

# Synthesis and luminescent properties of novel Cu (II), Zn (II) polymeric complexes based on 1,10-phenanthroline and biphenyl groups

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**Abstract.** A fully conjugated ligand 4,4'-bis(1,10-phenanthroline-[5,6-d]imidazole-2-yl)-biphenyl (BPIBP) based on 1,10-phenanthroline and biphenyl groups was firstly synthesized. The corresponding polymeric complexes, BPIBP (1) with Cu(II) (2) and Zn(II) (3), were synthesized and characterized by FT-IR, elemental Analysis, conductivity measurement. UV-Vis and fluorescence spectra at room temperature revealed that both the polymeric complexes 2 and 3 emit blue luminescence at 453 and 452 nm ( $\lambda_{em, max}$ ) in DMSO solution and blue/green luminescence at 527 and 536 nm ( $\lambda_{em, max}$ ) in solid state respectively, and the maximum wavelengths of the polymeric complexes 2 and 3 are red shifted, compared with the ligand 1. Thermal property measurements show that they have good thermal stability.

**Keywords.** Polymeric complexes; luminescence; 1,10-phenanthroline; biphenyl.

## 1. Introduction

Recently, polymeric metal complexes have attracted most researchers' interests,<sup>1–4</sup> because they not only exhibit the properties of polymers, but also possess properties of inorganic and organic small molecule metal complexes, such as good thermal stability, processibility and easy film-forming ability. The polymeric metal complexes are considered as promising light-emitting materials, which have good electron transition and intramolecular charge transfer transitions properties.<sup>2–4</sup>

1,10-phenanthroline has a rigid framework and possesses a superb ability to chelate many metal ions via two nitrogen donors, which show potential for technological applications, due to their high charge transfer mobility, bright light-emission and good electro- and photo-active properties.<sup>5–10</sup> In our work, 1,10-phenanthroline and biphenyl are inter-linked through imidazol rings to form the ligand. The introduction of biphenyl unit enhances  $\pi$ -conjugation and rigidity of the ligand. The ligand chelated metal ion to form corresponding polymeric

complexes, these polymeric metal complexes emission will possibly be enhanced, because the  $\pi$ -conjugation structure can lead to decrease the loss of energy by thermal vibrational decay and enhance their thermal stability.

Thus, we designed and synthesized two novel polymeric complexes: 4,4'-bis(1,10-phenanthroline-[5,6-d]imidazole-2-yl)-biphenyl (BPIBP) with Cu(II), Zn(II), and systematically investigated photoluminescent properties of these complexes for the first time. These polymeric complexes are considered to be promising materials for organic electroluminescent diodes (OLEDs), further work on fabricating organic electroluminescent devices is under investigation.

## 2. Experimental

### 2.1 Materials

All of the chemicals and reagents were purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China) and were used without any further purification. All solvents used in this work were freshly distilled and kept in 4A sifter.

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## 2.2 Instrument and measurements

The FT-IR spectra were obtained on a Perkin-Elmer Spectrum One Fourier transform infrared spectrometer (KBr pellet). NMR spectra were recorded on a Bruker NMR 400 spectrometer operating at 400 MHz at room temperature in DMSO- $d_6$  or  $CDCl_3$  using TMS as the internal reference. Thermogravimetric analysis (TGA) was conducted under nitrogen atmosphere at a heating rate  $20\text{ K min}^{-1}$  with a Shimadzu TGA-7, glass-transition temperature ( $T_g$ ) was determined by differential scanning calorimetry (DSC) at a heating rate of  $20^\circ\text{C min}^{-1}$  with a Perkin-Elmer DSC-7 thermal analyzer. Elemental analysis for C, H, and N was carried out using a Perkin-Elmer 2400 II instrument. Molar conductivity measurements were carried out in DMSO solution ( $10^{-4}\text{ mol/L}$ ) using model LF Digi 55 conductivity. Ultraviolet-visible (UV-Vis) spectra were measured with a Lambda 25 spectrophotometer. The fluorescence spectra were conducted on a Perkin-Elmer LS55 luminescence spectrometer with a xenon lamp as the light source. The solubility of the polymers was determined using polymeric complexes in appropriate solvent at room temperature.

## 2.3 Synthesis of 4,4'-diformylbiphenyl

Hexamethylenetetraamine (6.80 g, 48 mmol) was dissolved in ethanol (90 mL), 4,4'-bis(chloromethyl)biphenyl (3.00 g, 12 mmol) was added at  $40^\circ\text{C}$ . The mixture was stirred 1.5 h at  $45\text{--}50^\circ\text{C}$ . The precipitate was collected, washed with ethanol for two times and dried, and then acetic acid (40 mL, 50%) was added. The mixture was heated to reflux for 10 h and filtrated. The filtrate was cooled overnight and the crystals were attained. The crystals were purified further by crystallization from absolute ethanol to give 0.93 g (36.9%). Mp:  $137\text{--}138^\circ\text{C}$   $^1\text{H NMR}$  ( $CDCl_3$ ,  $\delta/\text{ppm}$ ): 10.09 (2H, s, CHO), 8.00 (4H, d, H-Ph), 7.80 (4H, d, H-Ph); IR (KBr,  $\text{cm}^{-1}$ ): 3134, 2838, 2744, 1693, 1601, 1394, 1212, 814.

## 2.4 Synthesis of 1,10-phenanthroline-5,6-dione

A mixture of 1,10-phenanthroline (5.0 g, 28 mmol) and KBr (5.0 g, 42 mmol) was added to a three-necked flask equipped with a dropping funnel, and then an ice cold mixture of concentrated  $\text{H}_2\text{SO}_4$  (50 mL) and  $\text{HNO}_3$  (50 mL) was dropped. The mixture was heated to reflux for 6 h. The hot yellow

solution was poured over 600 mL of ice water and neutralized carefully with NaOH until neutral to slightly acidic pH was attained. Extraction with  $\text{CHCl}_3$  was followed by drying with anhydrous  $\text{MgSO}_4$  and removal of solvent, and the precipitate was purified further by crystallization from absolute ethanol to give 4.44 g (80%). Mp:  $271\text{--}272^\circ\text{C}$ ;  $^1\text{H NMR}$  ( $CDCl_3$ ,  $\delta/\text{ppm}$ ): 9.12 (2H, d, H-Py), 8.51 (2H, d, H-Py), 7.58 (2H, d, H-Py); IR (KBr,  $\text{cm}^{-1}$ ): 3436, 3075, 1701, 1645, 1581, 1568, 1462, 1427, 1321, 1301, 1207, 1117, 1064, 1000, 929, 809, 737.

## 2.5 Synthesis of 4,4'-bis(1,10-phenanthroline-[5,6-d]imidazole-2-yl)-biphenyl (BPIBP) (1)

A mixture of 1,10-phenanthroline-5,6-dione (1.261 g, 6 mmol), ammonium acetate (9.25 g, 120 mmol), 4,4'-diformylbiphenyl (0.63 g, 3 mmol) and glacial acetic acid (100 mL) was added to a three-necked flask and refluxed for 3 h, and then cooled to room temperature. The precipitate was collected, washed enough with  $\text{H}_2\text{O}$  for three times, and dried *in vacuo* at  $60^\circ\text{C}$ , a greenish yellow powder was obtained. Yield 1.42 g (80%).  $^1\text{H NMR}$  (DMSO,  $\delta/\text{ppm}$ ): 13.9 (2H, s, H-Py), 9.1 (4H, d, H-Py), 8.9 (4H, d, H-Py), 8.4 (4H, d, H-Py), 8.1 (4H, d, H-Ph), 7.8 (4H, d, H-Ph). IR (KBr,  $\text{cm}^{-1}$ ): 3404, 1612, 1548, 1477, 1455, 822, 738, 696, 663.

## 2.6 Synthesis of polymeric metal complexes BPIBP-Cu (II) (2)

A methanol solution (10 mL) of  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  (0.064 g, 0.375 mmol) was added to a chloroform (20 mL) of the ligand BPIBP (0.148 g, 0.25 mmol). The reaction mixture was stirred for 24 h at room temperature. Then the solvent was evaporated under reduced pressure, the residue was filtrated, the green precipitate was collected. Yield 0.150 g (83%). Melting point is higher than  $300^\circ\text{C}$ . IR (KBr,  $\text{cm}^{-1}$ ): 3472, 1628, 1401, 1078, 990, 953, 807, 725, 554. Anal. Calc. for Cu ( $\text{C}_{38}\text{H}_{22}\text{N}_8\text{Cl}_2$ ): C, 62.92; H, 3.06; N, 15.45. Found: C, 62.21; H, 2.9367; N, 15.06.  $\Lambda_m$  ( $\text{cm}^2\ \Omega^{-1}\ \text{mol}^{-1}$ ): 25.0.

## 2.7 Synthesis of polymeric metal complexes BPIBP-Zn (II) (3)

In the same manner as described for **2**, the reaction of BPIBP (0.148 g, 0.25 mmol) and  $\text{ZnCl}_2$  (0.051 g,

0.375 mmol) afforded yellow solid complex **3**. Yield 0.146 g (80%). Melting point is higher than 300°C. IR (KBr,  $\text{cm}^{-1}$ ): 3485, 1630, 1402, 1072, 1003, 953, 839, 731, 642, 548. Anal. Calc. for  $\text{Zn}(\text{C}_{38}\text{H}_{22}\text{N}_8\text{Cl}_2)$ : C, 62.78; H, 3.05; N, 15.41. Found: C, 62.47; H, 2.90; N, 15.18.  $\Lambda_m$  ( $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$ ): 16.0.

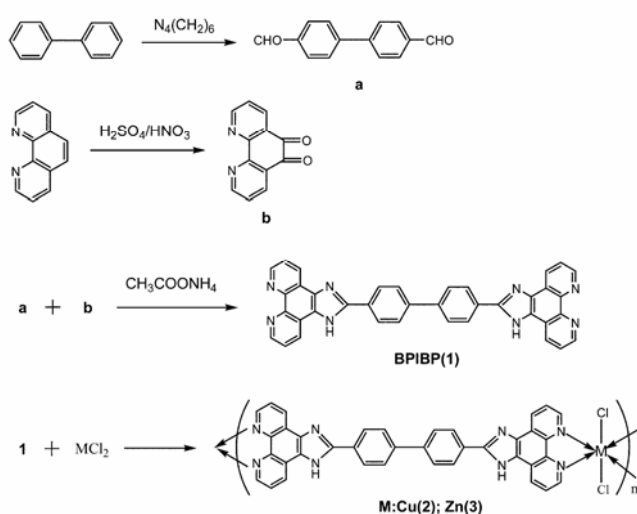
### 3. Results and discussion

#### 3.1 Synthesis and characterization

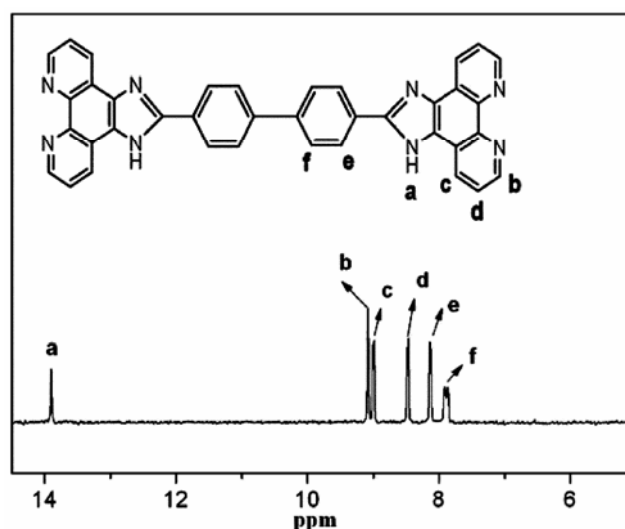
All synthesis routes are shown in scheme 1. 1,10-phenanthroline-5,6-dione were synthesized according to the published literature.<sup>11</sup> The novel ligand was synthesized on the basis of the method for imidazole ring preparation established by Steck and Day.<sup>12</sup> The corresponding polymeric metal complexes were afforded in high yield. All polymeric metal complexes were synthesized by the reaction of BPIBP with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{ZnCl}_2$  in a stoichiometric amount. All polymeric metal complexes had good solubility DMSO, but were hardly soluble in common solvents, such as THF,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ . The poor solubility of metal complexes suggested their polymeric nature. The polymerization condition was mild. All the attempts to prepare good quality crystals were failed. All these polymeric complexes were fully characterized by FT-IR, UV-Vis, elemental analysis and conductance measurements.

The  $^1\text{H}$  NMR spectrum of the ligand BPIBP in DMSO solvent is shown in figure 1. The observed  $^1\text{H}$  NMR spectrum indicates that each half of the ligand is equivalent due to the presence of internal symmetry. The proton signals at  $\delta$  9.1, 8.9, 8.4, 8.1, 7.8 ppm can be easily assigned to each of the corresponding hydrogen respectively, which indicate the presence of the phenanthroline and benzene rings. The proton signal at  $\delta$  13.9 ppm corresponds to H–N proton of the imidazole rings. In the IR spectrum of the ligand, the absorption peak of N–H is observed at  $3404 \text{ cm}^{-1}$ , the absorption peak at 1612 and  $1548 \text{ cm}^{-1}$  are assigned to N=C and C=C bond stretching frequency, respectively. All these results prove that the ligand has been successfully synthesized.

By comparison with the ligand, the FT-IR spectra of polymeric metal complexes are found to have similar bands. The C=N band in the polymeric complexes **2** and **3** shifts to  $1628$  and  $1630 \text{ cm}^{-1}$ , the C=C band shifts to  $1401$  and  $1402 \text{ cm}^{-1}$ , respectively. Other bands in the complexes have some different extent of shifting, which are similar to the description given in the literature.<sup>13,14</sup> The shift of all bands of the polymeric complexes is attributed to the fact that the ligand was coordinated with the metal ions. At the same time, some new sharp bands are observed at  $554 \text{ cm}^{-1}$  for **2** and  $548 \text{ cm}^{-1}$  for **3**, which assigned to the  $\nu$  (M–N) stretching vibration.<sup>15,16</sup> In addition, the molar conductance values of the polymeric complexes **2** and **3** in DMSO solutions ( $10^{-4} \text{ M}$ ) are 25 and  $16 \text{ cm}^2 \Omega^{-1} \text{mol}^{-1}$ , which



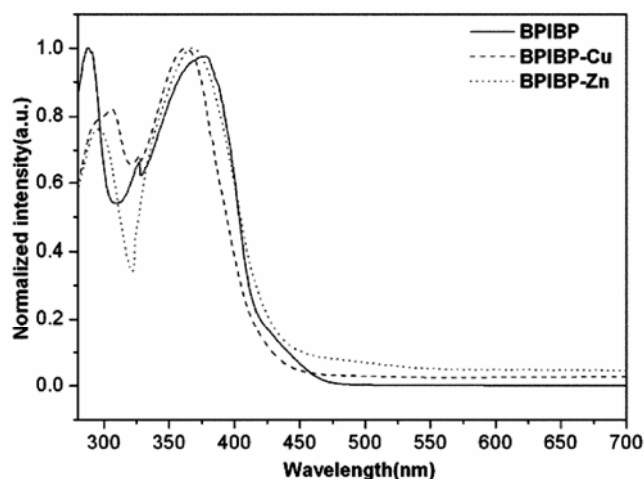
**Scheme 1.** The synthesis routes of the ligand **1** and the polymeric complexes **2** and **3**.



**Figure 1.**  $^1\text{H}$  NMR spectrum of the ligand **1**.

**Table 1.** Optical properties of the ligand **1** and the polymeric complexes **2–3**.

Compounds	Absorption (nm)	Fluorescence spectra			
		In DMSO ( $10^{-4}$ M)		In solid state	
		$\lambda_{\max}$ (em)	$\lambda_{\max}$ (ex)	$\lambda_{\max}$ (em)	$\lambda_{\max}$ (ex)
<b>1</b>	288, 326, 378	439	339	503	414
<b>2</b>	306, 363	453	391	527	453
<b>3</b>	295, 368	452	371	536	436

**Figure 2.** UV-Vis spectra of the ligand **1** and the polymeric complexes **2** and **3** in DMSO ( $1 \times 10^{-4}$  M).

are lower than the reported range for electrolytes in DMSO solutions.<sup>17</sup> There are weak electrovalent bond between chlorine ions and metal ions, these results are consistent with the light-electrolytes nature of the complexes. These data indicate that the ligand successfully chelated to metal ions.

### 3.2 UV-Vis absorption spectra

The UV-Vis absorption spectra of the three compounds **1–3** in DMSO solution at room temperature are shown in figure 2. The ligand has three absorption bands at around 288, 326 and 378 nm, which originate from  $\pi-\pi^*$  transition of phenanthroline ring,  $\pi-\pi^*$  transition of biphenyl ring and intraligand  $\pi-\pi^*$  transition of the conjugated backbone, respectively. The maximum absorptions of the polymeric complexes **2, 3** are 363 and 368 nm, which can be assigned to intraligand  $\pi-\pi^*$  transition of the conjugated backbone (BPIBP) and metal-to-ligand charge transfer (MLCT) transition. In the absorption spectra of the polymeric complexes **2** and **3**,

the characteristic absorption peaks of phenanthroline rings at 306 and 295 nm reduce, which can be attributed to the increasing conjugated degree of the polymeric complexes.

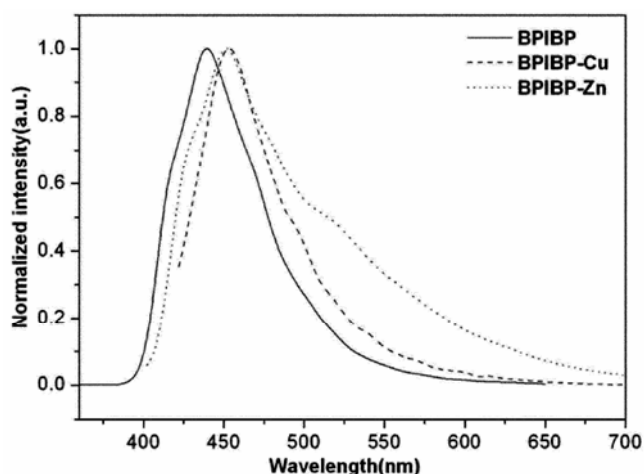
### 3.3 Fluorescence emission spectra

Luminescent properties of the three compounds **1–3** were investigated in DMSO solution and in solid state (powder) at room temperature. The fluorescence emission spectra of ligand **1** and the polymeric complexes **2, 3** are shown in figures 3 and 4. The luminescent data of the compounds are summarized in table 1. The fluorescent spectra of the polymeric complexes **2** and **3** display maximum emission wavelengths ( $\lambda_{\text{em, max}}$ ) at 453 and 452 nm with excitation wavelengths at 391 and 371 nm in DMSO solution, and maximum emission wavelengths ( $\lambda_{\text{em, max}}$ ) at 527 and 536 nm with excitation wavelengths at 453 and 436 nm in the solid state, respectively. The results indicate that the polymeric complexes have blue light emission in DMSO solution and blue/green light emission in the solid state, respectively. The emission of the polymeric complexes **2, 3** in the solid state predominantly originate from metal-to-ligand charge transfer (MLCT) transition.

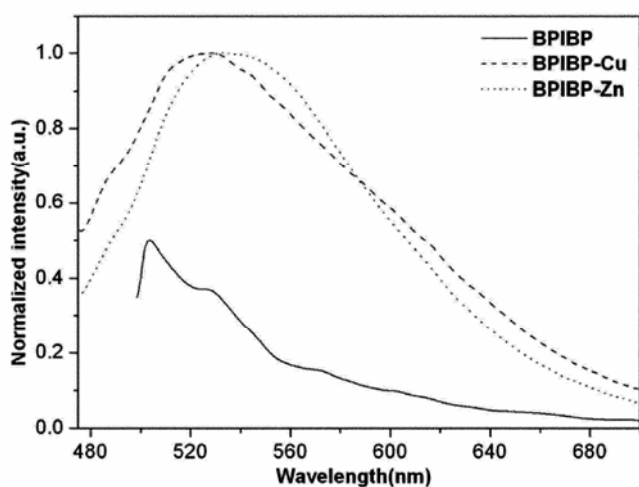
The fluorescence spectra of the polymeric complexes exhibit a red shift in both solid state and DMSO solution, compared with that of the ligand. The reason has two facets: the coordination of metal ions enhances the mobility of the electron transition in backbone due to back-coupling  $\pi$ -bond between the metal and the ligand, and decreases the electron transition energy of intraligand charge transfer. On the other hand, the ligand is coordinated with metal ions to form additional five-member rings, which increase the  $\pi-\pi^*$  conjugation length and the conformational coplanarity, accordingly reduces the energy gap between the  $\pi$  and  $\pi^*$  molecular orbital of

the ligand.<sup>18</sup> In addition, the plane structure and rigidity of the polymeric complexes are enhanced compared with the ligand, which decrease energy loss and are apt to emit fluorescence.

In the solid state, as shown in figure 4, the ligand **1** emits very weak luminescence, which can be assigned to  $\pi-\pi^*$  transition.<sup>19,20</sup> However, the polymeric complexes **2**, **3** emit intensive blue/green light, implying the energy transfer process from metal to ligand take place. The introduction of metal ions enhances the conformational rigidity in the molecule structure and reduces the non-radiative decay of the MLCT excited state, so the polymeric complexes are apt to emit fluorescence. In addition, although coordinating with the same ligand BPIBP,



**Figure 3.** Emission spectra of the ligand **1** and the polymeric complexes **2** and **3** in DMSO ( $1 \times 10^{-4}$  M).



**Figure 4.** Emission spectra of the ligand **1** and the polymeric complexes **2** and **3** in the solid state at room temperature.

the maximum emission of the polymeric complex **3** ( $\lambda_{em} = 536$  nm) has a larger red shift than **2** ( $\lambda_{em} = 527$  nm). The shift may be attributed to the difference in the excited state between the polymeric complexes **2** and **3**, the polymeric complex **3** with Zn(II) ( $d^{10}$  configuration) could show a larger geometrical rearrangement (depleting the antibonding orbitals between the metal and the ligand) and causing a far larger red shifts in the emission spectrum.<sup>21</sup>

To understand the effect on the emission energy from the free ligand to the complex, a similar theoretical reason has been studied.<sup>22</sup> The highest occupied molecular orbital (HOMO) of complex is a  $\pi$  orbital, localized on the non-coordinating nitrogen atom and carbon atom in the phenanthroline and imidazole rings, owing to the low symmetry. Compared with the free ligand, the energy of the HOMO level of the complex is much lower than that of the free ligand. The lowest unoccupied molecular orbital (LUMO) of the complex is a  $\pi^*$  orbital consisting of mostly atomic orbitals from one of the pyridyl rings. There are essentially few contributions from the imidazole ring in the LUMOs of the complexes. The role of the metal ion is to increase coplanarity, conformational rigidity in the molecule structure and to decrease the  $\pi-\pi^*$  energy gap. The results lead to a red shift in the transition energy from ligand to metal center.

### 3.4 Thermal stability

The thermal analyses are shown in table 2. For the polymeric complexes **2** and **3**, the first decomposition stages occurred in the range 30–296 and 30–274 °C with a corresponding weight loss 17.83% for **2** and 17.64% for **3**, respectively, which were assigned to the loss of absorbed water molecules. The second stages of decomposition were observed at 296–444 °C (8.12% weight loss) and 274–506 °C (4.55% weight loss), which may be caused by the

**Table 2.** Thermal properties of the polymeric complexes **2–3**.

Samples	M.p. (°C)	$T_d^a$ (°C)	$T_g^b$ (°C)	Char yield <sup>c</sup> (%)
<b>2</b>	300	296	253	14.60
<b>3</b>	300	274	203	15.84

<sup>a</sup>The initial degradation temperature of the complexes **2** and **3** by TGA at a heating rate  $20 \text{ K/min}^{-1}$

<sup>b</sup>Glass-transition temperature determined by DSC at a heat rate of  $20 \text{ K/min}^{-1}$

<sup>c</sup>Residual wt% at 800 °C in nitrogen

main chain decomposition of polymeric complexes. While the third stages occurred in the temperature ranges 444–800°C and 506–800°C with a corresponding weight loss 59.90 and 61.97%, which were attributed to the moiety degradation of the imidazole skeleton. The char yield % is about 15 wt% even at 800°C. The DSC traces of the polymeric complexes **2** and **3** show high  $T_g$ : 253 and 203°C (table 2).

From the result of TGA, the polymeric complexes are found to have formed stable five-member chelated ring,<sup>23–25</sup> which may be attributed to the fact that the M–N bond is highly polarized.<sup>26</sup> All the complexes possess a very high transition temperature, which are critical for electroluminescence device stability and good lifetime.<sup>27</sup>

#### 4. Conclusion

Two novel polymeric complexes **2** and **3** were successfully synthesized and characterized. The fluorescent spectra of complexes **2** and **3** displayed blue/green luminescence at 527 and 536 nm ( $\lambda_{em, max}$ ) in solid state and blue luminescence at 453 and 452 nm ( $\lambda_{em, max}$ ) in DMSO solution, respectively. The polymeric complexes have good thermal stability with initial decompose temperature at above 250°C. We expect that the two polymeric complexes can be used as OLEDs.

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