Crystal Structures and Thermodynamics/kinetics of Zn(II)

Coordination Polymers with Helical Chains

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Abstract: Solvothermal reactions of Zn(II) acetates and four V-shaped carboxylates ligands in the presence of 1,4-Bis(2-methyl-imidazol-1-yl)butane afforded four interesting Zn(II) coordination polymers with helical chains, namely, $\{[\text{Zn}(\text{bib})(\text{atibdc})] \cdot 2\text{H}_2\text{O}\}_n$ (**1**), $\{[\text{Zn}(\text{bib})(\text{atbip})] \cdot \text{H}_2\text{O}\}_n$ (**2**), $[\text{Zn}(\text{bib})(2,2'\text{-tda})]_n$ (**3**) and $\{[\text{Zn}(\text{bib})(5\text{-tbipa})] \cdot \text{EtOH}\}_n$ (**4**), (H_2atibdc = 5-amino-2,4,6-triiodoisophthalic acid, H_2atbip = 5-amino-2,4,6-tribromoisophthalic acid, $2,2'\text{-H}_2\text{tda}$ = 2,2'-thiodiacetic acid, $5\text{-H}_2\text{tbipa}$ = 5-tert-butyl-isophthalic acid). **1** reveals a 3D chiral framework with three kinds of helical chains along *a*, *b* and *c* axis. **2** shows a 2D step-type chiral framework with right-handed helical chains. **3** displays a wavelike 2D layer network possessing alternate left- and right-handed helical chains. **4** presents a four-connected 3D framework with zigzag and *meso*-helical chains. The different spacers and substituent group of carboxylic acid ligands may lead to the diverse network structures of **1–4**. The fluorescent properties of complexes **1–4** were studied. In addition, the thermal decompositions properties of **1–4** were investigated by simultaneous TG/DTG–DSC technique. The apparent activation energy *E* and the pre-exponential factor (*A*) of skeleton collapse for the complexes **1–4** are calculated by the integral Kissinger's method and Ozawa–Doyle's method. The activation energy *E* ($E_1=209.658 \text{ kJ}\cdot\text{mol}^{-1}$, $E_2=250.037 \text{ kJ}\cdot\text{mol}^{-1}$, $E_3=225.300 \text{ kJ}\cdot\text{mol}^{-1}$, $E_4=186.529 \text{ kJ}\cdot\text{mol}^{-1}$) demonstrates that the reaction rate of the melting

decomposition is slow. The thermodynamic parameters ($\Delta H^\ddagger$, $\Delta G^\ddagger$ and $\Delta S^\ddagger$) at the peak temperatures of the DTG curves were also calculated. $\Delta G^\ddagger > 0$ indicates that the skeleton collapse is not spontaneous. $\Delta H_d > 0$ suggests that the skeleton collapse is endothermic, corresponding to the intense endothermic peak of the DSC curve. The structural stability could be illustrated from the point of thermodynamics and kinetics.

Keywords: Coordination Polymers; Crystal Structure; Helix; Thermodynamics; Kinetics

1. Introduction

Fun Helical structures have attracted intense interest in coordination chemistry not only for their ubiquitous appearance in nature, a typical example being the DNA molecule, but also for their practical implications in multidisciplinary areas, such as optical devices, biomimetic chemistry, asymmetric catalysis chemistry, and structural biology [1–5]. However, there is less study of thermodynamic and kinetic analyses. Understanding thermal behavior of solid materials by means of thermal analyses appeared in many fields, such as estimation of the decomposition temperature of devices, prediction of the aging of concretes, determination of the safety conditions of explosive materials, etc [6]. Kinetic data play a significant role in the development of theoretical models aiming to postulate mechanisms for thermal decomposition [7, 8].

In general, deployment of V-shaped or flexible ligands with suitable metal centers has been proven to be the most successful strategy for helical CPs synthesis [9, 10]. We select flexible 1,4-bis(2-methylimidazol-1-yl) butane(bib) and V-shaped carboxylates mix-ligands. Bib with long spacer $-(CH_2)_4-$ between two imidazolyl rings is an interesting bridging ligand, which can adopt mutable conformations and geometries *via* bending, rotating, or twisting to meet preferential coordination geometries to metal ions in the assembly process [11–14]. V-shaped dicarboxylates

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are introduced because the two carboxylate groups located at appropriate angles (approximately 120°), which may allow it to connect metal ions to generate 1D helical chains [15, 16]. In this work, four interesting Zn(II) coordination polymers with helical chains have been obtained. Bib presents *cis*-conformation in title CPs rather than *trans*-conformation in previous CPs [13]. The fluorescent properties of complexes **1–4** were studied. The thermodynamics and kinetics of their thermal decomposition were studied using the TG/DTG–DSC techniques. The enthalpy, apparent activation energy and pre-exponential constant of the melting decomposition reaction were calculated.

2. Experimental

2.1. Materials and general methods

1,4-Bis(2-methyl-imidazol-1-yl)butane and 5-amino-2,4,6-tribromoisophthalic acid were prepared by published procedures [14, 17]. All other chemicals for synthesis were commercially available. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 2400C elemental analyzer. The IR spectra were recorded using KBr pellets on a Nicolet Avatar 360 FTIR spectrometer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8-ADVANCE using Cu K α radiation ($\lambda = 1.5418$ Å). The thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed on a Q600 SDT thermal analyzer instrument. Luminescent spectra were performed on a Perkin-Elmer LS55 luminescence spectrometer.

2.2 Synthesis of Complexes **1–4**

A mixture of Zn(Ac)₂·2H₂O (0.051 g, 0.2 mmol), H₂atibdc (0.120 g, 0.2 mmol) and bib (0.044 g, 0.2 mmol) in EtOH (8 mL) and water (2 mL) was heated in a stainless steel reactor with Teflon liner (25 mL) at 150 °C for 36 h and cooled to ambient temperature at a rate of 10 °C h⁻¹. The resulting colorless block crystals of this complex were isolated by washing with mother liquor and dried in air. The yield was 70.20% based on Zn. Anal. Elemental analysis: calc. for C₂₀H₂₄ZnI₃N₅O₆: C, 27.65; H,

2.76; N, 8.06; found: C, 28.21; H, 2.96; N, 8.43. IR (KBr pellet): 3431m, 3127 m, 2928w, 1611m, 1509m, 1383s, 1328m, 1284m, 1257m, 1154m, 1097w, 1009w, 930w, 784w, 742w, 676w, 628w, 556 w, 506w cm^{-1} .

$\{[\text{Zn}(\text{bib})(\text{atbip})]\cdot\text{H}_2\text{O}\}_n$ (**2**)

The same synthetic method as that for **1** was used except that H_2atibdc was replaced by H_2atbip (0.042 g, 0.1 mmol). Colorless block crystals of **2** were isolated by washing with mother liquor and dried in air. The yield was 65.31% based on Zn. Anal. Calc.(%) for $\text{C}_{20}\text{H}_{20}\text{ZnBr}_3\text{N}_5\text{O}_5$ (715.51): C, 33.56; H, 2.80; N, 9.78. Found: C, 35.24; H, 2.34; N, 11.02. IR (KBr, cm^{-1}): 3132 (s), 2941 (w), 1640 (s), 1510 (m), 1318 (s), 1074 (m), 737 (m), 586 (m), 504 (m).

$\{[\text{Zn}(\text{bib})(2,2'\text{-tda})]\}_n$ (**3**)

The same synthetic method as that for **1** was used except that H_2atibdc was replaced by 2,2'- H_2tda (0.025 g, 0.1 mmol). Colorless block crystals of **3** were isolated by washing with mother liquor and dried in air. The yield was 39.08% based on Zn. Anal. Calc.(%) for $\text{C}_{16}\text{H}_{22}\text{SN}_4\text{ZnO}_4$ (431.81): C, 44.46; H, 5.09; N, 12.97. Found: C, 44.39; H, 4.59; N, 12.72. IR (KBr, cm^{-1}): 3450 (m), 3119 (w), 2932 (m), 2864 (m), 1598 (m), 1546 (s), 1346 (s), 1283 (s), 1217 (w), 1157 (m), 933 (w), 763 (w), 680 (s), 631 (w).

$\{[\text{Zn}(\text{bib})(5\text{-tbipa})]\cdot\text{EtOH}\}_n$ (**4**)

The same synthetic method as that for **1** was used except that H_2atibdc was replaced by 5- H_2tbipa (0.025 g, 0.1 mmol). Colorless block crystals of **4** were isolated by washing with mother liquor and dried in air. The yield was 46.43% based on Zn. Anal. Calc.(%) for $\text{C}_{26}\text{H}_{36}\text{ZnN}_4\text{O}_5$ (549.96): C, 56.73; H, 6.55; N, 10.18. Found: C, 56.69; H, 6.49; N, 10.16. IR (KBr, cm^{-1}): 3528 (s), 3466 (s), 3128 (s), 2964 (m), 2870 (s), 1857 (w), 1632 (m), 1575 (w), 1460 (m), 1373 (w), 1268 (w), 1155 (s), 1011 (w), 912 (m), 819 (m), 781 (m), 752 (s), 728 (s), 678 (w), 625 (w).

2.3 Crystallography

Suitable single crystals of **1–4** were carefully selected under an optical microscope and glued to thin glass fibers. The single crystal X-ray data were collected on a

Bruker APEX CCD diffractometer using graphite monochromated Mo-K α radiation ($\lambda=0.71073$ Å) at 296 K. The structures were solved by the direct methods with SHELXS-97 and refined by full matrix least squares refinements based on F^2 [18]. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms added to their geometrically ideal positions and refined isotropically. The final chemical formulas of **1–4** were confirmed by the elemental microanalyses, infrared spectroscopy data and TGA data. Selected crystallographic data as well as structure refinement results of compounds **1–4** are listed in Table S1, and selected bond lengths and angles are given in Table S2 (Supporting information).

3. Results and discussion

3.1 Structure description

Complex **1** crystallizes in the orthorhombic chiral space group $P2_12_12_1$. Its asymmetric unit contains one independent Zn(II) ion, one bib, one atibdc²⁻ anion and two free water molecules. The four-coordinated Zn(II) center exhibits a distorted tetrahedral coordination geometry ZnN_2O_2 , with two oxygen atoms (O1, O3) from two separate H_2atibdc ligands and two nitrogen atoms (N2, N4) from different bib ligands (Fig. 1a). The Zn–O and Zn–N bond lengths are in range of 1.957–1.965 Å and 1.990(7)–1.991(7) Å, respectively. Consistent with the $P2_12_12_1$ space group of **1**, helices can be observed along all of the *a*, *b* and *c* directions. Along the *a* direction, bib adopts the *cis*-conformation (scheme S1a) to bridge the Zn(II) ion into a 1D right-handed $[\text{Zn}(\text{bib})]_n$ helical chain with a pitch of 10.643 Å, where the distances between two adjacent Zn(II) ions are 8.495 Å, and the Zn $\cdots$ Zn $\cdots$ Zn angles are 77.570° (Fig. 1b). Along the *b* direction, atibdc²⁻ anion links Zn(II) ion to give a 1D left-handed $[\text{Zn}(\text{atibdc})]_n$ helical chain with a pitch of 14.373 Å, where the distances between two adjacent Zn(II) ions are 9.614 Å, and the Zn $\cdots$ Zn $\cdots$ Zn angles are 96.750° (Fig. 1c). Along the *c* direction, four zinc(II) ions are bridged by two bibs and two atibdc²⁻ ligands to form left-handed $[\text{Zn}_4(\text{bib})_2(\text{atibdc})_2]_n$ helical chains with a pitch of 18.214 Å (Fig. 1d), respectively. It is worth noting that left-handed

$[\text{Zn}_4(\text{bib})_2(\text{atibdc})_2]_n$ helical chains by sharing the Zn(II) ions generate 2D network on the *ab* plane (Fig. 1e). From a topological viewpoint, the final structure can be regarded as a 4-connected 3D **dia** network with a point symbol of 6^6 by denoting the Zn(II) ion as a four-connected node (Fig. 1f).

Complex **2** crystallizes in the monoclinic chiral space group $P2_1$. The asymmetric unit is composed of one Zn(II), one bib, one H_2atbip , and one free water molecule. Zn(II) is four-coordinated by two N (N1 and N3) atoms from two different bib ligands and two O (O1 and O3) atoms from two different H_2atbip , forming a distorted tetrahedral coordination geometry (Fig. 2a). In complex **2**, the Zn–O and Zn–N bond lengths are in the range of 1.940(11)–1.946(11) Å, and 1.967(13)–1.984(12) Å, respectively. Each bib adopts the *cis*-conformation (Scheme S1b) to bridge the Zn(II) ions into 1D straight chains. What is more, the adjacent Zn(II) ions are linked by the H_2atbip ligand to give a series of right-handed helical chains along the *b* axis with a pitch of 15.121 Å, where the distances between two adjacent Zn(II) ions are 10.036 Å, and the Zn···Zn···Zn angles are 97.757° . Consequently, the adjacent Zn(II) ions link 1D bib straight chains and 1D right-handed helical chains to form a 2D step-type framework. From the topological point of view, the whole structure of **2** can be considered as a **sql** network with the point symbol of $(4^4\cdot6^2)$ (Fig. 2b).

Complex **3** crystallizes monoclinic space group $P2_1/n$ whose asymmetric unit is composed of one independent Zn(II) ion, one bib linker and one deprotonated $2,2'\text{-tda}^{2-}$ anion. The central Zn(II) ion is four-coordinated by two O atoms (O1, O3) from two different $2,2'\text{-tda}^{2-}$ anions and two different N atoms (N1, N4) from two bib ligands to generate a distorted ZnO_2N_2 tetrahedral coordination geometry (Fig. 3a). The Zn–O and Zn–N bond lengths are in the range of 1.937(4)–1.960(4) Å and 2.021(5)–2.021(5) Å, respectively. Each bib adopts the *cis*-conformation (Scheme S1c) to bridge the Zn(II) ions into a 1D zigzag chain with Zn···Zn···Zn angle of 129.803° and Zn···Zn distance of 9.039 Å. What is more, the adjacent Zn(II) ions are linked by

the 2,2'-tda²⁻ ligands to give 1D left- and right-handed helical chains along the *a* axis with a pitch of 16.322 Å, where the distances between two adjacent Zn(II) ions are 8.161 Å, and the Zn···Zn···Zn angles are 180° (Fig. 3b). Finally, the left- and right-handed helical chains [Zn(2,2'-tda)]_n are alternately bridged by bib to form an 2D wavelike framework. From the topological point of view, the whole structure of **3** can be considered as a **sql** network with the point symbol of (4⁴·6²) (Fig.3c).

Complex **4** crystallizes in the orthorhombic space group *Pna*2₁ whose asymmetric unit contains one independent Zn(II) ion, one bib linker, one deprotonated 5-tbipa²⁻ anion and one free EtOH molecule. Each Zn(II) ion is four-coordinated to two carboxylic oxygen atoms from two distinct 5-H₂tbipa ligands [Zn-O = 1.941(5)-1.978(5) Å] and two nitrogen atoms from two bib ligands [Zn-N = 1.999(6)-2.007(7) Å] to form a distorted ZnO₂N₂ tetrahedral geometry (Fig. 4a). The conformation of bib is shown in Scheme S1d, each bib adopts the *cis*-conformation to bridge the Zn(II) ions into a 1D *meso*-helical chain [Zn(bib)]_n with a long pitch of 18.699 Å. Each 5-tbipa²⁻ connects to two Zn(II) ions through two carboxyl groups to yield a 1D zigzag chain with Zn···Zn···Zn angles of 131.963° and Zn···Zn distances of 9.617 Å (Fig. 4b). Consequently, the adjacent Zn(II) ions link the 1D *meso*-helical chain [Zn(bib)]_n and 1D infinite zigzag chain [Zn(5-tbipa)]_n to form a 3D framework. From the topological point of view, the whole structure of **4** can be considered as a 4-connected network with the point symbol of (6⁵·8) (Fig. 4c)

Effects of substituent on the Structure

Many researchers have demonstrated that the structural diversities of complexes are undoubtedly related to the secondary ligand directed inclusion [19–21]. Hence, in this work, we selected the flexible bib and four V-shaped carboxylates ligands. From the structure description above, it has depicted that the substituent plays an important role in the formation of the diverse structures and topologies. When V-shaped carboxylate coligand H₂atibdc is introduced into the Zn(II)-bib system, a 3D chiral framework **1** is obtained. Atibdc²⁻ bridges Zn(II) to form left-handed [Zn(atibdc)]_n helical chain. But

when we use another dicarboxylate atbip²⁻ with three Br groups in **2** instead of three I groups in **1**, a 2D step-type chiral framework **2** is obtained. Atbip²⁻ bridges Zn(II) to form right-handed helical chains [Zn(atbip)]_n. The different atom radius between bromine and iodine results in bib bridging Zn(II) ions into straight chains in **2** and helical chains in **1** in the process of self-assembly. As a result, the different structures are formed in **1** and **2**. When 2,2'-H₂tad is introduced into the Zn(II)-bib system in **3**, a wavelike 2D layer network is obtained. Because the flexibility of 2,2'-H₂tad is better than others, 2,2'-tad²⁻ is linked with Zn(II) ions to form left- and right-handed helical chains [Zn(2,2'-tad)]_n in **3**. When 5-H₂tbipa is introduced into the Zn(II)-bib system in **4**, a 3D framework is obtained. 5-H₂tbipa connects Zn(II) only to form zigzag chains rather than helix due to the fairly high steric hindrance of tert-butyl group. Therefore, the results imply that the different spacers and substituent group of carboxylic acid ligands play important roles in constructing different degrees and structures.

3.2 PXRD Analysis

The experimental PXRD patterns of **1–4** are basically identical to the respective simulated patterns, indicating the high phase purity of the bulk products of **1–4** (Fig. S1, Supporting Information).

3.3 Thermal Decomposition

TG/DTG and DSC curves, under a linear heating rate of 5 K·min⁻¹ with a nitrogen atmosphere were obtained to explore the melting decomposition behavior of complexes **1–4** (Fig. 5). For complex **1**, the TG/DTG curve shows that complex **1** undergoes two mass-loss stages before 352 °C. The first weight loss stage starts at 40 °C and ends at 100 °C, accompanied by about 4.13% weight loss, which is attributed to the loss of two free water molecules (4.11%), and corresponding to the small endothermic process in the DSC curve. An abrupt weight loss is observed from 288 °C to 352 °C, considered as the collapse of the main framework and corresponding to the intense endothermic process in the DSC curve. The DSC curve shows that an intense endothermic process starts at 342 °C and ends at 400 °C, with the peak temperature of 375 °C, and enthalpy of the process is 1699.2 J/mol. For

complex **2**, the TG/DTG curve shows that complex **2** undergoes two mass-loss stages before 400 °C. The first weight loss stage starts at 30 °C and ends at 100 °C, accompanied by a weight loss of 2.52%, which is attributed to the loss of one free water molecule(calc. 2.58%), and corresponding to the small endothermic process in the DSC curve. The second weight loss stage shows an abrupt weight loss of 31.11%, maybe due to the release of bib ligand and corresponding to the intense endothermic process in the DSC curve. The DSC curve shows that the intensest endothermic process starts at 274 °C and ends at 364 °C, with the peak temperature of 308 °C, and enthalpy of the process is 1413.4 J/mol. For complex **3**, simultaneously, the TG/DTG curve shows an abrupt weight loss is observed from 278 °C to 350 °C, considered as the collapse of the main framework and consisting with the intense endothermic process in the DSC curve. The DSC curve shows that an intense endothermic process starts at 285 °C and ends at 404 °C, with the peak temperature of 322 °C, and enthalpy of the process is 2670.6 J/mol. For complex **4**, the TG/DTG curve reveals that complex **4** undergoes two mass-loss stages before 400 °C. The first weight loss stage starts at 80 °C and ends at 100 °C, accompanied by a weight loss of 7.92%, which is attributed to the loss of one free EtOH molecule(calc. 7.71%), and corresponding to a small endothermic process in the DSC curve. An abrupt weight loss is observed from 300 °C to 388 °C, considered as the collapse of the main framework and in agreement with the intense endothermic process in the DSC curve. the DSC curve shows that the intensest endothermic process starts at 332 °C and ends at 376 °C, with the peak temperature of 362 °C, and enthalpy of the process is 3443.1 J/mol. Obviously, 3D framework exhibits higher thermal stability than 2D framework [22].

3.4 Non-isothermal kinetics analysis

In order to investigate the thermokinetics for the decomposition of **1–4**, we employed Kissinger's method [23] and Ozawa–Doyle's method [24] to obtain the apparent activation energy (E) and the pre-exponential factor (A) in the current work, which are universally applied in this field, using the peak temperatures measured at four

different heating rates of 2, 5, 8, 10 K min⁻¹. The Kissinger and Ozawa–Doyle equations are as follows, respectively:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\frac{AR}{E} - \frac{E}{R} \frac{1}{T_p} \quad (1)$$

$$\lg \beta + \frac{0.4567E}{RT_p} = C \quad (2)$$

Where T_p is the peak temperature (K); A is the pre-exponential factor (s⁻¹); E is the apparent activation energy (J mol⁻¹); R is the gas constant (J mol⁻¹ K⁻¹); β is the linear heating rate (K min⁻¹) and C is a constant.

Based on the peak temperatures measured with four different heating rates of (2, 5, 8, and 10) K min⁻¹, the kinetic parameters were obtained and are listed in [Table 1](#). The calculated results using the two methods were similar. By substituting the activation energy E and pre-exponential factor A into eqs 3 to 5 [25], thermodynamic parameters of the complexes at the temperatures were evaluated.

$$A \exp(-E/RT) = \nu \exp(-\Delta G^\ddagger/RT) \quad (3)$$

$$\Delta H^\ddagger = E - RT \quad (4)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (5)$$

Where ν is the Einstein vibration frequency, $\nu = k_B T/h$ (k_B and h are Boltzmann and Planck constants, respectively), $\Delta G^\ddagger$ is the Gibbs energy of activation, $\Delta H^\ddagger$ is the enthalpy of activation, and $\Delta S^\ddagger$ is the entropy of activation. The value of entropy, enthalpy, and the Gibbs free energy of activation at the peak temperatures are shown in [Table 2](#).

The activation energy E , 209.658 kJ·mol⁻¹, 250.037 kJ·mol⁻¹, 225.300 kJ·mol⁻¹, 186.529 kJ·mol⁻¹ in [Table 1](#) demonstrates that the reaction rate of the skeleton collapse is slow, which can be explained by the influence of activation energy on the reaction rate: the greater activation energy, the slower reaction rate [26]. The Arrhenius equation is expressed as follows: $\ln k_1 = 15.048 - 209.658 \times 10^3/RT$ for **1**, $\ln k_2 = 20.474 - 250.037 \times 10^3/RT$ for **2**, $\ln k_3 = 17.682 - 225.300 \times 10^3/RT$ for **3**, $\ln k_4 = 13.032 - 186.529 \times 10^3/RT$ for **4**, which can be applied to estimate the rate constants

of the initial thermodecomposition processes of **1–4**. From Table 2, it can be seen that $\Delta G^\ddagger > 0$ indicates that the skeleton collapse is not spontaneous. $\Delta H^\ddagger > 0$ suggests that the reaction is endothermic, which is agreement with the intense endothermic peak of the DSC curve.

3.5 Solid-state Photoluminescence

The emission spectra of **1–4** were examined in the solid state at room temperature, shown in Fig. 6. The free ligand bib displays photoluminescence with emission maxima at 400 nm ($\lambda_{\text{ex}} = 330$ nm), assigned to $\pi^* \rightarrow \pi$ transition of bib [27, 28]. The carboxylate ligands display photoluminescence with emission maxima 470 nm ($\lambda_{\text{ex}} = 340$ nm) for H₂atibdc, 469 nm ($\lambda_{\text{ex}} = 340$ nm) for H₂atbip, 330 nm ($\lambda_{\text{ex}} = 300$ nm) for 2,2'-H₂tada, and 510 nm ($\lambda_{\text{ex}} = 340$ nm) for 5-H₂tbipa [29–32]. The emission bands of these carboxylate ligands can be assigned to the $\pi^* \rightarrow n$ transition as previously reported [33]. To the best of our knowledge, the emission of carboxylate belongs to $\pi^* \rightarrow n$ transitions which is very weak compared to that of the $\pi^* \rightarrow \pi$ transition of bib, so the carboxylates almost have no contribution to the fluorescent emission of as-synthesized CPs [34]. The emission spectra have broad peaks with maxima 475 nm ($\lambda_{\text{ex}} = 400$ nm) for **1**, 475 nm ($\lambda_{\text{ex}} = 385$ nm) for **2**, 500 nm ($\lambda_{\text{ex}} = 300$ nm) for **3**, 460 nm ($\lambda_{\text{ex}} = 300$ nm) for **4**. In comparison to the free bib ligand, the emission bands for **1–4** are red-shift by 75 nm, 75 nm, 100 nm, 60 nm. According to the literature, Zn(II) ion is difficult to oxidize or reduce because of the d^{10} configuration. As a result, the emissions of these CPs are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature [35]. Thus, they may be assigned to a mixture characteristics of intraligand and ligand-to-ligand charge transition (LLCT), as reported for other Zn(II) CPs constructed from mixed N-donor and O-donor ligands [36]. The enhancement of luminescence in d^{10} complexes may be attributed to ligand chelation to the metal center which effectively increases the rigidity of the ligand and reduces the loss of energy by radiation less decay. The emissions for **1–4** are smaller than that of free bib ligand probably due to the solvent molecules or the system of pH made the emissions for **1–4** reducing. And what's more, the difference of the emission

behaviors for **1–4** probably derives from the differences in the rigidity of solid-state crystal packing.

4. Conclusions

In summary, four new Zn(II) CPs with helical chains have been successfully obtained under the same solvothermal conditions. **1** and **4** present 3D frameworks, **2** and **3** show 2D frameworks and bib all displays *cis*-conformation in **1–4**. The different spacers and substituent group of carboxylic acid ligands may lead to the diverse network structures of **1–4**. The thermodynamics and kinetics of **1–4** were investigated by simultaneous TG/DTG-DSC techniques. The TG curves exhibit that the 3D framework exhibits higher thermal stability than 2D framework. The thermodynamic parameters ($\Delta H^\ddagger$, $\Delta G^\ddagger$, and $\Delta S^\ddagger$) at the peak temperatures of the DTG curves were calculated. $\Delta G^\ddagger > 0$ indicates that the skeleton collapse is not spontaneous. $\Delta H_d > 0$ suggests that the skeleton collapse is endothermic, which is agreement with the intense endothermic peak of the DSC curve. In addition, the activation energy E ($E_1=209.658$ kJ·mol⁻¹, $E_2=250.037$ kJ·mol⁻¹, $E_3=225.300$ kJ·mol⁻¹, $E_4=186.529$ kJ·mol⁻¹) demonstrates that the reaction rate of the melting decomposition is slow.

Supporting Information

The crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 1012489 for **1**, 1405653 for **2**, 1404866 for **3**, and 1404867 for **4**. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Powder XRD patterns, Luminescences of free ligand bib and complexes **1–4**, Structure refinement results, and selected bond lengths and angles of **1–4**

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Figure and table captions

Table 1 Kinetic parameters of the complexes **1–4**

Table 2 Thermodynamic parameters of the complexes **1–4**

Fig.1 (a) The coordination environment of Zn(II) ion in **1**. (b) The $[\text{Zn}(\text{bib})]_n$ right-handed helical chain; (c) The $[\text{Zn}(\text{atibdc})]_n$ left-handed helical chain; (d) The $[\text{Zn}_4(\text{bib})_2(\text{atibdc})_2]_n$ left-handed helical chain; (e) 2D layer in the ab plane; (f) 3D 4-connected network.

Fig.2 (a) The coordination environment of Zn(II) ion in **2**. (b) Left: View of the right-handed. Right: Schematic representation of the 2D step-type network.

Fig.3 (a) The coordination environment of Zn(II) ion in **3**; (b) View of the left- and right-handed chains; (c) Schematic representation of the 2D wavelike network.

Fig.4 (a) The coordination environment of Zn(II) ion in **4**; (b) View of the zigzag chain and *meso*-helical chain; (c) Schematic representation of the 3D network.

Fig.5 G/DTG-DSC curves of the complexes **1(a)**, **2(b)**, **3(c)** and **4(d)**

Fig.6 Luminescences of free ligand bib and complexes **1–4**.

Table 1 Kinetic parameters of the complexes **1–4**

complexes	$\beta(\text{K min}^{-1})$	$T_p(\text{K})$	$E(\text{kJ}\cdot\text{mol}^{-1})$		$\ln A(\text{S}^{-1})$
			Kissinger	Ozawa–Doyle	
1	2	623 $\pm$ 0.1	209.798	209.518	15.048
	5	627 $\pm$ 0.1			
	8	641 $\pm$ 0.1			
	10	643 $\pm$ 0.1			

2	2	572 $\pm$ 0.1	251.621	248.452	20.474
	5	581 $\pm$ 0.1			
	8	587 $\pm$ 0.1			
	10	589 $\pm$ 0.1			
3	2	583 $\pm$ 0.1	226.163	224.435	17.682
	5	595 $\pm$ 0.1			
	8	600 $\pm$ 0.1			
	10	603 $\pm$ 0.1			
4	2	617 $\pm$ 0.1	186.119	186.938	13.031
	5	635 $\pm$ 0.1			
	8	641 $\pm$ 0.1			
	10	643 $\pm$ 0.1			

Table 2 Thermodynamic parameters of the complexes **1–4**

complexes	β	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	T_p	ΔH_d
	K $\cdot$ min $^{-1}$	kJ $\cdot$ mol $^{-1}$	kJ $\cdot$ mol $^{-1}$	J $\cdot$ mol $^{-1}\cdot$ K $^{-1}$	K	kJ $\cdot$ mol $^{-1}$
1	2	209.7	204.5	-8.4	623.0 $\pm$ 0.1	1741.0 $\pm$ 0.1
	5	209.7	204.4	-8.4	627.0 $\pm$ 0.1	
	8	209.7	204.3	-8.3	641.0 $\pm$ 0.1	
	10	209.7	204.3	-8.3	643.0 $\pm$ 0.1	
Mean		209.7	204.4 $\pm$ 0.1	-8.4 $\pm$ 0.1		
2	2	250.1	245.3	-8.4	572.0 $\pm$ 0.1	1422.8 $\pm$ 0.1
	5	250.1	245.2	-8.4	581.0 $\pm$ 0.1	
	8	250.1	245.2	-8.4	587.0 $\pm$ 0.1	
	10	250.1	245.1	-8.4	589.0 $\pm$ 0.1	
Mean		250.1	245.2 $\pm$ 0.1	-8.4		
3	2	225.3	220.5	-8.4	583.0 $\pm$ 0.1	2677.1 $\pm$ 0.1
	5	225.3	220.4	-8.3	595.0 $\pm$ 0.1	
	8	225.3	220.3	-8.3	600.0 $\pm$ 0.1	

	10	225.3	220.3	-8.3	603.0±0.1	
Mean		225.3	220.4±0.1	-8.3±0.1		
	2	186.6	181.4	-8.5	617.0±0.1	
	5	186.6	181.2	-8.4	635.0±0.1	
4	8	186.6	181.2	-8.3	641.0±0.1	3443.1±0.1
	10	186.6	181.1	-8.3	643.0±0.1	
Mean		186.6	181.2±0.1	-8.4±0.1		

Standard deviations: $s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}}$

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

(a)

(b)

(c)

(d)

Fig.6