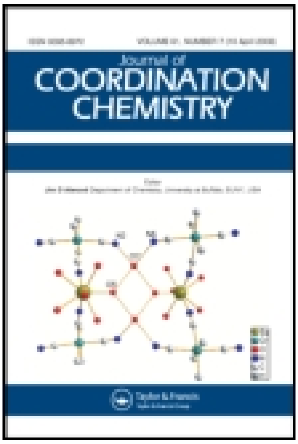

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

# Template construction of a series of supramolecular coordination polymers via 6,7-dihydro-5H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-4,8-diium cation

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To cite this article: Zhenhua Zhang, Yunyin Niu, Seikweng Ng, Benlai Wu & HongWei Hou (2011): Template construction of a series of supramolecular coordination polymers via 6,7-dihydro-5H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-4,8-diium cation, Journal of Coordination Chemistry, 64:10, 1683-1694

To link to this article: http://dx.doi.org/10.1080/00958972.2011.579117

*Journal of Coordination Chemistry*
Vol. 64, No. 10, 20 May 2011, 1683–1694

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# Template construction of a series of supramolecular coordination polymers *via* 6,7-dihydro-5H-[1,4]diazepino [1,2,3,4-lmn][1,10]phenanthroline-4,8-diium cation

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(*Received 22 December 2010; in final form 18 March 2011*)

Five cation-induced complexes, (phen-dzp) [$ZnBr_3N_3$] (**1**), (phen-dzp) [$ZnCl_2Br_2$] (**2**), (phen-dzp) $(H_3O)_2$ [$Fe(CN)_6$] (**3**), $(phen\text{-}dzp)_2$ [$Cu_2I_6$] (**4**), and $[(phen\text{-}dzp)(Ag_2Br_4)]_n$ (**5**) [phen-dzp $= (C_{15}H_{14}N_2)^{2+}$, 6,7-dihydro-5H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline-4,8-diium], have been synthesized *via* self-assembly in solution. The crystal structures of **1–3** show that they all crystallize in monoclinic systems with mononuclear structures. Compound **4** is a binuclear coordination polymer. Complex **5** possesses a 2-D supramolecular layer with the organic cation phen-dzp trapped in it; interestingly, each inorganic polymeric planar layer is composed of large, decagon rings formed by sharing four $Br^-$ and four [$Ag_2Br_4$] quadrilateral units with six adjacent decagon rings. The results provide insights into template effects of synthetic approaches on the construction of supramolecular compounds. The structures of **1–5** have been characterized by elemental analysis, infrared spectra, and single-crystal X-ray crystallography. Solid-state photoluminescence properties of **1–5** have been determined.

*Keywords*: Template effect; Photoluminescence property; X-ray crystal structure

## 1. Introduction

Although the term template effect was first used and defined at the beginning of the 1960s [1], surprising discoveries and new applications in the field of supramolecular chemistry in the 1990s provoked a boom in the subject. More and more examples cover the relevance of the template effect under the heading of rational synthesis. Metal ions can act as templates with neutral molecules, hydrogen bonds, and electrostatic interactions and also supporting formation of supramolecular compounds. A template is described as temporary or external if it is eliminated at the end of a synthesis and not incorporated into the end product [2]. If molecular compounds originally present are also found in the end product, it is defined as a permanent template [3]. Supramolecular compounds, especially coordination polymers directed by organic cations [4–9], have become one of the most active areas of chemical engineering and molecular science.

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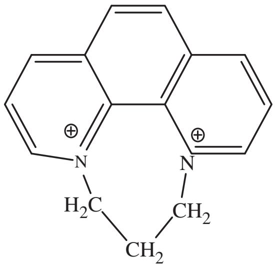
*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
DOI: 10.1080/00958972.2011.579117



Scheme 1. Organic cation phen-dzp.

Our recent studies reported a cuprous thiocyanate polymer directed by the azotic heterocyclic organic template 1,5-*bis*(pyridinium) pentane cation [10].

In order to explore self-assembly and mechanism in M–X supramolecular coordination polymers, we select Cu(+), Ag(+), Zn(2+), and Fe(2+) as metal cations and phen-dzp as organic cation-template in this article. Five supramolecular compounds were obtained and structurally characterized. In all the structures, the organic cation is a permanent template which serves to counterbalance the charge on the inorganic anion and induce formation of the whole supramolecular structure.

## 2. Experimental

### 2.1. *General*

Commercial reagents were used without purification and all experiments were carried out in open atmosphere. 1,10-Phenanthroline monohydrate and 1,3-dibromoalkane were used as received. Other chemicals were obtained from commercial sources and used as received. Elemental analyses of all crystals were performed on a VARIO EL (Heraeus) CHNS analyzer. Infrared (IR) spectra were recorded using a Bruker Tensor 27 spectrophotometer from 4000 to 400 $\mathrm{cm}^{-1}$ using KBr pellets. The fluorescence spectra of **1**–**5** were recorded using a HITACHI F-4500 (fluorescence spectrophotometer) in a 1-cm quartz cell. The excitation and emission bandwidths were set at 5 nm.

### 2.2. *Synthesis*

**2.2.1. Synthesis of 6,7-dihydro-5H-[1,4]diazepino[1,2,3,4-lmn][1,10]phenanthroline 4,8-diium (phen-dzp).** The phen-dzp (scheme 1) [11, 12] was synthesized from 1,10-phenanthroline monohydrate (5 mmol, 1 g) and 1,3-dibromoalkane (10 mmol, 2.02 g) was heated to 70–80°C, and refluxed for 6 h giving yellow precipitate. The reaction mixture was cooled to room temperature, the precipitate was collected, recrystallized with methanol and ether, and dried in vacuum; 2.3 g yellow powder was obtained (80% yield).

Table 1. Crystal data and structure refinement for **1–5**.

| | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| Empirical formula | $C_{15}H_{14}Br_3N_5Zn$ | $C_{15}H_{14}Br_2Cl_2N_2Zn$ | $C_{21}H_{20}FeN_8O_2$ | $C_{15}H_{14}CuI_3N_2$ | $C_{15}H_{14}Ag_2Br_4N_2$ |
| Formula weight | 569.41 | 518.37 | 472.30 | 666.52 | 757.66 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | *P*2(1) | *P*2(1)/*n* | *P*2(1)/*n* | *P*2(1)/*n* | *P*2(1)/*c* |
| Unit cell dimensions (Å, °) | | | | | |
| $a$ | 8.224(2) | 7.1829(6) | 13.0731(2) | 12.732(2) | 8.8671(5) |
| $b$ | 11.935(3) | 16.0542(14) | 13.2508(2) | 8.5688(15) | 13.3994(8) |
| $c$ | 9.002(3) | 14.7411(13) | 12.5115(2) | 15.759(3) | 17.6184(11) |
| $\alpha$ | 90 | 90 | 90 | 90 | 90 |
| $\beta$ | 91.554(4) | 93.4140(10) | 93.435(1) | 92.465(3) | 104.3320(10) |
| $\gamma$ | 90 | 90 | 90 | 90 | 90 |
| Volume (Å$^3$), $Z$ | 883.1(4), 2 | 1696.9(3), 4 | 2163.46(6), 4 | 1717.7(5), 4 | 2028.2(2), 4 |
| Calculated density $\rho$ (Mg m$^{-3}$) | 2.141 | 2.029 | 1.450 | 2.577 | 2.481 |
| Absorption coefficient (mm$^{-1}$) | 8.184 | 6.468 | 0.733 | 6.658 | 9.810 |
| $F$ (000) | 548 | 1008 | 976 | 1224 | 1408 |
| Crystal size (mm$^3$) | 0.32 × 0.28 × 0.24 | 0.23 × 0.21 × 0.19 | 0.35 × 0.20 × 0.10 | 0.43 × 0.40 × 0.39 | 0.18 × 0.16 × 0.16 |
| $\theta$ range for data collection (°) | 2.26–26.00 | 2.54–25.20 | 2.2–28.5 | 2.10–25.50 | 0.93–25.49 |
| Reflections collected | 5057 | 9350 | 4442 | 9026 | 6771 |
| Independent reflections | 3366 (0.0291) | 3160 (0.0240) | 3160 (0.0222) | 3160 (0.0461) | 2290 (0.0326) |
| Max./min. transmission | 0.2441/0.1793 | 0.3729/0.3178 | 0.2865/0.1932 | 0.1810/0.1619 | 0.3028/0.2712 |
| Data/restraints/parameters | 3366/1/218 | 3160/24/212 | 3160/12/313 | 3160/0/191 | 2290/0/204 |
| Goodness-of-fit on $F^2$ | 0.941 | 1.079 | 1.035 | 1.045 | 1.110 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0975$,<br>$wR_2 = 0.2620$ | $R_1 = 0.0547$,<br>$wR_2 = 0.1816$ | $R_1 = 0.0305$,<br>$wR_2 = 0.0870$ | $R_1 = 0.0594$,<br>$wR_2 = 0.1785$ | $R_1 = 0.0731$,<br>$wR_2 = 0.2137$ |
| $R$ indices (all data) | $R_1 = 0.1069$,<br>$wR_2 = 0.2748$ | $R_1 = 0.0626$,<br>$wR_2 = 0.1896$ | $R_1 = 0.0348$,<br>$wR_2 = 0.0904$ | $R_1 = 0.0650$,<br>$wR_2 = 0.1809$ | $R_1 = 0.0790$,<br>$wR_2 = 0.2238$ |

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

Table 2. Selected bond lengths (Å) and angles (°) within the coordination spheres in **1**–**5**.

| | | | | | |
|---|---|---|---|---|---|
| **1** | | | | | |
| Br(1)–Zn(1) | 2.309(4) | Br(2)–Zn(1) | 2.357(3) | Br(3)–Zn(1) | 2.319(3) |
| N(3)–Zn(1) | 2.025(16) | N(3)–N(4) | 1.16(3) | N(4)–N(5) | 1.09(2) |
| Br(1)–Zn(1)–Br(3) | 108.32(13) | N(3)–Zn(1)–Br(2) | 107.9(6) | Br(1)–Zn(1)–Br(2) | 108.97(14) |
| Br(3)–Zn(1)–Br(2) | 110.95(11) | N(3)–Zn(1)–Br(1) | 114.9(6) | N(3)–Zn(1)–Br(3) | 105.8(6) |
| **2** | | | | | |
| Cl(1)–Zn(1) | 2.35(2) | Cl(2)–Zn(1) | 2.31(2) | Br(1)–Zn(1) | 2.307(10) |
| Br(2)–Zn(1) | 2.434(8) | N(1)–C(1) | 1.342(8) | N(1)–C1(2) | 1.374(8) |
| N(1–C(15) | 1.485(8) | N(2)–C(10) | 1.330(8) | N(2)–C(11) | 1.382(7) |
| N(2)–C(13) | 1.489(7) | Br(1)–Zn(1)–C(l2) | 108.7(7) | Br(1)–Zn(1)–C(l2) | 106.9(6) |
| C(1)–N(1)–C(12) | 121.1(5) | C(1)–N(1)–C(15) | 117.7(5) | C(12)–N(1)–C(15) | 120.2(5) |
| Br(1)–Zn(1)–Br(2) | 111.0(3) | C(l1)–Zn(1)–Br(2) | 108.7(7) | Br(1)–Zn(1)–C(l2) | 106.9(6) |
| C(10)–N(2)–C(11) | 120.4(5) | C(10)–N(2)–C(13) | 119.1(5) | C(11)–N(2)–C(13) | 119.4(5) |
| **3** | | | | | |
| Fe(1)–C(18) | 1.8699(16) | Fe(1)–C(19) | 1.8856(16) | Fe(1)–C(16) | 1.9124(15) |
| Fe(1)–C(20) | 1.9179(16) | Fe(1)–C(21) | 1.9209(16) | Fe(1)–C(17) | 1.9218(16) |
| N(3)–C(16) | 1.157(2) | N(4)–C(17) | 1.162(2) | N(5)–C(18) | 1.153(2) |
| N(6)–C(19) | 1.162(2) | N(7)–C(20) | 1.160(2) | N(8)–C(21) | 1.162(2) |
| C(18)–Fe(1)–C(19) | 88.36(7) | C(19)–Fe(1)–C(16) | 91.89(7) | C(18)–Fe(1)–C(20) | 92.79(7) |
| C(19)–Fe(1)–C(20) | 90.41(7) | C(16)–Fe(1)–C(20) | 85.78(6) | C(18)–Fe(1)–C(21) | 90.92(7) |
| C(19)–Fe(1)–C(21) | 88.01(7) | C(16)–Fe(1)–C(21) | 90.52(6) | C(18)–Fe(1)–C(17) | 89.61(7) |
| C(16)–Fe(1)–C(17) | 90.19(6) | C(20)–Fe(1)–C(17) | 91.56(7) | C(21)–Fe(1)–C(17) | 90.15(6) |
| **4** | | | | | |
| I(1)–Cu(1) | 2.632(2) | I(2)–Cu(1) | 2.635(2) | I(3)–Cu(1) | 2.701(2) |
| I(3)–Cu(1) | 2.736(3) | N(1)–C(1) | 1.340(17) | N(1)–C(5) | 1.378(18) |
| N(1)–C(13) | 1.500(17) | N(2)–C(6) | 1.364(18) | N(2)–C(11) | 1.488(18) |
| N(2)–C(10) | 1.337(18) | I(1)–Cu(1)–I(2) | 110.61(9) | I(1)–Cu(1)–I(3) | 109.31(8) |
| I(2)–Cu(1)–I(3) | 115.60(9) | I(1)–Cu(1)–I(3) | 113.83(9) | I(3)–Cu(1)–I(3) | 101.13(8) |
| C(1)–N(1)–C(5) | 121.8(12) | C(1)–N(1)–C(13) | 117.4(12) | C(5)–N(1)–C(13) | 119.7(11) |
| C(6)–N(2)–C(11) | 120.1(11) | C(10)–N(2)–C(6) | 120.6(13) | C(10)–N(2)–C(11) | 118.1(13) |
| **5** | | | | | |
| Br(1)–Ag(1) | 2.8111(18) | Br(2)–Ag(1) | 2.8513(16) | Br(3)–Ag(1) | 2.8322(17) |
| Br(4)–Ag(1) | 2.9169(16) | Br(1)–Ag(2) | 2.8264(18) | Br(2)–Ag(2) | 2.8372(16) |
| Br(3)–Ag(2) | 2.8966(16) | Br(4)–Ag(2) | 2.8665(16) | Ag(2)–Ag(1) | 3.100(2) |
| N(1)–C(1) | 1.262(18) | N(1)–C(5) | 1.389(17) | N(1)–C(13) | 1.548(16) |
| N(2)–C(6) | 1.421(17) | N(2)–C(10) | 1.313(19) | N(2)–C(11) | 1.467(16) |
| Br(1)–Ag(1)–Ag(2) | 56.88(4) | Br(2)–Ag(1)–Ag(2) | 56.76(4) | Br(3)–Ag(1)–Br(4) | 100.88(5) |
| Br(1)–Ag(1)–Br(4) | 110.15(5) | Br(2)–Ag(1)–Br(4) | 105.06(5) | Br(4)–Ag(2)–Ag(1) | 135.01(6) |
| Br(3)–Ag(2)–Ag(1) | 122.65(6) | Br(1)–Ag(2)–Br(2) | 113.60(5) | Br(1)–Ag(2)–Br(4) | 112.55(5) |
| Br(2)–Ag(2)–Br(4) | 113.47(6) | Br(1)–Ag(2)–Br(3) | 104.10(6) | Br(2)–Ag(2)–Br(3) | 109.84(5) |
| Br(4)–Ag(2)–Br(3) | 102.18(5) | Br(4)–Ag(2)–Ag(1) | 135.01(6) | Br(3)–Ag(2)–Ag(1) | 122.65(6) |
| C(10)–N(2)–C(6) | 122.3(13) | C(10)–N(2)–C(11) | 117.9(11) | C(6)–N(2)–C(11) | 118.6(12) |
| C(1)–N(1)–C(5) | 124.0(13) | C(1)–N(1)–C(13) | 117.2(11) | C(5)–N(1)–C(13) | 117.4(11) |

**2.2.2. Synthesis of 1.** An ethanol solution of phen-dzp · 2Br (0.388 g, 1 mmol) was added to a stirring colorless solution of $ZnCl_2$ (0.134 g, 1.0 mmol) dissolved in 10 mL of DMF/$H_2O$ (volume ratio of 4 : 1) in the presence of excess $NaN_3$ (0.325 g, 5.0 mmol). The solution was then filtered and slowly evaporated in a vial at room temperature. White crystals of **1** suitable for X-ray analysis were obtained after 3 days in 56% yield. Anal. Calcd for $C_{15}H_{14}Br_3N_5Zn$ (%): C, 31.61; H, 2.46; N, 12.29. Found (%): C, 31.65; H, 2.43; N, 12.30. IR (KBr, $cm^{-1}$): 712 $\upsilon$(C–C); 1461 $\upsilon$(C=N); 697 $\upsilon$(pyridine).

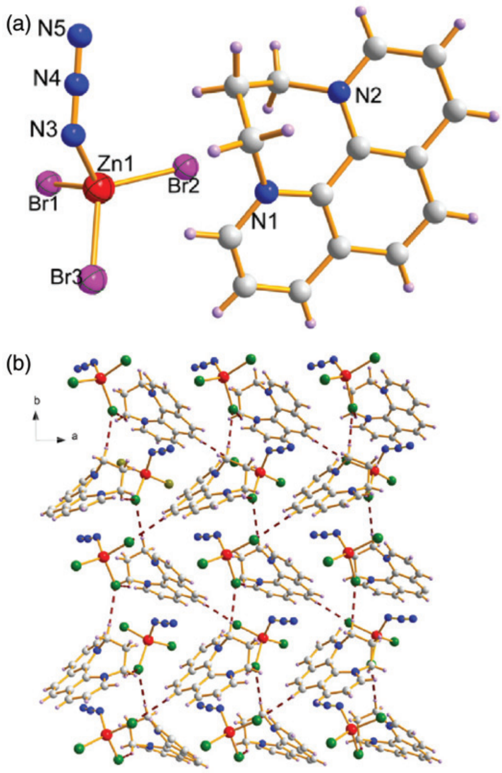


Figure 1. (a) The basic structural unit of **1**. (b) Packing structure of **1**.

**2.2.3. Synthesis of 2.** A methanol solution of phen-dzp · 2Br (0.388 g, 1 mmol) was added to a stirring colorless solution of $ZnCl_2$ (0.134 g, 1.0 mmol) dissolved in 10 mL of $DMF/H_2O$ (volume ratio of 4 : 1). The solution was then filtered and slowly evaporated in a vial at room temperature. White crystals of **2** suitable for X-ray analysis were obtained after 7 days in 41% yield. Anal. Calcd for $C_{15}H_{14}Br_2Cl_2N_2Zn$ (%): C, 34.72; H, 2.70; N, 5.40. Found (%): C, 34.73; H, 2.68; N, 5.52. IR (KBr, $cm^{-1}$): 712 $\upsilon$(C–C); 1461 $\upsilon$(C=N); 697 $\upsilon$(pyridine); 2020 $\upsilon$(N$\equiv$N=N).

**2.2.4. Synthesis of 3.** A methanol solution of phen-dzp · 2Br (0.388 g, 1 mmol) was added to a stirring colorless solution of $K_4Fe(CN)_6$ (0.33 g, 1.0 mmol) dissolved in 10 mL of $DMF/H_2O$ (volume ratio of 4 : 1). The solution was then filtered and slowly evaporated in a vial at room temperature. Black crystals of **3** suitable for X-ray analysis were obtained after 7 days in 63% yield. Anal. Calcd for $C_{21}H_{20}FeN_8O_2$ (%): C, 53.39; H, 4.23; N, 23.58. Found (%): C, 53.35; H, 4.25; N, 23.56. IR (KBr, $cm^{-1}$): 712 $\upsilon$(C–C); 1461 $\upsilon$(C=N); 697 $\upsilon$(pyridine); 2040 $\upsilon$(C$\equiv$N).

**2.2.5. Synthesis of 4.** An ethanol solution of phen-dzp · 2Br (0.388 g, 1 mmol) was added to a stirring pale yellow solution of CuI (0.190 g, 1.0 mmol) dissolved in 10 mL of

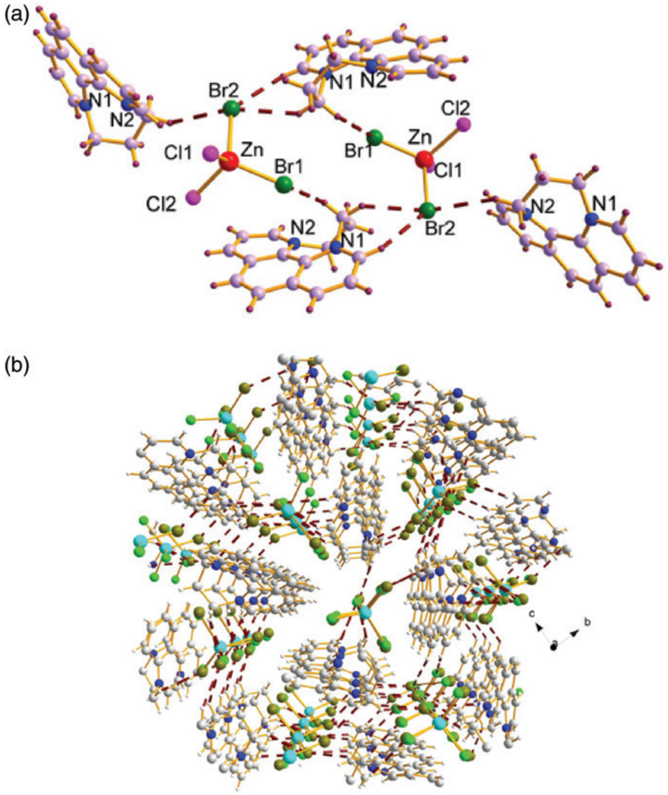


Figure 2. (a) The basic structural unit of **2**. (b) Packing structure of **2**.

DMF/$H_2O$ (volume ratio of 3 : 1) in the presence of excess KI (1.83 g, 5.0 mmol). The solution was then filtered and slowly evaporated in a vial at room temperature. Yellow crystals of **4** suitable for X-ray analysis were obtained after several weeks in 32% yield. Anal. Calcd for $C_{15}H_{14}CuI_3N_2$ (%): C, 27.00; H, 2.10; N, 4.20. Found (%): C, 26.98; H, 2.08; N, 4.23. IR (KBr, $cm^{-1}$): 710 $\upsilon$(C–C); 1469 $\upsilon$(C=N); 695 $\upsilon$(pyridine).

**2.2.6. Synthesis of 5.** A methanol solution of phen-dzp · 2Br (0.388 g, 1 mmol) was added to a stirring pale yellow solution of AgBr (0.188 g, 1.0 mmol) dissolved in 10 mL of DMF/$H_2O$ (volume ratio of 3 : 1) in the presence of excess KBr (0.36 g, 5.0 mmol). The reaction vessel was left to stand 3 days at room temperature. Large dark-yellow crystals of **5** suitable for X-ray analysis were obtained in 73% yield. Anal. Calcd for $C_{15}H_{14}Ag_2Br_4N_2$ (%): C, 23.76; H, 1.85; N, 3.69. Found (%): C, 23.74; H, 1.86; N, 3.67. IR (KBr, $cm^{-1}$): 711 $\upsilon$(C–C); 1465 $\upsilon$(C=N); 690 $\upsilon$(pyridine).

### 2.3. *X-ray crystallography*

Data were collected for five crystals on a Bruker APEX CCD area-detector diffractometer using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.7103$ Å).

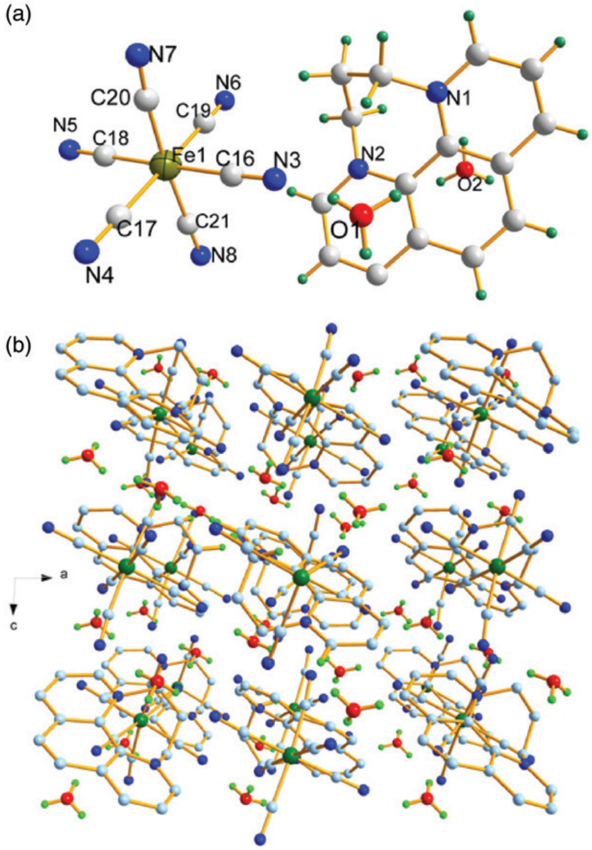


Figure 3. (a) The basic structural unit of **3**. (b) 3-D architecture of **3**.

The X-ray intensities were corrected for absorption using a semi-empirical procedure [13]. The crystal structure was solved by direct methods and refined by full-matrix least squares based on $F^2$ [14]. Crystal data and structure refinement parameters for **1**–**5** are given in table 1, and selected bond lengths and angles in table 2.

## 3. Results and discussion

### 3.1. *IR spectra*

Typical absorption bands at 3750–3000 $cm^{-1}$ (m, broad) and around 1650–1400 $cm^{-1}$ are assignable to the presence of water and the skeleton vibration of 1,10-phenanthroline monohydrate. The spectrum of phen-dzp has characteristic bands due to $\upsilon$(C–C), $\upsilon$(C=N), and pyridine at 713, 1466, and 699 $cm^{-1}$. Relative to the terminal $C\equiv N$ stretch at 2040 $cm^{-1}$ in the IR spectrum of **3**, the terminal $N\equiv N{=}N$ stretch is at 2020 $cm^{-1}$ in **1**.

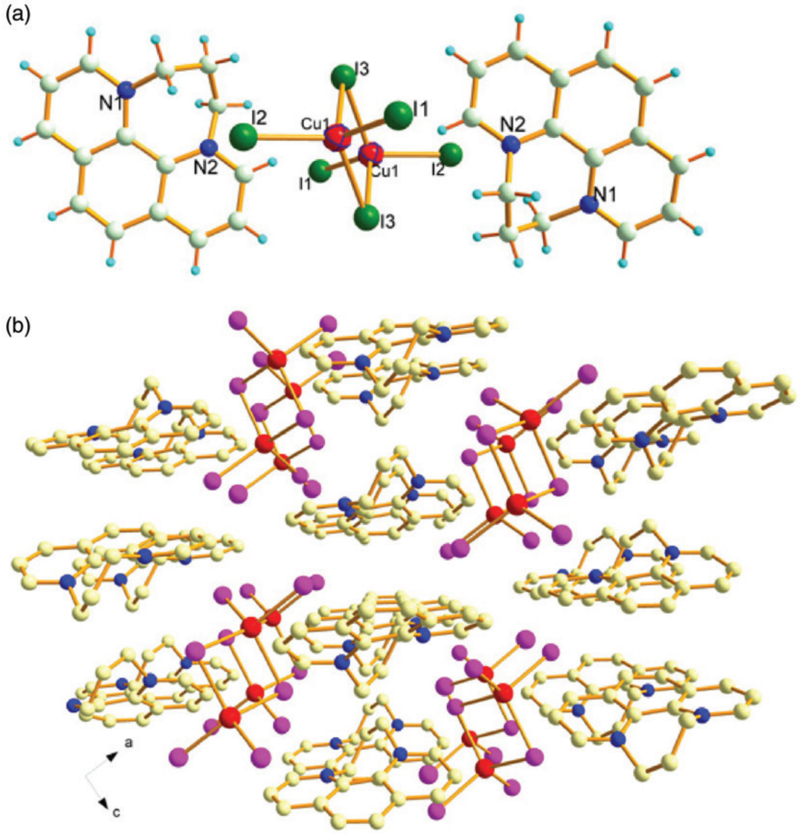


Figure 4. (a) A drawing of the copper(I) coordination environment in **4**. (b) The supramolecular architecture of **4** in the *ac* plane.

## 3.2. *The crystal structures of 1–5*

**3.2.1. Crystal structure of (phen-dzp) [$ZnBr_3N_3$] (1).** Single-crystal structure analysis reveals that **1** crystallized in monoclinic system with space group *P*2(1). The structural unit of **1**, shown in figure 1(a), consists of one $Zn^{2+}$, three $Br^-$, one $N_3^-$, and one phen-dzp. The Zn is four-coordinate with three $Br^-$ and one N to form tetrahedral geometry; the bond lengths range from 2.025(16) Å to 2.357(3) Å and bond angles vary from 105.8(6)° to 114.9(6)°. Within each unit, $Br^-$ connects with phen-dzp$^{2+}$ through a hydrogen bond, forming a 2-D architecture through weak hydrogen-bond interactions (shown in figure 1b). The organic cation plays a role of permanent template in the structure.

**3.2.2. Crystal structure of (phen-dzp) [$ZnCl_2Br_2$] (2).** The structure of **2** is similar to **1**, crystallized in monoclinic system with space group *P*2(1)/*n*. The structural unit of **2**, shown in figure 2(a), consists of one $Zn^{2+}$, two $Br^-$, two $Cl^-$, and one phen-dzp. The Zn is four-coordinate with two $Br^-$ and two $Cl^-$ in a tetrahedron. The bond lengths of

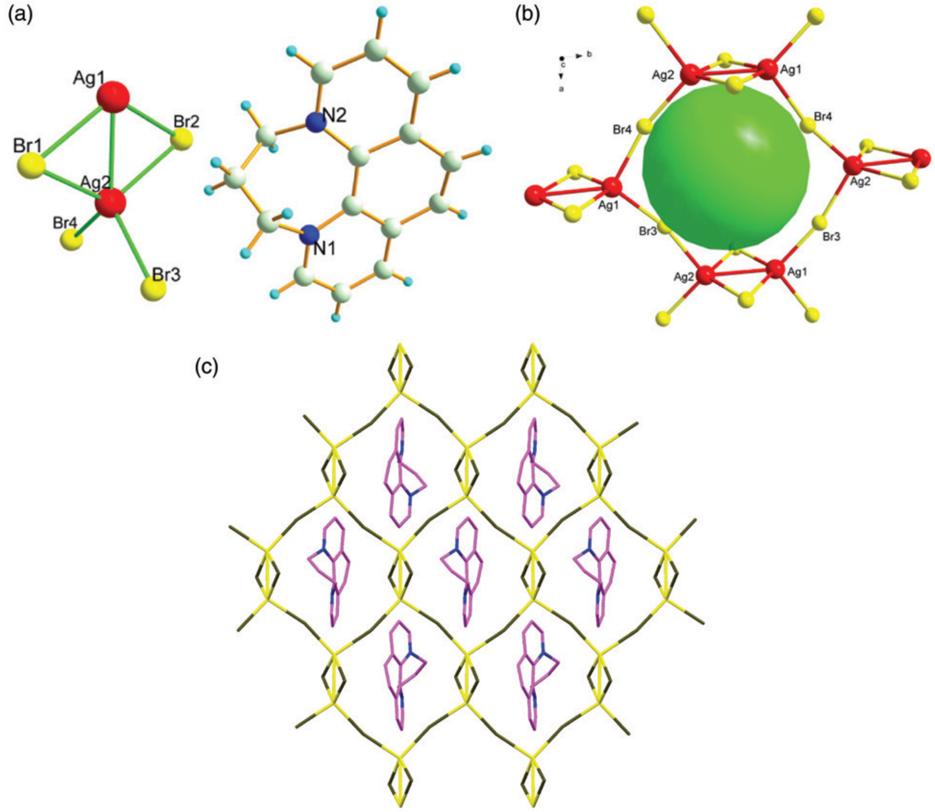


Figure 5. (a) A drawing of the silver(I) coordination environment in **5**. (b) The decagon ring of **5**. (c) Packing structure of **5** in the *ac* plane.

Zn–Br and Zn–Cl range from 2.282(15) Å to 2.434(8) Å and bond angles vary from 104.3(8)° to 108.7(7)°. With each unit, two $Br^-$ connect with three phen-dzp$^{2+}$ through hydrogen bonds. In both **1** and **2**, there exist hydrogen-bond interactions [15] forming a 3-D architecture (shown in figure 2b). In the solid state, the phen-dzp$^{2+}$ array around the anion spreads infinitely along the *b*-axis.

### 3.2.3. Crystal structure of (phen-dzp)$(H_3O)_2$ $[Fe(CN)_6]$ (3).

Single-crystal structure analysis revealed that **3** crystallized in monoclinic system with space group $P2(1)/n$. The structural unit of **3** is shown in figure 3(a), which consists of one $[Fe(CN)_6]^{4-}$ and two phen-dzp cations and two $H_3O^+$. The Fe is six-coordinate by six $CN^-$ groups with Fe–C bond lengths from 1.8699(16) Å to 1.9218(16) Å and bond angles from 85.78(6)° to 92.79(7)°. The organic cation is a permanent template counterbalancing the charge on $[Fe(CN)_6]^{4-}$ (figure 3b).

### 3.2.4. Crystal structure of $(phen\text{-}dzp)_2$ $[Cu_2I_6]$ (4).

Single-crystal structure analysis reveals that **4** consists of $[C_{15}H_{14}N_2]^{2+}$ as a structure-directing agent and $[Cu_2I_6]^{4-}$. Compound **4** is a binuclear polymer. In the polyanionic framework $[Cu_2I_6]^{4-}$, as shown

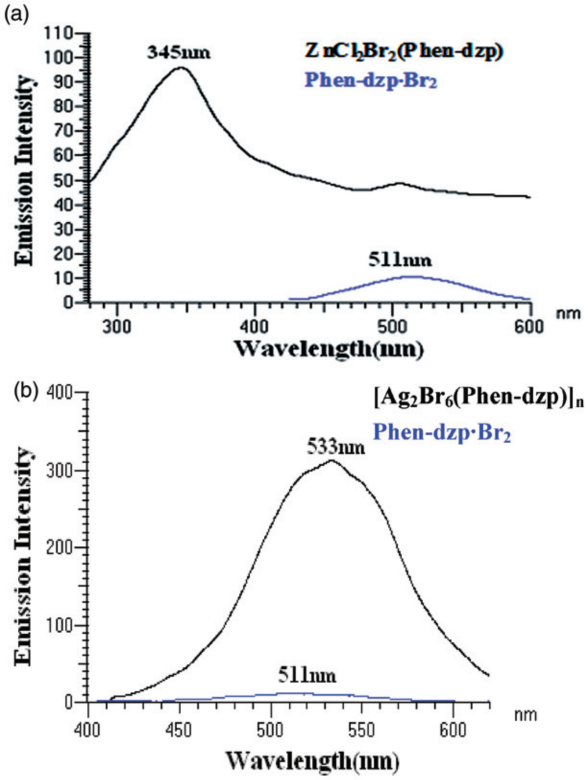


Figure 6. (a) Solid-state fluorescence spectrum of **2** and phen-dzp · 2Br at room temperature. (b) Solid-state fluorescence spectrum of **3**. (c) Solid-state fluorescence spectra of **4** and phen-dzp · 2Br at room temperature. (d) Fluorescence spectra of **5** and phen-dzp · 2Br at room temperature.

in figure 4(a), the coordination environments of coppers are identical. Each is four-coordinate in a distorted tetrahedral geometry by two $\mu_2$-$I^-$ and two terminal $I^-$. The bond distances around Cu are 2.632(2) Å to 2.701(2) Å and the bond angles range from 109.31(8)° to 115.60(9)°. The two Cu ions are bridged by two $\mu_2$-$I^-$ with a Cu · · · Cu distance of 3.4538 Å. From the *b*-axis, phen-dzp$^{2+}$ array around the polyanionic chains (figure 4b). We have synthesized $\{[Cu_2(SCN)_4(\text{phen-dzp})]\}_n$ [16], to compare with zinc chloride and potassium ferrocyanide, the halogen/pseudohalogenoocuprates (I) and the organic cation-template form complexes easily.

**3.2.5. Crystal structure of $[(\text{phen-dzp})(Ag_2Br_4)]_n$ (5).** The X-ray single-crystal structure analysis reveals that **5** crystallizes in the monoclinic system with space group *P*2(1)/*c*. Complex **5** is a 2-D polymeric architecture with phen-dzp$^{2+}$ trapped in the infinite 2-D inorganic $[Ag_2Br_4]_n$ network. In the polymeric structure, the basic unit is $[Ag_2Br_4]$. The unit structure is shown in figure 5(a). In $[Ag_2Br_4]$, two Ag ions are connected by two $\mu_2$-$Br^-$ forming quadrilateral rings. If we ignore the interaction of Ag–Ag [3.100(2) Å], Ag forms tetrahedral geometry. Bond distances around Ag(1) are

2.8111(18) Å to 2.9169(16) Å and around Ag(2) from 2.8264(18) Å to 2.8966(16) Å; bond angles around Ag(1) range from 105.06(5)° to 117.77(5)° and around Ag(2) from 102.18(5)° to 113.60(5)°. Six Ag ions from four quadrilateral rings and four $\mu_2$-$Br^-$ formed a decagon (figure 5b). So each inorganic polymeric planar net is composed of large decagons formed by sharing four $Br^-$ and four $[Ag_2Br_4]$ quadrilateral units with six adjacent decagons. Topologically, in **5** the network can be identified as a regular 2-D (6,3) net (Supplementary material). In the whole structure, the phen-dzp, acting as anti configuration, interlude irregularly in the 2-D network of the inorganic polymer (figure 5c).

### 3.3. *Solid-state photoluminescence properties of 1–5*

Luminescent properties of MOFs are of interest owing to their higher thermal stability than pure organic ligands and the ability to affect the emission wavelength and intensity by metal coordination [17]. The solid spectra of **2**–**5** at room temperature are illustrated in figure 6. The phen-dzp organic cation emits at 511 nm under excitation at 390 nm. No photoluminescence was observed for **1**. Excitation of the solid samples at 256 nm (for **2**), 460 nm (for **3**), 410 nm (for **4**), and 400 nm (for **5**) produces emissions with the peak maxima at 345 nm (for **2**), 688 nm (for **3**), 547 nm (for **4**), and 533 nm (for **5**). Comparable with the organic cation, a blue shift of 166 nm in **2** and a red shift in **3**–**5** have been observed. The emissions of **2** are tentatively ascribed to a ligand-to-metal charge transfer while those of **3**–**5** are attributed to a ligand-to-ligand charge transfer.

## 4. Conclusion

We have prepared and characterized five compounds. The structures of **1–3** show that they are monoclinic systems with mononuclear structures. The crystal structure of **4** is a binuclear polymer while **5** possesses a 2-D supramolecular network. The striking structural difference among **1**–**5** is simply caused by one identical organic cation which is mainly attributed to the template effects during the reactions. This presentation summarizes the most important results on use of phen-dzp cation as an organic cation-template for the synthesis of a range of metal halide/pseudohalide assemblies. The phen-dzp in these compounds, acting as charge-compensating counterions, play an important role in the crystal packing with the polymeric anionic layers or networks. Further efforts are in progress to extend this method to other metal halides/pseudohalides to evaluate the influences of cation structure modifications and different anions on the resulting supramolecular structures as well to elucidate the mechanism of inorganic polymeric framework formation.

## Supplementary material

Supporting information: CCDC-800258, CCDC-800261, CCDC-800260, CCDC-800259, and CCDC-723106 contain the supplementary crystallographic data for **1–5**.

These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033 or Email: deposit@ccdc.cam.ac.uk.

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