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PAPER

Versatile trifunctional chemosensor of rhodamine derivative for Zn^{2+}, Cu^{2+} and His/Cys in aqueous solution and living cells†

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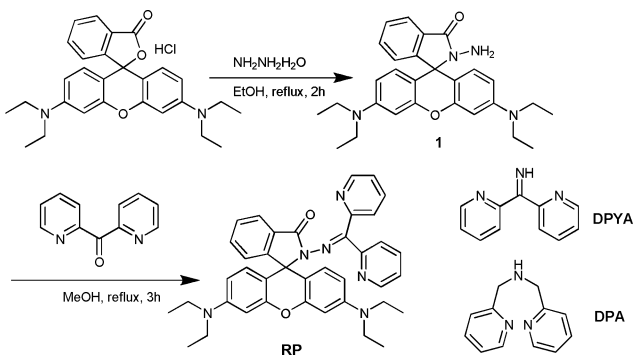
On the basis of rhodamine, a versatile trifunctional chemosensor **RP** has been synthesized. It can selectively and sensitively recognize Cu^{2+} and Zn^{2+} in different solutions. Based on the zinc-containing [**RP**@Zn^{2+}] complex, it shows highly selective recognition for His/Cys. Fluorescent imaging of Zn^{2+} in living cells was also obtained.

In the past few years, considerable attention has been devoted to the development of fluorimetric and/or colorimetric chemosensors for selective and sensitive detection of heavy transition metal (HTM) ions,[1] because these ions play important roles in environmental, biological and chemical systems. Among the various essential HTM ions, zinc and copper are the second and third most abundant of the essential nutrients required for normal cell growth and development, and they play a critical role in metabolic processes.[2] However, as well as deficiency of these ions, ion overload can also result in a variety of diseases, such as Parkinson's, epileptic seizures and renal and liver damage.[3]

Besides HTM, we are also concerned about the physiological action of amino acids. As the essential component of many proteins, histidine (His) and cysteine (Cys) play a crucial role in living systems.[4] The deficiency of histidine in plasma may lead to an impaired nutritional state in patients with chronic kidney disease and the deficiency of cysteine may lead to many conditions such as a hematopoiesis decrease, slow growth, hair depigmentation, leucocyte loss, psoriasis and so on.[5] Therefore, the development of sensitive and selective chemosensors for zinc, copper, His or Cys is necessary and indispensable. To date, there are many reported fluorimetric and/or colorimetric chemosensors for zinc,[6] copper[7] and cysteine,[8] respectively. However, relatively few examples of chemosensors for histidine have been reported.[9] Similarly, rarely have bifunctional chemosensors for both Zn^{2+} and Cu^{2+} been reported,[10] and their properties have been investigated only in organic solvents. Recently, Liu[11] reported a bifunctional sensor that can recognise Zn^{2+} and Cu^{2+} in a buffer solution (containing 50% CH_3CN as a co-solvent).

High sensitivity and specificity is usually the primary concern when designing a metal ion sensor, so chemists have taken many possible parameters into consideration to improve selectivity and specificity. However, in fact, a real tested sample usually contains multiple heavy metal ions, and the chemosensor is sensitive to the environment. Based on this, if we can design a multifunctional chemosensor by modulating the selectivity to various metal ions with a change in media, it would be interesting and more convenient for real applications. Recently, Hu[12] reported a probe that can selectively detect Pb^{2+} and Hg^{2+} by varying the ratios of CH_3CN to water. Wang and Peng[12] reported a probe that can selectively detect Au^{3+} and Hg^{2+} in different aqueous solutions. Xu and Qian[13] developed two fluorescent probes, which can selectively recognise Cd^{2+}, Hg^{2+} and Pb^{2+} *via* judicious choice of aqueous buffer solutions.

Herein, we report a novel chemosensor **RP** that uses rhodamine as the fluorophore and dipyridin-2-ylmethanimine (DPYA) as the receptor. The **RP** sensor was readily synthesized from rhodamine B (see Scheme 1 and Section 2 of the ESI†). The structure of **RP** was verified by ^1H NMR, ^{13}C NMR and HRMS (Fig. S1, ESI†).



Scheme 1 Synthesis of **RP** and structures of **DPYA** and **DPA**.

As a rhodamine B derivative with a spirolactam group, the free **RP** remained colorless and did not exhibit apparent absorption above 500 nm in DMSO/H_2O (v/v = 10 : 1, 2 mM Tris-HCl, pH 7.8). Upon addition of Cu^{2+} (2.0 equiv.) to a solution of **RP** in DMSO/H_2O, the absorption at around 563 nm was significantly enhanced, along with an obvious color change from colorless to purple and this indicated that the spirolactam form was

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opened. However, under the same conditions, there was almost no enhancement of the absorption at around 563 nm in the presence of 2.0 equivalent of the other tested ions, and all solutions were still colorless (Fig. 1). Upon addition of Cu^{2+} to the solution of **RP**, the spirolactam form was opened, but no enhancement of fluorescence was observed, we supposed the fluorescence was quenched due to the well-known paramagnetic effect of Cu^{2+}.[14] Therefore, **RP** was a highly selective colorimetric "naked eye" probe for Cu^{2+} in DMSO/H_2O (v/v = 10 : 1, 2 mM Tris-HCl, pH 7.8).

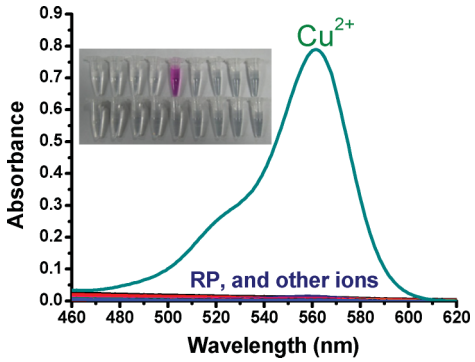


Fig. 1 UV-Vis absorption spectra and photographs of **RP** (10 μM) in the presence of various metal ions (20 μM) in DMSO/H_2O (v/v = 10 : 1, 2 mM Tris-HCl, pH 7.8). Inset: from left to right, then from top to bottom: **RP**, and **RP** with Co^{2+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, Cr^{3+}, Cd^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Ni^{2+}, Ba^{2+}, K^+, Li^+, Ag^+.

As we know, di-2-picolylamine (DPA) is not only used as the receptor for Cu^{2+} fluorescent probes,[7j] but is usually used as the receptor for Zn^{2+} fluorescent probes.[6d,h,k] Considering the structural similarity of DPA with DPYA, we thought DPYA could bind with Zn^{2+} also. On the other hand, the selectivity of rhodamine-based chemosensors for ions was remarkably affected by the solvent,[12a,15] so further investigations of the selectivity of **RP** in other media were also carried out.

RP is also nearly colorless and non-fluorescent in ethanol/water due to its stable spirolactam form. Upon addition of Zn^{2+} to a solution of **RP** in ethanol/water, an instantaneous change from nearly colorless to pink and significant enhancement of fluorescence with an emission maximum at 581 nm was observed (Fig. 2); the results clearly indicated that the spirolactam form was opened. Fig. 2 showed that addition of Cd^{2+} induced a slight increase in fluorescent intensity, *ca.* 10% compared to Zn^{2+}. The other ions produced minor changes in the fluorescence spectra. Therefore, this interesting feature revealed that **RP** was also a highly selective fluorescent probe for Zn^{2+} in ethanol/water solution.

Based on the aforementioned results, we predicted that the change in the selectivity of **RP** in different solutions is due to the difference in polarity and viscosity of DMSO and CH_3CH_2OH , which causes a change in the shape, size, coordination geometry and binding capacity of the receptor of **RP**.

Metal ion complexes are considered to be ideal approaches for amino acid recognition. Some metal complexes have been reported to recognize cysteine and homocysteine.[8g] The selectivity of a zinc-containing [**RP**@Zn^{2+}] complex for 20 natural amino acids was determined. Upon addition of twenty amino acids to the solution of [**RP**@Zn^{2+}], only histidine and cysteine caused a

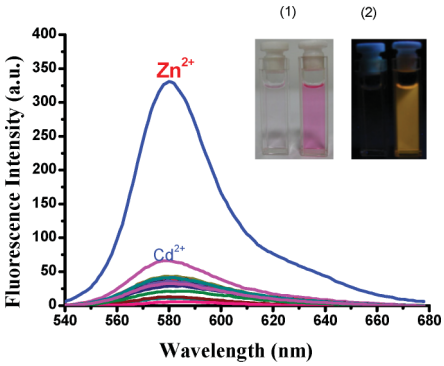


Fig. 2 The fluorescence spectra of **RP** (10 μM) in the presence of 10 μM of various metal ions such as Fe^{3+}, Cr^{3+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Hg^{2+}, Ba^{2+}, Na^+, K^+ in Tris-$HClO_4$ aqueous buffer (10 mM, pH 7.4, containing 40% ethanol as a co-solvent). (λ_{ex} = 530 nm). Inset: The photographs showed (1) the color change and (2) the fluorescent change (irradiated at 365 nm) of **RP** (10 μM) in the presence of 10 μM of Zn^{2+}.

significant decrease in the absorption at around 563 nm and the fluorescence at 583 nm along with the color change from pink to nearly colorless instantaneously (Fig. 3). Some of the other amino acids induced a slight quenching of fluorescence intensity, no more than 25% compared to His/Cys. Therefore, [**RP**@Zn^{2+}] is a selective colorimetric "naked eye" and fluorescence "on–off" switch probe for His/Cys in aqueous solution. To the best of our knowledge, this is the first example of a colorimetric and fluorimetric dual-responsive probe for His.

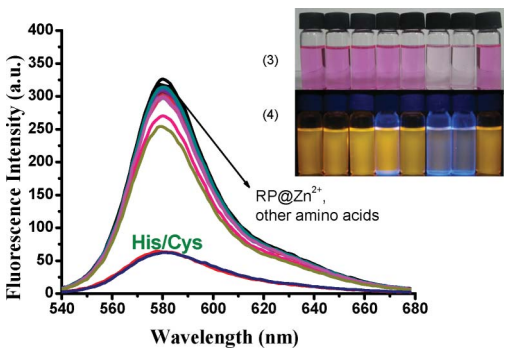


Fig. 3 The fluorescence spectra of [**RP**@Zn^{2+}] (10 μM **RP** and 10 μM Zn^{2+}) in the presence of 100 μM of various amino acids such as Gly, Ala, Val, Leu, Ile, Pro, Phe, Tyr, Trp, Ser, Thr, Cys, Met, Asn, Gln, Asp, Glu, Lys, Arg and His in Tris-$HClO_4$ aqueous buffer (10 mM, pH 7.4, containing 40% ethanol as a co-solvent). (λ_{ex} = 530 nm). Inset: The photographs showed (3) the color change and (4) the fluorescent change (irradiated at 365 nm) of [**RP**@Zn^{2+}] (10 μM **RP** and 10 μM Zn^{2+}) in the presence of 100 μM of various amino acids; From left to right: (1) Arg, (2) Thr, (3) Leu, (4) Asn, (5) Asp, (6) His, (7) Cys, (8) Trp.

Titration of **RP** with Cu^{2+}, Zn^{2+} and His/Cys was then conducted by UV-Vis and/or fluorescence spectroscopy (Fig. 4). The results indicate that **RP** or [**RP**@Zn^{2+}] is extremely sensitive towards Cu^{2+}, Zn^{2+}, or His/Cys. Based on Job's plot analysis, **RP** forms a 1 : 1 stoichiometric complex with Cu^{2+} or Zn^{2+} (Fig. S4, ESI†). Moreover, this binding mode is supported by the presence of a peak at m/z = 786.16 or m/z = 784.10 corresponding to [**RP** + Zn + ClO_4]$^+$ or [**RP** + Cu + ClO_4]$^+$ in the ESI-MS spectrum

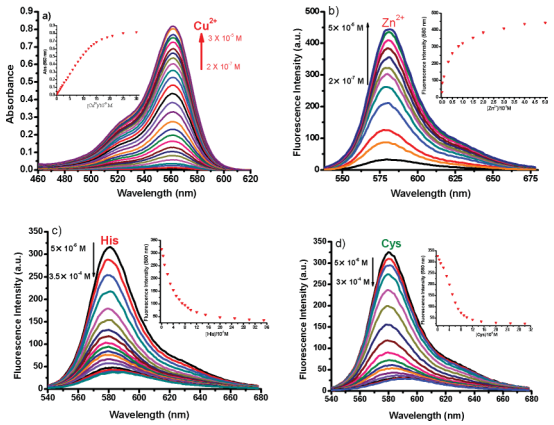
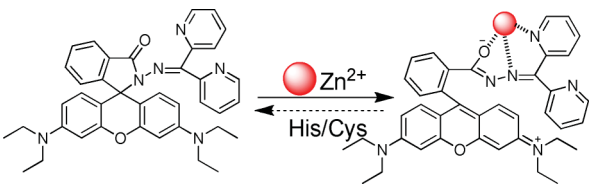


Fig. 4 UV-Vis absorption spectra of **RP** (10 μM) upon addition of (a) Cu^{2+} (0.2–30 μM) in DMSO/H_2O (v/v = 10 : 1, 2 mM Tris-HCl, pH 7.8); Fluorescence spectra of **RP** (10 μM) upon addition of (b) Zn^{2+} (0.2–50 μM) in CH_3CH_2OH/H_2O (40 : 60, v/v, 10 mM Tris-$HClO_4$, pH 7.4). Fluorescence spectra of **[RP@Zn²⁺]** (10 μM **RP** and 10 μM Zn^{2+}) upon addition of (c) His (5–350 μM) and (d) Cys (5–300 μM) in CH_3CH_2OH/H_2O (40 : 60, v/v, 10 mM Tris-$HClO_4$, pH 7.4).

(Fig. S5, ESI†). The association constants between **RP** and various metal ions were determined to be 2.3×10^6 M^{-1} for Zn^{2+} and 3.8×10^3 M^{-1} for Cd^{2+} in CH_3CH_2OH–H_2O (40 : 60, v/v, 10 mM Tris-$HClO_4$, pH 7.4) and 2.4×10^6 M^{-1} for Cu^{2+} in DMSO/H_2O (v/v = 10 : 1, 2 mM Tris-HCl, pH 7.8).

To get an insight into the binding mode, ^{1}H NMR titration experiments were measured. As shown in Fig. S6†, a set of new peaks appeared with the addition of Zn^{2+} into the solution of **RP** in CD_3CN. The apparent downfield shift of H_1 or $H_{1'}$ in the presence of Zn^{2+} suggested that the nitrogen atom of the pyridine ring participates in the binding. Moreover, the integration of the ^{1}H NMR spectrum indicated that only one nitrogen atom of the pyridine ring participates in the binding. Taken together, based on the above results, the coordinating property of Zn^{2+}, ESI-MS spectrum and the Job's plot, we proposed a plausible binding mode for the sensor **RP** with Zn^{2+} as shown in Scheme 2. Though one of the two pyridine moieties in **RP** was found not to be involved in metal chelation, its presence could change the rigidity and the size of the metal binding cavity and result in a varied selectivity pattern.[16] Because of the poor solubility of His in CD_3CN, ^{1}H NMR titration experiments of His were not successful. With addition of His/Cys into the solution of **[RP@Zn²⁺]** in a buffer solution, a significant decrease in the fluorescence was observed, which may be attributed to the stronger binding capacity of Zn^{2+} with His/Cys. Addition of Cu^{2+} to the DMSO-d_6 solution of **RP** caused the disappearance of proton signals at 7.15–7.40 ppm and 8.40–8.50 ppm, revealing formation of a Cu^{2+} complex (Fig. S7, ESI†). It is well-known that Cu^{2+} is paramagnetic and almost universally causes peaks to disappear in ^{1}H NMR spectra upon complex formation.[17]



Scheme 2 Proposed binding mode of **RP** with Zn^{2+}.

To further demonstrate the practical biological application of the **RP** sensor, fluorescence imaging experiments were carried out in living cells. HeLa cells were incubated with **RP** for 30 min, followed by the addition of 6.0 equiv. Zn^{2+} and 3.0 equiv. pyrithione at 37 °C and then incubated for another 30 min. The cells were washed three times with a PBS buffer solution (containing 2.0% methanol). Fig. 5 shows that when HeLa cells were treated with the **RP** sensor only, weak fluorescence was detected. By contrast, bright red fluorescence was noted when HeLa cells were incubated with the **RP** sensor treated with Zn^{2+}. The results suggest that the **RP** sensor is cell membrane permeable and can also be used for imaging of Zn^{2+} in living cells and potentially *in vivo*.

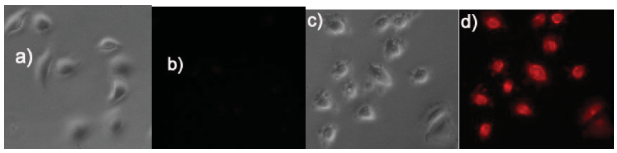


Fig. 5 (a) Bright-field transmission image of HeLa cells pre-incubated with the **RP** sensor (10 μM) for 30 min, washed three times; (b) Fluorescence image of (a); (c) Bright-field transmission image of HeLa cells pre-incubated with the **RP** sensor (10 μM) for 30 min, washed three times, and then treated with Zn^{2+} (6.0 equiv.) and pyrithione (3.0 equiv.); (d) Fluorescence image of (c).

In conclusion, we have reported a versatile rhodamine-based trifunctional chemosensor **RP**. It can sensitively and selectively recognize Cu^{2+} in DMSO/H_2O (v/v = 10 : 1, 2 mM Tris-HCl, pH 7.8) by naked eye through a drastic color change from colorless to purple and Zn^{2+} in CH_3CH_2OH/H_2O through an off–on fluorescence emission along with a color change from nearly colorless to pink. To the best of our knowledge, this work provides the first example of one bifunctional chemosensor that can sensitively and selectively recognize Cu^{2+} and Zn^{2+} respectively in different aqueous solutions. Interestingly, the zinc-containing [**RP**@Zn^{2+}] complex is also a colorimetric and fluorimetric dual-responsive probe for His/Cys. Furthermore, we have demonstrated that the **RP** sensor is applicable for Zn^{2+} imaging in living HeLa cells.

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