

Color responses of novel receptors for AcO^- and a test paper for AcO^- in pure aqueous solution

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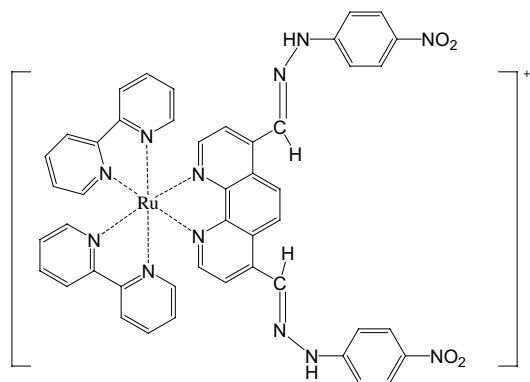
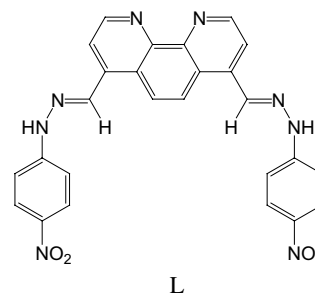
Abstract—An efficient AcO^- sensor L which contains 1,10-phenanthroline-based and nitrophenylhydrazine-based groups, and its water-soluble Ru(II) complex were synthesized, characterized and studied in this Letter. Via UV–vis experiments and ^1H NMR titration in DMSO solution, it was found that there were potential hydrogen bonds between the $\text{N}=\text{CH}$ and AcO^- after the deprotonation of two $-\text{NH}$ during the reaction of L or its Ru complex with anions. Furthermore, an easy-to-prepare test paper was developed to detect AcO^- at 10 mg/L in pure aqueous solution.

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The design and synthesis of efficient sensors that can recognize and sense anions selectively through the means of electrochemical and optical responses is currently an increasing field in supramolecular chemistry due to their important roles played in biological, industrial, and environmental process.¹ It is well known that amides,² (thio)ureas,³ ammonium,⁴ imidazole,⁵ and imidazolium⁶ are particularly effective in the reaction with anions through the formation of hydrogen bonds between the active N–H group and the anions, and there are many receptors of them with molecular clefts or cavities, which can discern anions with different geometries. Furthermore, with the strong inducement of the anions, proton transfer often takes place during the host–anion reactions.⁷ Compared with the F^- and H_2PO_4^- sensors, AcO^- sensors are limited for most of the AcO^- receptors usually have a stronger affinity for F^- . Here, we report an AcO^- sensor L which contains 1,10-phenanthroline-based and *p*-nitrophenylhydrazone-based groups, and its *cis*-Ru(bipy)₂²⁺ complex which have high selectivity for AcO^- . Moreover, based on the high selectivity and water-solubility of this Ru(II) complex, we prepare an AcO^- test paper for practical application.

This novel hydrozone L is synthesized by the 4,7-dicarbonylaldehyde-1,10-phenanthroline and *p*-nitrophenylhydrazine. As a good colorific group, *p*-nitrophenylhydrazone

is introduced for visual anion detection, moreover, the introduction of Ru containing group not only strengthens the affinity of the host with anions, but also makes it



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water-soluble and able to detect the anions in pure water. By the UV–vis experiments and the ^1H NMR titrations, it is observed that L and its Ru(II) complex have high selectivity for AcO^- with dramatic color changes: L has the color change from faint yellow to green, and the Ru complex has the color change from purple to green with the addition of AcO^- .

From an overall consideration of solubility and polarity, the UV–vis experiments of the hosts with anions were performed in DMSO solution at 298.2 ± 0.1 K. As shown in Figure 1 of L with different anions as TBA salts, the intensity of the absorption peak at 434 nm was remarkably decreased with a simultaneous growth of a new peak at 622 nm as the anion concentration increased, which was accompanied by the color change from yellow to green (Fig. 3). The spectral changes during the AcO^- addition was more obvious than that of

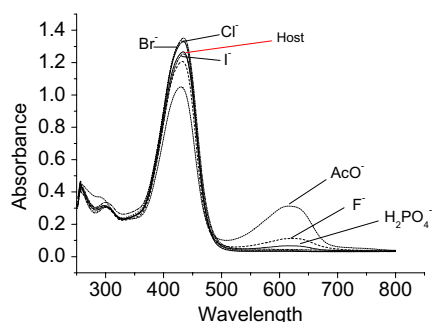


Figure 1. UV–vis titration of ligand L in DMSO (4×10^{-5} M) solution upon the addition of different anions (1×10^{-4} M).

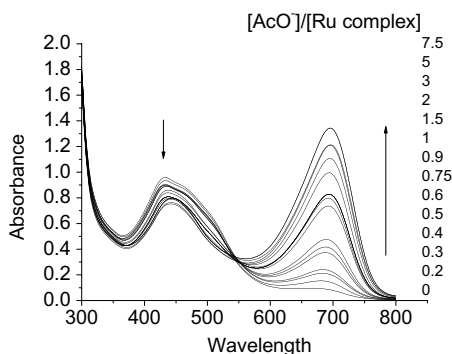


Figure 2. UV–vis titration of Ru complex in DMSO (4×10^{-5}) solution upon the addition of AcO^- as TBA salts.

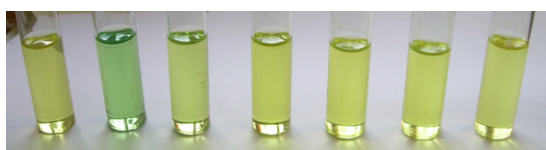


Figure 3. Color changes observed for L in DMSO solution (1×10^{-5} M) upon the addition of 10 mol equiv of anions as TBA salts. From left to right: host, host + AcO^- , host + F^- , Host + H_2PO_4^- , Host + Cl^- , host + Br, host + I^- .

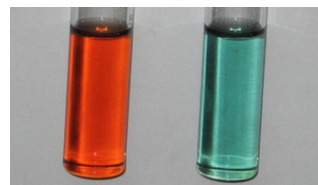


Figure 4. Color change of $\text{cis-Ru}(\text{bipy})_2^{2+}$ complex mixing (4×10^{-5} M) with AcO^- (4×10^{-5} M).

F^- and H_2PO_4^- . In addition, from Figure 2, the Ru complex titration with AcO^- exhibited a broad strong absorption peak at 430 nm with a shoulder at about 463 nm, which was assigned to the metal-to-ligand charge transfer (MLCT) of $\text{Ru}(\text{bipy})_2^{2+}$ moiety coupled with the *p*-nitrophenylhydrozone centered charge transfer (CT).⁸ Also, a new peak at 696 nm appeared and increased with the color change from purple to green (Fig. 4) upon the addition of AcO^- . The addition of basic anions such as F^- or H_2PO_4^- also triggered the similar but more weaker absorption spectral changes for the $\text{cis-Ru}(\text{bipy})_2^{2+}$ complex compared to AcO^- . However, other anions including Cl^- , Br^- , I^- did not cause noticeable spectral changes or color changes, even in the presence of a large excess of them. The job-plot experiments revealed that the L and its Ru(II) complex both reacted with the AcO^- to form 1:1 complexes (via a total concentration of 4.0×10^{-4} M). By nonlinear least-squares fitting⁹ at $\lambda_{\text{max}} = 696$ nm, the association constants K_a of L, Ru(II) complex with AcO^- are 3.91×10^4 , 8.96×10^5 , respectively, according to the following equation:

$$X = X_0 + (X_{\text{lim}} - X_0) \left\{ c_{\text{H}} + c_{\text{G}} + 1/K_a - [(c_{\text{H}} + c_{\text{G}} + 1/K_a)^2 - 4c_{\text{H}}c_{\text{G}}]^{1/2} \right\} / 2c_{\text{H}}$$

To further investigate the anion–sensor reaction mechanism, ^1H NMR titration was carried out. From Figure 5, before the 2 equiv of AcO^- was added, the peak of H_1 ($-\text{NH}$) was broad and appeared downfield, while other H_s did not show any obvious changes ($a \rightarrow b \rightarrow c$). Therefore, it showed that there was a hydrogen bond between $-\text{NH}$ and AcO^- . After two or

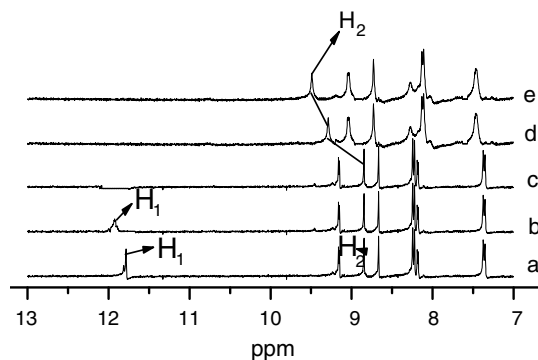


Figure 5. Partial ^1H NMR (400 MHz) spectra of host L (2×10^{-5} M) in $\text{DMSO}-d_6$ upon the addition of AcO^- . (a) Free, (b) 1 equiv of AcO^- , (c) 2 equiv of AcO^- , (d) 3 equiv of AcO^- , (e) 4 equiv of AcO^- .

more equiv of AcO^- were added, the $-\text{NH}$ -acetate resonance disappeared, instead, the peak of $\text{H}_2(-\text{CH})$ had now clearly downshifted (from 8.82 to 9.29 to 9.48 ppm, $c \rightarrow d \rightarrow e$) revealing at higher concentrations of acetate, the $-\text{NH}$ deprotonated. At the same time, the $-\text{N}=\text{CH}$ reacted with acetate to form a strong potential hydrogen bond (when deprotonation happened, the acetate and the acetic acid coexisted in the solution, surely the acetate was as a base to bind with the $-\text{CH}$ not the acetic acid). At last, the receptor reacts with the anions to form a 1:1 supramolecular complex (the job plots are given in the [Supplementary data](#)) in the DMSO solution. The whole reaction process was shown in [Figure 6](#). This phenomenon may be attributed to its basicity and geometry configuration to converge the two $-\text{NH}$ groups at a point via $-\text{NH}$ -anions hydrogen binding that required twisting the $-\text{CH}=\text{N}-\text{NHAr}$ groups substantially out of the plane of the phenanthroline ring, this results in some odd bond angles, such that the extended conjugation will be diminished, and the receptor cannot have such remarkably high affinities with only two NH hydrogen bond donor groups. On the contrary, with the two $\text{N}=\text{CH}$ as binding sites, the geometry will be more suitable for the formation of stable $\text{N}=\text{CH}$ -anions hydrogen bonds. Furthermore, it will make the electron deficient phenanthroline have more delocalization space. The $-\text{CH}$ had a chemical shift at 8.817 ppm which made it possible to bind with the basic anions. The angle of two oxygen atoms in triangular acetate is 120° , which allowed for a better matching of geometry between the two $\text{N}=\text{CH}$ compared to other anions such as F^- and H_2PO_4^- . The complexation of Ru in L will only act to intensify this effect, so the Ru complex had more association constants with anions than its ligand L.

It is generally accepted that receptors for anions based on hydrogen binding interactions cannot be served as efficient sensors in pure aqueous media for the strong protic solvent competition. When water was added into the DMSO solution of $\text{Ru}(\text{bipy})_2^{2+}$ complex with AcO^- , the green color faded and it indicated that the protic solvent water would compete with the anionic guest for the

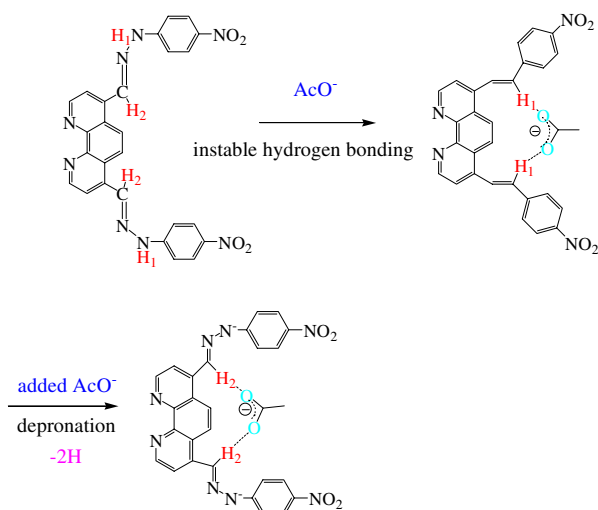


Figure 6. The proposed reaction mechanism of the receptor with AcO^- .

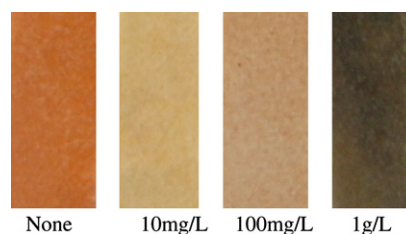


Figure 7. The color changes of the test papers for detecting acetate ion in neutral aqueous solution with different NaAcO concentrations.

binding sites of the receptors. For this reason, it cannot be an efficient sensor for anions in aqueous solution though it was water soluble. To avoid the competing solvent effect of the water, we prepared a test paper based on the water solubility of $\text{cis-Ru}(\text{bipy})_2^{2+}$ complex. (This test paper was made by putting a filter paper into the acetone solution of the Ru complex (10^{-4}M) for 24 h and then drying it in the air). This paper was then placed into acetate solution in water, dried it in the air to remove water gradually, which resulted in a color change in the paper. It can detect the presence of minute AcO^- in pure aqueous solution at 10 mg/L ([Fig. 7](#)). To our knowledge, there are many traditional methods such as ^{19}F NMR spectroscopy for detecting F^- and other anion recognitions were taken in a mixed solution of water and an organic solvent. However, there are few simple methods or instruments to detect AcO^- in pure aqueous solution, we hope that this interesting and easy-to-prepare test paper will be extensively applicable in daily life.

In a word, a new hydrozone L and its water-soluble $\text{cis-Ru}(\text{bipy})_2^{2+}$ complex as the colorimetric anion sensors were synthesized, characterized and studied in this Letter, they both have high selectivity for AcO^- than other anions such as H_2PO_4^- , F^- , Cl^- , Br^- , I^- . Furthermore, an interesting and easy-to-prepare test paper of $\text{cis-Ru}(\text{bipy})_2^{2+}$ complex for the detection of AcO^- in pure aqueous solution was developed for detecting AcO^- in aqueous solution. This test paper successfully resolves the competition of water-guest for the binding sites. We hope that this test paper will be put into use in the future.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2007.10.034](https://doi.org/10.1016/j.tetlet.2007.10.034).

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