

## Anion-Directed Assembly of Macrocycle and Helix

Xuanjun Zhang, Xiao-Ping Zhou, and Dan Li\*

Department of Chemistry, Shantou University, Shantou 515063, People's Republic of China

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**ABSTRACT:** Self-assembly of the flexible ligand *N,N'*-bis(3-pyridylmethyl)thiourea (bpt) with ZnCl<sub>2</sub> and CdCl<sub>2</sub> in the absence and presence of KSCN yielded a short series of novel complexes (**1–4**) with macrocyclic, helical, double-helical, and 1D polymeric structures. Different metal ions, hydrogen bonds, and counteranions play significant roles in the final crystal structures. The NCS<sup>−</sup> anion was found to favor the formation of helical structures, whereas the Cl<sup>−</sup> anion favored macrocycle formation in the present system. Photoluminescence (PL) measurement results revealed that complex **2** (Zn(bpt)(SCN)<sub>2</sub>) with a helical structure exhibits enhanced emissions compared to those of the ligand and other complexes. The anion-directed assembly as well as the interesting emissions may provide useful information for further design of metal–organic compounds with novel structures and properties.

Crystal engineering based on self-assembly provides a powerful tool for the design and construction of supramolecules with unique structural motifs and tunable physical properties.<sup>1,2</sup> Metal-containing cages, clusters, macrocycles, and helical polymers are receiving increasing attention, since they can combine the properties of metal centers (e.g., optical, magnetic, or structural) with the recognition abilities of organic ligands to yield assemblies with potential applications in catalysis, magnetism, and chemical sensors.<sup>3,4</sup> By carefully selecting metal ions and organic ligands that contain multiple heterocyclic rings acting as bridges, it is possible to affect the controlled assembly of diverse molecular architectures, such as polygons, macrocycles, and coordination polymers.

Bis-monodentate ligands with longer chains offer some flexible polymeric characteristics. The combination of these ligands with appropriate metal ions under the proper synthetic conditions can lead to several kinds of structures, such as discrete cycles, infinite linear chains, and helices.<sup>5,6</sup> However, with flexible building blocks, the structures become less predictable.<sup>7</sup> In addition, the self-assembly of these architectures is highly influenced by factors such as the solvent system,<sup>8</sup> templates,<sup>9a,b</sup> metal ions, and counterion;<sup>9c,10</sup> thus, the exploration of synthetic routes is a long-term challenge.

In this work, *N,N'*-bis(3-pyridylmethyl)thiourea (bpt) was selected as a spacer for the construction of different supramolecular structures. We found that different metal ions and counteranions play significant roles in the final crystal structures. Herein, we report the synthesis, crystal structure, and photoluminescence of a short series of coordination complexes with macrocyclic, helical, double-helical, and 1D polymeric structures.

## Experimental Section

**Materials and Measurements.** All chemicals were obtained from commercial sources and used as received. The photoluminescence (PL) measurements were carried out on crystalline samples, and the spectra were collected with a Perkin-Elmer LS 55B spectrofluorimeter.

**Crystal Structure Determination.** The crystal structures were determined by single-crystal X-ray analyses. Data collections were performed using a Bruker-AXS SMART CCD area detector diffractometer with Mo K $\alpha$  radiation with an  $\omega$ -scan mode ( $\lambda = 0.71073$  Å). The structures were solved with direct methods (complexes **1–3**) and Patterson methods (complex **4**) using the SHELXTL program<sup>11</sup>

\* To whom correspondence should be addressed. Fax: +86-754-2902767. E-mail: dli@stu.edu.cn.

Table 1. Crystallographic Data for the Complexes 1–4

	1	2	3	4
empirical formula	C <sub>13</sub> H <sub>14</sub> Cl <sub>2</sub> N <sub>4</sub> SZn	C <sub>15</sub> H <sub>14</sub> N <sub>6</sub> S <sub>3</sub> Zn	C <sub>28</sub> H <sub>36</sub> CdCl <sub>2</sub> N <sub>8</sub> O <sub>2</sub> S <sub>2</sub>	C <sub>28</sub> H <sub>28</sub> CdN <sub>10</sub> S <sub>4</sub>
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>m</i>	<i>C</i> 2/ <i>c</i>
<i>T</i> (K)	293(2)	293(2)	293(2)	293(2)
<i>a</i> (Å)	7.605(6)	14.5933(13)	9.428(4)	23.410(14)
<i>b</i> (Å)	15.220(12)	5.7422(5)	22.396(9)	11.034(7)
<i>c</i> (Å)	13.828(11)	23.212(2)	7.908(3)	15.373(9)
$\beta$ (deg)	90.83(10)	106.13(2)	105.95(7)	126.41(10)
<i>V</i> (Å <sup>3</sup> )	1600.4(2)	1868.6(3)	1605.5(12)	3195.6(3)
<i>Z</i>	4	4	2	4
<i>D<sub>c</sub></i> (g cm <sup>−3</sup> )	1.638	1.564	1.581	1.549
<i>F</i> (000)	800	896	780	1512
$\mu$ (mm <sup>−1</sup> )	1.996	1.660	1.017	0.982
$\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073
cryst size (mm)	0.60 × 0.42 × 0.30	0.65 × 0.43 × 0.40	0.60 × 0.65 × 0.80	0.6 × 0.4 × 0.38
2 $\theta$ <sub>max</sub> (deg)	55.7	55.76	54.94	55.74
no. of collected rflns ( <i>R</i> <sub>int</sub> )	9809/0.018	15 250/0.063	4842/0.020	9647/0.017
<i>N<sub>o</sub></i> ( <i>I</i> > 2.0 $\sigma$ ( <i>I</i> ))	3657	4322	1861	3645
no. of params refined	198	282	110	195
<i>S</i>	1.048	1.007	1.170	1.040
<i>R</i> 1 <sup>a</sup>	0.0275	0.0647	0.0337	0.0285
<i>wR</i> 2 <sup>b</sup>	0.0676	0.1313	0.0911	0.0726
largest diff peak and hole (e Å <sup>−3</sup> )	0.285 and −0.240	0.805 and −0.600	0.690 and −0.751	0.446 and −0.398

$$^a R1(F_o) = \sum |F_o| - |F_c| / \sum |F_o|; ^b wR2(F_o) = (\sum w|F_o| - |F_c|)^2 / \sum |F_o|^2)^{1/2}; w = [\sigma^2(F_o) + (0.002F_o)^2]^{-1}.$$

and refined anisotropically with SHELXTL using full-matrix least-squares procedures. The structural plots were drawn using SHELXTL and Mercury.<sup>11b</sup> Crystal data and experimental details for the complexes are given in Table 1. Selected bond lengths and angles are given in Table 2.

**Synthesis of [Zn(bpt)Cl<sub>2</sub>]<sub>2</sub> (1).** ZnCl<sub>2</sub> (0.2 mmol, 0.027 g) and bpt (0.2 mmol, 0.052 g) were put into a Teflon-lined autoclave of 20 mL capacity. Water was added to the autoclave, up to 80% of the total volume. The autoclave was heated to 110 °C for 10 h. After the mixture was cooled to room temperature, the colorless crystals were filtered and washed with water. Yield: 74% (59 mg, 0.15 mmol). Anal. Calcd for C<sub>13</sub>H<sub>14</sub>N<sub>4</sub>SCl<sub>2</sub>Zn (394.6): C, 39.56; H, 3.58; N, 14.20. Found: C, 39.74; H, 3.68; N, 13.97.

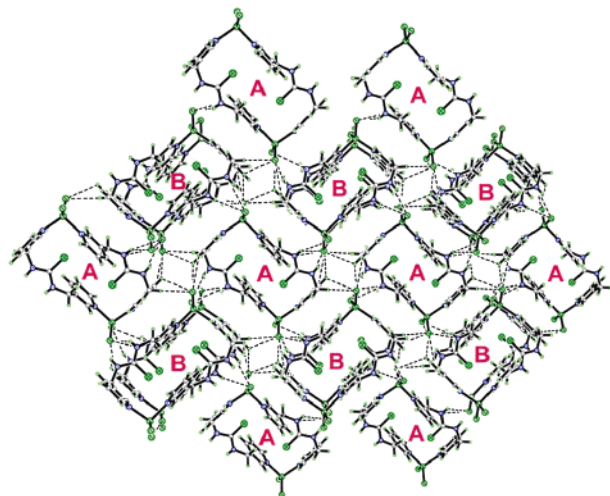
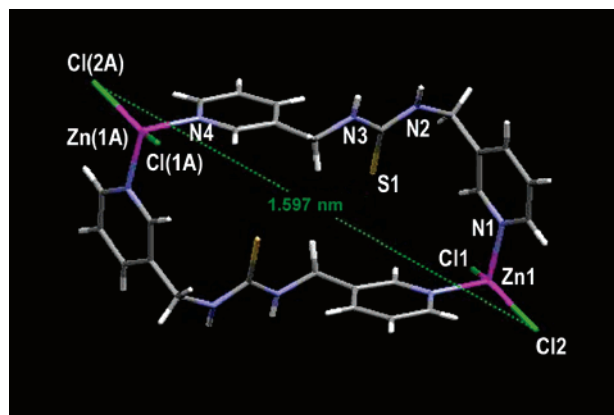
**Synthesis of [Zn(bpt)(SCN)<sub>2</sub>]<sub>n</sub> (2).** ZnCl<sub>2</sub> (0.2 mmol, 0.027 g), KSCN (0.4 mmol, 0.039 g), and bpt (0.2 mmol, 0.052 g) were put into a Teflon-lined autoclave of 20 mL capacity. Water was added to the autoclave up to 80% of the total volume. The autoclave was heated to 110 °C for 10 h. After the mixture was cooled to room temperature, the colorless crystals were filtered and washed with water. Yield: 77%

**Table 2.** Selected Interatomic Distances (Å) and Angles (deg)

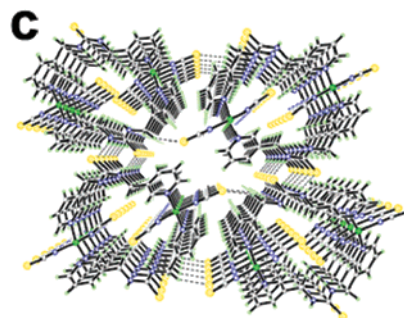
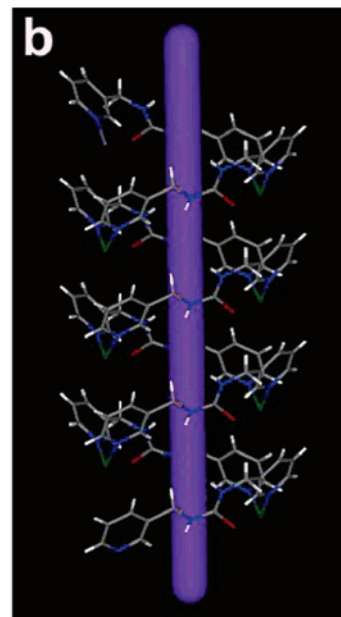
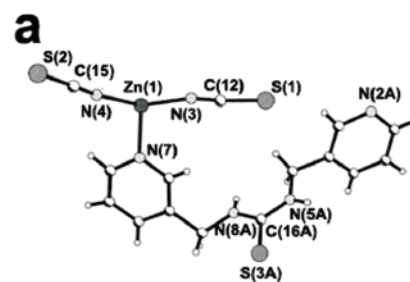
Compound 1			
Zn(1)–N(1)	2.055(15)	Zn(1)–N(4A)#1	2.044(15)
Zn(1)–Cl(1)	2.222(5)	Zn(1)–Cl(2)	2.231(5)
S(1)–C(7)	1.677(17)	N(1)–C(5)	1.337(2)
N(4A)#1–Zn(1)–N(1)	99.47(6)	N(1)–Zn(1)–Cl(1)	105.57(5)
N(1)–Zn(1)–Cl(2)	108.42(5)		
Compound 2			
Zn(1)–N(3)	1.954(4)	Zn(1)–N(7)	2.035(4)
S(1)–C(12)	1.660(6)	C(16A)–S(3A)	1.697(5)
N(4)–Zn(1)–N(3)	119.94(19)	N(4)–Zn(1)–N(7)	108.66(17)
Compound 3			
Cd(1)–N(1)#1	2.398(2)	Cd(1)–Cl(1)	2.602(13)
N(1)#1–Cd(1)–N(1)	180.0	N(1)#1–Cd(1)–N(1)#2	95.17(11)
N(1)–Cd(1)–Cl(1)#1	88.44(6)	N(1)#1–Cd(1)–Cl(1)#1	91.56(6)
Compound 4			
Cd(1)–N(1)	2.3591(17)	Cd(1)–N(5)	2.348(2)
S(2)–C(14)	1.626(2)	S(1A)–C(7A)	1.692(2)
N(4A)#1–Cd(1)–N(1)	178.11(6)	N(5)–Cd(1)–N(1)	91.77(7)

(67.7 mg, 0.154 mmol). Anal. Calcd for  $C_{15}H_{14}N_6S_3Zn$  (439.87): C, 40.95; H, 3.21; N, 19.10. Found: C, 41.06; H, 3.27; N, 18.94.

**Synthesis of  $[Cd(bpt)_2Cl_2 \cdot 2CH_3OH]_n$  (3).** At room temperature,  $CdCl_2 \cdot 2.5H_2O$  (0.1 mmol, 0.023 g) in 10 mL of water was added to a methanol solution of bpt (0.2 mmol, 0.052 g) dropwise. The mixture was stirred for 5 min and filtered. Colorless crystals suitable for X-ray single-crystal analysis were obtained after standing for 2 days at room temperature. Yield: 87% (66.5 mg, 0.087 mmol). Anal. Calcd for  $C_{28}H_{36}N_8S_2O_2Cl_2Cd$  (764.07): C, 44.08; H, 4.71; N, 14.66. Found: C, 44.10; H, 4.83; N, 14.34.



**Figure 1.** Macrocylic structure of **1** with two  $-NH-$  groups in a cis configuration (top) and the packing in the crystal showing two different arrangements (bottom).

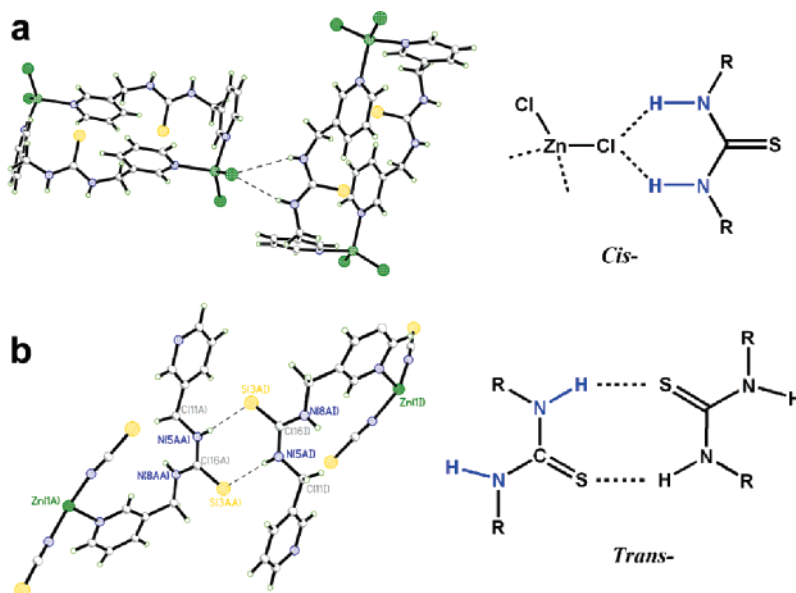


**Figure 2.** (a) Asymmetric unit of the chiral polymer of **2**. (b) Helical structure of **2**,  $CNS^-$  anions have been omitted for clarity. (c) Helix array of **2** along the  $b$  axis, interconnected via  $C-H \cdots S$  and  $N-H \cdots S$  hydrogen bonds.  $CNS^-$  anions have been omitted for clarity.

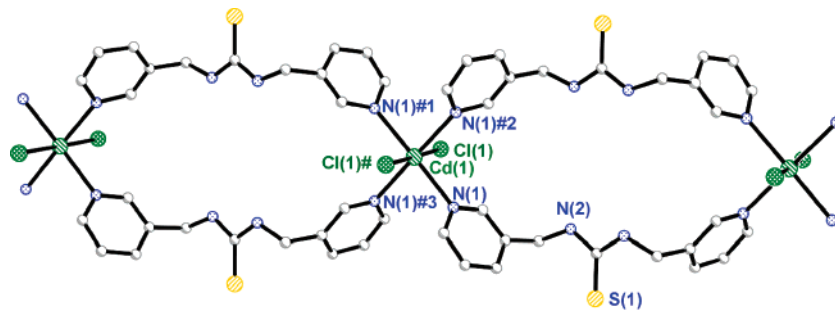
**Synthesis of  $[Cd(bpt)_2(SCN)_2]_n$  (4).**  $CdCl_2$  (0.1 mmol, 0.023 g),  $KSCN$  (0.2 mmol, 0.019 g), and bpt (0.2 mmol, 0.052 g) were put into a Teflon-lined autoclave of 20 mL capacity. Water was added to the autoclave up to 80% of the total volume. The autoclave was heated to 110 °C for 10 h. After the mixture was cooled to room temperature, colorless crystals mixed with some yellow powder were obtained. Yield: 67% (49.93 mg, 0.067 mmol). Anal. Calcd for  $C_{28}H_{28}CdN_{10}S_4$  (745.26): C, 45.08; H, 3.76; N, 18.79. Found: C, 45.26; H, 3.88; N, 18.71.

## Results and Discussion

The syntheses of complexes **1**, **2**, and **4** were carried out via a moderate hydrothermal approach (110 °C). Higher temperatures or longer reaction times resulted in the hydrolysis of the ligand or decomposition of the complexes, leading to the corresponding sulfides (ZnS and CdS). In comparison with the case for other Zn and Cd salts (such as  $ZnCl_2$ ,  $Zn(SCN)_2$ , and



**Figure 3.** (a) N–H···Cl hydrogen bonds in **1**. (b) Double N–H···S hydrogen bonds between two chains in **2**.



**Figure 4.** 1D polymeric structure of **3** with repeated macrocycles.

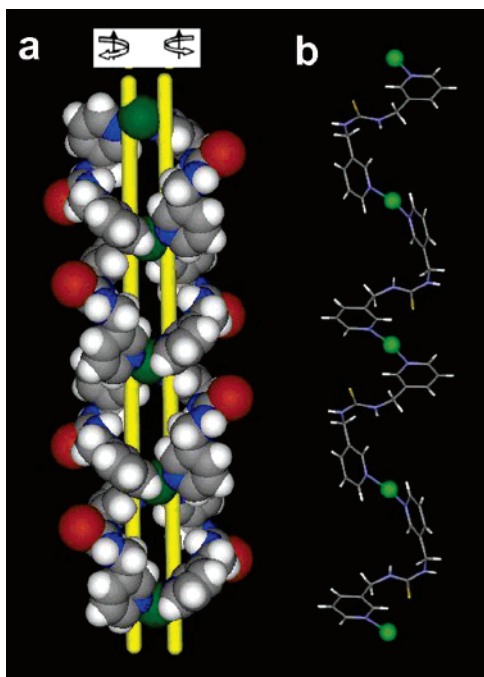
$\text{Cd}(\text{SCN})_2$ , the presence of  $\text{CdCl}_2$  can more easily result in the hydrolysis of the ligand, generating  $\text{S}^{2-}$  at temperatures higher than  $100\text{ }^\circ\text{C}$ , which can react with  $\text{Cd}^{2+}$  to form a yellow  $\text{CdS}$  precipitate. A lower reaction temperature ( $<100\text{ }^\circ\text{C}$ ) and shorter reaction time only led to some powdered products. Thus, complex **3** was synthesized at room temperature in a methanol/ $\text{H}_2\text{O}$  system.

Complex **1** has a macrocyclic structure constructed from two  $\text{ZnCl}_2$  units and two bpt ligands. As shown in Figure 1, the  $\text{Zn}^{\text{II}}$  atom is in a distorted-tetrahedral  $\text{ZnN}_2\text{Cl}_2$  geometry, being coordinated with two Cl anions and two N atoms of separated bpt ligands. The whole molecule is of nanometer scale ( $\text{Zn1}\cdots\text{Zn(1A)} = 12.276\text{ \AA}$ ;  $\text{Cl2}\cdots\text{Cl(2A)} = 15.967\text{ \AA}$ ), and there is nothing included within the macrocycles. Two  $-\text{NH}-$  groups are in a cis configuration. It is known that the halide anion can be selectively recognized by  $-\text{NH}-$  groups in urea derivatives.<sup>12</sup> The cis configuration with two  $-\text{NH}-$  groups in a chelating mode facilitates the binding with the Cl atom via  $\text{N}-\text{H}\cdots\text{Cl}$  interactions. The chloride anion coordinated to a transition metal is expected to reduce its hydrogen-bond-acceptor character significantly. However, it was anticipated that enough residual electron density would remain on the chloride ligands such that they might still interact with compound containing  $-\text{NH}-$  or  $-\text{NH}_2$  in a manner similar to that for the free anions, although less strongly.<sup>13</sup> In the crystal, the macrocycles exhibit two arrangements (A and B) and are interconnected via  $\text{N}-\text{H}\cdots\text{Cl}$  ( $\text{H}\cdots\text{Cl} = 2.992\text{ \AA}$ ) hydrogen bonds to form supramolecules (Figure 1, bottom).

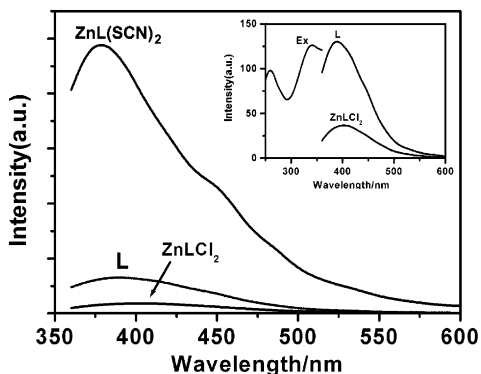
Hydrothermal treatment of  $\text{ZnCl}_2$ ,  $\text{KSCN}$ , and bpt in a molar ratio of 1:2:1 yielded the novel helical polymer **2**, the asymmetric unit of which was shown in Figure 2a. The  $\text{Zn}^{\text{II}}$  atom is also in a distorted-tetrahedral geometry, being coordinated by four N atoms from two  $\text{NCS}^-$  anions and two bpt ligands. The infinite chains form helices (Figure 2b), which were interconnected by  $\text{N}-\text{H}\cdots\text{S}$  ( $\text{H}\cdots\text{S} = 2.558\text{ \AA}$ ) and  $\text{C}-\text{H}\cdots\text{S}$  ( $\text{H}\cdots\text{S} = 2.802\text{ \AA}$ ) hydrogen bonds to form novel 3D supramolecular structures with tubular arrays along the  $b$  axis (Figure 2c). Different from those in **1**, the two  $-\text{NH}-$  groups are in a trans configuration (Figure 3), forming double  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonds between chains.

Figure 4 shows the 1D polymeric structure of **3** with repeated macrocycles. The Cd atom is in a distorted-octahedral geometry coordinated with four N atoms from four separated bpt ligands and two  $\text{Cl}^-$  anions. Similar to those in **1**, two  $-\text{NH}-$  groups of the ligand are in a cis configuration. However, the  $-\text{NH}-$  groups here are inside the macrocycle, which inhibits the formation of  $\text{N}-\text{H}\cdots\text{Cl}$  interactions.

Reaction of  $\text{CdCl}_2$ ,  $\text{KSCN}$ , and bpt in a molar ratio of 1:2:2 yielded **4** with a novel double-helical structure (Figure 5). The Cd atom is in a distorted-octahedral geometry coordinated with four N atoms from four separated bpt ligands and two N atoms from  $\text{NCS}^-$  anions. The Cd atoms and the ligands on each side of the  $\text{Cd}\cdots\text{Cd}\cdots\text{Cd}$  chain form a single-helical chain, respectively. Figure 5b shows a separated right-handed helical chain. The left- and right-handed double helices are equally separated by the  $\text{Cd}\cdots\text{Cd}\cdots\text{Cd}$  chain along the 1D structure. This kind of



**Figure 5.** (a) Double-helical structure of **4**, with Cd atoms and the ligands on each side of the Cd...Cd...Cd chain forming single helical chains, respectively: (red) S; (blue) N; (gray) C; (green) Cd; (white) H. (b) A separated right helical chain. CNS<sup>-</sup> anions have been omitted for clarity.



**Figure 6.** Solid-state photoluminescence of the ligand and complexes. Inset: detailed photoluminescence spectra of the ligand and complex **1** for comparison.

double helix is different from some reported double or triple helices, in which helical chains are entangled with each other with one axis along the 1D structure.<sup>3c,14</sup> In the crystal, the double helices are linked by multiple N—H...S and C—H...S interactions, forming a stable supramolecular structure. Although the structure based on self-assembly is highly influenced by many factors, it appeared that the NCS<sup>-</sup> anion favors the formation of helical structures to some extent, whereas the Cl<sup>-</sup> anion favors the formation of macrocycles in this system.

Photoluminescence measurements were carried out in the solid state at room temperature. The ligand emits at ca. 389 nm upon an excitation of 341 nm. The complex **1** had the almost the same emission peak position, but the intensity was relatively weak. Interestingly, complex **2** exhibited a greatly enhanced emission compared to those of the ligand and complex **1** (Figure 6). Since the emission peak positions of the complexes were almost the same as that of the ligand bpt, they should be due to

neither ligand-to-metal nor metal-to-ligand charge transfer and can be ascribed to the intraligand  $\pi^*-\pi$  charge transfer of *N,N'*-bis(3-pyridylmethyl)thiourea (bpt). The enhancement of complex **2** is probably related to its helical structure. This phenomenon was also observed previously in some coordination polymers and was proposed to be due to enhancement of the ligand rigidity.<sup>15</sup> Complex **3** and **4** exhibited relatively weak emissions, which may be a result of the heavy-atom effect of cadmium.

In conclusion, a series of complexes with macrocyclic, repeated macrocyclic, helical, and double-helical structures have been synthesized by self-assembly of a flexible ligand and appropriate metal salts. We found that anions and hydrogen bonds play important roles in the crystal structures of the complexes. It appears that the NCS<sup>-</sup> anion favors the formation of helical structures, whereas the Cl<sup>-</sup> anion favors the formation of macrocycles in the present system. All of the complexes exhibited solid-state photoluminescence, and the zinc complex **2**, with a helical structure, exhibited enhanced emission compared to the free ligand and other complexes, which may be induced by its helical structure with relatively enhanced rigidity of the ligand. The anion-directed assembly as well as interesting photoluminescence may provide useful information for further design of metal-organic compounds with novel structures and properties.

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**Supporting Information Available:** CIF files giving crystallographic data for compounds **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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