)(H O)] ·5nH O (4)

Compound 4 was synthesized similarly to 2, except H btc was used instead of H (m-bdc). Colorless block crystals were obtained in approximately 65% yield based on Zn. Anal. Calcd. for C H N O Zn (760.26): C, 36.34; H, 3.58; N, 9.21%. Found: C, 36.32; H, 3.56; N, 9.19%. IR (KBr, cm^{1}): 3416(m), 2026(w), 1618(s), 1562(m), 1426(m), 1376(s), 1183(m), 1066(w), 1035(m), 913(w), 766(w), 714(m), 687(w), 612(w), 548(w), 460(w), 414(w).

2.7 X-ray Crystallography

Intensity data were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo-K radiation (= 0.71073 Å) at room temperature. Empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares based on F^2 using the SHELXTL-97 program [19]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of organic ligands were generated geometrically. Selected bond distances and bond angles for 1–4 are listed in Table 1 –4.

3. Results and Discussion

3.1 Structure Description of 1

Single-crystal X-ray analysis reveals that 1 crystallizes in the triclinic system, space group P, with a = 7.165(6), b = 11.482(10), c = 19.018(17) Å, = 88.973(16)°, = 85.533(16)°, = 72.386(17)°, Z = 1, and exhibits a mononuclear structure, as shown in Fig. 1a [Figure 1: see original paper]. The asymmetric unit of 1 consists of one Zn(II) cation, two (bppc) anions, two coordinated water molecules, and three lattice water molecules. Zn(1) is hexa-coordinated by three nitrogen atoms [N(1), N(3), N(4)] and one oxygen atom O(3) from (bppc) anions, plus two oxygen atoms [O(5), O(6)] from coordinated water molecules, adopting a distorted octahedral geometry. The N(1), N(3), N(4), and O(3) atoms form the equatorial plane, while O(5) and O(6) occupy the axial positions. The Zn–N and Zn–O bond lengths range from 2.059(8)–2.203(10) Å and 1.928(7)–2.234(7) Å, respectively, consistent with values reported for Zn-pyridyl and Zn-carboxylate complexes [20]. In 1, two (bppc) anions coordinate to a Zn(II) cation through monodentate (Scheme 1a) and tridentate chelating (Scheme 1b) modes to form a mononuclear structure. Adjacent mononuclear units are interconnected via intermolecular hydrogen bonding interactions between nitrogen atoms of (bppc) ligands and oxygen atoms of coordinated water molecules (N(2) ⋯ O(5), 2.828 Å), and between oxygen atoms of coordinated water molecules and oxygen atoms of (bppc) ligands (O(6) ⋯ O(1), 2.737 Å) to form a 1D chain (Fig. 1b). These chains are further connected through hydrogen bonding interactions between N atoms of (bppc) ligands and O atoms of lattice water molecules (N(10) ⋯ O(7) = 2.721 Å), and between O atoms of coordinated water molecules and O atoms of lattice water molecules (O(7) ⋯ O(6) = 2.582 Å) to generate a 2D supramolecular structure (Fig. 1c).

3.2 Structure Description of 2

Single-crystal X-ray analysis reveals that 2 crystallizes in the triclinic system, space group P, with a = 9.9357(11), b = 10.5755(12), c = 21.343(2) Å, = 80.253(2)°, = 79.653(2)°, = 76.851(2)°, and Z = 2. Compound 2 displays a dinuclear structure, as shown in Fig. 2a [Figure 2: see original paper]. The asymmetric unit of 2 contains two crystallographically independent Zn(II) cations, two (bppc) anions, one (m-bdc)^{2} anion, four coordinated water molecules, and seven lattice water molecules. Zn1 is coordinated by three nitrogen atoms from one (bppc) anion (Zn(1)-N(1) = 2.284(3) Å, Zn(1)-N(3) = 2.126(3) Å, Zn(1)-N(4) = 2.176(3) Å) and three oxygen atoms from the (m-bdc)^{2} anion and two coordinated water molecules (Zn(1)-O(5) = 1.969(3) Å, Zn(1)-O(9) = 2.158(3) Å, Zn(1)-O(10) = 2.110(3) Å, Zn(1)-O(10) = 2.186(3) Å), exhibiting a distorted octahedral coordination geometry. Zn2 shows similar coordination geometry to Zn1. In 2, one (bppc) anion coordinates to a Zn(II) cation through a chelating mode (Scheme 1b) to form a mononuclear unit, and two such units are bridged by a (m-bdc)^{2} anion in a - ^{1}: ^{1} coordination mode to form a dinuclear [Zn (bppc) (m-bdc)(H O)] structure. Adjacent dinuclear units are interconnected via intermolecular hydrogen-bonding interactions between O atoms of (m-bdc)^{2} anions, N atoms of (bppc) ligands, and O atoms of coordinated water molecules (N(2) ⋯ O(10), 2.678 Å; O(12) ⋯ O(4), 2.844 Å) to form a one-dimensional chain (Fig. 2b). These chains are further extended into a 2D supramolecular layer (Fig. 2c).

3.3 Structure Description of 3

Single-crystal X-ray analysis reveals that 3 crystallizes in the orthorhombic system, space group Pna2 , with a = 17.7527(15), b = 17.5479(15), c = 7.3095(6) Å, and Z = 4. Compound 3 is a one-dimensional chain structure, as shown in Fig. 3a [Figure 3: see original paper]. The asymmetric unit of 3 consists of one Zn(II) cation, one (bppc) ligand, one (m-Hbdc) counter anion, two coordinated water molecules, and one lattice water molecule. Zn(1) is hexa-coordinated by three nitrogen atoms (N(1), N(3), N(4)) and one oxygen atom O(2) from one (bppc) anion, plus two oxygen atoms (O(7), O(8)) from two coordinated water molecules, adopting a distorted octahedral geometry. The N(1), N(3), N(4), and O(2) atoms comprise the equatorial plane, while O(7) and O(8) occupy the axial positions. Each (bppc) anion coordinates to one Zn(II) atom through its chelating nitrogen atoms, and the Zn(II) atoms are further bridged by carboxylate oxygen atoms of another (bppc) anion (Chart 2c) to form a linear 1D chain (Fig. 3b). These linear chains are extended into a 2D supramolecular structure through intermolecular hydrogen bonding interactions between O atoms of coordinated and lattice water molecules (O(7)$\cdots$O(9) = 2.721 Å), as well as between O atoms of lattice water molecules and the (m-Hbdc) counter anion (O(9) $\cdots$ O(5) = 2.921 Å, O(9) $\cdots$ O(3) = 2.759 Å) (Fig. 3c). This 2D supramolecular structure is further extended into a 3D supramolecular architecture through additional hydrogen-bonding interactions involving coordinated water molecules, (m-Hbdc) counter anions, and (bppc) anions (Fig. 3d).

3.4 Structure Description of 4

Single-crystal X-ray diffraction analysis reveals that 4 crystallizes in the monoclinic system, space group P2 /c, with a = 14.726(2), b = 14.613(2), c = 13.7709(19) Å, = 111.2552(2)°, and Z = 4. Compound 4 displays a two-dimensional supramolecular structure composed of one-dimensional chains. The asymmetric unit of 4 contains two crystallographically independent Zn(II) cations, one (bppc) anion, one (btc)^3 anion, three coordinated water molecules, and five lattice water molecules. As shown in Fig. 4a [Figure 4: see original paper], Zn(1) is coordinated by three nitrogen atoms from one (bppc) ligand (Zn(1)-N(1) = 2.210(4) Å, Zn(1)-N(3) = 2.135(4) Å, Zn(1)-N(4) = 2.242(4) Å), one carboxylic oxygen atom of the (btc)^3 anion (Zn(1)-O(6) = 1.993(4) Å), and two oxygen atoms from two different coordinated water molecules (Zn(1)-O(9) = 2.098(4) Å, Zn(1)-O(10) = 2.113(4) Å), showing a distorted octahedral coordination geometry. Zn(2) is coordinated by one nitrogen atom and one oxygen atom from one (bppc) ligand (Zn(2)-N(5) = 2.122(4) Å, Zn(2)-O(1A) = 2.070(4) Å), three carboxylic oxygen atoms of the (btc)^3 anion (Zn(2)-O(3C) = 1.945(4) Å, Zn(2)-O(7A) = 2.358(5) Å, Zn(2)-O(8A) = 2.089(5) Å), and one oxygen atom from a coordinated water molecule (Zn(2)-O(11) = 2.285(6) Å), also displaying a distorted octahedral coordination geometry. Each (bppc) ligand adopts a -^{1}: ^{3}: ^{1} mode (Chart 2d) to link Zn(1) and Zn(2). Each Zn(1) atom is further bridged by one (btc)^3 anion in a -^{1}: ^{2}: ^{1} coordination mode to form a 1D chain (Fig. 4b), and the (btc)^3 anions further extend the 1D chain into a 2D supramolecular layer structure (Fig. 4c). To simplify the multidimensional structure into a node-and-connection net, Zn(1) and Zn(2) can be considered as 2- and 4-connected nodes, respectively, while the (bppc) ligand and (btc)^3 anions serve as 3-connected linkers. Topological analysis reveals that compound 4 has a {4.6.8}{4.62.82.10}{62.8}{6} topology (Fig. 4d).

3.5 Effect of pH Value and Auxiliary Ligand on the Structures of 1-4

Compounds 1-4 were prepared as single-phase crystalline products via hydrothermal reactions of the Hbppc ligand and ZnCl with or without corresponding O-donor auxiliary ligands. Our experimental and structural results prompted investigation into how reaction conditions affect the final architectures. Compounds 1 and 2 were synthesized under identical reaction conditions except for the presence of O-donor auxiliary ligands. The H (m-bdc) ligand in 2 is completely deprotonated and coordinates with Zn(II), resulting in a structure distinct from that of 1. Complexes 2 and 3 were synthesized under the same conditions except for reaction pH (pH = 5.5 for 2 and pH = 6.5 for 3). The pH influence on structure is rooted in the protonation state of the Hbppc ligand. At pH = 5.5 in compound 2, the Hbppc ligand is not protonated and (m-bdc)^{2} coordinates to Zn(II) as an O-donor auxiliary ligand. In contrast, at pH = 6.5 in compound 3, the Hbppc ligand is deprotonated to coordinate with Zn(II) and satisfy the coordination requirements of the metal center, while [H(m-bdc)] exists as a guest molecule to balance charge and stabilize the framework. Compounds 3 and 4 were also isolated under identical conditions except for different auxiliary ligands (H (m-bdc) for 3 and H btc for 4), resulting in 3 possessing a 1D ladder-chain structure while 4 exhibits a 2D layer structure.

3.6 Luminescent Properties

Organic-inorganic coordination polymers, particularly those with d^{1} metal centers, have been extensively investigated for their fluorescent properties and potential applications as fluorescent-emitting materials, such as in light-emitting diodes (LEDs) [21]. Therefore, we studied the photoluminescence properties of 1–4 and the free Hbppc ligand in the solid state (Fig. 5 [Figure 5: see original paper]). The free Hbppc ligand shows intense emission bands at 420 and 466 nm (= 290 nm), assignable to ligand-centered charge transitions, specifically * → n and * → transitions [22]. Bimodal emissions are observed at 500 nm for 1, 477 nm for 2, 471 nm for 3, and 526 nm for 4 upon excitation at 280 nm. As previously reported [23,24], the solid aromatic carboxylate ligands 1,3-H bdc and H btc are nearly non-fluorescent in the 400–600 nm range at ambient temperature. Compared with free Hbppc, the main peaks in 1–4 are red-shifted, likely resulting from ligand-to-metal charge transfer (LMCT) [25]. Notably, lower-energy emissions were also detected at 388 nm for 1, 395 nm for 2, and 390 nm for 3, attributable to intraligand * → transitions.

3.7 Thermogravimetric Analysis

To characterize the thermal stability of compounds 1–4, their thermal decomposition behavior was investigated from 30 to 1000 °C under nitrogen atmosphere using thermogravimetric analysis. Compound 1 first loses lattice water molecules below 104 °C, with an observed weight loss of 7.1% consistent with the calculated value (7.7%). The second weight loss stage occurs from 108 to 150 °C, corresponding to departure of coordinated water molecules (Calcd. 5.1%; Found: 4.9%). Above 348 °C, the compound begins to lose ligands and decompose (Fig. 6a [Figure 6: see original paper]). For 2, the weight loss of 18.28% below 116 °C corresponds to removal of both lattice and coordinated water molecules (calcd. 18.62%). Subsequently, a weight loss of 14.84% between 160 and 325 °C indicates loss of H (m-bdc) (calcd. 15.04%), after which the framework begins to collapse (Fig. 6b). Compound 3 begins losing water molecules and free H (m-bdc) molecules below 345 °C, with decomposition of residual components starting above 360 °C (Fig. 6c). The framework of compound 4 remains intact until heated to 338 °C, after which it begins to collapse (Fig. 6d). These TGA results indicate that all four coordination frameworks possess excellent thermal stability.

4. Conclusion

In summary, four new compounds have been synthesized through the assembly of Hbppc, different auxiliary ligands, and zinc salts under hydrothermal conditions. Compounds 1–4 exhibit intriguing 0D, 1D, and 2D structures. Their structural diversity demonstrates that both the pH value of the reaction system and the auxiliary ligand play significant roles in the structural self-assembly process. Additionally, hydrogen bonding interactions contribute substantially to the formation of supramolecular architectures. Moreover, compounds 1–4 exhibit intense emissions, indicating they may be promising candidates as luminescent materials.

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Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for 1

Zn(1)-O(3) | 1.928(7) | Angle | |

Zn(1)-N(1)	2.174(9)	O(3)-Zn(1)-O(5)	93.4(3)
Zn(1)-O(5)	2.234(7)	O(3)-Zn(1)-N(3)	174.0(4)
Zn(1)-N(3)	2.059(8)	O(6)-Zn(1)-N(1)	90.5(3)
Zn(1)-O(6)	1.969(3)	N(1)-Zn(1)-N(4)	149.9(3)
Zn(1)-N(4)	2.203(10)	N(3)-Zn(1)-N(1)	74.9(4)
Zn(1)-O(5)	2.127(8)	O(3)-Zn(1)-O(6)	90.0(3)
Zn(1)-N(1)	2.284(3)	O(3)-Zn(1)-N(4)	99.0(4)
Zn(2)-O(7)	1.938(3)	O(6)-Zn(1)-N(4)	90.3(3)
Zn(2)-N(6)	2.242(3)	N(3)-Zn(1)-O(5)	86.8(3)
		N(3)-Zn(1)-N(4)	75.0(3)
		O(3)-Zn(1)-N(1)	111.1(4)
		O(6)-Zn(1)-O(5)	176.0(3)
		N(1)-Zn(1)-O(5)	90.2(3)
		N(3)-Zn(1)-O(6)	89.6(3)
		N(4)-Zn(1)-O(5)	87.1(3)

Table 2 . Selected Bond Lengths (Å) and Bond Angles (°) for 2

Zn(1)-O(5)	1.969(3)	Zn(1)-O(10)	2.110(3)
Zn(1)-N(1)	2.284(3)	Zn(1)-N(4)	2.175(3)
Zn(1)-O(9)	2.158(3)	Zn(2)-O(11)	2.109(3)
Zn(1)-N(3)	2.126(3)	Zn(2)-N(8)	2.103(3)
Zn(1)-O(10)	2.186(3)		
Zn(2)-O(7)	1.938(3)		
Zn(2)-N(6)	2.242(3)		

Angle		Angle	
O(5)-Zn(1)-O(9)	86.99(12)	O(9)-Zn(1)-N(4)	89.65(12)
O(5)-Zn(1)-O(10)	96.94(13)	O(10)-Zn(1)-O(9)	175.86(12)
O(5)-Zn(1)-N(1)	159.25(12)	O(10)-Zn(1)-N(1)	87.00(11)
O(5)-Zn(1)-N(3)	123.82(11)	O(10)-Zn(1)-N(3)	89.26(12)
O(5)-Zn(1)-N(4)	87.91(11)	O(10)-Zn(1)-N(4)	87.09(11)
O(9)-Zn(1)-N(1)	87.48(11)	N(3)-Zn(1)-O(9)	87.48(11)
O(9)-Zn(1)-N(3)	94.46(11)	N(3)-Zn(1)-N(1)	72.61(11)
O(9)-Zn(1)-N(4)	89.65(12)	N(3)-Zn(1)-N(4)	76.11(11)
O(10)-Zn(1)-O(9)	175.86(12)	N(4)-Zn(1)-N(1)	148.21(11)
O(10)-Zn(1)-N(1)	87.00(11)	O(7)-Zn(2)-O(11)	94.70(12)
O(10)-Zn(1)-N(3)	89.26(12)	O(7)-Zn(2)-O(12)	85.43(11)
O(10)-Zn(1)-N(4)	87.09(11)	O(7)-Zn(2)-N(6)	96.55(12)
N(3)-Zn(1)-O(9)	87.48(11)	O(7)-Zn(2)-N(8)	165.96(12)
N(3)-Zn(1)-N(1)	72.61(11)	O(7)-Zn(2)-N(9)	114.65(12)
N(3)-Zn(1)-N(4)	76.11(11)	O(11)-Zn(2)-O(12)	176.20(12)
N(4)-Zn(1)-N(1)	148.21(11)	O(11)-Zn(2)-N(6)	85.71(11)
		O(11)-Zn(2)-N(9)	89.22(12)
		O(12)-Zn(2)-N(6)	90.51(11)
		N(8)-Zn(2)-O(11)	94.97(12)
		N(8)-Zn(2)-O(12)	84.25(11)

	N(8)-Zn(2)-N(6)	74.07(11)
	N(8)-Zn(2)-N(9)	75.65(11)
	N(9)-Zn(2)-O(12)	94.17(12)
	N(9)-Zn(2)-N(6)	148.70(11)

Table 3 . Selected Bond Lengths (Å) and Bond Angles (°) for 3

Zn(1)-O(2)#1	1.9517(16)	Zn(1)-O(8)	2.215(3)
Zn(1)-O(7)	2.141(2)	Zn(1)-N(1)	2.192(2)
Zn(1)-O(8)	2.215(3)	Zn(1)-N(3)	2.0879(18)
Zn(1)-N(1)	2.192(2)	Zn(1)-N(4)	2.183(2)
Zn(1)-N(3)	2.0879(18)		
Zn(1)-N(4)	2.183(2)		

Angle		Angle	
O(2)#1-Zn(1)-O(7)	89.49(13)	O(7)-Zn(1)-N(4)	87.84(10)
O(2)#1-Zn(1)-O(8)	92.42(13)	N(3)-Zn(1)-O(7)	91.59(10)
O(2)#1-Zn(1)-N(1)	105.54(10)	N(4)-Zn(1)-O(8)	88.09(10)
O(2)#1-Zn(1)-N(3)	178.46(16)	N(3)-Zn(1)-O(8)	86.43(10)
O(2)#1-Zn(1)-N(4)	103.51(10)	N(4)-Zn(1)-N(1)	150.95(8)
O(7)-Zn(1)-O(8)	175.81(10)	N(1)-Zn(1)-O(8)	91.04(11)
O(7)-Zn(1)-N(1)	92.03(10)	N(3)-Zn(1)-N(4)	75.44(8)

Table 4 . Selected Bond Lengths (Å) and Bond Angles (°) for 4

Zn(1)-O(6)#1	1.993(4)	Zn(1)-O(9)	2.098(4)
Zn(1)-N(1)	2.210(4)	Zn(1)-N(3)	2.135(4)
Zn(2)-O(1)#2	2.070(4)	Zn(2)-O(11)	2.285(6)
Zn(2)-O(8)#3	2.089(5)	Zn(1)-O(10)	2.113(4)
Zn(1)-O(9)	2.098(4)	Zn(1)-N(4)	2.242(4)
Zn(1)-N(3)	2.135(4)	Zn(2)-O(7)#3	2.358(5)
Zn(2)-O(3)	1.945(4)	Zn(2)-N(5)	2.122(4)

Angle		Angle	
O(6)#1-Zn(1)-O(9)	92.43(16)	O(9)-Zn(1)-N(4)	88.47(16)
O(6)#1-Zn(1)-O(10)	91.51(19)	O(10)-Zn(1)-N(1)	93.39(16)
O(6)#1-Zn(1)-N(1)	124.44(15)	O(10)-Zn(1)-N(3)	84.03(18)
O(6)#1-Zn(1)-N(3)	161.10(15)	O(10)-Zn(1)-N(4)	85.36(16)
O(6)#1-Zn(1)-N(4)	87.28(14)	N(1)-Zn(1)-N(4)	148.27(14)
O(9)-Zn(1)-O(10)	172.51(18)	N(3)-Zn(1)-N(1)	74.27(14)
O(9)-Zn(1)-N(1)	89.61(15)	N(3)-Zn(1)-N(4)	74.07(14)
O(9)-Zn(1)-N(3)	90.20(15)	O(1)#2-Zn(2)-O(7)#3	93.18(17)
O(1)#2-Zn(2)-O(8)#3	93.55(18)	O(3)-Zn(2)-O(11)	86.4(2)
O(1)#2-Zn(2)-O(11)	172.97(18)	O(3)-Zn(2)-N(5)	114.16(17)
O(1)#2-Zn(2)-C(23)#3	95.80(18)	O(3)-Zn(2)-C(23)#3	119.4(2)
O(3)-Zn(2)-O(1)#2	98.40(17)	O(7)#3-Zn(2)-C(23)#3	28.96(18)
O(3)-Zn(2)-O(7)#3	91.47(16)	O(8)#3-Zn(2)-O(7)#3	58.57(16)
O(3)-Zn(2)-O(8)#3	148.37(18)	O(8)#3-Zn(2)-O(11)	79.7(2)
O(8)#3-Zn(2)-N(5)	93.73(17)	N(5)-Zn(2)-O(7)#3	151.62(15)

O(8)#3-Zn(2)-C(23)#3 | 29.72(19) | N(5)-Zn(2)-O(11) | 87.8(2) | O(11)-Zn(2)-O(7)#3 | 81.6(2) | N(5)-Zn(2)-C(23)#3 | 122.89(18) | O(11)-Zn(2)-C(23)#3 | 77.3(2) | | |

Chart 1. Structure of the Hbppc ligand

Chart 2. Syntheses of compounds 1-4

Scheme 1. Coordination modes of the (bppc) ligand in 1-4

Fig. 1. (a) Coordination environment of the Zn(II) cations in 1; (b) 1D chain structure of 1; (c) Perspective view of the 2D supramolecular framework

Fig. 2. (a) Coordination environment of the Zn(II) cations in 2; (b) View of the 1D chain formed by hydrogen bonds; (c) 2D supramolecular framework formed by hydrogen bonds

Fig. 3. (a) Coordination environment of the Zn(II) cation in 3; (b) View of the 1D chain of 3; (c) 2D supramolecular framework of 3; (d) Perspective view of the 3D supramolecular framework of 3

Fig. 4. (a) Coordination environment of the Zn(II) atom in 4; (b) View of the 1D chain of 4; (c) 2D layer framework of 4; (d) Topological network of 4

Fig. 5 [Figure 5: see original paper]. Solid-state emission spectra of the Hbppc ligand and complexes 1-4 at room temperature

Fig. 6 [Figure 6: see original paper]. TGA curves for 1 (a), 2 (b), 3 (c) and 4 (d)

Note: Figure translations are in progress. See original paper for figures.

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