Polyhedron 33 (2012) 347-352

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and characterization of a series of transition metal polypyridyl complexes and the pH-induced luminescence switch of Zn(II) and Ru(II) complexes

Hui-Hua Xu, Xian Tao, Yue-Qin Li, Ying-Zhong Shen*, Yan-Hong Wei

Applied Chemistry Department, School of Material Science & Engineering, Nanjing University of Aeronautics & Astronautics, Nanjing 210016, PR China

ARTICLE INFO

Article history: Received 15 September 2011 Accepted 25 November 2011 Available online 3 December 2011

Keywords: Imidazo[4,5-f][1,10]phenanthroline Transition metal complex UV-Vis absorption Luminescence Fluorescence pH switch

ABSTRACT

Five new transition metal complexes, formulated as $[Zn(DMBPIP)_3](PF_6)_2$ (1), $[Ni(DMBPIP)_3](PF_6)_2$ (2), $[Co(DMBPIP)_3](PF_6)_2$ (3), $[Fe(DMBPIP)_3](PF_6)_2$ (4), $[Ru(DMBPIP)_3](PF_6)_2$ (5) {where DMBPIP = 2-(3',5'-dimethoxybiphenyl-4-yl)-1*H*-imidazo[4,5-*f*] [1,10]phenanthroline} were synthesized and characterized by means of elemental analysis, IR, ¹H NMR, ¹³C{¹H} NMR, standard spectroscopy techniques and cyclic voltammetry. The pH effects on UV–Vis absorption and luminescence spectra of the Zn(II) and Ru(II) complexes are studied, and ground- and excited-state ionization constants of the two complexes are derived. The two complexes acting as pH-induced "off-on-off" luminescence switches through protonation and deprotonation in buffer solution at room temperature are studied and discussed as well.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Small molecules that can be used as sensors, switches and logic gates has received much attention in the last three decades [1,2], which are of tremendous significance to the development of miniaturized device components [3]. Molecular switches, which can be converted from one state to another through molecular level property changes by external stimuli such as light, electric field or chemical reaction, have attracted a great deal of attentions [4]. Transfer of protons as an external stimulation has attracted a lot of interest because it could be simply controlled and can induce the switching of properties such as luminescence and UV-Vis absorption for pH sensors. The pH sensors are not only fundamental molecular switches but also can be used to measure pH and pCO₂ in the biological and environmental systems [5]. Besides, the pH responsive luminescence switches could be used to mimic many of life processes, such as the functions and activities of "switch on" or "switch off" enzymes within a narrow pH window [6,7]. However, it is noticed that many pH sensor researches have primarily focused on organic molecules. Investigations of transition metal complexes have attracted less attention and their great potential as pH sensors has not fully explored. In order to synthesize this class of sensors, the most import factor is the introduction of a pH sensitive functional group into the ligand such as polypyridine. Imidazo [4,5-f] [1,10] phenanthroline derivatives are poor π acceptors and good π -donors and have the appreciable ability to control orbital energies by proton transfer [8]. Their metal complexes with imidazole rings uncoordinated to the metal center are good emitters with proton induced on–off emission switching characteristics through a reversible acid–base interconversion of imidazole group. Several mononuclear and dinuclear metal polypyridine complexes of this type have been reported [8–14].

In this paper, a new imidazo[4,5-*f*][1,10]phenanthroline derivative, namely 2-(3',5'-dimethoxybiphenyl-4-yl)-1*H*-imidazo[4,5*f*][1,10]phenanthroline (DMBPIP) and its transition metal complexes [M(DMBPIP)₃](PF₆)₂ (M = Zn, Ni, Co, Fe, Ru) were synthesized and characterized. And UV–Vis absorption and luminescence spectra of the Zn(II) and Ru(II) complexes in response to pH changes are studied as well.

2. Experimental

1,10-Phenanthroline-5,6-dione [15], 3,5-dimethoxyphenylboronic acid [16] were synthesized according to the literature methods. All other chemicals used were of analytical reagent grade quality from commercial sources and were used without further purification.

Melting points were measured on a WRS-1B digital melting point apparatus and are uncorrected. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Advance 300 or a Bruker DRX500 spectrometer in DMSO- d_6 solution with TMS as internal standard. IR spectra were recorded on a Bruker Vector 22 as KBr pellets in the 400–4000 cm⁻¹ region. Elemental analyses were carried out on a Perkin-Elmer 240 C elemental analyzer. Absorption spectra were recorded with a UV-2550 UV–Visible spectrophotometer.





^{*} Corresponding author. Tel.: +86 25 52112906/84765; fax: +86 25 52112626. *E-mail address*: yz_shen@nuaa.edu.cn (Y.-Z. Shen).

^{0277-5387/\$ -} see front matter @ 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2011.11.049

Luminescence spectra were obtained with an Eclipse Fluorescence spectrometer. Cyclic voltammetry was recorded on a CHI 660C electrochemical work station using a platinum wire as working electrode, a platinum plate as counter electrode, and an Ag/AgCl electrode as the reference. 0.1 M tetra-*n*-butylammonium perchlorate (*n*-Bu₄NClO₄) dissolved in anhydrous acetonitrile was employed as the supporting electrolyte. The concentration of the complexes were 2×10^{-3} mol/L. Prior to electrochemical measurement, the solution was deoxygenated with bubbling nitrogen for 30 min.

The pH dependence of the ground-state and excited-state properties of the complexes was studied with UV–Vis absorption and luminescence spectra, respectively. UV–Vis absorption and luminescence pH spectroscopic titrations of the two complexes were carried out in acetonitrile–Briton–Robinson buffer (1:1) solution with 0.2 mol/L NaCl to maintain a constant ionic strength. The pH changes were also measured with a PHS-3C pH meter. All spectral changes with pH were reversible.

2.1. Synthesis of 3',5'-dimethoxybiphenyl-4-carbaldehyde

4-Bromobenzaldehyde (4.63 g, 25 mmol) and 3,5-dimethoxyph enylboronic acid (5.46 g, 30 mmol) were dissolved in toluene (100 mL). A solution of 1 M K₂CO₃ (50 mL) was added, and the mixture was stirred with nitrogen bubbling for a while, then Ph(PPh₃)₄ (0.4634 g, 0.4 mmol) was added. The mixture was refluxed for 10 h in an atmosphere of nitrogen. After cooling to the room temperature, the organic layer was separated and the aqueous layer was extracted twice with 20 mL portions of toluene. The combined organic layer was washed twice with NaHCO₃ solution and water respectively, then dried over MgSO₄, filtered and the solvent was evaporated. Recrystallized from petroleum ether/dichloromethane (1:4, v/v), the pure 3',5'-dimethoxybiphenyl-4-carbaldehyde (4.31 g, 71.2% based on 4-bromobenzaldehyde) was obtained as a white solid. Mp: 68.1–68.5 °C.

2.2. Synthesis of 2-(3',5'-dimethoxybiphenyl-4-yl)-1H-imidazo[4,5f][1,10]phenanthroline (DMBPIP)

A mixture of 3',5'-dimethoxybiphenyl-4-carbaldehyde (2.10 g, 10 mmol), 1,10-phenanthroline-5,6-dione (3.39 g, 14 mmol), ammonium acetate (15.42 g, 200 mmol) in glacial acetic acid (100 mL) was refluxed for about 5 h. After cooling to room temperature, the reaction mixture was poured into 50 mL of distilled water and neutralized to pH = 7 with an aqueous ammonia solution. The precipitate was filtered off, washed with distilled water, and finally recrystallized from petroleum ether/ethanol (1:10, v/v) to afford 2-(3',5'-dimethoxybiphenyl-4yl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline as a yellow product. Yield: 3.25 g(75.2% based on 3',5'-dimethoxybiphenyl-4-carbaldehyde). Mp: >350 °C. Anal. Calc. for C₂₇H₂₀N₄O₂: C, 74.98; H, 4.66; N, 12.95. Found: C, 74.87; H, 4.61; N, 12.98%. ¹H NMR (DMSO-*d*₆, 300.13 MHz): δ 13.82 (s, N-H, 1 H), 9.09-9.04 (m, H_a, 2 H), 8.97-8.94 (m, H_c, 2 H), 8.38 (d, J = 8.5 Hz, H_d, 2 H), 7.96 (d, J = 8.5 Hz, H_b, 2 H), 7.90–7.81 (m, H_e, 2 H), 6.94 (d, J = 2.2 Hz, H_f, 2 H), 6.57 (t, J = 2.2 Hz, H_g, 1 H), 3.86 (s, OCH₃, 6 H). IR (KBr): v = 3086 (w), 2939 (w), 2835 (w), 1599 (m), 1453 (m), 1157 (m), 742 (m) cm⁻¹.

2.3. Synthesis of $[Zn(DMBPIP)_3](PF_6)_2(1)$

A DMF (10 mL) solution of DMBPIP (0.6485 g, 1.5 mmol) was added dropwise to $Zn(OAc)_2 \cdot 2H_2O$ (0.1095 g, 0.5 mmol) dissolved in DMF (10 mL) and refluxed for 12 h. The resulting clear solution was cooled to room temperature and treated in situ anion exchange reaction by adding excess NH₄PF₆ aqueous solution. A yellow precipitate was filtered, washed with water and diethyl ether, and dried under vacuum (0.6596 g, 79.8% based on DMBPIP). Mp: >350 °C. Anal. Calc. for $C_{81}H_{60}N_{12}O_6P_2F_{12}Zn$: C, 58.87; H, 3.66; N, 10.17. Found: C, 58.79; H, 3.62; N, 10.12%. ¹H NMR (DMSO- d_6 , 300.13 MHz): δ 9.28 (d, *J* = 8.0 Hz, H_c, 2 H), 8.47–7.80 (m, H_d, H_a, H_b, H_e, 8 H), 6.90 (s, H_f, 2 H), 6.56 (s, H_g, 1 H), 3.84 (s, OCH₃, 6 H). ¹³C NMR (DMSO- d_6 , 75.47 MHz): δ 160.3, 151.3, 145.9, 145.8, 140.9, 140.6, 137.1, 133.5, 127.9, 126.8, 126.2, 125.6, 104.2, 99.0, 54.7 ppm. IR (KBr): ν = 3382 (w), 3085 (w), 2939 (w), 2839 (w), 1605 (m), 1456 (m), 1156 (m), 849 (s), 735 (m), 559 (m) cm⁻¹.

2.4. Synthesis of $[Ni(DMBPIP)_3](PF_6)_2$ (2)

The synthesis of **2** was similar to that of **1** except that NiCl₂·2H₂O (0.1185 g, 0.5 mmol) was used instead of $Zn(OAc)_2$ ·2H₂O. Yield: 0.6448 g, 78.4% based on DMBPIP. M.p.: >350 °C. *Anal.* Calc. for C₈₁H₆₀N₁₂O₆P₂F₁₂Ni: C, 59.10; H, 3.67; N, 10.20. Found: C, 59.15; H, 3.69; N, 10.14%. IR (KBr): v = 3376 (w), 3082 (w), 2939 (w), 2838 (w), 1605 (m), 1456 (m), 1155 (m), 847 (s), 734 (m), 558 (m) cm⁻¹.

2.5. Synthesis of $[Co(DMBPIP)_3](PF_6)_2$ (3)

The synthesis of **3** was similar to that of **1** except that $CoCl_2 \cdot 6H_2O$ (0.1186 g, 0.5 mmol) was used instead of $Zn(OAc)_2 \cdot 2H_2O$. Yield: 0.6546 g, 79.5% based on DMBPIP. Mp: >350 °C. *Anal.* Calc. for $C_{81}H_{60}N_{12}O_6P_2F_{12}Co:$ C, 59.10; H, 3.67; N, 10.20. Found: C, 59.16; H, 3.64; N, 10.17%. IR (KBr): v = 3377 (w), 3080 (w), 2937 (w), 2838 (w), 1605 (m), 1456 (m), 1156 (m), 846 (s), 734 (m), 558 (m) cm⁻¹.

2.6. Synthesis of $[Fe(DMBPIP)_3](PF_6)_2(4)$

The synthesis of **4** was similar to that of **1** except that FeCl₂·4H₂O (0.0997 g, 0.5 mmol) was used instead of Zn(OAc)₂·2H₂O. Yield: 0.6628 g, 80.7% based on DMBPIP. Mp: >350 °C. *Anal.* Calc. for C₈₁H₆₀N₁₂O₆P₂F₁₂Fe: C, 59.20; H, 3.68; N, 10.22. Found: C, 59.17; H, 3.67; N, 10.25%. ¹H NMR (DMSO-*d*₆, 500.13 MHz): δ 9.06–8.96 (m, H_c, 2 H), 8.42–8.39 (m, H_d, 2 H), 7.96–7.64 (m, H_a, H_b, H_e, 6H), 6.91 (s, H_f, 2H), 6.57 (s, H_g, 1H), 3.85 (s, OCH₃, 6H) ppm. ¹³C NMR (DMSO-*d*₆, 75.47 MHz): δ 162.9, 161.6, 152.4, 147.5, 142.2, 131.2, 131.2, 128.0, 127.9, 127.5, 127.2, 126.2, 106.5, 100.2, 55.9 ppm. IR (KBr): ν = 3377 (w), 3079 (w), 2936 (w), 2836 (w), 1602 (m), 1458 (m), 1155 (m), 845 (s), 727 (m), 558 (m) cm⁻¹.

2.7. Synthesis of $[Ru(DMBPIP)_3](PF_6)_2$ (5)

The synthesis of **5** was similar to that of **1** except that RuCl₃·3H₂O (0.1278 g, 0.5 mmol) was used instead of $Zn(OAc)_2 \cdot 2H_2O$ and dimethylformamide was used instead of ethanol. Yield: 0.6046 g, 71.6% based on DMBPIP. Mp: >350 °C. *Anal.* Calc. for C₈₁H₆₀N₁₂O₆P₂-F₁₂Ru: C, 57.62; H, 3.58; N, 9.95. Found: C, 57.59; H, 3.60; N, 9.99%.¹H NMR (DMSO-*d*₆, 500.13 MHz): δ 9.11–9.03 (m, H_c, 2 H), 8.43–8.37 (m, H_d, 2 H), 8.06–7.96 (m, H_a, H_b, 4 H), 7.82–7.80 (m, H_e, 2 H), 6.94 (s, H_f, 2 H), 6.59 (s, H_g, 1 H), 3.86 (s, OCH₃, 6 H). ¹³C NMR (DMSO-*d*₆, 75.47 MHz): δ 162.9, 161.6, 150.6, 148.4, 145.9, 141.9, 130.9, 130.2, 128.1, 127.6, 127.2, 126.7, 105.6, 100.4, 55.9 ppm. IR (KBr): ν = 3393 (w), 3081 (w), 2938 (w), 2838 (w), 1602 (m), 1458 (m), 1156 (m), 848 (s), 725 (m), 558 (m) cm⁻¹.

3. Results and discussion

3.1. Synthesis and characterization

An outline of the synthesis of the ligand 2-(3',5'-dimethoxybiphenyl-4-yl)-1*H*-imidazo[4,5-f][1,10]phenanthroline (DMBPIP) is presented in Scheme 1, and the chemical structure of the related complexes was shown in Fig. 1. 3',5'-Dimethoxybiphenyl-4-carbaldehyde was prepared according to a Suzuki cross-coupling reaction starting from 4-bromobenzaldehyde and 3,5-dimetho xyphe nylboronic acid. The ligand DMBPIP was prepared by a condensation reaction between one equivalent of 1,10-phenanthroline-5,6dione and one equivalent of 3',5'-dimethoxybiphenyl-4-carbaldehyde in the presence of an excess of ammonium acetate in refluxing acetic acid. All the related transitional metal complexes 1-5were produced by refluxing three equivalents of DMBPIP with one equivalent of each metal chloride or metal acetate in DMF, respectively and then treating in situ anion exchange reaction by adding excess NH₄PF₆ in order to precipitate the complexes from their mother solution.

The ¹H NMR, ¹³C NMR data and the important IR frequencies are given in Section 2, and the ¹H NMR spectra of [Fe(DMB- $PIP_{3}(PF_{6})_{2}$ (**4**) and DMBPIP are compared in Fig. S1, the characteristic infrared absorption bands of the free ligand DMBPIP and its complexes are given in Table 1. In general, the NMR and IR spectra of the complexes are quite similar and can be used to detect the coordination of phenanthroline nitrogens by comparison of the free ligand. The ¹H NMR spectrum of DMBPIP displays 7 signals in the aromatic region between 9.09 and 6.57 ppm with the expected multiplicities, a singlet at 13.82 ppm for the N-H peak and a singlet at 3.86 ppm for the methoxy peak. The ¹H NMR spectra of the complexes shows the expected peaks in the aromatic and aliphatic regions as well. Upon M(II) coordination, the H_a chemical shift for DMBPIP experienced a large upfield shift. This is because the coordination of nitrogen atoms on the aromatic ring to M(II) leads to the electron deficiency of H_a, and accordingly the deshielding effect on the protons of H_a [17,18]. In addition, the chemical shifts of N-H protons in the complexes have not been examined, probably because this proton is very active and exchanges quickly between the two nitrogens of the imidazole ring in solution [19,20]. As can be seen from Table 1, the IR spectra of the complexes show bands at 1602–1605 cm⁻¹ (C=N) and 1456-1458 cm⁻¹ (C=C), all shifted to lower frequencies when compared to free ligand DMBPIP, suggesting complexation. A new band at $558-559 \text{ cm}^{-1}$ can be assigned to M-N stretching and a strong band at 845-849 cm⁻¹ can be ascribed to the counter anion PF_6^- [21].



Fig. 1. The chemical structure of $[M(DMBPIP)_3](PF_6)_2$ (M = Zn, Ni, Co, Fe, Ru) (general atom numbering also given for NMR description).

Table 1	
Characteristic IR bands (cm ⁻¹)	of the ligand and its complexes.

Sample	v (C=N)	v (C=C)	PF_6^-	v (M–N)
DMBPIP	1599	1453		
1	1605	1456	849	559
2	1605	1456	847	558
3	1605	1456	846	558
4	1602	1458	845	558
5	1602	1458	848	558

3.2. Absorption and emission spectra

The UV–Vis absorption spectra of complexes **1–5** in CH₃CN solution at room temperature are displayed in Figs. 2 and 3, respec-

OCH4



Scheme 1. The synthetic route of ligand DMBPIP.

tively. The corresponding spectral data are listed in Table 1. All the complexes show three intense bands around 240–250 nm, 290–301 nm and 314–332 nm, which could be assigned to intraligand charge transfer (ILCT). Low-energy absorptions were observed at 531 nm for the Fe(II) complex **4** and 466 nm for the Ru(II) complex **5**, corresponding to the metal-ligand charge transfer (MLCT) absorptions. These values and assignments are consistent with those of a number of related complexes in the literature [22–24].

The luminescence emission spectra of the complexes 1 and 5 in CH₃CN solution are shown in Fig. 3. It can be seen from Fig. 3 and Table 1, the complex 1 exhibits maximum emission band at 485 nm in CH₃CN with excitation wavelength at 330 nm. As Zn(II) is difficult to oxidize or to reduce owing to their d^{10} electronic configuration, the emission of 1 should be neither ligand-metal charge transfer (LMCT) nor metal-ligand charge transfer (MLCT) in nature. It is tentatively attributed to the intraligand charge transfer (ILCT) of ligands [25]. A CH₃CN solution of complex 5 on excitation at 465 nm exhibited an emission maximum at 600 nm, which could be assigned as a triplet metal-ligand charge-transfer transition (³MLCT), on the basis of literature assignment of analogous Ru(II) metal complexes [26,27]. These results indicate that the complexes 1 and 5 emit cyan/orange luminescence in CH₃CN solution respectively. For the complexes 2, 3 and 4, there are no emission luminescence spectra can be observed. The reasons are that Ni(II), Co(II) and Fe(II) are open-shell cations with available oxidation states [28] and that the transition metal (M)-fluorophore (F) communication is too strong compared with the other interactions for commonly used receptor (R) [29].

3.3. Electrochemistry

Cyclic voltammograms of the complexes **2–5** are compared Table 2. The Ni(II), Co(II), Fe(II), Ru(II) complexes display metal-based irreversible cyclic voltammetric response in DMF–0.1 M TBAP. The Zn(II) complex **1** does not show any metal-based redox process, suggesting the stability of the bivalent metal oxidation state in the Zn^{II} species [30]. The Ni(II) complex **2** undergoes oxidation to the Ni^{III} species giving an $E_{1/2}$ value of 0.98 V for the Ni^{II}/Ni^{III} couple [31]. The Co^{II}/Co^{III} oxidation occurs at a higher potential, giving an $E_{1/2}$ value of 1.02 V. The Fe^{II}/Fe^{III} couple is observed at 1.15 V. Such a high redox potential renders stability to the Fe^{II} state with a lowspin electronic configuration. The Ru^{II}/Ru^{III} oxidation occurs at 0.93 V versus Ag/AgCl electrode which is lower than that of [Ru(b-py)₃]²⁺ [32] complex due to the presence of more delocalized π systems. At negative potentials, each complex shows well shaped reduction (one) waves with $E_{1/2}$ in the potential range of –1.11



Fig. 2. UV–Vis absorption spectra of complexes $[Ni(DMBPIP)_3](PF_6)_2$ (**2**), $[Co(DMB-PIP)_3](PF_6)_2$ (**3**) and $[Fe(DMBPIP)_3](PF_6)_2$ (**4**) in CH₃CN with the concentration of 2×10^{-5} M.



Fig. 3. UV–Vis absorption and normalized luminescence spectra of complexes $[Zn(DMBPIP)_3](PF_6)_2$ (1) and $[Ru(DMBPIP)_3](PF_6)_2$ (5) in CH₃CN with the concentration of 2×10^{-5} M at room temperature.

to -1.67 V, which can be assigned to the reduction of the ligand DMBPIP.

3.4. PH effects on UV-Vis and emission spectra

The UV–Vis absorption spectra of $[Zn(DMBPIP)_3](PF_6)_2$ (1) and $[Ru(DMBPIP)_3](PF_6)_2$ (5) in neutral CH₃CN/H₂O (1:1, v/v) are shown in Figs. S2 and 4, respectively. The two complexes exhibit intraligand π – π * absorption band at 222–228, 283–291 and 317–324 nm. The metal–ligand charge transfer (MLCT) transition band of complex 5 is shown at 466 nm. The emission peak of complex 1 and 5 in CH₃CN/H₂O (1:1, v/v) solution at pH = 7 located at 450 and 600 nm, respectively (Figs. S2 and 4).

The UV–Vis absorption spectra of complex 1 and 5 in CH₃CN/ Britton-Robinson (BR) buffer (1:1, v/v) as a function of pH are shown in Figs. S3 and 5, respectively. It is clear from Figs. S3 and 5 that the two complexes underwent two successive deprotonation processes over a pH range of 1.8–11.9. For **1**, upon raising pH from 1.8 to 6.6, the π - π ^{*} transitions at 222, 283 and 324 nm were all slightly increasing in the intensities (Fig. S3a). Spectral changes were attributed to the concurrent dissociation of three protons on protonated imidazole rings. Further increasing pH from 6.6 to 11.9, the deprotonation on neutral imidazole rings occurred. Band at 222 nm was obviously decreasing in the intensities. Bands at 283 and 324 nm were red-shifted to 289 and 337 nm, respectively, and were slightly decreasing in the intensities (Fig. S3b). Quantitative analysis of the absorption changes at 280 nm does show two deprotonation processes, as shown by nonlinear sigmoidal fits of the data in the inset of Fig. S3. So, two ground-state ionization constants of pK_{a1} = 4.32, pK_{a2} = 10.28 were obtained. Absorption spectral changes of complex 5 are similar to that of complex 1. Upon raising pH from 1.8 to 6.8, the absorbance for the MLCT band at 466 nm and the π - π ^{*} transitions at 228, 291 and 317 nm were all slightly increasing in the intensities (Fig. 5a). Further increasing pH from 6.8 to 11.9, the absorption intensity at 228 nm was slightly decreasing. Bands at 291, 317 and 466 nm were red-shifted to 301, 344 and 485 nm, respectively, and were decreasing in the intensity (Fig. 5b). Two ground-state ionization constants were derived to be $pK_{a1} = 4.36$ and $pK_{a2} = 8.04$ by nonlinear sigmoidal fit of the data in the insets of Fig. 5.

Luminescence spectral changes of complexes **1** and **5** in $CH_3CN/$ Britton–Robinson (BR) buffer (1:1, v/v) as a function of pH is shown in Figs. S4 and 6, respectively. For **1**, upon raising pH from 1.8 to 6.8, emission intensity increased by about 14.5-fold, and the emission maxima were blue-shifted from 600 to 442 nm (Fig. S4a). Complex **1** acted as an off–on switch over this pH range. Upon

Table 2	
Optical and	electrochemical data of the complexes.

Compound	Absorption ^a $\lambda_{abs} (nm) (\varepsilon (1000 L mol^{-1} cm^{-1}))$	Emission ^a λ _{max} (nm)	$E_{1/2}^{\mathrm{Ox}}/V^{\mathrm{b}}$	$E_{1/2}^{\text{Red}}/V^{\text{b}}$
1	249 (43), 290 (109), 332 (107)	485	_	-
2	246 (69), 292 (169), 330 (165)	-	0.98	-1.53
3	250 (52), 291 (130), 331 (132)	-	1.02	-1.16
4	247 (60), 301 (137), 321 (139), 531 (19)	-	1.15	-1.60
5	246 (73), 293 (180), 314 (160), 466 (33)	600	0.93	-1.57

^a The data were obtained in CH₃CN at room temperature.

^b The electrochemical data were measured in DMF containing a 0.1 M tetra-*n*-butylammonium perchlorate using a platinum wire electrode as a working electrode and were reported vs. Ag/AgCl electrode.



Fig. 4. UV–Vis absorption and normalized luminescence spectra of complex 5 in neutral CH_3CN/H_2O (1:1, v/v) at room temperature.

increasing pH from 8.7 to 11.9, the emission intensity was found to decrease by about 83.0% (Fig. S4b). Over this pH region, complex 1 acted as an on-off emission switch. For 5, upon raising pH from 2.0 to 5.7, the intensity of the emission increased by about 14.4% with the emission maxima blue-shifted from 601 to 598 nm (Fig. 6a). Complex **5** acted as an off-on switch over this pH range, as shown in the inset of Fig. 6a. On the contrary, the emission intensity was found to sharply decrease by 57.3% as the pH further increased from 5.7 to 10.9 with the emission maxima red-shifted from 598 to 604 nm (Fig. 6b). Over this pH region, complex 5 acted as an on-off emission switch. This process may involve rapid radiationless decay [33]. It has been well known that the energy of the metal-centered excited state depends on the ligand field strength. The negative charge on the deprotonated imidazole rings can be delocalized over the whole π framework, which lowers the ligand field strength around the metal center and in turn lowering the metal σ^* orbitals [34,35]. The emission intensities versus pH profiles of the complexes (the insets of Figs. S4 and 6) shows that a luminescence



Fig. 5. Changes of UV–Vis absorption spectra of $[Ru(DMBPIP)_3](PF_6)_2$ (5) upon raising the pH: (a) from 1.8 to 6.8, (b) from 6.8 to 11.9.



Fig. 6. Changes of emission spectra of $[Ru(DMBPIP)_3](PF_6)_2$ (**5**) upon raising the pH: (a) from 2.0 to 5.7, (b) from 5.7 to 10.9.

off-on-off switching action was achieved by the two deprotonation processes of the protonated imidazole moieties on the complexes.

Excited-state ionization constants, pK_a^* , could be correlated with pK_a thermodynamically on the basis of the Förster cycle [36] by Eq. (1), in which *T* is temperature (298 K) and v_B and v_{HB} are pure 0–0 transitions in cm⁻¹ for the deprotonated and the protonated forms, respectively. In practice, v_B and v_{HB} are often difficult or even impossible to obtain. A good approximation is to use the emission maxima for v_B and v_{HB} since the protonation equilibrium is almost certainly established between the ³MLCT states [37].

$$pK_{a}^{*} = pK_{a} + (0.625/T)(v_{B} - v_{HB})$$
(1)

Therefore, for the Ru(II) complex **5**, by using the emission band maxima of both deprotonated and protonated species studied for $v_{\rm B}$ and $v_{\rm HB}$ in Eq. (1), two excited state ionization constants $pK_{\rm a}^*$ values of $pK_{\rm a1}^*$ = 4.54 and $pK_{\rm a2}^*$ = 7.71 were obtained.

4. Conclusions

In summary, a series of transition metal complexes with 2-(3',5'dimethoxybiphenyl-4-yl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline as ligand have been synthesized and fully characterized. The luminescence of complexes **1** and **5** emit cyan/orange luminescence at 485 and 600 nm in CH₃CN solution respectively, while the other complexes quench luminescence. The Zn(II) and Ru(II) complexes, in CH₃CN/Britton–Robinson (BR) buffer (1:1, v/v) were found to exhibit two separated protonation/deprotonation steps in ground and excited states, respectively, and act as on–off–on type emission switches. They have potential utility as a chemical sensor to detect pH variations of external environment due to their interesting photon-dependent photophysical properties.

Acknowledgement

This work was supported by National Science and Technology of Major Project (2009ZX02039101-02).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.11.049.

References

- [1] P. Goswami, D.K. Das, J. Lumin. 131 (2011) 760.
- [2] A.P. de Silva, K.C. Loo, B. Amorelli, S.L. Pathirana, M. Nyakirang'ani, M. Dharmasena, S. Demarais, B. Dorcley, P. Pullay, A. Salih, J. Mater. Chem. 15 (2005) 2791.
- [3] Y. Shiraishi, R. Miyamot, T. Hirai, Tetrahedron Lett. 48 (2007) 6660.
- [4] S. Xiao, T. Yi, Y. Zhou, Q. Zhao, F. Li, C. Huang, Tetrahedron 62 (2006) 10072.
- [5] F. Cheng, N. Tang, J. Chen, F. Wang, L. Chen, Inorg. Chem. Commun. 14 (2011) 852.
- [6] T. Gunnlaugsson, J.P. Leonard, K. Snchal, A.J. Harte, J. Am. Chem. Soc. 125 (2003) 12062.
- [7] P. Pallavicini, V. Amendola, C. Massera, E. Mundum, A. Taglietti, Chem. Commun. (2002) 2452.
- [8] F. Liu, K. Wang, G. Bai, Y. Zhang, L. Gao, Inorg. Chem. 43 (2004) 1799.
- [9] F. Cheng, N. Tang, J. Chen, F. Wang, L. Chen, Inorg. Chem. Commun. 13 (2010) 757.
- [10] F. Cheng, N. Tang, Inorg. Chem. Commun. 11 (2008) 506.
- [11] S.H. Fan, A.G. Zhang, C.C. Ju, L.H. Gao, K.Z. Wang, Inorg. Chem. 49 (2010) 3752.
- [12] M.J. Han, L.H. Gao, Y.Y. Lü, K.Z. Wang, J. Phys. Chem. B 110 (2006) 2364.
- [13] L. Xu, P.X. Liu, G.L. Liao, X. Chen, H. Chao, L.N. Ji, Aust. J. Chem. 63 (2010) 700.
- [14] J. Gao, Z.P. Wang, C.L. Yuan, H.S. Jia, K.Z. Wang, Spectrochim. Acta, Part A 79 (2011) 1815.
- [15] W. Paw, R. Eisenberg, Inorg. Chem. 36 (1997) 2287.
- [16] R.M. Rosen, D.A. Wilson, C.J. Wilson, M. Peterca, B.C. Won, C. Huang, L.R. Lipski, X. Zeng, G. Ungar, P.A. Heiney, V. Percec, J. Am. Chem. Soc. 131 (2009) 17500.
- [17] H. Chao, R.H. Li, C.W. Jiang, H. Li, L.N. Ji, X.Y. Li, J. Chem. Soc., Dalton Trans. 1 (2001) 1920.
 [20] M. M. M. K.Z. Magar, J. Dam, Chem. P. 112 (2002) 11020.
- [18] Y.Z. Ma, H.J. Yin, K.Z. Wang, J. Phys. Chem. B 113 (2009) 11039.
- [10] J.Z. Wu, B.H. Ye, L. Wang, L.N. Ji, J.Y. Zhou, R.H. Li, Z.Y. Zhou, J. Chem. Soc., Dalton Trans. (1997) 1395.
- [20] L.F. Tan, X.H. Liu, H. Chao, L.N. Ji, J. Inorg. Biochem. 101 (2007) 56.
- [21] S. Vidhisha, K.L. Reddy, K.A. Kumar, Y.P. Kumar, S. Satyanarayana, Transition Met. Chem. 35 (2010) 1027.
- [22] D. Pomeranc, V. Heitz, J.C. Chambron, J.P. Sauvage, J. Am. Chem. Soc. 123 (2001) 12215.
- [23] C. Goze, J.C. Chambron, V. Heitz, D. Pomeranc, X.J. Salom-Roig, J.P. Sauvage, A.F. Morales, F. Barigelletti, Eur. J. Inorg. Chem. 20 (2003) 3752.
- [24] D. Martineau, M. Beley, P.C. Gros, S. Cazzanti, S. Caramori, C.A. Bignozzi, Inorg. Chem. 46 (2007) 2272.
- 25] X. Duan, Y. Li, S. Zang, C. Zhu, Q. Meng, CrystEngComm 9 (2007) 758.
- [26] C. Girardot, G. Lemercier, J.C. Mulatier, J. Chauvin, P.L. Baldeck, C. Andraud, Dalton Trans. 31 (2007) 3421.
- [27] C. Goze, C. Sabatini, A. Barbieri, F. Barigelletti, R. Ziessel, Eur. J. Inorg .Chem. (2008) 1293.
- [28] Ö.A. Bozdemir, O. Büyükcakir, E.U. Akkaya, Chem. Eur. J. 15 (2009) 3830.
- [29] Z. Xu, Y. Xiao, X. Qian, J. Cui, D. Cui, Org. Lett. 7 (2005) 889.
- [30] R. Mithun, P. Biswarup, K.P. Ashis, D.J. Eluvathingal, N. Munirathinam, R.C. Akhil, Inorg. Chem. 46 (2007) 11122.
- [31] J.C. Philip, P. George, A.B. Christos, Bioorg. Med. Chem. 17 (2009) 6054.
- [32] D.I. Simone, C.A.L. Francisco, B.F.S. Albérico, R.S. Andreza, C.T. Antônio, F.S.D.
- Juliana, S.L. Benedito, M.C. Rose, Inorg. Chem. 46 (2007) 5744.
 [33] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, Coord. Chem. Rev. 84 (1988) 85.
- [34] R.H. Fabian, D.M. Klassen, R.W. Sonntag, Inorg. Chem. 19 (1980) 1977.
- [35] J.M. Kelly, C. Long, C.M. O'Connell, J.M. Vos, H.A. Tinnemans, Inorg. Chem. 22 (1983) 2818.
- [36] E.V. Donckt, Progress in Reaction Kinetic, fifth ed., Pergamon Press, Oxford, England, 1970 (Ed.: G. Poter).
- [37] G.Y. Zheng, Y. Wang, D.P. Rillema, Inorg. Chem. 35 (1996) 7118.