Two new competitive coordination-directed zinc(II) complexes, \([\text{Zn}_2(\text{bpp})_2(\text{na})_4]_n\) (1) and \([\text{Zn}(\text{bpp})_2(\text{nas})_2]_n\) (2) (bpp = 1,3-bi(4-pyridyl)propane, na = 1-naphthoate, and nas = 2-amino naphthalene-1-sulfonate), were hydrothermally synthesized by varying carboxylate- or sulfonate-containing coligands. Structural analyses reveal that complex 1 modified by terminal na spacers possesses a bent one-dimensional chain bridged by ditopic bpp linkers. By contrast, complex 2 with two monodentate nas ligands exhibits a two-dimensional layered structure extended by four equatorial bpp connectors. Obviously, the increase on the dimensionality of 2 than 1 is significantly resulting from the competitive coordination of the two mixed ligands with differently tunable binding groups to variable metal polyhedra. In addition, both complexes with analogously high thermal stability display strong fluorescent emissions at room temperature resulting from the ligand-to-metal or intraligand charge-transfer, suggesting their hopeful applications as efficient fluorescent materials.

**Keywords:** competitive coordination, 1,3-bi(4-pyridyl)propane, crystal structure, fluorescence

**Introduction**

Rational design and successful preparation of novel coordination polymers (CPs) have recently attracted considerable attention due to their intriguing structural diversities\(^1\) and potential applications as selective catalysts,\(^2\) gas adsorbents,\(^3\) molecule-based magnets,\(^4\) and fluorescent materials.\(^5\)–\(^7\) It is well known that the structural diversities of the reported CPs can be significantly dominated by variously tuneable factors from both the reactants or surroundings. Some external perturbations, such as temperature, pH value, solvent, template molecule, and so on, can essentially direct the types and connection manners of structural subunits and the dimensionality of the resulting CPs. Additionally, the coordination preference of the single or mixed ligands toward the metal coordination polyhedra can more importantly govern the structural novelty and unpredictability, which can further influence the structure-dependent optical, electronic, or magnetic properties of the targeted CPs. For example, resulting from competitive or synergic binding of the mixed ligands to the same metal ion with variable coordination spheres, several interesting samples with different structures and the same compositions have been successively fabricated from the reaction systems of the Cu\(^{II}/\)Co\(^{II}\)-triazolate-sulfonisophthalate and Cu\(^{II}\)-triazolate-citrate,\(^8\)–\(^10\) which exhibit interesting transformations on the structure and magnetic behaviors. Herein, to further investigate the competitive coordination ability of the mixed ligands with different binding groups to transition metal ions, two O-donor-based coligands respectively with functional carboxylate and sulfonate moieties, 1-naphthoic acid (Hna) and 2-amino naphthalene-1-sulfonate acid (Hnas), were chosen as gate the competitive coordination ability of the mixed ligands with the two different coligands toward the metal coordination polyhedra can more importantly govern the structural novelty and unpredictability, which can further influence the structure-dependent optical, electronic, or magnetic properties of the targeted CPs. For example, resulting from competitive or synergic binding of the mixed ligands to the same metal ion with variable coordination spheres, several interesting samples with different structures and the same compositions have been successively fabricated from the reaction systems of the Cu\(^{II}/\)Co\(^{II}\)-triazolate-sulfonisophthalate and Cu\(^{II}\)-triazolate-citrate,\(^8\)–\(^10\) which exhibit interesting transformations on the structure and magnetic behaviors. Herein, to further investigate the competitive coordination ability of the mixed ligands with different binding groups to transition metal ions, two O-donor-based coligands respectively with functional carboxylate and sulfonate moieties, 1-naphthoic acid (Hna) and 2-amino naphthalene-1-sulfonate acid (Hnas), were chosen as gate the competitive coordination ability of the mixed ligands with the two different coligands toward the metal coordination polyhedra can more importantly govern the structural novelty and unpredictability, which can further influence the structure-dependent optical, electronic, or magnetic properties of the targeted CPs.
Experimental

Materials and Instruments

Bpp, Hnas, and Hna were purchased from Acros and other analytical-grade starting materials were obtained commercially and used as received without further purification. Doubly deionized water was employed for the conventional synthesis. IR spectra were collected on a Nicolet IR-200 spectrometer with KBr pellets in the range 4000–400 cm⁻¹. Elemental analyses for C, H, and N were determined on a Perkin Elmer 2400 C elemental analyzer. TGA experiments were carried out on a Shimadzu simultaneous DTG-60A thermal analysis instrument with a heating rate of 10°C min⁻¹ from room temperature to 800°C under a nitrogen atmosphere (flow rate 10 mL min⁻¹). Fluorescence spectra of the polycrystalline powder samples of 1 and 2 were performed on a Fluorolog-3 fluorescence spectrophotometer from Horiba Jobin Yvon at room temperature.

Syntheses

For [Zn₂(bpp)₂(na)₄]₄⁻ (1), a mixture of Hna (68.9 mg, 0.4 mmol), bpp (79.2 mg, 0.4 mmol), Zn(NO₃)₂·6H₂O (118.8 mg, 0.4 mmol), NaOH (24.0 mg, 0.6 mmol), and doubly deionized water (12.0 mL) was sealed in a 23.0 mL stainless steel vessel and heated at 160°C for 120 hours under autogenous pressure. After the mixture was cooled to room temperature at a rate of 5°C h⁻¹, colorless block-shaped crystals suitable for single-crystal X-ray diffraction analysis were isolated directly, washed with ethanol, and dried in air. Yield: 36.0% (based on Hna), C₇₀H₅₆Zn₂N₄O₈: Anal. Calcd. for C 60.96; H 4.89; N 9.27%; Found C 60.82; H 4.91; N 9.43%. IR (KBr): ν = 3431 (w), 3330 (w), 3041 (w), 1622 (s), 1561 (m), 1507 (m), 1475 (m), 1430 (m), 1359 (m), 1200 (s), 1161 (m), 1048 (m), 820 (m), 751 (w), 674 (w), 622 (m), 552 (w), 514 (w), 461 (w) cm⁻¹.

Crystallography

Diffraction intensities for both 1 and 2 were collected on a computer-controlled Bruker APEX-II QUAZAR diffractometer equipped with graphite-monochromated Mo-Kα radiation with a radiation wavelength of 0.71073 Å by using the o-φ scan technique at room temperature. The program SADABS was used for integration of the diffraction profiles. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically. After the positions of H attached to oxygen atom were located in difference Fourier syntheses and then fixed geometrically as riding atoms. Crystallographic data and experimental details for structural analyses were summarized in Table 1. Selected bond distances and angles for 1 and 2 were

|                  | 1                              | 2                              |
|------------------|---------------------------------|---------------------------------|
| Formula          | C₇₀H₅₆Zn₂N₄O₈                  | C₄₆H₄₄ZnN₆S₂O₆                 |
| Fw               | 1211.93                         | 906.36                          |
| Crystal system   | monoclinic                      | orthorhombic                    |
| Space group      | P2₁/n                           | Pnna                           |
| a/Å              | 13.0436(13)                     | 23.2875(15)                    |
| b/Å              | 12.8352(12)                     | 10.9470(7)                     |
| c/Å              | 35.802(4)                       | 16.6440(10)                    |
| β/°              | 98.881(2)                       | 90.0                            |
| V/Å³             | 5922.1(10)                      | 4243.0(5)                      |
| Z                | 4                               | 4                               |
| Dₚ/g cm⁻³        | 1.359                           | 1.419                           |
| μ/µm⁻¹           | 0.871                           | 0.735                           |
| h / k / l        | −15, 15 / −14, 15 / −41, 42     | −26, 27 / −11, 13 / −19, 19    |
| Max. and min.    | 0.8382 / 0.8878                 | 0.8670 / 0.8376                 |
| Reflections      | 31687 / 10462                   | 20845 / 7087                    |
| Unique            | 1                             | 1                               |
| Data / restraints | 10462 / 0 / 757                 | 7087 / 1 / 550                  |
| Parameters       | 1.003                          | 1.033                           |
| GOF on F²        | 2512                           | 1888                            |
| F(000)           | 0.0857                         | 0.0267                          |
| R₁ / wR₂ [I>2σ(I)] | 0.0559 / 0.1244                | 0.0369 / 0.0951                 |
| R₁ / wR₂ [all data] | 0.1587 / 0.1641               | 0.0431 / 0.0994                 |
| Δρ_max, Δρ_min | 0.663 / −0.348                 | 0.568 / −0.274                 |

a) R₁ = Σ||F₁|−|F₀||/Σ|F₀|, b) wR₂ = [Σ[w(F₀²−|F_C|²)]²/Σ[w(F₀²)]²]¹/².
Results and Discussion

Syntheses and FT-IR Spectra

Bulk products of crystalline 1 and 2 were hydrothermally prepared by the reactions of inorganic Zn(II) salt and flexible bpp molecule in the presence of Hna or Hnas coligand, in which aqueous NaOH solution was used to make O-donor-containing ligands deprotonation and further to facilitate their coordination with Zn(II) ion. Additionally, both complexes are air stable, insoluble in common organic solvents and can retain their crystalline integrity at ambient conditions for a considerable length of time.

In the IR spectra (Figure S1), weak absorption bands located at 3431 and 3330 cm\(^{-1}\) for 2 should be assigned to the stretch vibrations of exocyclic amino group of nas\(^{-}\) anion. Weak absorptions appeared at 3054 (for 1) and 3041 (for 2) cm\(^{-1}\) could be ascribed to the C–H stretching vibrations of aromatic ring. An absence of a characteristic band at 1675 cm\(^{-1}\) for a considerable length of time.

monodentate coordination mode to complete the coordination sphere of the Zn2 ion.

As shown in Figure 1b, both crystallographically unique bpp molecules in 1 adopt a bidentate bridging binding mode to alternately aggregate the two unique Zn(II) ions into a 1D zigzag chain with the Zn2 ion locating at a salt point.

Table 2. Selected bond distances (Å) and angles (°) for 1

| Bond/Dihedral Angle | Value 1 | Value 2 |
|---------------------|---------|---------|
| Zn(1)–O(1)          | 2.468(4)| 2.017(4)|
| Zn(1)–O(3)          | 2.034(4)| 2.465(5)|
| Zn(1)–N(1)          | 2.071(4)| 2.054(4)|
| Zn(2)–O(5)          | 2.046(6)| 2.463(6)|
| Zn(2)–O(7)          | 1.970(5)| 2.045(4)|
| Zn(2)–N(3)          | 2.059(5)|         |
| O(2)–Zn(1)–O(3)     | 141.47(17)| 110.32(16)|
| O(3)–Zn(1)–N(4)\(^\#1\) | 96.78(18)| 98.48(17)|
| O(3)–Zn(1)–N(1)     | 101.28(17)| 103.48(16)|
| O(2)–Zn(1)–O(4)     | 88.95(16)| 56.83(15)|
| O(4)–Zn(1)–O(1)     | 92.79(15)| 94.77(16)|
| O(4)–Zn(1)–O(1)     | 79.05(16)| 146.32(16)|
| O(7)–Zn(2)–O(5)     | 116.9(3)| 127.43(3)|
| O(5)–Zn(2)–N(2)     | 101.6(2)| 107.5(2)|
| O(7)–Zn(2)–O(6)     | 87.2(2)| 54.8(2)|
| N(2)–Zn(2)–O(6)     | 87.20(19)|         |

Symmetry codes: \(^\#1\) 3/2 – x, y – 3/2, 1/2 – z.

Table 2—3, respectively. Hydrogen-bonding parameters are included in Table 4.

Descriptions of Crystal Structures

Complex 1, [Zn\(_2\)(bpp)\(_2\)(na)\(_3\)]\(_3\)br, crystallizes in the monoclinic \(P2_1/n\) space group, possessing an infinite zigzag chain with hexa- and pentacoordinated Zn\(^{II}\) ions alternately extended by flexible bpp linkers. The asymmetric unit of 1 consists of two crystallographically independent Zn(II) ions, two neutral bpp molecules, and four deprotonated na\(^{-}\) anions in two different binding modes. As shown in Figure 1, the Zn1 ion in 1 is hexa-coordinated in a distorted O\(_6\)N\(_2\) octahedral coordination geometry completed by two bidentate chelating carboxylate groups from two na\(^{-}\) anions and two pyridyl N donors from two crystallographically unique bpp ligands. By contrast, the unique Zn2 ion is five-coordinated to two pyridyl N donors from two neutral bpp molecules and three carboxylate O atoms from two separate na\(^{-}\) anions, adopting a severely distorted square-pyramidal geometry with Addison parameter \(\tau = 0.32\). The \(\tau\) value is defined as an index of trigonality (\(\tau = 1\)) and square-pyramid (\(\tau = 0\)). The Zn–O and Zn–N distances are in the region of 1.970–2.468 Å (Table 2), falling into the normal range of Zn(II)-based complexes with mixed carboxylate or pyridyl ligands.[19] Four unique deprotonated na\(^{-}\) anions in 1 exhibit two different binding modes: three of them coordinate with the Zn\(^{II}\) ions in an asymmetric bidentate chelating fashion, and the last one adopts a...
The adjacent Zn(II)···Zn(II) distances are 13.6988(1) and 12.7354(1) Å, and the angle of three neighboring Zn(II) ions are 93.602(6) and 175.434(7)°. Each zigzag chain of 1 interacts with two neighbors by four different kinds of interchain C–H···O hydrogen interactions between bpp and sulfonated group of na⁻ ligands (Table 4), generating a scarcely observed twisted triple-chain substructure, as shown in Figure 1c. Adjacent triple-chain substructures of 1 are further hydrogen-bonded together into a higher-dimensional supra-molecular network of 1.

Complex 2, [Zn(bpp)₂(na)₂]ₙ, crystallizes in the orthorhombic Pna₂₁ space group, exhibiting a coplanar 2D layer extended by flexible bpp ligands. The asymmetric unit of 2 contains one crystallographically independent Zn(II) site, two neutral bpp ligands and two monodentate na⁻ anions for charge compensation. The unique Zn(II) ion is hexacoordinated by four equatorial N donors from the pyridyl group and two axially sulfonate O atoms from deprotonated na⁻ anions, exhibiting a slightly distorted octahedral coordination geometry with one axial Zn–O6 bond considerable longer by 0.4 Å than those of Zn–O and Zn–N distances (Table 3). The bpp entity adopts a bidentate mode, leading to macrocyclic C₈H₇O₆ anion shows a diptopic connector. Thus, the Zn(II) ion can be considered as a four-connected node, and the neutral bpp ligand acts as a ditopic connector. Thus, the Zn(II) ion in 2 is infinitely extended by four equatorial bpp ligands in a bidentate mode, leading to macrocyclic [Zn₄(bpp)]₄²⁻ subunit-based 2D layer. Topologically, each Zn(II) ion can be considered as a four-connected node, and the neutral bpp ligand acts as a ditopic connector. Thus, the 2D layer of 2 belongs to an infinite (4 4) sheet (Figure 2b).

Adjacent 2D layers of 2 are linked together to form 3D supramolecular architecture by interlayer N–H···O interactions between the amino group and sulfonate moiety of na⁻ anions (Figure 2c and Table 4).

Apparently, the increase of the dimensionality from 1D chain (for 1) to 2D layer (for 2) is structurally due to the flexible bpp ligand, and the O-donor coligands play key roles on the construction of the metal coordination polyhedron and the assembly of the higher level ordered supramolecular architecture.

**Thermal Stability**

TGA experiments of 1 and 2 were carried out to explore their thermal stability and the results were presented in Figure 3. Complex 1 exhibits a one-step weight-loss stage once the temperature is higher than 215°C, ascribing to the continuous decomposition of bpp ligand and deprotonated na⁻ anions. The final product of 1 above 800°C is ZnO (obsd. 14.7%, calcd. 13.4%). Analogous to 1, polymeric sample of 2 can also be thermally stable up to 215°C and is followed by a

**Table 3. Selected bond distances (Å) and angles (°) for 2**

|       | Zn(1)–N(1) | Zn(1)–N(2) | Zn(1)–N(4) | Zn(1)–O(1) | Zn(1)–O(6) | N(3)–Zn(1)–N(4) | N(3)–Zn(1)–O(1) | N(1)–Zn(1)–O(1) | N(1)–Zn(1)–N(4) |
|-------|------------|------------|------------|------------|------------|-----------------|-----------------|-----------------|-----------------|
| Zn(1)–N(1) | 2.100(3)  | 2.159(3)  | 2.532(2)  | 0.930  | 1.990  | 1.973  | 1.973  | 1.973  | 1.973  |
| Zn(1)–N(3) | 2.124(3)  | 2.159(3)  | 2.532(2)  | 0.930  | 1.990  | 1.973  | 1.973  | 1.973  | 1.973  |
| Zn(1)–O(1) | 2.152(3)  | 2.159(3)  | 2.532(2)  | 0.930  | 1.990  | 1.973  | 1.973  | 1.973  | 1.973  |
| N(3)–Zn(1)–N(4) | 94.19(11)  | 92.24(10)  | 96.50(10)  | 98.76(10)  | 96.82(11)  | 96.82(11)  | 96.82(11)  | 96.82(11)  | 96.82(11)  |

Symmetry codes: #1 x − 1/2, 3/2 − y, z; #2 x + 1/2, 1/2 − y, z.

**Figure 2.** (a) Local coordination environment of ZnII in 2 (hydrogen atoms were omitted for clarity. Symmetry codes: A = x − 1/2, 3/2 − y, z; B = x + 1/2, 1/2 − y, z); (b) 2D network of 2 with ZnII ions extended by ditopic bpp connecters (The terminal nas⁻ ligands were omitted for clarity) and the topological representation; (c) 3D supramolecular architecture of 2 by interlayer N–H···O interactions.

**Table 4. Selected hydrogen bond lengths (Å) and angles (°) for 1–2**

|       | D–H···A | d (D–H) | d (H···A) | d (D···A) | DHA |
|-------|---------|---------|----------|----------|-----|
| 1     | C23–H23···O3#1 | 0.930 | 2.551 | 3.255(5) | 133.41 |
| 2     | N5–H5A···O3 | 0.860 | 1.990 | 2.667(1) | 134.81 |
| 3     | C24–H24···O1#1 | 0.930 | 2.491 | 3.291(4) | 145.01 |
| 4     | C29–H29B··O1#1 | 0.970 | 2.580 | 3.405(3) | 143.05 |
| 5     | C67–H67··O4#3 | 0.930 | 2.480 | 3.309(6) | 148.23 |
| 6     | C35–H35··O6#2 | 0.930 | 2.531 | 3.344(6) | 146.00 |

*Symmetry codes for 1: #1 3/2 − x, 1/2 + y, 1/2 − z; #2 1 − x, 1 − y, 1 − z; #3 3/2 − x, y − 1/2, 1/2 − z; for 2: #1 1 − x, 1 − y, z+ 0.5, #2 0.5 − x, y − 0.5, z − 0.5.
continuous weight-loss stage between 215 and 660°C. The obvious weight-loss stage is corresponding to the broken of the extended structure and the decomposition of the mixed bpp and nas\(^-\) ligands. The remained substance beyond 660°C is calculated to be ZnO (obsd. 8.81%, calcd. 8.98%). Thus, the two polymeric complexes with different dimensionality exhibit analogous high thermal stability.

**Luminescent Properties**

The emissions of the two solid-state samples were measured at room temperature, together with the free Hna and Hnas ligands for comparison. As shown in Figure 4, complex 1 exhibits one intense band at 496 nm upon excitation at 280 nm. By contrast, a strong emission at 412 nm is observed in 2 upon excitation at 315 nm. Under comparable experimental conditions, free Hna species shows a strong emission at 421 nm (\(\lambda_{ex} = 370\) nm) and the Hnas ligand gives a broad maximum at 462 nm (\(\lambda_{ex} = 349\) nm). Therefore, the observed luminescence for 1 should be ascribed to the ligand-to-metal charge transfer and the emission for 2 is due to intraligand electron-charge. The slight difference of the complexes from the free ligands is probably resulting from the deprotonation of Hna/Hnas and the coordination behavior of the na\(^-\)/nas\(^-\) to Zn(II) ion.[20]

### Conclusions

In summary, two fluorescent Zn(II)-bpp complexes with 1D zigzag chain and 2D coplanar layer have been hydrothermally prepared by incorporating with two different O-donor coligands. Structurally, the competitive coordination of the flexible bpp and carboxylate/sulfonate-based coligand significantly dominates the extension of the polymeric frameworks with different dimensionality. Resulting from the intraligand and ligand-to-metal charge transfer, both complexes with good thermal stability can exhibit strong emissions with variable intensities, suggesting their potential applications as luminescent materials.

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### Supplementary Material

Supplemental data for this article can be accessed at the publisher's website. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-986982 and CCDC-986983 (for 1–2) (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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