

A Molecular Helix: Self-Assembly of Coordination Polymers from d^{10} Metal Ions and 1,10-Phenanthroline-5,6-dione (pdon) with the Bridges of SCN^- and Cl^- Anions

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ABSTRACT: Novel complexes of (half)-filled d-configurations, including $[Zn(pdion)(SCN)(\mu-Cl)(H_2O)]_n$ (**1**), $[Cd_2(pdion)_2(\mu_{1,3}SCN)_4]_n$ (**2**), $[Hg(pdion)_2Cl_2]$ (**3**), and $[Mn(pdion)_2(SCN)_2]$ (**4**) ($pdion = 1,10$ -phenanthroline-5,6-dione), were synthesized and structurally characterized by single crystal X-ray diffraction. Self-assembly behaviors of these metal ions with anions are essentially different, although some of them are elements of the same group. Various supramolecular interactions of H-bonding, $\pi \cdots \pi$ stacking, and C–X \cdots π ($X = H, O$, and S) are observed in the structures. In **1**, central Zn^{2+} cations are connected to form an infinite one-dimensional (1D) zigzag chain by bridged Cl^- and further extended to two-dimensional layers via weak interactions. Complex **2** consists of dinuclear units doubly bridged by two end-to-end (EE) SCN^- anions and linked to 1D molecular helix along the b -axis with a long pitch of 13.077 Å. The helix displays racemic mixtures in the crystal. Complexes **3** and **4** are six-coordinated with distorted octahedron geometry. $pdion$ serves as a terminal ligand in complexes. Spectroscopic and electrochemical properties of $pdion$ and the complexes are studied in dimethyl sulfoxide (DMSO) solution at room temperature. Circular dichroism (CD) spectral results suggest that there is phenomenon of spontaneous resolution in the DMSO solution for the spiral structure **2**.

Introduction

In recent years, there has been rapidly increasing interest in the design and synthesis of metal organic frameworks (MOFs) employing various secondary building units (SBUs) linked via coordination reactions, supramolecular contacts, such as van der Waals contacts, $\pi \cdots \pi$ stacking, hydrogen bonding, and hydrogen (non-hydrogen) \cdots π interactions, or their combination in order to understand molecular self-assembly principles and design molecular recognition devices. On the basis of crystal engineering of coordination polymers, a great deal of fascinating structures with their potential applications as functional materials have been reported.¹ Self-assembly of organic and inorganic compounds with metal centers is one of the most efficient and widely utilized approaches for the construction of such polymers. However, a major challenge in this approach is the predictability of the polymeric structures since many factors such as coordination geometry of the metals, nature of the ligands, metal-to-ligand ratio, solvent system, template, pH value of solution, and counterions will influence the framework formation.² Thus, systematic research is required for understanding the roles of the factors in the formation of frameworks. Extensive studies have been carried out to give many new one-, two-, and three-dimensional (1D, 2D, and 3D) frameworks through the coordination of metal atoms with organic N-donors such as bipyridine, 1,10-phenanthroline, and related derivatives.³

1,10-Phenanthroline-5,6-dione (pdon) is a versatile ligand for the assembly of metal organic materials.⁴ It may serve as a terminal or planar bridging ligand in the construction of

multinuclear complexes and has the ability to form stable complexes with a wide variety of metal ions analogous to 1,10-phenanthroline and carries an *o*-quinone moiety with pH-dependent electroactivity. So, metal complexes with the ligand potentially allow for the variation and control of redox properties over a wide range as well as the fine-tuning of potentials through pH changes.⁵ The diketone functionality can also easily be transformed to other chelating groups such as a diamine or a dioxime.⁶ Moreover, it is also a versatile organic linker that can form bridges through amine condensation or a combination of coordination and condensation.⁷ SCN^- is a linear ligand with two donor atoms and may coordinate through terminal modes or bridging modes or both, with great potential in building a coordination network.⁸ It can adopt end-to-end (EE) and end-on (EO) fashions via the nitrogen and sulfur atoms to build coordination networks as well as interlink the 1D or 2D molecules into frameworks via the noncovalent interactions.⁹ A series of new coordination polymers with interesting structures based on the bridging SCN^- ligand along with their magnetic properties have been reported.¹⁰ The significance of this research work is to report the self-assembly synthesis of pdon, SCN^- , and Cl^- based on the influence of different d^{10} and d^5 metal ions such as Zn^{2+} , Cd^{2+} , Hg^{2+} , and Mn^{2+} . It is noted that two crystal structures exhibit a 1D zigzag or helical chain through different inorganic anions.

Experimental Section

Materials and Apparatus. All chemicals were reagent grade and commercially available, and were used without further purification. The infrared spectra were recorded as KBr pellets on a Shimadzu 8300 FT-IR spectrometer. Samples for elemental analysis were

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Table 1. Summary of Data Collections and Structure Refinements for Complexes **1–4**

	1	2	3	4
formula	C ₁₃ H ₈ ClN ₃ O ₃ SZn	C ₂₈ H ₁₂ Cd ₂ N ₈ O ₄ S ₄	C ₂₄ H ₁₂ Cl ₂ HgN ₄ O ₄	C ₂₆ H ₁₂ MnN ₆ O ₄ S ₂
<i>M</i> _r	387.1	877.5	691.87	591.48
temperature (K)	298(2)	298(2)	298(2)	298(2)
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
space group	<i>P</i> c	<i>P</i> 2(1)/ <i>c</i>	<i>F</i> <i>d</i> <i>d</i> 2	<i>P</i> n
<i>a</i> (Å)	8.8115(13)	13.1392(15)	42.098(4)	11.1626(15)
<i>b</i> (Å)	12.2454(18)	13.0766(14)	8.3101(8)	8.0501(12)
<i>c</i> (Å)	7.2356(12)	17.2116(18)	12.9061(8)	15.1800(8)
α	90	90	90	90
β (°)	108.886(10)	91.253(1)	90	107.706(2)
γ	90	90	90	90
<i>V</i> (Å ³)	738.7(2)	2956.5(6)	4515.0(7)	1299.5(3)
crystal size	0.16 × 0.09 × 0.04	0.23 × 0.18 × 0.17	0.2 × 0.2 × 0.2	0.35 × 0.18 × 0.08
<i>Z</i>	2	4	8	2
ρ_c (g cm ⁻³)	1.740	1.971	2.036	1.596
μ (mm ⁻¹)	2.00	1.77	7.10	0.71
<i>F</i> (000)	388	1712	2640	598
θ range (°)	3.0–25.1	2.4–25.4	3.0–21.1	2.8–21.6
limiting indices	$-9 < h < 10$ $-10 < k < 14$ $-8 < l < 7$	$-15 < h < 10$ $-15 < k < 14$ $-20 < l < 20$	$-36 < h < 50$ $-9 < k < 9$ $-15 < l < 15$	$-13 < h < 8$ $-9 < k < 9$ $-18 < l < 18$
goodness of fit	1.04	1.024	1.08	1.036
reflections collected	3794	14211	5632	6377
reflections unique	1300	5065	1039	3599
<i>R</i> _{int}	0.038	0.094	0.067	0.041
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.054, 0.139	0.092, 0.217	0.030, 0.067	0.054, 0.125
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.059, 0.142	0.174, 0.249	0.038, 0.070	0.08, 0.137
largest diff peak, hole (e Å ³)	−0.65 and 0.63	−1.46 and 5.59	−0.48 and 0.66	−0.54 and 0.67

dried under a vacuum, and the analysis was performed with a CHN-O-Rapid instrument. Luminescence spectrum was recorded on a CARY Eclipse fluorescence spectrophotometer at room temperature. The electronic spectra in dimethyl sulfoxide (DMSO) were recorded with a Hewlett-Packard HP-8453 Chemstation spectrophotometer. The circular dichroism (CD) spectrum of the complex **2** in DMSO solution was recorded by means of a Jasco J-810 spectropolarimeter. Electrospray ionization mass spectra (ESI-MS) were recorded with a Quattro Micro API instrument (Waters, USA) in DMSO/methanol solution. A CHI 660C electrochemical workstation (Shanghai CH Instrument Company, China) was used for all of the electrochemical measurements such as cycle voltammetry (CV). A glassy carbon electrode (GCE) of 3-mm diameter was used as working electrode; a platinum wire and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. These experiments were conducted at RT in a 0.1 M DMSO solution of 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as a supporting electrolyte, which was recrystallized three times from ethyl acetate and dried in vacuo at 90 °C for 72 h.^{4b} The solutions were deoxygenated by bubbling with nitrogen. The X-ray diffraction pattern for the 1D spiral structures of **2** was obtained on a Miniflex–Rigaku II diffractometer using Cu Kα radiation ($\lambda = 1.54056$ Å).

Synthesis of Complexes 1–4. pdon was oxidized from its parent compound 1,10-phenanthroline. The processes of preparation and purification were easily followed from the literature.^{4f} Pure products were yellow-orange needles, mp 257 °C. IR data (cm⁻¹): 3457(s), 1689(s), 1559(s), 1460(m), 1415(s), 1291(m), 1206(w), 1115(w), 1063(w), 926(w), 808(w), 736(m), 671(w), 613(w), 541(w). Complexes **1–4** were prepared by a similar procedure. MCl₂ (0.1 mmol, M = Zn(**1**), Cd(**2**), Hg(**3**), and Mn(**4**)) dissolved in 5.0 mL of aqueous solution was dropwise added to a 10 mL of methanol solution containing pdon (0.021 g, 0.1 mmol) at room temperature, and the mixture was reacted with stirring for 0.5 h. KSCN (0.0195 g, 0.2 mmol) was added dropwise with a constant stirring. The insoluble components were removed by filtration, and the filtrate was allowed to stand at room temperature. The light yellow (**1–2**) and orange red (**3–4**) crystals were collected after slow evaporation at room temperature for about 2 weeks, respectively.

[Zn(pdona)(SCN)(μ-Cl)(H₂O)]_n (**1**). Yield 49%. Elemental analysis calcd. (%) for C₁₃H₈ClN₃O₃SZn: C 40.33, H 2.08, N 10.85; found: C 40.19, H 2.14, N 10.99; FT-IR data (cm⁻¹): 3452(s), 2082(s), 1703(s), 1631(w), 1579(m), 1424(m), 1383(w), 1300(w), 1130(w), 1024(w), 803(w), 731(w).

[Cd₂(pdona)₂(SCN)₄]_n (**2**). Yield 16.7%. Elemental analysis calcd. (%) for C₂₈H₁₂Cd₂N₈O₄S₄: C 38.32, H 1.38, N 12.77; found: C 38.32, H 1.35, N 12.73; FT-IR data(cm⁻¹): 3444(s), 2113(s), 1695(s), 1571(s), 1460(w), 1428(m), 1421(s), 1304(w), 1206(w), 1121(w), 1017(w), 925(w), 834(w), 736(m), 697(w), 456(w).

[Hg(pdona)₂Cl₂] (**3**). Yield 41.7%. Elemental analysis calcd. (%) for C₂₄H₁₂Cl₂HgN₄O₄: C 41.66, H 1.75, N 8.10; found: C 41.43, H 2.05, N 8.61; FT-IR data (cm⁻¹): 3444(s), 1701(s), 1571(s), 1467(s), 1428(s), 1310(m), 1258(w), 1206(w), 1122(w), 1069(w), 1017(w), 932(w), 828(w), 736(m), 691(w), 626(w), 547(w).

[Mn(pdona)₂(SCN)₂] (**4**). Yield 17%. Elemental analysis calcd. (%) for C₂₆H₁₂MnN₆O₄S₂: C 52.80, H 2.04, N 14.21; found: C 52.87, H 2.12, N 14.29; FT-IR data (cm⁻¹): 3444(s), 2073(s), 1696(s), 1571(s), 1474(m), 1421(s), 1297(m), 1121(w), 1023(w), 932(w), 821(w), 730(m), 691(w), 547(w), 468(w).

X-ray Crystallography. All the data of the complexes **1–4** were collected on a Bruker Smart Apex II diffractometer equipped with 1K CCD instrument by using a graphite monochromator utilizing Mo-Kα radiation ($\lambda = 0.71073$ Å) at RT. Cell parameters were determined using SMART software.¹¹ Data reduction and corrections were performed using SAINTPlus. Absorption corrections were made via SADABS.¹² The structures were solved by direct methods with the program SHELXS-97 and refined by full-matrix least-squares methods on all *F*² data with SHELXL-97.¹³ Non-H atoms were refined anisotropically. Hydrogen atoms attached C were added theoretically and treated as riding on the concerned atoms. H atoms of coordinational water molecules in **1** were located from difference Fourier maps and refined from their global *U*_{iso} values. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. Crystallographic data of complexes **1–4** are shown in Table 1. Selected bond lengths and bond angles were given in Table 2. The CIF files deposited in the Cambridge Crystallographic Data Center (CCDC reference numbers 741165, 741166, 749581, and 741164 for compounds **1–4**, respectively) can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html; or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K. [fax: (+44)-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

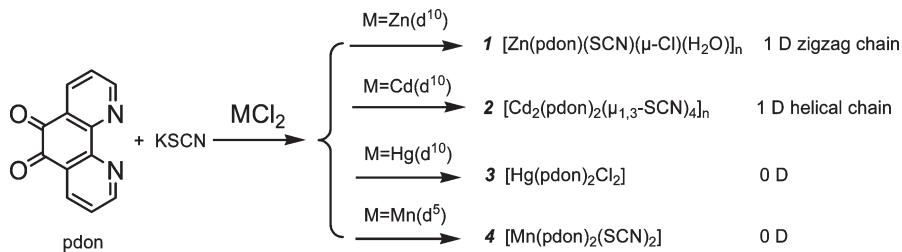
Results and Discussion

Synthesis and Characterization. The analogous d¹⁰ or d⁵ complexes with bridges of organic molecules, terephthalic

Table 2. Selected Bond Distances (\AA) and Angles ($^\circ$) for Complexes **1–4^a**

Complex 1					
Zn1–N1	2.357(14)	Zn1–N2	2.390(13)	Zn1–N3	2.197(14)
Zn1–Cl1	2.565(4)	Zn1–O3	2.435(13)	O1–C11	1.20(2)
O2–C12	1.239(18)	Zn1–Cl1 ⁱ	2.713(5)	N1–Zn1–Cl1	93.6(3)
Cl1–Zn1–Cl1 ⁱ	93.59(7)	Zn1–Cl1–Zn1 ⁱⁱ	137.11(18)	N1–Zn1–N2	70.9(4)
Complex 2					
Cd1–S2	2.845(4)	Cd1–S3	2.739(4)	Cd2–S1	2.823(4)
Cd2–S4	2.748(3)	Cd1–N5	2.223(13)	Cd1–N8	2.237(12)
Cd2–N6	2.244(12)	Cd2–N7	2.213(11)	Cd1–N1	2.360(12)
Cd1–N2	2.393(10)	Cd2–N3	2.375(11)	Cd2–N4	2.364(9)
O1–C11	1.25(2)	O2–C12	1.21(2)	O3–C23	1.260(19)
O4–C24	1.243(19)				
N5–C25–S1	176.5(12)	N6–C26–S2	176.1(14)	N1–Cd1–N2	70.7(4)
N4–Cd2–N3	69.0(4)				
Complex 3					
Hg1–N2	2.532(9)	Hg1–N1	2.457(9)	Hg1–Cl1	2.524(3)
C11–O1	1.173(17)	C12–O2	1.215(18)		
N2–Hg1–N1	65.1(3)	N2–Hg1–Cl1	91.6(2)	N1–Hg1–Cl1	107.3(2)
Cl1–Hg1–Cl1 ⁱⁱⁱ	102.49(19)				
Complex 4					
Mn1–N5	2.117(6)	Mn1–N6	2.117(8)	Mn1–N1	2.249(5)
Mn1–N3	2.280(5)	Mn1–N2	2.291(5)	Mn1–N4	2.310(5)
O1–C11	1.192(10)	O2–C12	1.197(10)	O3–C23	1.191(8)
O4–C24	1.222(8)	N1–Mn1–N2	72.06(18)	N3–Mn1–N4	70.8(2)

^aSymmetry codes: (i) $x, -y + 1, z + 1/2$; (ii) $x, -y + 1, z - 1/2$; (iii) $-x + 1/2, -y + 3/2, z$.

Scheme 1

acid, or 5-bromo-*p*-phthalic acid, as well as mononuclear complexes have been reported earlier.¹⁴ To construct polymers, we introduced the three potential bridges, dot (Cl^-), line (SCN^-), and plane (pdon) into the reaction system. The self-assembly process of **1–4** was achieved as set out in Scheme 1. Namely, they were obtained from the ligands of 1,10-phenanthroline-5,6-dione and thiocyanate reacting with the d^{10} or d^5 metal chloride in aqueous methanol solution at room temperature. The results indicated that under the same synthetic conditions, only two coordinated polymers were realized in the assembly of the four d^{10} or d^5 metal ions, despite every recipe including all three potential bridges. The pdon ligand only served as a terminal ligand and occupied two coordinated sites of the metal ions in the four complexes. Although Zn^{2+} , Cd^{2+} , and Hg^{2+} are elements of the same group, their self-assembly behaviors were essentially different. The architectures may relate to crystal and ionic radii (\AA , C.N.6) of metal ions, Mn (0.81, 0.67), Zn (0.88, 0.74), Cd (1.09, 0.95), and Hg (1.16, 1.02).¹⁵ The infrared absorption spectra showed a small shift to higher energy of C=O stretching of the pdon in **1–4** and the free ligand at 1703, 1695, 1701, 1696, and 1689 cm^{-1} , respectively. $\text{C}\equiv\text{N}$ stretching of thiocyanate in complexes **1**, **2**, and **4** were at 2082, 2113, and 2073 cm^{-1} , respectively. The products were further confirmed by elemental analyses.

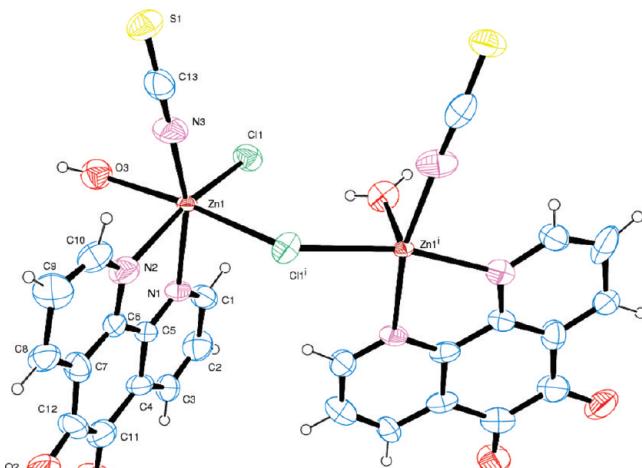


Figure 1. ORTEP diagram of complex **1**, showing the two building units and coordination environments of Zn and Cl-bridge ions in the coordination polymer **1**, symmetry code: (i) $x, 1 - y, 1/2 + z$.

Description of the Crystal Structures

Complex **1** crystallizes in the $P\bar{c}$ space group. As shown in Figure 1, the asymmetric unit of complex **1** displays a Zn^{2+}

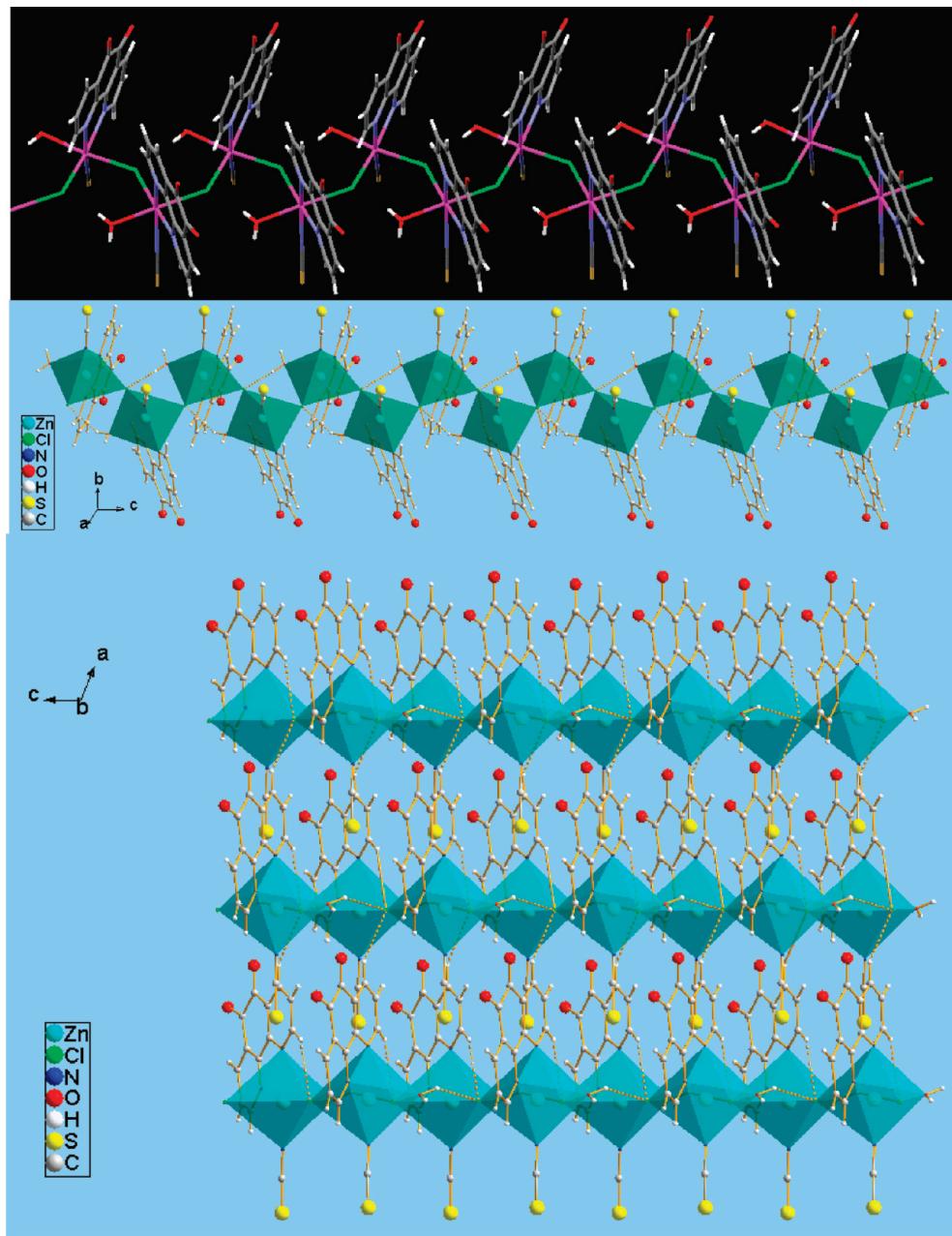


Figure 2. Perspective view of complex **1**, showing a 1D chain (top and mid) with a Cl-bridge and 2D supramolecular network (bottom) by weak interactions in the coordination polymer **1**.

center with a distorted octahedral environment of $\{\text{ZnN}_3(\mu\text{-Cl})_2\text{O}\}$, coordinated by three N atoms from pdon and SCN^- , one O atom from a water molecule, and two bridged Cl^- anions. Both Cl-bridges are located in a cis-configuration in this complex. $\text{Zn}-\text{N}(\text{pdon})$ bond distances are 2.357(14) and 2.390(13) Å, respectively. The $\text{Zn}-\text{N}(\text{SCN})$ bond length [2.197(14) Å] is slightly longer than that of $\text{Mn}-\text{N}(\text{SCN})$ [2.113(5) and 2.120(6) Å] of complex **4**. $\text{Zn}-\text{Cl}$ bond distances [2.565(4) and 2.713(5) Å] are longer than that in the previous reports.¹⁶ The bond angle of $\text{N}1-\text{Zn}1-\text{N}2$ [70.9(4)] is comparable to the reported complexes.¹⁷ The $\text{Cl}1-\text{Zn}1-\text{Cl}1$ angle is 93.59(7)° (see Table 2). The structure of **1** shows that the Cl^- anion as a bridge connects two Zn^{2+} ions along the *c* direction to form a 1D zigzag chain (Figure 2). In the chain, the distance of two adjacent Zn is 4.912(1) Å, and the angle of the bridging Cl atom linking two metal centers ($\text{Zn}-\text{Cl}-\text{Zn}$) is 137.11(18)°, while the angle of three adjacent $\text{Zn}\cdots\text{Zn}\cdots\text{Zn}$ is 94.87(2)°.

There are a lot of weak intra- and interchain interactions in **1** (Figure 3 and Table S1, Supporting Information), such as $\text{O}-\text{H}\cdots\text{O}$, $\text{O}-\text{H}\cdots\text{Cl}$, $\text{C}-\text{H}\cdots\text{O}$, $\text{C}-\text{H}\cdots\pi$, $\text{C}=\text{O}\cdots\pi$, $\text{C}-\text{S}\cdots\pi$ interactions between the coordination water molecules and the Cl atoms, adjacent chains as well. Interestingly, the S atom of thiocyanate inserts interspace of two pdon ligands of adjacent chains, showing a sandwich structure of weak interactions in which the distances of $\text{S}\cdots\pi$ ($\text{Cg}1^{\text{iii}}$ and $\text{Cg}2^{\text{ii}}$, $\text{ii} -1+x, y, z$; $\text{iii} -1+x, y, -1+z$) are 3.617(16) and 3.705(15) Å.

As depicted in Figures 4 and 5, and Table 2, complex **2** consists of dinuclear units doubly bridged by two end-to-end (EE) SCN anions and linked to a 1D helical chain along the 2_1 screw axis with direction [0, 1, 0]. The two independent Cd atoms are octahedrally coordinated in a N-chelate ring from pdon, two N-coordinated SCN bridges, and two S-coordinated SCN bridges, respectively. Thus, each Cd molecular

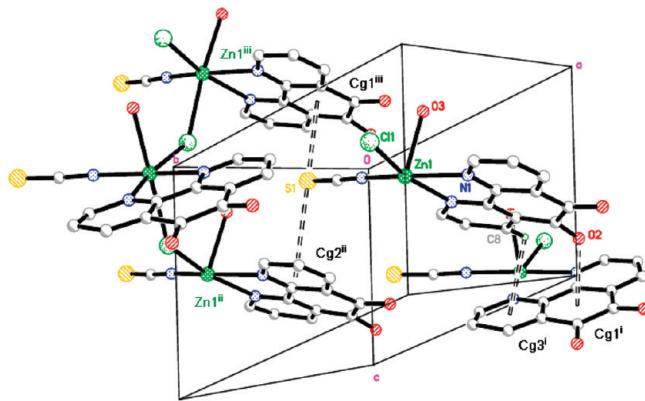


Figure 3. The C–H $\cdots\pi$, C=O $\cdots\pi$ and C–S $\cdots\pi$ interactions (double dashed lines) between neighboring molecules in complex **1**, symmetry codes: (i) $x, -y, z + 1/2$; (ii) $-1 + x, y, z$; (iii) $-1 + x, y, -1 + z$; ring label: Cg1 C4–C7/C12/C11, Cg2 N1/C1–C5, Cg3 N2/C6–C10.

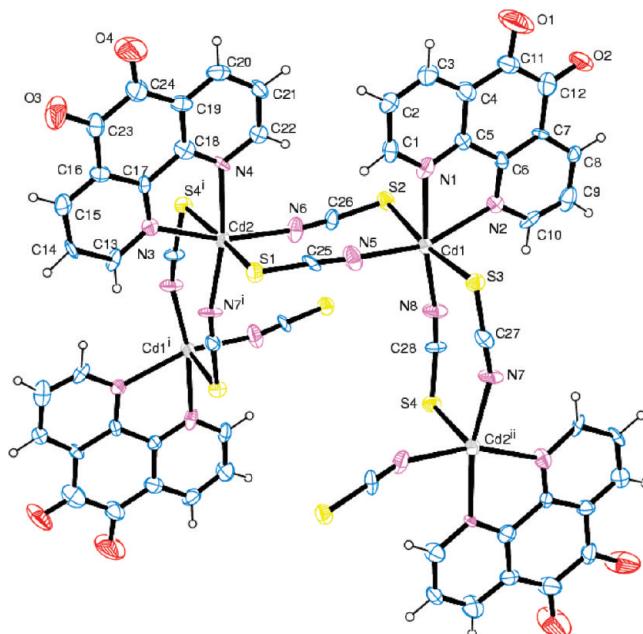


Figure 4. ORTEP diagram of complex **2**, showing the two building units and coordination environments of Cd and double SCN-bridge ions in the coordination polymer **2**, symmetry codes: (i) $1 - x, -1/2 + y, 5/2 - z$; (ii) $1 - x, 1/2 + y, 5/2 - z$.

fragment shows an octahedral CdN₄S₂ coordination arrangement with a trans-configuration. In this coordination geometry, four N and two S atoms are located at an equatorial plane and two apexes, respectively. The chelated angle of the strained five-member ring around Cd1 (N1–Cd1–N2) is 70.7(4) $^{\circ}$, while around Cd2 the angle is 69.0(4) $^{\circ}$. The two sets of $\mu_{1,3}$ -SCN bridges are not equivalent, which is evident from their bond parameters data (Table 2). The bridging SCN⁻ does not show deviation from linearity (N5–C25–S1, 176.5(12) $^{\circ}$ and N6–C26–S2, 176.1(14) $^{\circ}$). We can see the same structure that consists of a network of metal chains bridged together by pairs of thiocyanate groups in reported compounds,¹⁸ and there is scarcely any difference in the bonds between Cd and bridging thiocyanate compared with the literature.¹⁹ But the reported Cd–N(SCN) distance [2.2378(8)–2.390 Å]²⁰ is longer than that of the present complex (average 2.229(12) Å). There are C=O $\cdots\pi$ and $\pi\cdots\pi$ interactions (double dashed

lines) between neighboring molecules in complex **2** to stabilize its crystal structure (Figure 5 and Table S1, Supporting Information).

Architecturally, the crystal structure of **2** builds a couple of a molecular helix (Figure 6) with a long pitch of 13.077 Å, outer diameter of 20.648(13) Å, and minimum overhang distances close to a 2_1 screw axis of 7.524(6) Å (S1 \cdots S4ⁱ, i $1 - x, 1/2 + y, 5/2 - z$ and 7.512(6) Å (S3 \cdots S2ⁱⁱ, ii $x, y - 1, z$). Here, double thiocyanate bridges integrate the connectors tightly and chelated pdons play steps of the helix, in which, distances of two adjacent Cd are 5.893(2) (Cd1 \cdots Cd2) and 5.776(2) Å (Cd1 \cdots Cd2ⁱ), and angles of three adjacent Cd are 105.08(2) (Cd2 \cdots Cd1 \cdots Cd2ⁱ) and 111.36(2) $^{\circ}$ (Cd1 \cdots Cd2ⁱ \cdots Cd1ⁱ). Complex **2** exhibits racemic mixtures in the solid state, but a positive Cotton effect of circular dichroism (CD) spectroscopy was detected for **2** in DMSO solution (see section Circular Dichroism).

X-ray crystallographic analysis revealed that complexes **3** and **4** are mononuclear species as shown in Figures 7 and 8. The metal centers are six-coordinated in a slightly distorted octahedron by two pdon ligands and *cis*-Cl⁻ (**3**) or *cis*-SCN⁻ (**4**) anions, forming a coordination environment of MnN₆ or HgN₄Cl₂ in which the four N atoms come from pdon ligands and the other two N from a SCN anion in **3** or two Cl atoms from Cl anions in **4**. The Mn–N(pdon) distances are in the range of 2.249(5)–2.310(5) Å, which is comparable to the corresponding bond distances in *cis*-[Mn(bipy)₂(NCS)₂] (bipy = 2,2'-bipyridine) [2.286(8)–2.312(8) Å] and *cis*-[Mn(bipy)₂(Cl)₂] [2.270(3)–2.342(3) Å].¹⁷ The Mn–N(SCN) [2.117(6) and 2.117(8) Å] distances are shorter than that in the reported literature [Mn–N(SCN) 2.139(3) Å].^{17c} In **4**, the Mn–N(SCN) distances are also shorter than the Mn–N(pdon) distances. The Hg–N distances of **3** are the longest in four complexes, in a range of 2.457(9)–2.532(9) Å. The N–M–N chelated angles in both complexes formed by each pdon are 72.06(18), 70.8(2) (**4**), and 65.1(3) $^{\circ}$ (**3**), which are very close to the corresponding angles found in *cis*-[Mn(bipy)₂(Cl)₂] (70.2)^{17b} and *cis*-[Mn(bipy)₂(SCN)₂] (70.4)^{17a}.

The crystal structures of complexes **1**–**4** indicate that under the synthesis conditions of this work, pdon acted only as a terminal ligand. The bond lengths of C=O ranging from 1.21 to 1.26 Å (Table 2) exhibit the character of a double bond, indicating the pdon participates in coordination mainly in the form of quinone. For the ambidentate thiocyanate ligand, Teo suggested that its coordination be classified into 6 types and 15 designs.²¹ Complexes **1** and **4** display Ib mode while **2** exists in IIa mode according to their opinion.

Fluorescence Properties. The emission spectra of complexes pdon, **1**, **2**, **3**, and **4** in DMSO solution at room temperature are depicted in Figure 9. The intense emissions occurred at 330 nm ($\lambda_{ex} = 279$ nm) for pdon, **2** and **4**, while 340 nm ($\lambda_{ex} = 279$ nm) for **1** and **3**, can be attributed to the $\pi\cdots\pi^*$ intraligand transitions.²² Complexes **1** and **3** display a 10 nm slight red shift compared with that of complexes **2**, **4** and the free pdon, probably due to the difference of metal ions and coordination environment.²³ In complex **1**, hydrogen-bonding interaction may also have an effect on the red shift.²² Additionally, complex **3** shows obviously weaker fluorescence than that of free ligand and complexes **1**, **2**, and **4**, which may be attributed to the quenching effect of the Hg²⁺ metal ion.²⁴

Electronic Spectra. Figure 10 shows the UV–Vis absorption spectra of the ligand as well as complexes **1**–**4** in DMSO. All of them exhibit two very strong absorption bands at

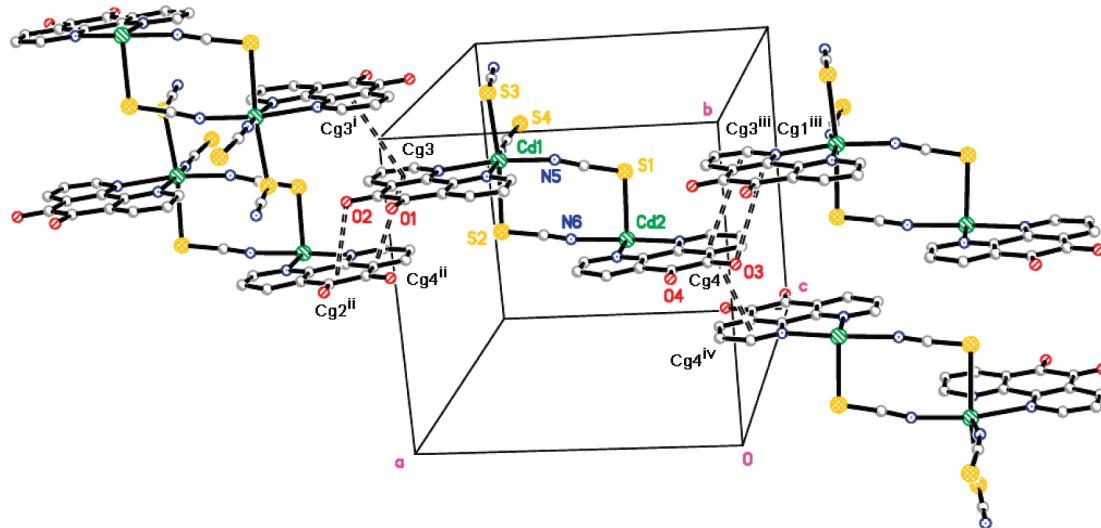


Figure 5. The $\text{C}=\text{O}\cdots\pi$ and $\pi\cdots\pi$ interactions (double dashed lines) between neighboring molecules in complex **2**, symmetry codes: (i) $2-x$, $2-y$, $-z$; (ii) $1+x$, y , z ; (iii) $-1+x$, y , z ; (iv) $-x$, $1-y$, $-z$; ring label: Cg1 C4—C7/C12/C11, Cg2 C16—C19/C24/C23, Cg3 N2/C6—C10, Cg4 N3/C13—C17.

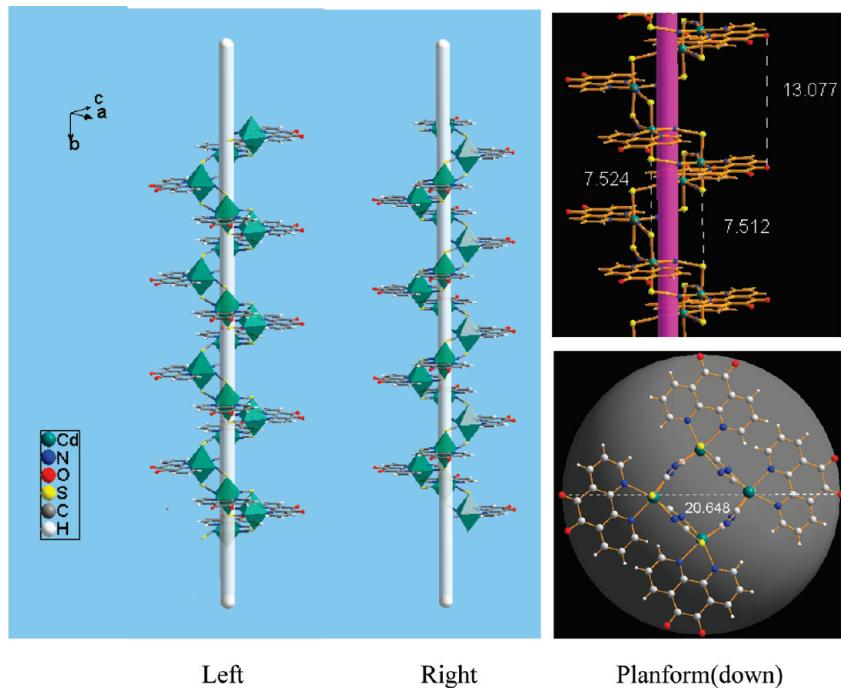


Figure 6. Perspective view of complex **2**, showing 1D helical chain in the coordination polymer.

262–265 and 295–300 nm due to the $\pi-\pi^*$ transitions.^{6a} The peaks are similar to that in the reported compounds pdon and $\text{Co}(\text{pdon})_3\text{PF}_6$.^{4b}

Circular Dichroism. Circular dichroism (CD) spectroscopy is a very useful and convenient technique to analyze characters of stereochemistry. Complex **2** crystallized in $P2_1/c$ space group with racemic mixtures with zero CD intensity in the solid state. What happens to this complex in the solution state? The CD spectrum of **2** in DMSO has been investigated because of its poor dissolution in other solvents. The CD spectrum of complex **2** shows positive Cotton effects in the wavelength range of 200–360 nm, which arise due to structural asymmetry in solution conformation (Figure 11). Does this activity come from left- or right-handed spirals of **2** or other active species, such as Δ or Λ -conformation mononuclear

$[\text{Cd}(\text{pdon})_2\text{X}_2]$ (X = counterion or solvent molecule), or $[\text{Cd}(\text{pdon})_3]^{2+}$, or both from the components of complex **2**? However, electrospray ionization mass spectrometry (ESI-MS) of **2** in DMSO does not show any mononuclear species with CD activity (Figure S1, Supporting Information). Powder XRD data on the bulk material is determined to detect other species present that escaped analysis by the single crystal X-ray study (Figure S2, Supporting Information). The experimental PXRD pattern of **2** is consistent with the simulation on the basis of the single crystal structure, respectively, indicating phase purity. So, this CD spectral result suggests that there is phenomenon of spontaneous resolution in DMSO solution for the spiral structure **2**. These positive Cotton effects may come from complex **2** with some degree of enantiomeric excess, the average degree

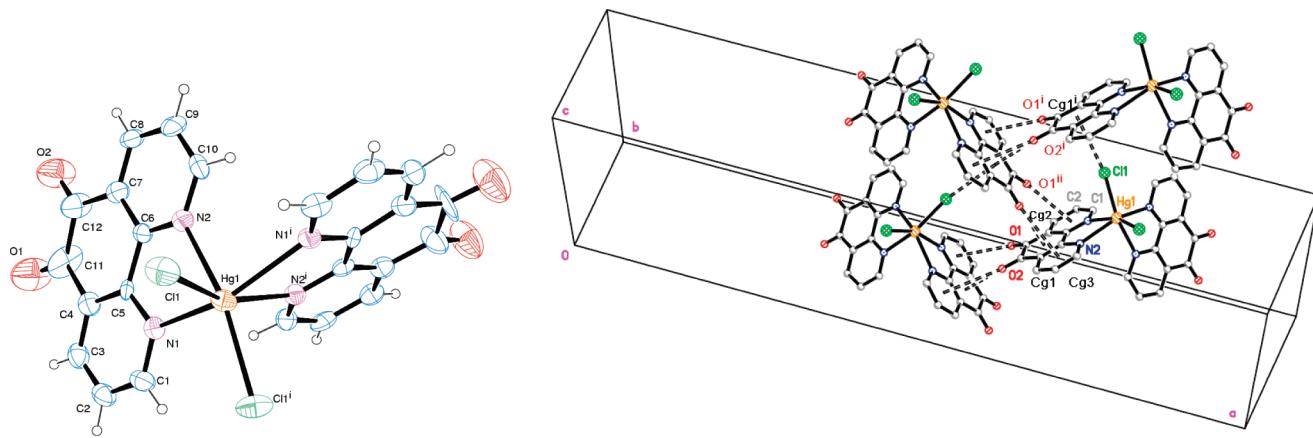


Figure 7. ORTEP diagram and weak interactions ($\text{C}=\text{O}\cdots\pi$ and $\text{Hg}-\text{Cl}\cdots\pi$, double dashed lines) in complex **3**, symmetry codes: left (i) $3/2-x$, $1/2-y$, z ; right (i) x , $y+1/2$, $z+1/2$; (ii) $-x+5/4$, $y+1/4$, $z+1/4$; ring label: Cg1 C4–C7/C12/C11, Cg2 N1/C1–C5, Cg3 N2/C6–C10.

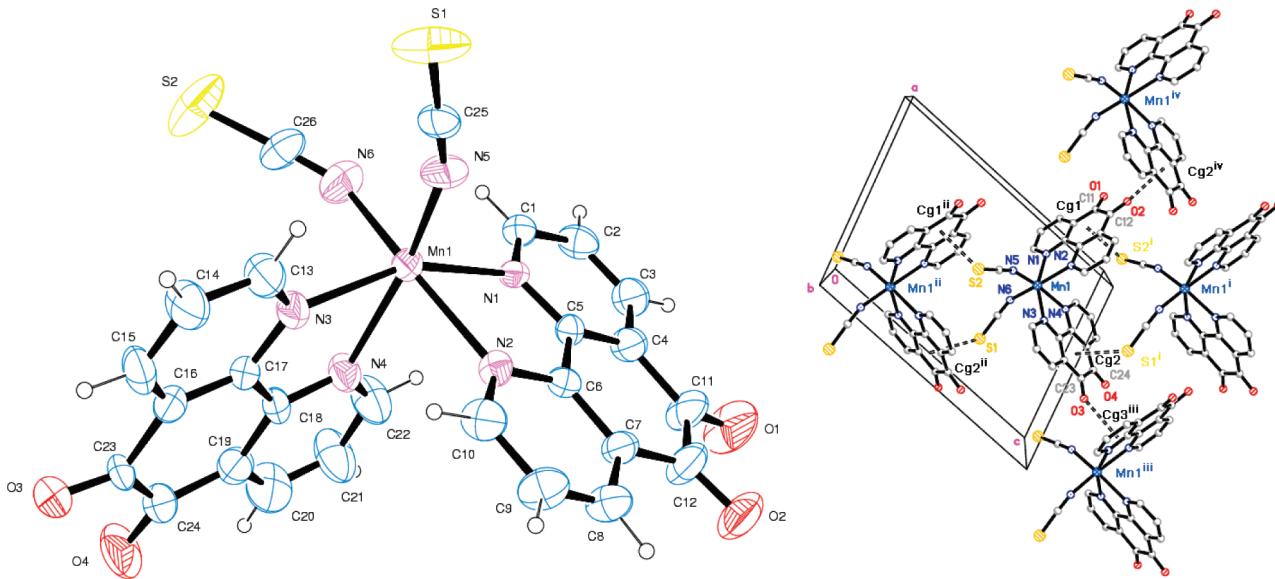


Figure 8. ORTEP diagram and weak interactions ($\text{C}=\text{O}\cdots\pi$ and $\text{C}-\text{S}\cdots\pi$, double dashed lines) in complex **4**, symmetry codes: (i) $x+1/2$, $2-y$, $z+1/2$; (ii) $-1/2+x$, $2-y$, $-1/2+z$; (iii) $-1/2+x$, $2-y$, $1/2+z$; (iv) $1+x$, y , z ; ring labels: Cg1 C4–C7/C12/C11; Cg2 C16–C19/C24/C23; Cg3 N1/C1–C5.

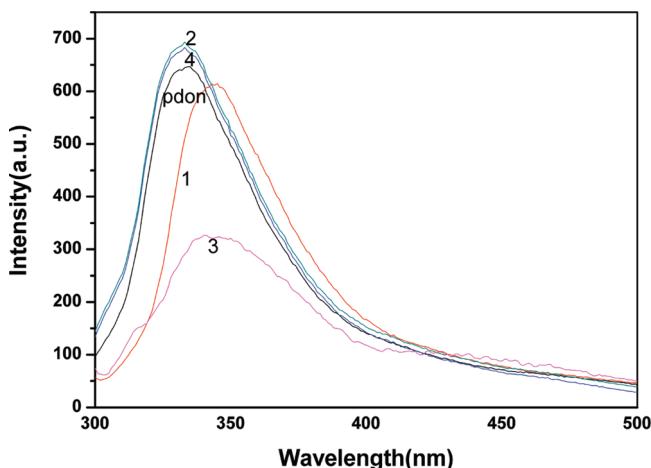


Figure 9. The fluorescence spectra of **1–4** In DMSO at room temperature ($[\text{C}] = 1 \times 10^{-5}$ M, $\lambda_{\text{ex}} = 279$ nm).

of twisting between left-hand and right-hand helical forms.²⁵ This interesting result is worthy of further investigation.

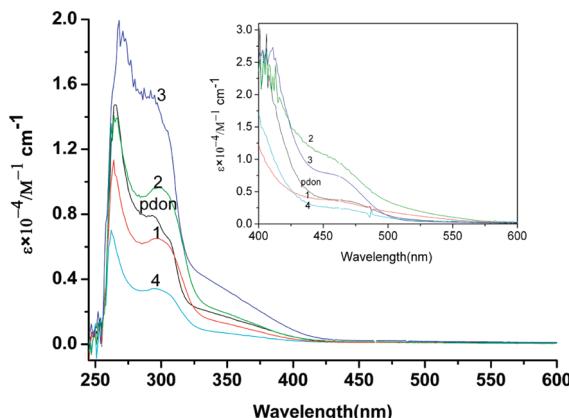


Figure 10. UV-vis spectra of pdon and complexes **1–4** in dimethyl sulfoxide ($[\text{C}] = 1.0 \times 10^{-4}$ M, inset 1.0×10^{-2} M).

Electrochemistry Characterization. The pdon ligand is electrochemically active due to the presence of *o*-quinone moiety. Electrochemical behavior is usually strongly dependent on whether an aprotic solvent such as acetonitrile or an aqueous

solvent. According to the references,²⁶ pdon ligand in acetonitrile shows two reversible one-electron-reduction waves. In aqueous solvent the process is the two-electron, two-proton reduction of the quinone to the hydroquinone so that only a single, pH-dependent electrochemical wave is observed. Because of the solubility of the complexes, their electrochemical behaviors in DMSO have been examined by cyclic voltammetry. The free pdon ligand shows two reversible one-electron-reduction waves with formal potentials of -0.4445 and -1.1973 V (Figure 12), representing the formation of the ion radical and dianion of the ligand. The potential of this wave is qualitatively similar to that of pdon ligand in acetonitrile (-0.45 , -1.25 V).^{4b} Complexes **1** and **2** show similar electrochemical behaviors (Figures S3 and S4, Supporting Information), indicating the ligand in the complexes still retain its redox activity in the supramolecular framework since Zn^{2+} and Cd^{2+} ions are difficult to oxidize or to reduce due to their d^{10} configuration.²⁷ In addition, it is observed that the peak potential of **1** and **2** shift positively compared with that of the free pdon ligand. This phenomenon suggests that metal ions influence the redox process of the ligand. In complex **4**, new couple peaks of $E = -0.067$ V are observed, which can be assigned to Mn^{3+}/Mn^{2+} transformation.²⁷

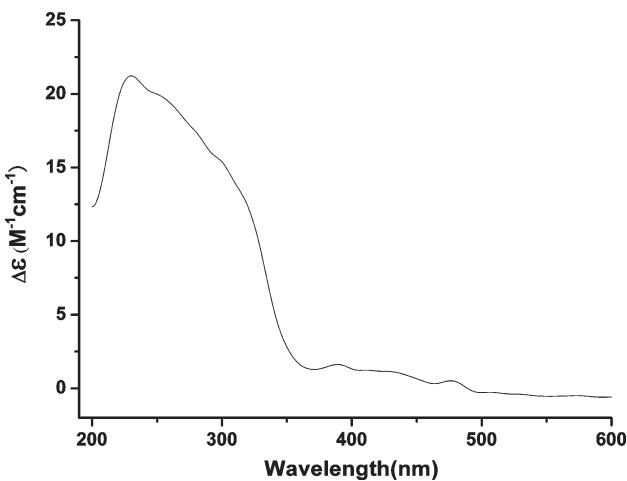


Figure 11. The CD spectrum for complex **2** in DMSO ($[C] = 2.0 \times 10^{-4}$ M).

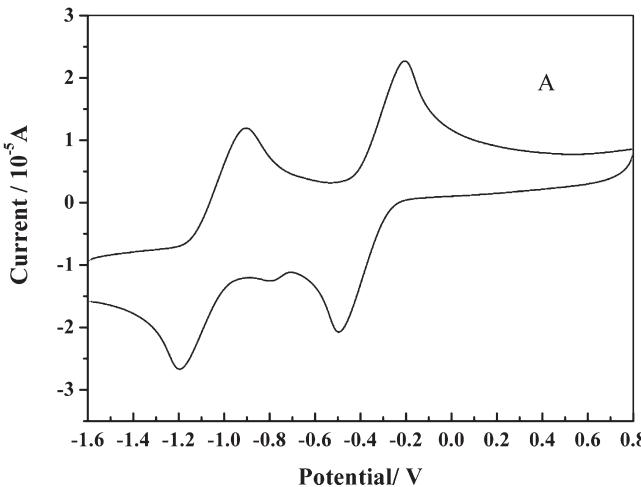


Figure 12. Cyclic voltammogram of the free pdon ligand (A) and complex **4** (B).

Conclusions

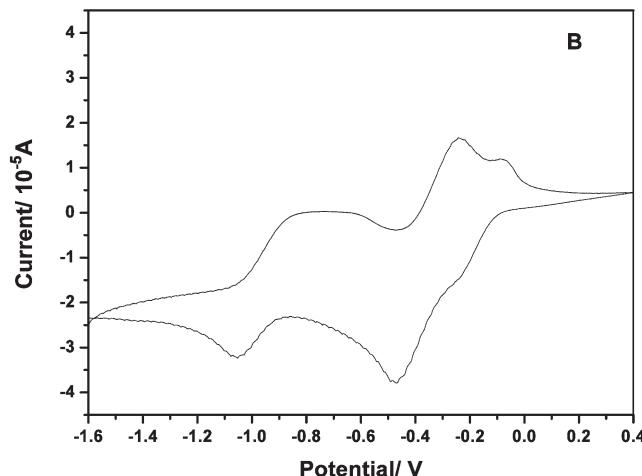
As the results of the self-assembly of four d^{10} and d^5 metal ions (Zn^{2+} , Cd^{2+} , Hg^{2+} , and Mn^{2+}) with SCN^- , Cl^- , and pdon bridges using the same metal-to-ligand ratios in aqueous-methanol solution, two complexes give rise to coordinated polymers with one-dimensional zigzag chain and one-dimensional molecular helix. Another two complexes are mononuclear species. These results indicate that although Zn^{2+} , Cd^{2+} , and Hg^{2+} are elements of the same group, their self-assembly behaviors with three bridges are essentially different. A positive Cotton effect of **2** in DMSO was observed, suggesting that there is a phenomenon of spontaneous resolution in DMSO solution for the spiral enantiomer. These positive Cotton effects may come from some degree of enantiomeric excess, the average degree of twisting between left-hand and right-hand helical forms. This phenomenon is worthy of further investigation.

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Supporting Information Available: (1) Hydrogen bonding and $C=O(S)\cdots\pi$ and $\pi\cdots\pi$ interaction for complexes **1–4**, (2) ESI-MS spectrum of complex **2**, (3) powder XRD patterns of experimental and simulation in RT for complex **2**, (4) cyclic voltammogram of complexes **1** and **2**, (5) crystallographic information files (CIF) for **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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