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pH responsive "off–on–off" luminescent switch of a novel ruthenium(II) complex $[Ru(bpy)_2(pipipH_2)]^{2+}$

Feng Gao [a,b], Hui Chao [a,c,*], Feng Zhou [a], Bin Peng [a], Liang-Nian Ji [a,b,*]

[a] *Key Laboratory of Bioinorganic and Synthetic Chemistry of Ministry of Education, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, XiGang XiLu 135#, Guangzhou 510275, China*
[b] *Department of Chemistry, Tongji University, Shanghai 200092, China*
[c] *State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China*

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Abstract

A novel ruthenium(II) complex, $[Ru(bpy)_2(pipipH_2)](ClO_4)_2 \cdot H_2O$ (1) ($pipipH_2$ = 2-(4-(1*H*-phenanthro[9,10-*d*]imidazol-2-yl)phenyl)-1*H*- imidazo[4,5-*f*][1,10] phenanthroline, bpy = 2,2′-bipyridine) has been found to act as a luminescent pH switch with extraordinary sensitivity through protonation and deprotonation of the bis-imidazole-containing ligand $pipipH_2$ in aqueous solution at room temperature.

Keywords: Ruthenium(II) complex; Protonation; Deprotonation; Luminescent pH switch

Molecular systems that respond to external stimuli have received much attention in recent years in connection with the design of molecular switches and molecular machines [1,2]. Transfer of protons can be regarded as one of the simplest chemical signals. Many life processes, such as enzymes, operate within a very narrow pH window, where their function or activity can be described as being "*on/off* switching" as a function of pH [3]. Attempts to mimic such "*off–on–off*" or "*on–off–on*" behavior by constructing luminescence devices that are modulated by a single *input*, e.g., pH, is of current interest [4–6]. However, it is noticed that this activity has primarily focused on organic molecules. Investigations of transition metal complexes have attracted much less attention, and their vast potential as pH sensors remains largely untapped. Recently, ruthenium complexes have received considerable attention as pH sensors due to their long excited-state lifetime and high luminescence quantum yield [7–11]. In our previous study, a dinuclear ruthenium(II) complex was developed to act as the pH sensor in which "*off–on–off*" luminescent switching can achieve via the protonation/deprotonation of imidazole-containing ligand [11]. As part of an ongoing systematic study aimed at the construction of sensitive pH-induced luminescent sensors and pH luminescent switches and the exploration of the underlying mechanism, we presented here the synthesis and pH luminescent switch properties of a mononuclear ruthenium(II) complex, $[Ru(bpy)_2(pipipH_2)](ClO_4)_2 \cdot H_2O$ (1), in which organic fluorescent group phenanthrene was introduced at one terminal with the aim of extending the π-electron systems and increasing the energy gap between the luminescent levels. As expected, complex **1** was found to be fully reversible pH controlled "*off–on–off*" luminescent signaling.

The synthesis of complex **1** was achieved as shown in Scheme 1. The ligands were synthesized on the basis of the method for imidazole ring preparation established by Steck and Day [12]. 2-(4-formylphenyl)imidazo-[4,5-*f*]

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[*] Corresponding authors. Address: Key Laboratory of Bioinorganic and Synthetic Chemistry of Ministry of Education, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, XiGang XiLu 135#, Guangzhou 510275, China. Fax: +86 20 84035497.
E-mail addresses: ceschh@mail.sysu.edu.cn (H. Chao), cesjln@mail.sysu.edu.cn (L.-N. Ji).

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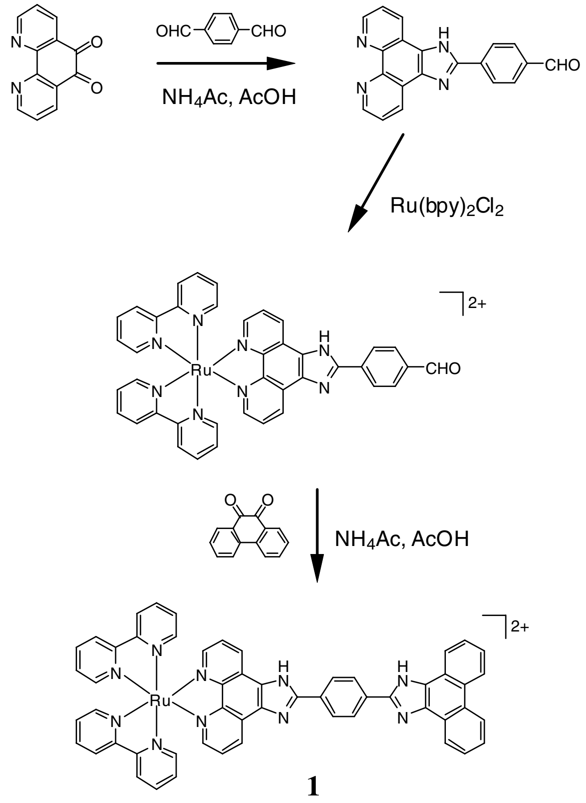

Scheme 1. Synthetic routines of Ru(II) complexes.

[1,10] phenanthroline (fmp) was obtained through condensation of 1,10-phenanthroline-5,6-dione with terephthalic aldehyde in refluxing glacial acetic acid containing ammonium acetate at a molar ratio of 1:1. The ligand pipipH_2 can be synthesized by the phenanthrene-9,10-dione with fmp. However, pipipH_2 is sparingly soluble in common organic solvents. Therefore, to prepare the complex **1**, we have carried out the condensation of phenanthrene-9,10-dione with the pre-coordinated fmp in $[Ru(bpy)_2(fmp)]^{2+}$ [13] as shown in Scheme 1. The product was purified by column chromagraphy on alumina with acetonitrile as eluent and characterized by ^{1}H NMR, ES-MS, IR, UV–Vis spectroscopy and elemental analyses.[1] (Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled in small quantity with care.)

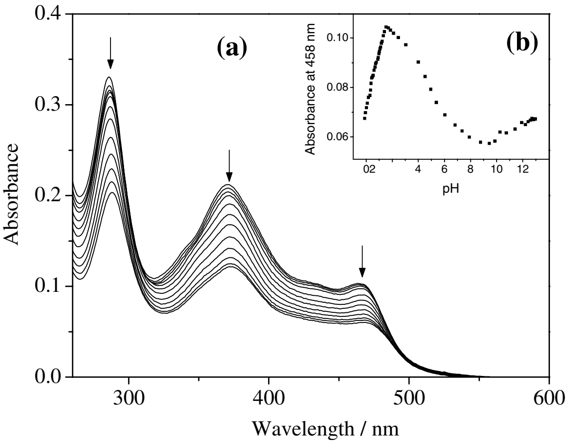

Fig. 1. The absorption spectra changes of complex **1** upon raising the pH. (a) Spectra changes in the range of 1.52–9.43. (b) The pH (0.08–12.96) effect on absorbance at 458 nm.

The pH dependence of the ground-state and excited-state properties of 1 were investigated using UV–Vis and luminescent spectra, respectively.[2] All spectral changes observed were reversible. Fig. 1a shows the changes of the UV–Vis spectra of complex **1** in the pH range 1.52–9.43 in aqueous Briton–Robinson buffer. An increase in pH causes a much more pronounced reduction in absorbance of the band at 286 nm (40%), 371 nm (43%) and the MLCT band at 464 nm (44%). The MLCT band displays a slight red shift (4 nm) with increasing pH. In the pH range of 0.08–1.52 and 9.43–12.96, the increase in pH causes significant increase in absorbance of all the three bands. The above spectral changes are attributed to the acid-base equilibria of complex 1 shown in Fig. 2. Three ground-state ionization constants obtained are $pK_{a1} = 0.6$, $pK_{a2} = 4.7$ and $pK_{a3} = 10.7$. The ligand pipipH_2 has two protonated sites and two deprotonated sites. The first protonation ($pK_{a2} = 4.7$), according to the spectral changes, should take place at the imidazole group of uncoordinated subunit. On the contrary, only the dissociation of the imidazole group in the coordinated subunit ($pK_{a3} = 10.7$) was observed in the pH range 0.08–12.96. This result is rationalized by the fact that the pK_a of the imino NH protons of free benzimidazole derivatives is usually around 14. Therefore, it shows clearly that in complex **1** the imidazole of the coordinated subunit is a stronger acid or a weaker base in comparison with that of the uncoordinated subunit. In the process of the luminescence titration, the emission spectra of complex **1** are strongly dependent on the buffer pH (Fig. 3) and three excited-state ionization constants are $pK^*_{a1} = 0.7$, $pK^*_{a2} = 5.4$ and $pK^*_{a3} = 11.4$. The emission intensity *vs.* pH profile of complex **1** (Fig. 3, inset), composed of three sigmoidal curves representing three separate processes, clearly shows the "*off–on–off*" switching process modulat-

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[1] *Selected data for complex 1*: Anal. Calcd for $C_{54}H_{36}N_{10}Cl_2O_8Ru \cdot H_2O$: C, 56.75; H, 3.35; N, 12.26. Found: C, 56.54; H, 3.41; N, 12.33%. ^{1}H NMR (ppm, DMSO-d_6): 14.12 (s, 1H), 13.85 (s, 1H), 9.10 (d, 2H, $J = 8.0$), 8.86 (d, 2H,$J = 8.0$), 8.83 (d, 2H,$J = 8.0$), 8.61 (t, 2H), 8.53 (d, 4H,$J = 8.0$), 8.21 (t, 2H), 8.10 (t, 2H), 8.00 (d, 2H,$J = 8.0$), 7.90 (d, 2H,$J = 8.0$), 7.86 (d, 2H, $J = 8.0$), 7.76 (q, 4H), 7.62 (m, 4H), 7.56(d, 2H), 7.36 (t,2H). ES-MS [CH_3CN, m/z]: 1025 ($[M-ClO_4]^+$), 924 ($[M-2ClO_4-H]^+$), 463 ($[M-2ClO_4]^{2+}$). ν_{max}/cm^{-1}: 3368w (br), 3075w, 1603 m, 1504 m, 1449 m, 1084vs (ClO_4), 851 s, 760 s, 724 m, 621 s. UV-Vis (CH_3CN): $\lambda_{max} = 459$ nm ($\varepsilon = 18800$ dm^3 mol^{-1} cm^{-1}), 382 (59200), 286 (82900).

[2] The UV–Vis and emission spectrophotometric pH titrations of the complex were investigated in aqueous Briton-Robinson buffer with 0.2 M NaCl to keep constant ionic strength in order to avoid any changes arising from a change in the environment of the medium.

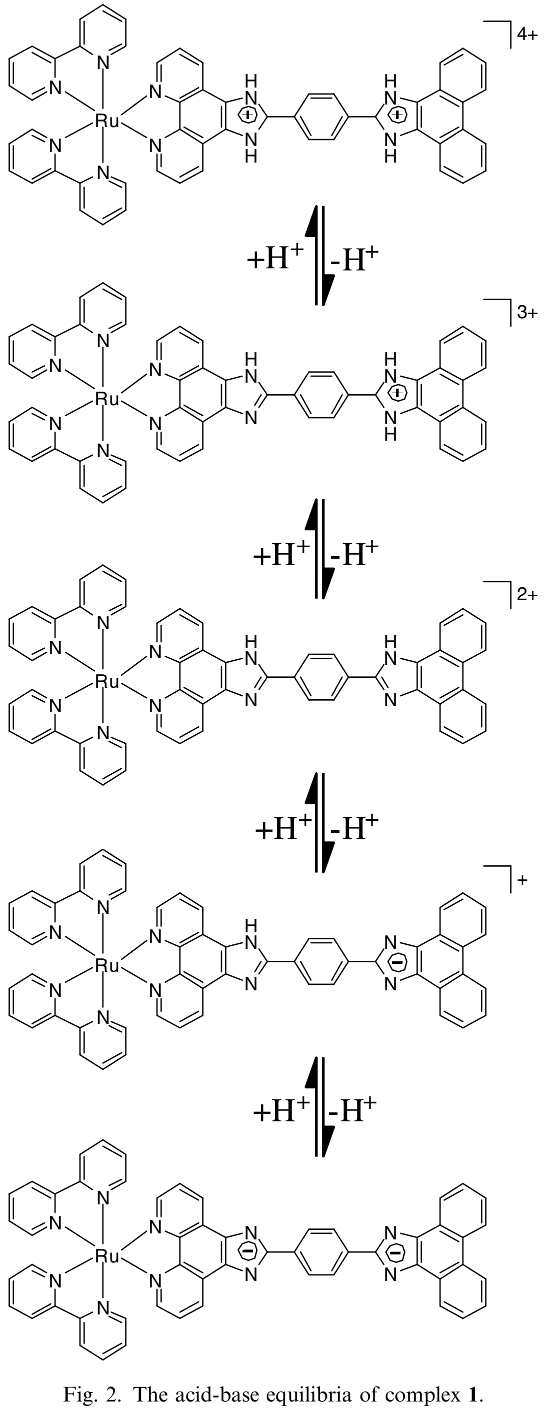

Fig. 2. The acid-base equilibria of complex **1**.

ing by pH value. In the first region, the emission intensity increases very sharply within the narrow range from pH 0.08 to 1.86, acting as a sensitive "*off–on*" switch with an emission enhancement factor of 2.6. The luminescence of complex **1** is quenched at a lower pH when the imidazole rings are protonated because the protonated species is a better electron acceptor than $[Ru(bpy)_3]^{2+}$ itself [14]. Contrastively, in the following two successive wider regions (1.86–10.25 and 10.25–12.96), the emission intensity decreases steadily to less than 2% of the original emission intensity, displaying the character of wide range pH

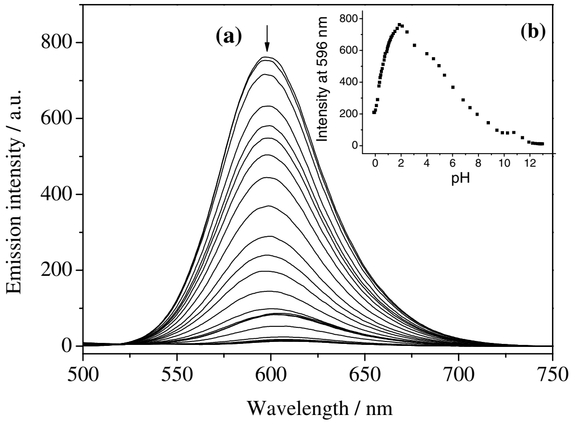

Fig. 3. The emission spectra changes of complex **1** upon raising the pH. (a) Spectra changes in the range of 1.86–12.96. (b) The pH (0.08–12.96) effect on emission intensity at 596 nm.

"*on–off*" light switch with a large luminescence on–off ratio of 65.3. This behavior may involve rapid radiationless decay [15]. It has been known that the energy of the metal-centered (MC) excited states depends on the ligand field strength, which in turn depends on the σ-donor and π-acceptor properties of the ligands [15]. The negative charge on the deprotonated imidazol substituent may be delocalized over the whole π framework, which decreases the σ-donor and increases the π-acceptor capacity of the pipipH$_2$ ligand, resulting in weakening of the ligand-field strength around the metal center and in turn lowering the metal σ^* orbitals [16–18]. Now we can see that, it is the introduction of pipipH$_2$ ligand that enables the complex **1** to act as not only a diprotic acid but also a diprotic base and displays an "*off–on–off*" luminescent switch depending on the solution pH.

In summary we have developed a novel mononuclear ruthenium(II) luminescence device that displays a clear and complete bell-shaped luminescent "*off–on–off*" switching as a function of pH in water through two different mechanisms, one involving luminescence quenching arising from the positive charge and the other originating rapid radiationless decay. Studies on the details of the mechanisms involved and design of new pH luminescent switches are in progress.

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References

[1] V. Bazani, F. Scandola, Supramolecular Photochemistry, Horwood, Chichester, 1991.

[2] V. Balzani, M. Venturi, A. Credi, Molecular Devices and Machines, Wiley-VCH, Weinheim, 2003.

[3] L. Stryer, Biochemistry, Freeman, New York, 1988.

[4] A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlangasson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 1515.

[5] T. Gunnlaugsson, J.P. Leonard, K. Sénéchal, A.J. Harte, J. Am. Chem. Soc. 125 (2003) 12062.

[6] Y. Diaz-Fernandez, F. Foti, C. Mangano, P. Pallavicini, S. Patroni, A. Perez-Gramatges, S. Rodriguez-Calvo, Chem. Euro. J. 12 (2006) 921.

[7] J.C. Ellerbrock, S.M. McLoughlin, A.I. Baba, Inorg. Chem. Commun. 5 (2002) 555.

[8] M. Haga, T. Takasugi, A. Tomie, M. Ishizuya, T. Yamada, M.D. Hossain, M. Inoue, Dalton Trans. (2003) 2069.

[9] F.R. Liu, K.Z. Wang, G.Y. Bai, Y.A. Zhang, L.H. Gao, Inorg. Chem. 43 (2004) 1799.

[10] M.J. Han, L.H. Gao, Y.Y. Lü, K.Z. Wang, J. Phys. Chem. B 110 (2006) 2364.

[11] H. Chao, B.H. Ye, Q.L. Zhang, L.N. Ji, Inorg. Chem. Commun. 2 (1999) 338.

[12] E.A. Steck, A.R. Day, J. Am. Chem. Soc. 65 (1943) 452.

[13] H. Chao, R.H. Li, C.W. Jiang, H. Li, L.N. Ji, X.Y. Li, J. Chem. Soc., Dalton Trans. (2001) 1920.

[14] R. Grigg, W.D.J.A. Norbert, J. Chem. Soc., Chem. Commun. (1992) 1300.

[15] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, Coord. Chem. Rev. 84 (1988) 85.

[16] R.H. Fabian, D.M. Klassen, R.W. Sonntag, Inorg. Chem. 19 (1980) 1977.

[17] J.M. Kelly, C. Long, C.M. O'Connell, J.G. Vos, H.A. Tinnemans, Inorg. Chem. 22 (1983) 2818.

[18] E.C. Constable, M.J. Hannon, A.M.W. Cargill Thompson, D.A. Tocher, J.V. Walker, Supramol. Chem. 2 (1993) 243.