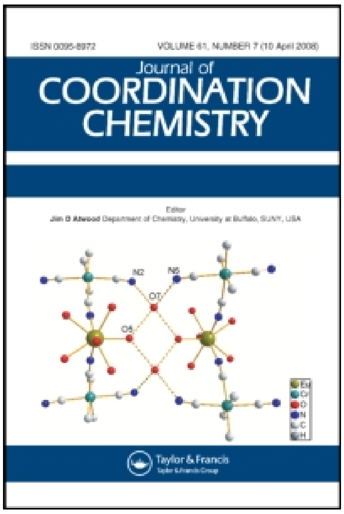

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Synthesis and luminescence of polymeric metal complexes based on 1,10-phenanthroline and 8-hydroxyquinoline

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Synthesis and luminescence of polymeric metal complexes based on 1,10-phenanthroline and 8-hydroxyquinoline

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A ligand containing different coordination groups, 5-([1,10]phenanthroline-[4,5-f]imidazo-2-yl)-8-hydroxyquinoline (PhenI8Q) has been synthesized and two corresponding polymeric metal complexes Cu(II) (**1**) and Zn(II) (**2**) were prepared by coordination polymerization of the ligand with copper(II) and zinc(II) halides, respectively. The ligand was characterized by ^{1}H-NMR, ^{13}C-NMR, and Fourier transform-infrared (FT-IR) and its corresponding polymeric metal complexes **1** and **2** were characterized by FT-IR, UV-Vis, elemental analysis, thermal gravimetric analysis, and conductivity measurements. The absorption spectra and luminescence of the ligand, **1**, and **2** were investigated by UV-Vis and fluorescence spectroscopy at room temperature. Compared with the ligand, the fluorescence spectra of the polymeric metal complexes exhibit blue shifts in dimethyl sulfoxide (DMSO) solution and bathochromic shifts in the solid state. Complexes **1** and **2** emit blue light with emission maximum ($\lambda_{\mathrm{f\,max}}$) at 449 and 431 nm in DMSO solution and at 485 and 484 nm in the solid state, respectively.

Keywords: Polymeric metal complexes; Luminescence properties; 1,10-Phenanthroline; 8-Hydroxyquinoline

1. Introduction

Since organic light emitting devices (OLEDs) using 8-hydroxyquinoline aluminum (Alq$_3$) as the emitting layer were reported to emit green light in 1987 [1], OLEDs have been a focus due to their potential applications in full color, flat panel displays and other emissive devices [2–5]. Progress with regard to low voltage, high brightness, and multi- or full-color emission has been made by selection of emitting materials, easy fabrication of large area, thin-film devices, durability, and thermal stability of OLEDs [6–8].

1,10-Phenanthroline is the parent of an important class of chelating agents that form coordination compounds with various metal ions [9, 10], possesses a rigid framework, and presents superb ability to coordinate many metal ions. The corresponding metal complexes show potential applications because of their high charge transfer mobility,

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strong absorption in the ultraviolet spectral region, bright red light emission, and good electro- and photo-active properties [11–13]. Complexes containing 8-hydroxyquinoline have emerged as one of the best green-emitting luminescent materials in OLEDs [14–16] due to the high luminescent and quantum efficiency. Chemical modifications between 8-hydroxyquinoline and 1,10-phenanthroline may satisfy application requirements to make an efficient and practical OLED device.

Many research groups have studied polymeric metal complexes with bis(benzimidazole) and bis(8-hydroxyquinoline) as emitting layers in OLEDs. Moreover, the luminescent efficiency and quantum efficiency have improved *via* molecular design and synthesis [17–20]. Emission color and charge transport properties of complexes can be changed by varying the central metal ion, the structure and the number of ligands [21]. However, polymeric metal complexes with different coordination groups have not been reported up to now.

In this article, a new kind of π-conjugate ligand with 5-([1, 10]phenanthroline-[4,5-f]imidazo-2-yl)-8-hydroxyquinoline (PhenI8Q) and the corresponding polymeric metal complexes **1** and **2** have been synthesized. We also investigated their thermal stabilities and fluorescence, where the results indicated that the two materials have thermal stability with luminescent properties for promising OLEDs.

2. Experimental

2.1. *Materials*

All materials were obtained from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China) and were used without purification. All solvents used in this study were of analytical grade.

2.2. *Instrument and measurements*

All chemicals used were of analytical grade. Solvents were purified by conventional methods.

All nuclear magnetic resonance (NMR) spectra, ^{1}H-NMR and ^{13}C-NMR, were performed in $CDCl_3$ or DMSO-d_6 on a Bruker 400 MHz spectrometer. ^{1}H-spectra were collected at 400 MHz using a spectral width of 6000 Hz, a relaxation delay of 3.5 s, 30 k data points, a pulse width of 38°, and TMS (0.00 ppm) as the internal reference. ^{13}C-NMR spectra were collected at 100 MHz using a spectral width of 25,000 Hz, a relaxation delay of 1.5 s, 75 k data points, a pulse width of 40°, and TMS (0.00 ppm) as the internal reference.

Fourier transform-infrared (FT-IR) spectra were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer in KBr discs from 450 to 4000 cm^{-1}.

Thermogravimetric analyses (TGA) were run on a Shimadzu TGA-7 Instrument (TA Instruments, Q50, V20.8 Build 34). Samples (10–15 mg) were loaded in alumina pans and ramped at 20°C min^{-1} to 800°C under dry N_2 with a flow rate of 60 mL min^{-1}.

Differential scanning calorimetry (DSC) was performed on materials using a Perkin-Elmer DSC-7 thermal analyzer (TA Instruments, Q10, V9.9 Build 303). The N_2 flow rate was 50 mL min^{-1}. Sample (5–10 mg) was placed in a pan with capping and ramped to the desired temperature at a rate of 20°C min^{-1}. The heat flow difference between the reference blank and the sample pan was recorded.

UV-Vis spectra were taken on a Lambda 25 spectrophotometer in DMSO. Samples were dissolved in DMSO and diluted to a concentration (10^{-4}–10^{-5} mol L^{-1}) where the absorption maximum was less than 10% for a 1 cm path length.

Photoluminescence spectra were taken on a Perkin-Elmer LS55 luminescence spectrometer in DMSO using 260-nm excitation for R-styrenylOS and 320-nm excitation for R-vinylstilbeneOS. Samples of R-styrenylOS from UV-Vis spectroscopy were used without dilution, while samples of R-vinylstilbeneOS from UV-Vis spectroscopy were diluted (10^{-5}–10^{-6} mol L^{-1}) to avoid excimer formation and fluorimeter detector saturation.

For elemental analysis, sample (5–10 mg) was placed in a Perkin-Elmer 2400 II instrument and measured for C, H, and N.

Molar conductance was measured by electric conductivity gauge model DDS-11A (Shanghai LeiCi XingJing Instrument Co., China) with DJS-1 type conducting electrode. The conductivity constant is 0.99. The calibration of the conductor meter was made by diluted water. The sample was dissolved in DMSO solution (10^{-4} mol L^{-1}).

2.3. *Synthesis*

2.3.1. Synthesis of 1,10-phenanthroline-5,6-dione. This compound was synthesized according to the methods in literature [22]. Yield (%): 96.5; ^{1}H-NMR ($CDCl_3$, δ, ppm): 9.118 (2H, d, H-Py), 8.514 (2H, d, H-Py), 7.584 (2H, d, H-Py).

2.3.2. Synthesis of 5-formyl-8-hydroxyquinoline. This compound was synthesized according to the published procedure [23]. Yield (%): 20.3; ^{1}H-NMR ($CDCl_3$, δ, ppm): 10.134 (1H, s, –CHO), 9.680 (1H, d, H-Py), 8.860 (1H, d, H-Py), 8.000 (1H, d, H-Ph), 7.661 (1H, d, H-Py), 7.210 (1H, d, H-Ph).

2.3.3. Synthesis of PhenI8Q. A mixture of 1,10-phenanthroline-5,6-dione (1.26 g, 6 mmol), ammonium acetate (9.24 g, 120 mmol), 5-formyl-8-hydroxyquinoline (1.04 g, 6 mmol), and glacial acetic acid (100 mL) was added to a 250-mL three-necked flask and refluxed for 2 h under N_2 and then cooled to room temperature. Filtering, collecting the precipitate, washing by H_2O (20 mL) for three times, and drying *in vacuo* at 60°C gave 1.39 g of light brown powder. Yield (%): 64. ^{1}H-NMR (DMSO, δ, ppm): 9.851 (1H, s, H-O), 9.022 (3H, d, H-Py), 8.971-8.952 (3H, m, H-Py), 8.190 (1H, m, H-Py), 7.812-7.735 (3H, m, H-Py), 7.294 (1H, d, H-Ph). ^{13}C-NMR (DMSO, δ, ppm): 154.97, 150.29, 148.30, 147.60, 143.42, 138.52, 135.26, 129.61, 129.10, 126.65, 123.16, 122.66, 121.47, 117.25, 110.66. IR (KBr, cm^{-1}): 3415, 1623, 1579, 1557, 1510, 1471, 1384, 806, 738, 624. Anal. Calcd for PhenI8Q ($C_{22}H_{13}ON_5$): C, 72.72; H, 3.61; N, 19.27. Found: C, 72.31; H, 3.41; N, 18.96.

2.3.4. Synthesis of PhenI8Q-Cu(II) (1). A methanol solution (10 mL) of $CuCl_2 \cdot 2H_2O$ (1.023 g, 6 mmol) was added to DMF solution (20 mL) of PhenI8Q (1.39 g, 4 mmol).

Then the reaction mixture was stirred for 24 h at 60°C. After filtration, the precipitate was washed with anhydrous methanol until the filtrate was colorless and then dried *in vacuo* for 8 h at 65°C to yield 1.93 g deep blue solid. Yield (%): 89. IR (KBr, cm^{-1}): 3409, 1647, 1581, 1541, 1512, 1455, 1369, 1100, 811, 724, 658, 570. Anal. Calcd for $[C_{22}H_{13}N_5CuCl_2]$: C, 54.87; H, 2.72; N, 14.54. Found: C, 54.65; H, 2.87; N, 14.38. Λ_m ($cm^2\,\Omega^{-1}\,mol^{-1}$): 15.0.

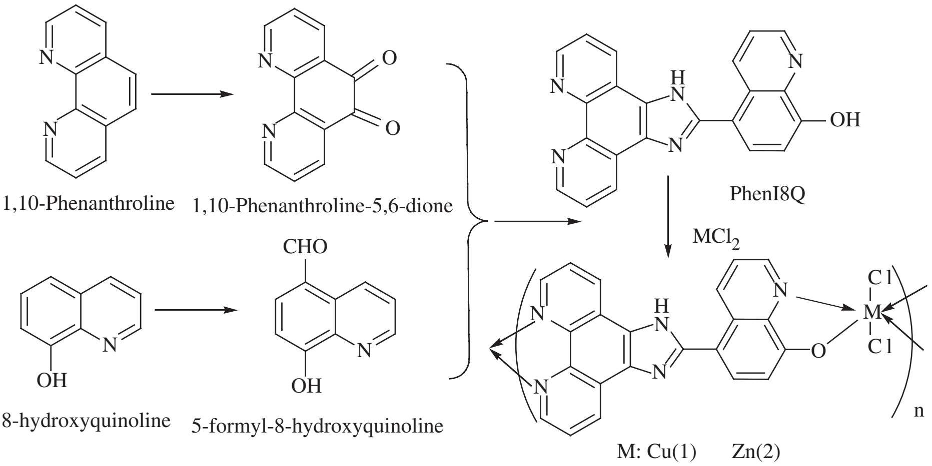
2.3.5. Synthesis of PhenI8Q-Zn(II) (2). PhenI8Q-Zn(II) was synthesized and purified by the same method as **1**. The methanol solution (10 mL) of $ZnCl_2$ (0.817 g, 6 mmol) was added to DMF solution (20 mL) of PhenI8Q (1.39 g, 4 mmol) to obtain a light-yellow solid of 1.85 g. Yield (%): 84. IR (KBr, cm^{-1}): 3411, 1654, 1598, 1539, 1513, 1450, 1358, 1079, 814, 736, 653, 574. Anal. Calcd for $[C_{22}H_{13}N_5ZnCl_2]$: C, 54.63; H, 2.71; N, 14.48. Found: C, 54.43; H, 2.93; N, 14.11. Λ_m ($cm^2\,\Omega^{-1}\,mol^{-1}$): 15.0, 11.0.

3. Results and discussion

3.1. *Synthesis*

The synthetic routes of PhenI8Q and the polymeric metal complexes are presented in scheme 1. PhenI8Q was synthesized based on the method of Steck *et al.* [24] through condensation of 1,10-phenanthroline-5,6-dione with 5-formyl-8-hydroxyquinoline in refluxing glacial acetic acid containing ammonium acetate at a molar ratio of 1 : 1 under N_2. As expected, PhenI8Q is soluble in CH_3OH, DMF, and DMSO.

The π-conjugated polymeric metal complexes **1** and **2** were synthesized with $CuCl_2 \cdot 2H_2O$ and $ZnCl_2$ in DMF *via* a standard approach, where the metal ions and the ligand coordinate to form polymers. The corresponding metal complexes were obtained in good yields. Both polymeric metal complexes have good solubility in DMSO, but poor solubility in common solvents, such as THF, CH_2Cl_2, and $CHCl_3$.



Scheme 1. Synthetic routes of PhenI8Q, **1**, and **2**.

3.2. *NMR and FT-IR spectra of the ligand*

The ^{1}H-NMR and ^{13}C-NMR spectra of PhenI8Q in DMSO are shown in figures 1 and 2. In the ^{1}H-NMR spectra of PhenI8Q, the proton signals at $\delta = 9.851$, 9.022, 8.971–8.952, 8.19, and 7.812–7.735 ppm are assigned to the corresponding protons of the pyridyl ring and the signal at 7.294 ppm is attributed to hydrogen proton of phenyl [22, 23]. The proton resonance on nitrogen of the imidazole ring is not observed because of the rapid exchange between the two nitrogens of the imidazole [25, 26]. There is no detectable signal for OH in $CDCl_3$ [27].

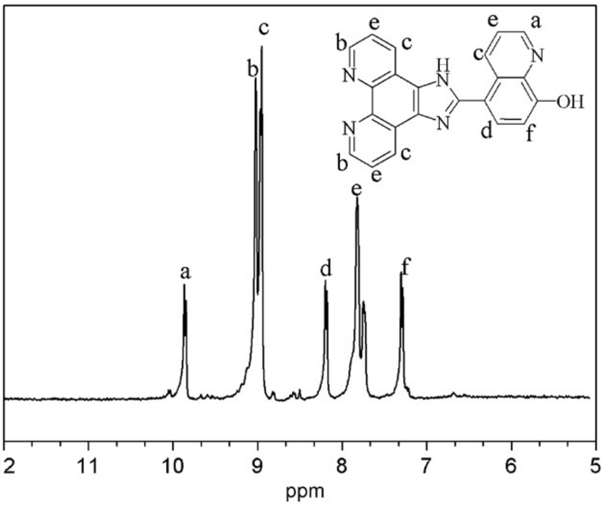


Figure 1. ^{1}H-NMR spectra of PhenI8Q in DMSO.

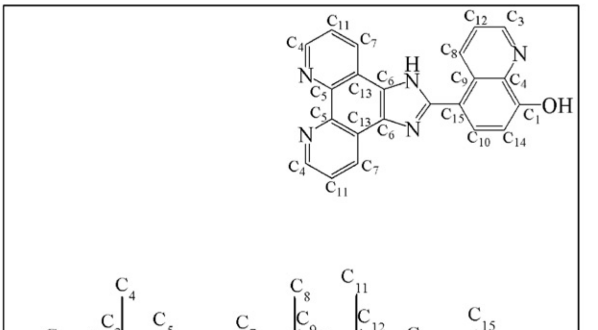


Figure 2. ^{13}C-NMR spectra of PhenI8Q in DMSO.

The ^{13}C-NMR spectrum shows expected signals of aromatic ring carbons (110.66 ~ 154.97 ppm); signals at 148.30, 147.60, 143.42, 135.26, 129.61, 129.10, 123.16, 122.66, and 121.47 ppm are assigned to C_3, C_4, C_5, C_7, C_8, C_9, C_{11}, C_{12}, C_{13} of the pyridyl ring. Signals at 154.97, 126.65, 117.25, and 110.66 ppm are assigned to C_1, C_{10}, C_{14}, C_{15} of the phenyl ring. Signals at 150.29 and 138.52 ppm are assigned to C_2 and C_6 of imidazole. From the NMR and FT-IR spectra above, the proton signals suggest the presence of the phenanthroline and quinoline rings.

An FT-IR spectrum of PhenI8Q is provided in "Supplementary material." A band at 3415 cm^{-1} is assigned to ν(OH). IR bands at 3400 cm^{-1} are assigned to ν(N–H) of the imidazole ring. Other bands observed in the regions around 1623 and 1579 cm^{-1} were assigned to ν(C = N) of 8-hydroxyquinoline and ν(C = C), respectively. The ν(C = N) vibration of the phenanthroline ring could not be assigned since the spectra were complicated by many bands in the 1300–1600 cm^{-1} region [28].

Elemental analyses, IR, and NMR spectroscopy of the products are in agreement with the formula of PhenI8Q.

3.3. *FT-IR spectra of the polymeric metal complexes*

The FT-IR spectra (Supplementary material) of **1** and **2** show red shifts compared with the ligand. N–H bands in **1** and **2** shift from 3400 to 3409 and 3411 cm^{-1}, respectively; C = N bands in **1** and **2** shift from 1623 to 1647 and 1654 cm^{-1}, respectively, C = C bands in **1** and **2** shift from 1510 to 1512 and 1513 cm^{-1}, respectively. Bands at 736, 738, and 750 cm^{-1} are assigned to bending of alkyl C–H plane for PhenI8Q, **1**, and **2**, respectively. In comparison to the ligand, there are intense bands at 1100 and 1079 cm^{-1} in **1** and **2**, respectively, associated with C–O vibrations of C–O–M [29]; furthermore, sharp O–H stretches disappear in the polymeric metal complexes, indicating the metal ions coordinate with 8-hydroxyquinoline. In **1** and **2**, new bands at 570 and 574 cm^{-1}, respectively, absent in the free ligand, can be attributed to metal–nitrogen bonds [30].

Other bands in the complexes have different extents of shifting similar to the description given in the literature [31, 32]. The shifts of all bands of the complexes are attributed to ligand coordinated with metal. Molar conductance of the polymeric metal complexes **1** and **2** in DMSO solutions (10^{-4} mol L^{-1}) are 15 and 11 cm^2 Ω^{-1} mol^{-1}, lower than the reported range for electrolytes in DMSO solutions [33]. These results are consistent with non-electrolytes.

3.4. *UV-Vis spectra*

Figure 3 displays UV-Vis absorption spectra of PhenI8Q, **1**, and **2** measured in dilute DMSO solutions and table 1 summarizes their peak positions. The band at 278–296 nm is best ascribed to the π–π* transition of phenanthroline and quinoline rings of the compounds. The band at 318–366 nm can be assigned to the π–π* transition of the conjugated backbone and n–π* transition in the quinoline ring and the phenanthroline ring [34]. Absorptions of the complexes blue-shift to 296 and 279 nm, respectively, for **1** and **2** due to pronounced steric crowding of **1** and **2**, which results in less coplanarity of the molecule after coordination with the metals [35].

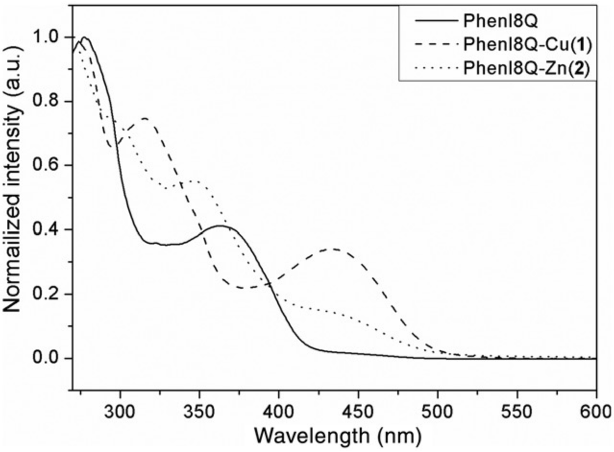


Figure 3. UV-Vis spectra of PhenI8Q, **1**, and **2** in DMSO.

Table 1. Optical properties of PhenI8Q, **1**, and **2**.

		Fluorescence spectra			
		DMSO (10^{-4} mol L^{-1})		Solid state	
Compounds	Absorption (nm)	λ_{max} (em)	λ_{max} (ex)	λ_{max} (em)	λ_{max} (ex)
PhenI8Q	278, 366	456	375	483	396
1	296, 349, 438	449	367	485, 529	312
2	279, 318, 439	431	342	484, 528	394

em, emission; ex, excitation.

Spectra of **2** show one new low-intensity absorption at 438 nm, which is due to metal-to-ligand charge transfer (MLCT) transition [36], and the low-intensity absorption at 439 nm of **1** may be assigned to a Cu(II) d–d transition [37].

3.5. Fluorescence spectra

Figure 4 shows the fluorescence emission spectra of PhenI8Q, **1**, and **2** in DMSO solution (summarized in table 1). Free PhenI8Q shows weak fluorescence emission at 456 nm in DMSO (10^{-4} mol L^{-1}), which might be assigned to ligand-localized fluorescence. Emission spectra of **1** and **2** may be ascribed to π–π^* and n–π^* transitions, with slight blue shifts, indicating that the n–π^* excited state plays a more important role in **1** and **2** than the π–π^* transition [38].

As shown in figure 5, PhenI8Q gives one intense emission at 483 nm and a very low-energy emission band in the solid state. Complexes **1** and **2** present one intense emission at 485 and 484 nm, respectively, assigned to ligand-localized fluorescence emission. Both also show low-energy emission at 529 and 528 nm, respectively, which may be

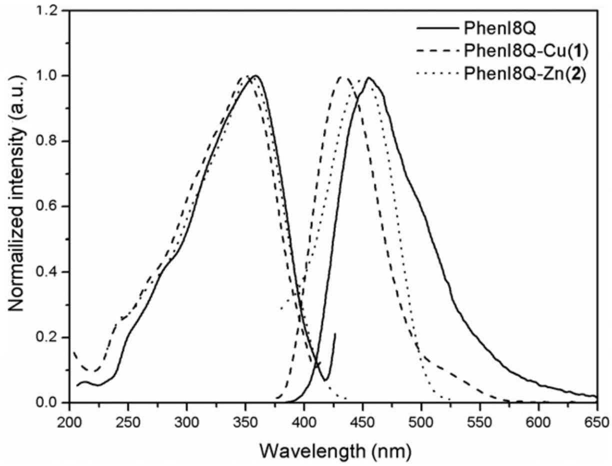


Figure 4. Excitation and emission spectra of PhenI8Q, **1**, and **2** in DMSO at room temperature.

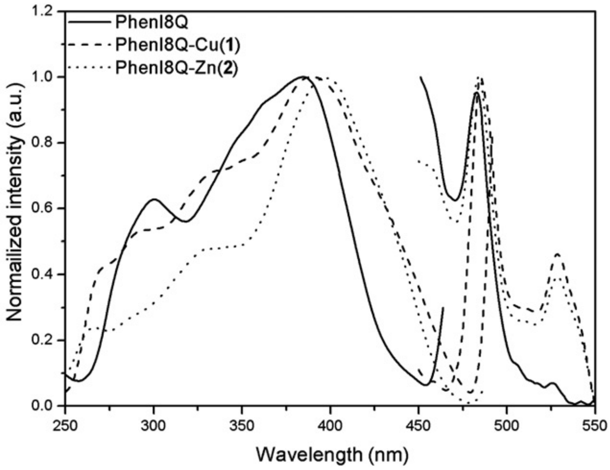


Figure 5. Excitation and emission spectra of PhenI8Q, **1**, and **2** in the solid state at room temperature.

associated with the charge transfer transitions involving metal dπ electrons and π^* orbital of the ligand [39, 40]. Comparing with the ligand, **1** and **2** both exhibit red shifts, which may be attributed to excimer formation between adjacent lumophores in the solid films [41].

3.6. *Thermal stability*

Thermal properties of **1** and **2** were evaluated by TGA and DSC, (table 2 and Supplementary material). The first decomposition stages occur at 30–270°C and 30–230°C with a corresponding mass loss of 3.47% for **1** and 4.79% for **2**, respectively,

Table 2. Physical thermal properties of PhenI8Q, **1**, and **2**.

Compounds	Color	m.p. (°C)	Yield (%)	T_d^a (°C)	T_g^b (°C)
PhenI8Q	Light brown	>300	64		
1	Deep blue	>300	89	270	220
2	Light yellow	>300	84	230	211

[a] The initial degradation temperature of **1** and **2** by TGA at a heating rate of 20°C min^{-1}.
[b] Glass transition temperature determined by DSC at a heating rate of 20°C min^{-1}.

assigned to loss of absorbed water and Cl^- or solvent. The second stages of decomposition are observed at 270–545°C (16.72 wt% loss) and 230–390°C (6.51 wt% loss), from main chain decomposition of the polymeric complexes. The third stages of decomposition occurred at 545–800°C and 390–790°C with a corresponding weight loss of 12.13% and 48.41%, from degradation of the imidazole skeleton.

The thermal behavior below the decomposition temperature was investigated by DSC that permitted determination of the glass transition temperature (T_g) of the polymeric metal complexes. The glass transition events of **1** and **2** are detected at 220°C and 211°C (table 2), respectively. T_g data indicate that both complexes possess high transition temperature, which may be an advantage for OLEDs, as materials with high transition temperature in the active emissive layer or carrier transporting layer may provide the device with greater longevity [42]. Further work on optimizing device performance is under investigation.

4. Conclusions

Two polymeric metal complexes, PhenI8Q-Cu(II) (**1**) and PhenI8Q-Zn(II) (**2**), containing 8-hydroxyquinoline and 1,10-phenanthroline were synthesized and characterized. The two materials have good stabilities and their thermal decomposition temperatures are 270 and 230°C. The fluorescence spectra of **1** and **2** displayed blue luminescence at 485 and 484 nm in the solid state and at 449 and 431 nm in DMSO solution, respectively. The two materials **1** and **2** show potential for OLEDs, and further work is needed to optimize device performance.

Acknowledgments

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References

[1] C.W. Tang, S.A. VanSlyke. *Appl. Phys. Lett.*, **51**, 913 (1987).
[2] C.W. Tang, S.A. Van Slyke. *J. Appl. Phys.*, **65**, 3610 (1989).

[3] J. Ittman, P. Martic. *J. Appl. Phys.*, **72**, 1957 (1992).
[4] T. Hayakawa, K. Furuhashi, M. Nogami. *J. Phys. Chem. B*, **108**, 11301 (2004).
[5] T.D. Anthopoulos, M.J. Frampton, E.B. Namdas, P.L. Burn, I.D.W. Samuel. *Adv. Mater.*, **16**, 557 (2004).
[6] P.E. Burrows, V. Bulovic, S.R. Forrest, L.S. Sapochak, D.M. McCarty, M.E. Thompson. *Appl. Phys. Lett.*, **65**, 2922 (1994).
[7] E.B. Namdas, A. Ruseckas, I.D.W. Samuel, S.-C. Lo, P.L. Burn. *J. Phys. Chem. B*, **108**, 1570 (2004).
[8] H. Liang, Q.J. Zhang. *Opt. Lett.*, **29**, 477 (2004).
[9] N. Armaroli. *Chem. Soc. Rev.*, **30**, 113 (2001).
[10] C. Kaes, A. Katz, M.W. Hosseini. *Chem. Rev.*, **100**, 3553 (2000).
[11] D.J. Hurley, Y. Tor. *J. Am. Chem. Soc.*, **124**, 3749 (2002).
[12] D. Felder, J.F. Nierengarten, F. Barigelletti, B. Ventura, N. Armaroli. *J. Am. Chem. Soc.*, **123**, 6291 (2001).
[13] N.S. Baek, H.K. Kim, G.T. Hwang, B. Kim. *Mol. Cryst. Liq. Cryst.*, **370**, 387 (2001).
[14] F. Auzel, G. Baldacchini, T. Baldacchini, P. Chiacchiaretta, R.B. Pode. *J. Lumin.*, **119–120**, 111 (2006).
[15] D.F. O'Brien, M.A. Baldo, M.E. Thompson, S.R. Forrest. *Appl. Phys. Lett.*, **74**, 442 (1999).
[16] J. Kido, K. Hongawa, K. Okuyama, K. Nagai. *Appl. Phys. Lett.*, **64**, 815 (1994).
[17] C. Zhong, R. Guo, Q. Wu, H. Zhang. *React. Funct. Polym.*, **67**, 408 (2007).
[18] J. Yu, Z. Chen, S. Miyata. *Chem. Vap. Deposition*, **7**, 66 (2001).
[19] H. Huang, C. Zhong, Y. Zhou. *Eur. Polym. J.*, **44**, 2944 (2008).
[20] J. Xie, L. Fan, J. Su, H. Tian. *Dyes Pigm.*, **59**, 153 (2003).
[21] G. Wang, F. Liang, Z. Xie, G. Su, L. Wang, X. Jing, F. Wang. *Synth. Met.*, **131**, 1 (2002).
[22] C. Zhong, H. Huang, A. He, H. Zhang. *Dyes Pigm.*, **579**, 77 (2008).
[23] H. Huang, C. Zhong, Y. Zhou. *Eur. Polym. J.*, **44**, 2945 (2008).
[24] F. Calderazzo, F. Marchetti, G. Pampaloni, V. Passarelli. *J. Chem. Soc., Dalton Trans.*, 4389 (1999).
[25] C.-W. Jiang, H. Chao, R.-H. Li, H. Li, L.-N. Ji. *Transition Met. Chem.*, **27**, 520 (2002).
[26] A.A. Van Dijk, R.M. Scheek, K. Dijkstra, G.K. Wolters, G.T. Robillard. *Biochemistry*, **31**, 9063 (1992).
[27] M. La Deda, A. Grisolla, I. Aiello, A. Crispini, M. Ghedini, S. Belviso. *J. Chem. Soc., Dalton Trans.*, **16**, 2424 (2004).
[28] B. Kirkan, R. Gup. *Turk. J. Chem.*, **32**, 9 (2008).
[29] G. Robert, H. Charles, R. Freiser, L. Friedel, E. Hilliard, W.D. Johnston. *Spectrochim. Acta*, **8**, 1 (1956).
[30] R. Pagadala, P. Ali, J.S. Meshram. *J. Coord. Chem.*, **62**, 4015 (2009).
[31] E.A. Steck, A.R. Day. *J. Am. Chem. Soc.*, **65**, 452 (1943).
[32] E. Sahin, S. Ìde, M. Kurt, S. Yurdakul. *J. Mol. Struct.*, **616**, 259 (2002).
[33] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[34] S. Dong, W. Wang, S. Yin, C. Li, J. Lu. *Synth. Met.*, **159**, 389 (2009).
[35] X.H. Zhang, B.J. Chen, X.Q. Lin, O.Y. Wong, C.S. Lee, H.L. Kwong, S.T. Lee, S.K. Wu. *Chem. Mater.*, **13**, 1565 (2001).
[36] P. Dapporto, M. Formica, V. Fusi, L. Giothi, M. Micheloni, P. Paoli, R. Pontellini, P. Rossi. *Inorg. Chem.*, **40**, 6186 (2001).
[37] B.A. Jazdzewski, P.L. Holland, M. Pink, V.G. Young, D.J.E. Spencer, W.B. Tolman. *Inorg. Chem.*, **40**, 6097 (2001).
[38] L. Feng, X. Wang, S. Zhaoc, Z. Chena. *Spectrochim. Acta, Part A*, **68**, 648 (2007).
[39] S. Ressalan, C.S.P. Iyer. *J. Lumin.*, **111**, 121 (2005).
[40] J. Lu, L. Zhang, L. Liu, G. Liu, D. Jia, D. Wu, G. Xu. *Spectrochim. Acta, Part A*, **71**, 1036 (2008).
[41] T.A. Hopkins, K. Meerholz, S. Shaheen, M.L. Anderson, A. Schmidt, B. Kippelen, A.B. Padias, H.K. Hall Jr, N. Peyghambarian, N.R. Armstrong. *Chem. Mater.*, **8**, 344 (1996).
[42] S. Tokito, H. Tanaka, K. Noda, A. Okada, Y. Taga. *Appl. Phys. Lett.*, **70**, 929 (1997).