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Bichromophoric Rhodamine–Iridium(III) Sensory System: Modulation of the Energy-Transfer Process through a Selective Sensing Behavior

Chunyan Wang and Keith Man-Chung Wong*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, People's Republic of China

Supporting Information

ABSTRACT: A newly designed bichromophoric rhodamine–iridium(III) system was found to show color/electronic absorption spectral changes and modulation of the energy-transfer process from rhodamine 6G to the iridium(III) luminophore upon selective Hg^{II} ion binding.

Since the first preparation of rhodamine in 1905,[1] rhodamine-based dyes have been widely used as fluorophoric and chromophoric probes in the past several decades.[2−5] Many derivatives of rhodamine are known to exist in two constitutional isomers with completely different spectroscopic properties in equilibrium,[5] in which the ring-closed spirolactam form is colorless and nonfluorescent while the ring-opened amide form displays an intense pink to red color and strong fluorescence. From the inspiration of the pioneering work of Czarnik and coworkers,[6] who utilize the ring-opening process of a rhodamine B hydrazide as a fluorescent chemosensor to selectively sense Cu^{2+} cation, various rhodamine-based turn-on fluorescent probes for metal cations or analytes of interest have been reported in the past few years.[7−12]

Although there are a few reports on the combination of the rhodamine sensing unit with another organic chromophore or luminophore, such as dansyl,[12a,b] pyrene,[12c] BODIPY,[12d,e] and 1,8-naphthalimide[10d] moieties, in a single molecule, to the best of our knowledge, the related construction of a bichromophoric array through the incorporation of a luminescent transition-metal complex into a rhodamine derivative with sensory functionality is relatively unexplored. The cyclometalated iridium(III) or polypyridyliridium(III) system has gradually become an important class of luminescent transition-metal complexes in recent years,[13,14] because of their wide tunability of the emission energy, less thermally accessible ^{3}MC state, high electrochemical reversibility, synthetic versatility, photostability, and chemical stability. As an extension of our interest in the design of luminescent chemosensors based on various transition-metal complexes,[15,16] herein we report the design and synthesis of a novel class of bichromophoric sensory assemblies, **1** and **2** (Scheme 1), from the combination of a rhodamine sensing derivative and luminescent cyclometalated iridium(III) complex. Their photophysical selective metal cation sensing behaviors and energy-transfer properties have also been investigated.

The rhodamine derivatives containing bidentate ligands, **L1** and **L2**, were prepared from the condensation reaction of 4-carboxaldehyde-4′-methyl-2,2′-bipyridine with rhodamine 6G hydrazide[11b] and rhodamine 6G ethylamine,[9c] respectively. The reaction of **L1** and **L2** with 0.5 equiv of a dinuclear iridium(III) precursor complex, $Ir_2(dpqx)_4Cl_2$ (dpqx = 2,3-diphenylquinoxaline),[14b] followed by metathesis with NH_4PF_6 afforded the bichromophoric rhodamine–iridium(III) derivatives, $[Ir(dpqx)_2(\mathbf{L1})]PF_6$ (**1**) and $[Ir(dpqx)_2(\mathbf{L2})]PF_6$ (**2**), in reasonable yield (Scheme 1).

The electronic absorption spectra of **1** and **2** in methanol at 298 K exhibit intense high-energy absorption bands at 298 and 366 nm and a less intense low-energy absorption band at 472 nm (Figure S1 in the Supporting Information). With reference to the spectroscopic studies of the other related iridium(III) 2,3-quinoxalinato complexes,[14] the low-energy absorption band is ascribed to a spin-allowed metal-to-ligand charge-transfer (MLCT) $[d\pi(Ir) \rightarrow \pi^*(dpqx)]$ transition. On the other hand, the weak shoulder that occurred beyond 500 nm is tentatively assigned as a spin-forbidden ^{3}MLCT transition, resulting from the spin–orbit coupling of an iridium(III) heavy atom. Upon excitation at 365 nm, complexes **1** and **2** in methanol at 298 K are found to show an intense emission band at 675 nm (Figure S1 in the Supporting Information), which is ascribed to the triplet excited state of MLCT $[d\pi(Ir) \rightarrow \pi^*(dpqx)]$ origin. Similar emission bands were also observed in the related iridium(III) 2,3-quinoxalinato complexes[14] (622−670 nm) and the rhodamine derivative-free model complex, $[Ir(dpqx)_2$(4-carboxaldehyde-4′-methyl-2,2′-bipyridine)$]PF_6$ (675 nm; Figure S2 in the Supporting Information). The observation of a rather weak emission at 550 nm characteristic of rhodamine 6G in **1** is probably due to the existence of the open form of rhodamine 6G in a trace amount, as a result of equilibrium or the sensitivity of the imine linker to hydrolysis.

The selective binding properties of **1** and **2** were investigated for various alkali and alkaline-earth as well as transition-metal cations, such as K^+, Na^+, Li^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Fe^{2+}, Cu^{2+}, and Hg^{2+}. Solutions of **1** and **2** in methanol exhibit drastic color changes from pale yellow to magenta selectively in the presence of a Hg^{II} ion, while only a pale-orange color was observed for the Cu^{II} ion (Figure 1), indicating that **1** and **2** can serve as a "naked-eye" indicator for the Hg^{II} ion.

Electronic absorption titration studies of **1** and **2** showed that a new absorption band at 530 nm emerges with an increase in the concentration of Hg^{II} ions in a methanol solution. The electronic absorption spectral changes of **1** in methanol upon the addition of a Hg^{II} ion are illustrated in Figure 2 (left) (Figure S3 in the Supporting Information for **2**), and the emergence of the absorption band at 530 nm is responsible for the magenta color

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Scheme 1. Synthetic Route of 1 and 2

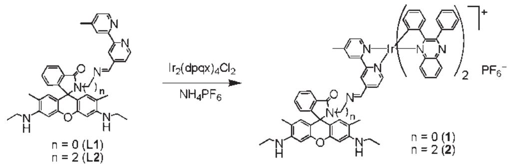

Figure 1. Photograph of **1** (8.38 μM in MeOH) showing the color change in the presence of various cations (40 equiv).

change. An interference experiment has been performed to examine the selectivity of **1**. Almost the same response was observed for the solution containing the same concentration of Hg^{II} ions and other metal cations (Figure S4 in the Supporting Information), indicative of the high selectivity of **1** toward the Hg^{II} ion. A similar absorption band was also observed upon the addition of acid to **1** and **2** (Figures S5 and S6 in the Supporting Information). In view of the fact that ring opening of the spirolactam of rhodamine derivatives is commonly induced by protonation,[7a] the observation of similar electronic absorption spectral changes clearly suggests conversion of the spirolactam form to the corresponding ring-opened amide upon the addition of acid and a Hg^{II} ion. The close resemblance of the experimental data to the theoretical fit is supportive of the binding mode of 1:1 stoichiometry [Figure 2 (left, inset)]. This 1:1 complexation mode has been further confirmed by the method of continuous variation showing a break point at a $[\mathbf{1}]/([\mathbf{1}] + [Hg^{2+}])$ mole fraction of 0.5 (Figure S7 in the Supporting Information). The log K_s values for Hg^{II} ion binding to **1** and **2** were found to be 4.55 (±0.09) and 3.63 (±0.04), respectively. The addition of an equimolar concentration of ethylenediaminetetraacetic acid to the solution mixture of **1** or **2** and Hg^{II} ion in methanol resulted in a color change from magenta back to the original pale-yellow color, suggesting that the Hg^{II} ion-induced ring-opening process of the rhodamine derivative is reversible in the present chemosensing system.

Emission titration experiments with a Hg^{II} ion or acid in methanol at room temperature were performed to investigate the change in the emission response of **1** to the ring opening of the rhodamine derivative. Upon excitation at the isosbestic wavelength of 365 nm, the emission intensity ratio of iridium(III)-based MLCT at 675 nm to rhodamine 6G at 555 nm was increased upon an increase in the concentration of Hg^{II} ions [Figure 2 (right)] or acid (Figure S8 in the Supporting Information). A log K_s value of 4.58 (±0.16) was obtained for binding of a Hg^{II} ion to **1** [Figure 2 (right, inset)]. The good agreement of this value with that obtained from the electronic absorption titration studies suggests that the emission enhancement of the iridium(III) luminophore is ascribed to the ring opening of the rhodamine derivative, similar to the electronic absorption spectral changes.

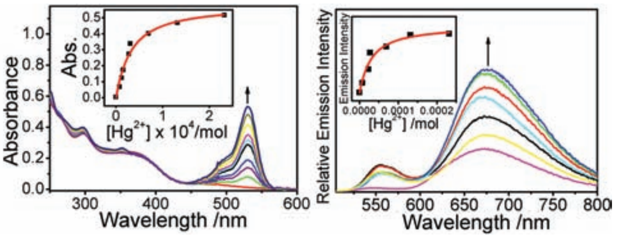

Figure 2. Electronic absorption (left) and corrected emission spectra of **1** in methanol (concentration = 8.12 μM) at 298 K upon the addition of various concentrations of Hg^{2+}. Insets show the plot of the absorbance at 530 nm (left) and the emission intensity (right) as a function of the concentration of Hg^{2+} with a theoretical fit.

It is interesting to note that complex **1** with the open form of rhodamine 6G exhibited an about 52-fold enhancement of iridium(III) emission at 675 nm (Figure S9 in the Supporting Information) upon excitation at 520 nm. In view of the fact that the rhodamine 6G donor absorbs strongly at 520 nm upon ring opening, the huge emission enhancement is mainly due to an efficient intramolecular energy-transfer process from rhodamine 6G to the cyclometalated iridium(III) moiety. Upon ring opening of rhodamine 6G, an intense excitation band at 530 nm in the excitation spectrum of **1**, monitored at the iridium(III) emission of 675 nm, emerged that was found to closely resemble the characteristic rhodamine 6G absorption band (Figure S8 in the Supporting Information, inset). This result further supports the occurrence of an efficient intramolecular energy-transfer process from rhodamine 6G to the iridium(III) luminophore upon ring opening of the rhodamine derivative. The observation of a less efficient energy transfer upon Hg^{II} ion binding, relative to the case in protonation, suggests the possibility of triplet relaxation, resulting from the heavy-atom effect upon Hg^{II} ion binding.

Complex **1** represents the first example with efficient energy transfer from a rhodamine donor to a luminescent transition-metal complex and such an energy-transfer process could be modulated by the ring opening of rhodamine 6G through the selective binding of Hg^{II} ions. In the present study, the luminescent cyclometalated iridium(III) chromophore in **1** is employed as an energy acceptor to report the sensing signal transmitted from the rhodamine derivative, which serves as a selective receptor as well as a latent energy donor. Furthermore, rhodamine 6G absorbs strongly at about 530 nm, resulting in a shift of the excitation of the iridium(III) luminophore to lower energy being possible (Figure S9 in the Supporting Information). No observable color or spectral changes of **1** were obtained upon the addition of a Hg^{II} ion in a solution mixture of EtOH−H_2O (1:1, v/v) or in a MeCN−H_2O mixture (10 mM HEPS, pH 7.0, 50% MeCN), indicative of the difficulty for the operation in the aqueous and/or aqueous−organic media.

In contrast, the emission spectra of **2** upon the addition of acid showed that the emission of rhodamine 6G was substantially enhanced, with no observable change in the emission intensity of the iridium(III) luminophore (Figure S9 in the Supporting Information), indicative of insignificant energy transfer from rhodamine 6G. Such an inefficient energy transfer in **2** is ascribed to the introduction of an ethyl group as a nonconjugated linker between rhodamine 6G and the iridium(III) luminophore. The discrepancy between the log K_s values obtained in **1** and **2** in the electronic absorption titration studies is ascribed to the difference in the separation distance of the amide group from the nitrogen atom on the imine unit, which is anticipated to participate in the binding process of the Hg^{II} ion. A higher concentration of Hg^{II} ions is required in **2** (Figure S3 in the Supporting Information), relative to **1**, to reach saturation in the electronic absorption titration studies, which is indicative of the lower binding affinity of **2** for the Hg^{II} ion, in accordance with the lower log K_s value obtained in **2**. Although **1** and **2** showed similar color and electronic absorption spectral changes upon ring opening of the same rhodamine derivative, the difference in their emission responses demonstrates that such an energy-transfer process could be regulated by the judicious design of the rhodamine-containing ligand.

In conclusion, a novel system of a bichromophoric chemosensor, with hybridization of the organic fluorophoric rhodamine sensing derivative and the luminescent cyclometalated iridium(III) complex, has been designed and synthesized. Selective Hg^{II} ion-sensing properties have been studied to show color/electronic absorption spectral changes. More importantly, such Hg^{II} ion binding has been found to modulate the energy-transfer process from rhodamine 6G to the iridium(III) luminophore upon ring opening of rhodamine 6G. As a "proof-of-principle" concept, the present result may open up new avenues for the fundamental understanding of the photophysical and selective sensory behaviors and the design of a new chemosensor system with hybridization of the organic fluorophoric rhodamine and the luminescent transition-metal complex.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details include syntheses and characterizations, photophysical spectra of **1**, and other electronic absorption and emission spectral changes of **1** and **2** upon the addition of a Hg^{II} ion and acid. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wongmc@hku.hk.

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