

Off-on-off Luminescent Switching of a Novel Ru(II) Complex

Bin DONG¹, Ke Zhi WANG^{1*}, Lin Pei JIN¹, Li Hua GAO²

¹Department of Chemistry, Beijing Normal University, Beijing 100875

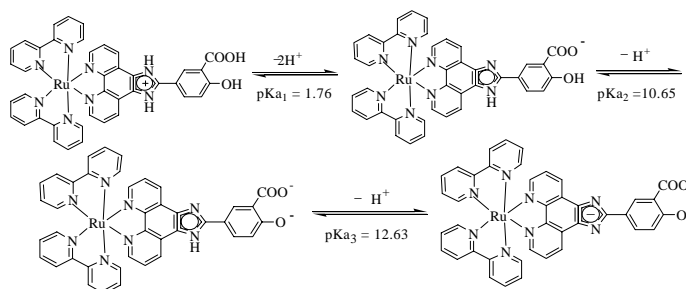
²College of Chemistry and Chemical Engineering, Beijing Technology and Business University, Beijing 100037

Abstract: UV-vis and luminescence spectroscopic titration experiments show that a novel Ru(II) complex exhibits off-on-off pH luminescent switching with a maximum on-off ratio of about 100.

Keywords: Ruthenium complex, pH-induced, luminescent switch.

There has been explosive interest in the synthesis and applications of novel Ru(II) polypyridyl complexes with respect to molecular sensors^{1,2}, switches³, and sensitizers of Grätzel solar cells based on nanocrystalline TiO₂⁴. Here we report a novel Ru(II) complex, which can serve as pH-induced remarkable off-on-off luminescent switch.

Scheme 1 The acid-base equilibria of the complex



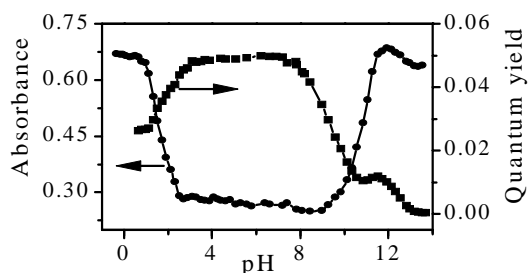
UV-vis absorption and emission spectroscopic pH titration experiments of the Ru complex with molecular structure shown in **Scheme 1** showed that the complex underwent three-step deprotonation processes upon raising pH from a strongly acidic solution of pH 0.67. The three step processes can be well illustrated in both the absorbance and the emission intensity vs. pH profiles shown in **Figure 1**.

The first step was assigned to the concurrent dissociation of the protons on the imino group (protonated cation) of the imidazole ring and on the carboxylic group since these two kinds of proton dissociation processes have been known to revive the Ru(II)

*E-mail: kzwang@bnu.edu.cn

complex emission^{5,6}. The second and third steps were ascribed to the deprotonations of the phenol group and the neutral imidazole ring. According to the reports, these two processes quench the Ru(II) complex emission^{5,7}. It is interesting to note that the complex can act as an off-on-off emission switch with a maximum on-off ratio (the ratio of the maximum emission quantum yield to the minimum one) of around 100, which is much more remarkable than the ratio of 5 of Ru(II) complex-based off-on-off switch⁵. The ratio is about 10 for bis (2,2'-bipyridyl) (5,5'-diaminomethyl-2,2'-bipyridyl) Ruthenium (II) and its analogues² and 6 for *p*-tert-butylcalix[4]arene-linked Ruthenium(II) trisbipyridyl complexes¹. The ground-state acidity constants⁶ were determined to be $\text{pK}_{\text{a}1} = 1.76$, $\text{pK}_{\text{a}2} = 10.65$ and $\text{pK}_{\text{a}3} = 12.63$, respectively, based on the inflection points of the absorption spectroscopic data in **Figure 1**.

Figure 1 Absorbance at 284 nm (circle) and fluorescence ($\lambda_{\text{ex}}=470$ nm) quantum yield (square) vs. pH profiles



In summary, the Ru (II) complex we synthesized was proved to be a promising sensing/switching material.

Acknowledgments

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