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A rhodamine-based dual chemosensor for the visual detection of copper and the ratiometric fluorescent detection of vanadium

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ABSTRACT

The optical properties of a novel, rhodamine-based derivative, synthesized by reacting rhodamine hydrazide and 5-chlorosalicylaldehyde in ethanol, were investigated in methanol:HEPES solution. The novel sensor displayed selectivity for Cu^{2+}, as evidenced by a colourless to dark red colour change, which was characterized using UV–visible spectroscopy and which also allowed visual detection of Cu^{2+}. In contrast, selectivity towards VO^{2+} was determined from changes in the emission spectra in the nanomolar range. This represents the first reported rhodamine-based sensor capable of detecting both Cu^{2+} and VO^{2+} using two different modes.

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1. Introduction

Rhodamine derivatives are excellent fluorophores and chromophores and have attracted considerable interest due to their very good photophysical properties [1–3], such as long absorption and emission wavelength, high fluorescence quantum yield (Φ), large extinction coefficient (ε), and high light stability. Rhodamine derivatives with a spirolactam-ring moiety, which is non-fluorescent and colourless, can be converted to the open-ring form in the presence of a proton or metal ion and display characteristically strong fluorescence emission and red colour [4]. Rhodamine-based spirolactams are considered to offer promise as molecular scaffolds and often are employed in OFF–ON fluorescent or colourimetric chemosensors [4,5]. Recently, several rhodamine-modified chemosensors have been developed for heavy- and transition-metal ions such as Cu^{2+} [6–19], Hg^{2+} [20–36], Fe^{3+} [36–40], Cr^{3+} [40–43], Cd^{2+} [44], Pb^{2+} [45] and Ag^{+} [46] because of the wide use of these metal ions and their subsequent impact on the environment and human health [47,48]. Copper is the third most abundant essential trace element in the human body after iron and zinc, and is important in many fundamental physiological processes in organisms. Copper has been shown to be a biochemically essential metal, such as, copper–zinc superoxide dismutase and its role in the enzymatic defense against oxygen toxicity. The detection of Cu^{2+} has important implications in the areas of environmental and biological analysis [6–19]. Vanadium is an essential trace element due to its significant roles in the environment, industry and physiological systems [49]. Laboratory and epidemiological evidence suggests that vanadium may also play a beneficial role in the prevention of heart-disease, despite its toxicity at ml^{-1} levels [50]. Vanadium remains a relatively unknown trace element, as it is still being targeted for use in various clinical applications worldwide. The development of an analysis method for vanadium is also same important [51].

Herein, we reported a novel dual chemosensor for detecting Cu^{2+} by UV–visible spectroscopy and VO^{2+} using fluorescence spectra. This chemosensor employs a rhodamine-based derivative (CSR), which was prepared by the reaction of excessive 5-chlorosalicylaldehyde (CS) and rhodamine hydrazide.

2. Experimental section

2.1. General

4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES; caution: stable; combustible; incompatible with strong oxidizing

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agents; protect from moisture) was purchased from Sigma–Aldrich. CSR was synthesized according to literature. HEPES solutions were adjusted to pH 7.0 by adding NaOH (0.1 M) to aqueous HEPES (10 mM). Cation salts were purchased from Shanghai city of China. All the common chemicals were of analytical grade.

A Beckman Φ50 pH meter was used to determined pH. UV–vis spectra were recorded on an HP8453 spectrophotometer. A PO-120 quartz cuvette (10 mm) was purchased from Shanghai city of China. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-300 MHz NMR spectrometer. Fluorescence spectra were measured on Cary Eclipse fluorescence spectrophotometer. Electrospray ionization (ESI) mass spectra were measured with an LC–MS 2010A (Shimadzu) instrument. A yellow single crystal of CSR was mounted on a glass fiber for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from reflections with 3.7–25.0° for CSR using a Bruker SMART APEX CCD automatic diffractometer. Data were collected at 223 K using Mo Kα radiation ($\lambda = 0.710713$ Å) and the ω-scan technique and corrected for Lorentz and polarization effect (SADABS) [52]. The structures were solved by direct methods (SHELX97) [53], and subsequent difference Fourier map and then refined in $F2$ using a full-matrix least-squares procedure and anisotropic displacement parameters.

2.2. Preparation of CSR

CSR was prepared in more high yield by reacting rhodamine hydrazide with excessive 5-chlorosalicylaldehyde (Fig. 1). Rhodamine hydrazide (0.46 g, 1 mmol; caution: toxic; contact with water or acids liberates toxic gas; can become highly flammable in use; danger of cumulative effects) was dissolved in 20 mL of absolute ethanol. An excessive of 5-chlorosalicylaldehyde (CS, 4 mmol) was added and the mixture was refluxed for 8 h. The ensuing solution was cooled, concentrated to 10 mL, and allowed to stand at 0 °C overnight in the refrigeratory. The precipitate was filtered and washed three times with 20 mL of cold ethanol. After drying under reduced pressure, the reaction afforded 0.43 g (76%) as a white solid. CSR compound. ^{1}H NMR ($CDCl_3$), δ (ppm): 1.15 (t, $J = 6.78$ Hz, 12H, CH_3), 3.34 (q, $J = 6.78$ Hz, 8H, CH_2), 6.27 (dd, $J = 8.29$ Hz, 2H), 6.49(m, 4H), 6.81 (d, $J = 8.76$ Hz, 2H,), 7.06 (s, 1H), 7.10–7.13 (d, $J = 8.75$ Hz, 1H), 7.18–7.20 (d, $J = 6.48$ Hz, 1H), 7.56 (m, 2H), 8.0 (d, $J = 6.27$ Hz, 1H), 9.00 (bs, 1H), 10.96 (bs, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 12.4, 44.2, 66.2, 97.8, 104.8, 108.0, 118.2, 119.1, 123.2, 124.0, 127.9, 128.5, 129.3, 130.1, 130.6, 133.2, 149.0, 150.1, 150.7, 153.2, 156.9, 164.2. ESI–MS: m/z 595.3 (55%, $[CSR + H]^+$), 617.3 (23%, $CSR + Na]^+$); [CSR] calculated 594.2. Crystal data for $C_{35}H_{35}ClN_4O_3$: crystal size: 0.5 × 0.5 × 0.4 mm, monoclinic, space group $Pca21$ (No. 29). $a = 21.467(6)$ Å, $b = 11.827(3)$ Å, $c = 12.344(3)$ Å, $V = 3134.04(3)$ Å^3, $Z = 4$, $T = 223$ K, $\theta_{max} = 25.0°$, 5104 reflections measured, 4447 unique ($R_{int} = 0.0747$). Final residual for 388 parameters and 5104 reflections with $I > 2\sigma(I)$: $R_1 = 0.1231$, $wR_2 = 0.2485$ and GOF = 1.27. The crystal structure is shown in Fig. 2.

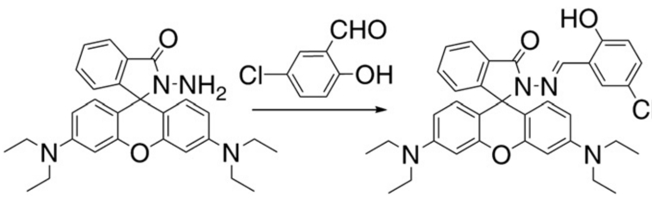

Fig. 1. Synthesis of CSR chemosensor.

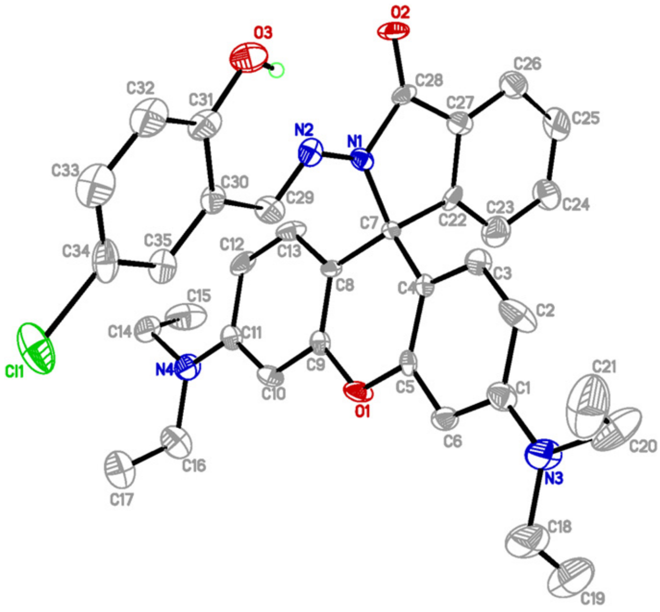

Fig. 2. Crystal structure of CSR, all hydrogen atoms were omitted for clarity.

2.3. Description of the structure of CSR

An intramolecular O3—H3…N2 hydrogen bond is observed in the molecular structure with the O3…N2 distance of 2.620(7) Å and the O3—H3…N2 angle of 146°, which is closed the six-membered pseudo-ring N2–C29–C30–C31–O3–H3. The dihedral angle between the spirolactam-ring system and xanthene ring plane is 88.53(2)°. Weak intermolecular C6—H6a…O3 hydrogen bonds also stabilize the crystal structure, forming one-dimensional infinite molecular chains along the c axis with the C6…O3 distance of 3.401 (9) Å and the C6—H6a…O3 angle of 159°.

2.4. General UV–vis and fluorescence spectra measurements

Since the chemosensor was not fully soluble in 100% aqueous media, methanol was used as a solubilizing medium. CSR stock solutions were prepared in methanol. The UV–vis and fluorescence spectra were obtained in mixed methanol/HEPES aqueous buffer (1:1, v/v, 10 mM, pH 7.0) solutions. Aqueous metal ion solutions were also prepared. Fluorescence measurements were carried out with a slit width of 10 nm.

2.5. Detection range

The UV–vis spectrum was characterized by a main band centred at 557 nm. The low detection threshold for Cu^{2+} was in the order of 10^{-6}–10^{-5} M and at this level the colour change was very obvious. The fluorescence emission was measured for each sample by exciting at 530 nm and spectra were measured from 540 to 700 nm. The sensitivity range for VO^{2+} was 10^{-7}–10^{-6} M.

3. Results and discussion

As a rhodamine derivative with a spirolactam group, CSR is non-fluorescent and colourless. Ring opening of the corresponding spirolactam gives rise to strong fluorescence emission and a pink colour. In a similar way, CSR as a ligand on a spirolactam-ring can induce colour change and a fluorescence change upon the addition of metal ions. The chemosensing behavior of CSR was investigated using UV–vis and fluorescence measurements.

The pH-titration experiments showed that the proper pH range for the determination of the Cu^{2+} ions was pH 6.0–10.0 in UV–vis spectra and for the detection of the VO^{2+} ions being pH 7.0–8.0 in fluorescence spectrum. These suggest that the chemosensor is suitable candidate for potential use in biological systems.

The UV–vis absorption spectrum of CSR in 50% CH_3OH solution (methanol:HEPES = 1:1, v/v, pH 7.0) had no absorption band from 400 to 800 nm. The absorption spectrum did not change significantly in the presence of 10^{-3} M concentrations of representative lanthanide ions (Eu^{3+}, Yb^{3+} etc), alkaline earth metal ions (Mg^{2+}, Ba^{2+} etc), or transition-metal ions (such as Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+}, Pb^{2+} etc) and the colour of the solutions containing these ions remained relatively unchanged. However, upon interaction with 10^{-5} M Cu^{2+} ions a new strong absorption peak for CSR appeared at 557 nm (Fig. 3a). When changes at 557 nm were monitored, good selectivity was observed for Cu^{2+} ion with a more than 30-fold increase in absorbance intensity (Fig. 3b). The effect caused by Cu^{2+} was so substantial that it could be detected by the naked-eye with a distinct solution colour change from colourless to dark red (Fig. 4). A titration was conducted with the CH_3OH–HEPES system containing 20 μL CSR ([CSR] = 20 μM), and Cu^{2+} (20 μM), and the end point was reached with a 1:1 molar ratio of CSR and Cu^{2+} (20 μL Cu^{2+}) (Fig. 5), This correlates to a quantitative detection of Cu^{2+} with CSR at micromolar levels (Fig. 5, inset). (Fig. 5, inset). This detection mode should be consistent with that reported previous by Xiang [6,7,13] and Zhou [19]. In the UV–vis spectra, the absorption at 557 nm for VO^{2+}-CSR was only 20% of that for Cu^{2+}-CSR (Fig. 3). The VO^{2+}-CSR solution was lighter red than the equivalent Cu^{2+}-CSR solution (Fig. 4).

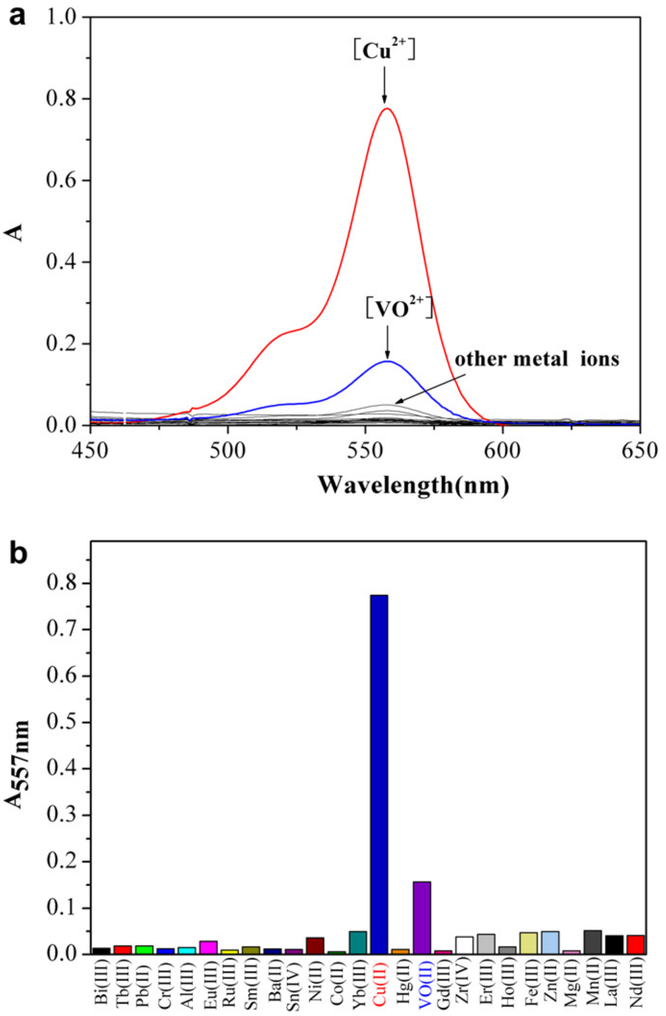

Fig. 3. (a) UV–vis spectra of CSR (20 μM) in the presence of various metal ions in methanol-HEPES (1:1, v/v, pH 7.0) solution; (b) Optical density of the probe CSR (20 μM) at 557 nm upon addition various metal ions.

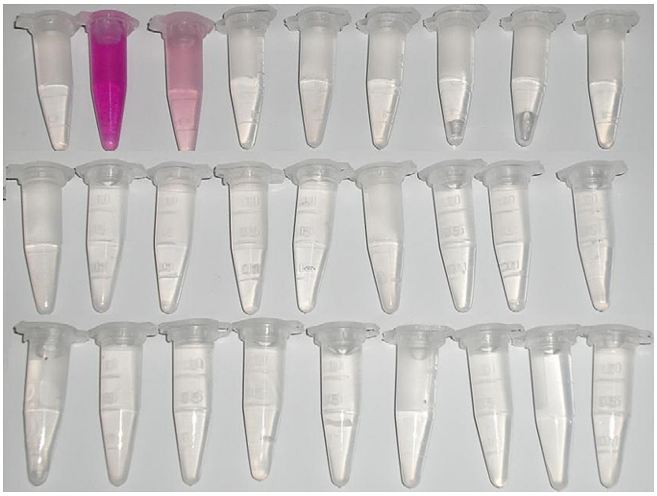

Fig. 4. Photograph of CSR (20 μM) in the presence of various metal ions (1000 μM except Cu^{2+} that is 20 μM) in methanol–HEPES (1:1, v/v, pH 7.0) solution. From left to right, then from top to bottom: CSR (20 μM), and CSR with Cu^{2+}, VO^{2+}, Bi^{3+}, Tb^{3+}, Pb^{2+}, Cr^{3+}, Al^{3+}, Eu^{3+}, Ru^{3+}, Sm^{3+}, Sn^{4+}, Ni^{2+}, Co^{2+}, Yb^{3+}, Hg^{2+}, Ga^{3+}, Zr^{4+}, Er^{3+}, Ho^{3+}, Fe^{3+}, Zn^{2+}, Mg^{2+}, Mn^{2+}, La^{3+}, Nd^{3+}.

The detailed fluorescence spectrum of CSR was plane when excited at 530 nm, (Fig. 6a) with no fluorescence intensity changes were observed in emission spectra with a wide range of environmentally and physiologically important metal ions: Bi^{3+}, Tb^{3+}, Pb^{2+}, Cr^{3+}, Al^{3+}, Eu^{3+}, Ru^{3+}, Sm^{3+}, Sn^{4+}, Ni^{2+}, Co^{2+}, Yb^{3+}, Hg^{2+}, Ga^{3+}, Zr^{4+}, Er^{3+}, Ho^{3+}, Fe^{3+}, Zn^{2+}, Mg^{2+}, Mn^{2+}, La^{3+}, Nd^{3+}, Na^{+}, and K^{+} (up to 500 equiv). However, under identical conditions, VO^{2+} significantly enhanced the fluorescence intensity. Nanomolar concentrations of VO^{2+} significantly enhanced the peak at 583 nm. The emission peak of CSR at 583 nm (λ_{ex} = 530 nm) increased dramatically upon addition of VO^{2+} (Fig. 6b). When 10 equiv VO^{2+} was added to the solution of CSR, a more than 40-fold increase in fluorescence intensity at 583 nm was observed, whereas 10 equiv Cu^{2+} induced only a 3.6-fold enhancement in emission at 577 nm. This indicated that except for Cu^{2+}, common coexisting metal ions did not interfere with the measurement of VO^{2+}. The stoichiometry

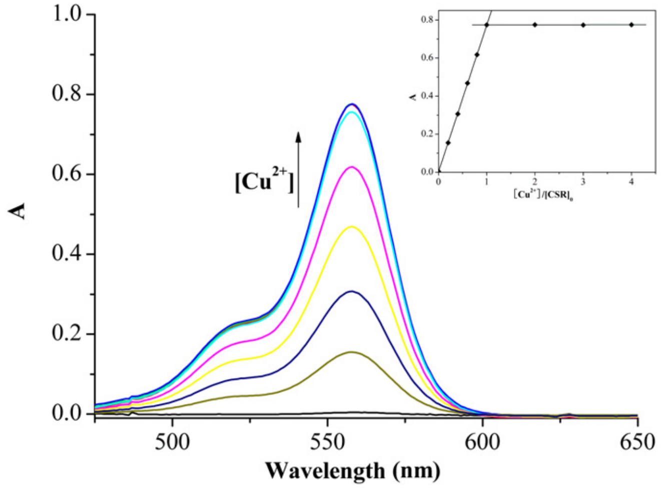

Fig. 5. Plot of absorbance intensity of CSR (20 μM) at 557 nm against $[Cu^{2+}]$ 0, 5, 10, 15, 20, 40, 60, 80 μM in methanol–HEPES (1:1, v/v, pH 7.0) solution.

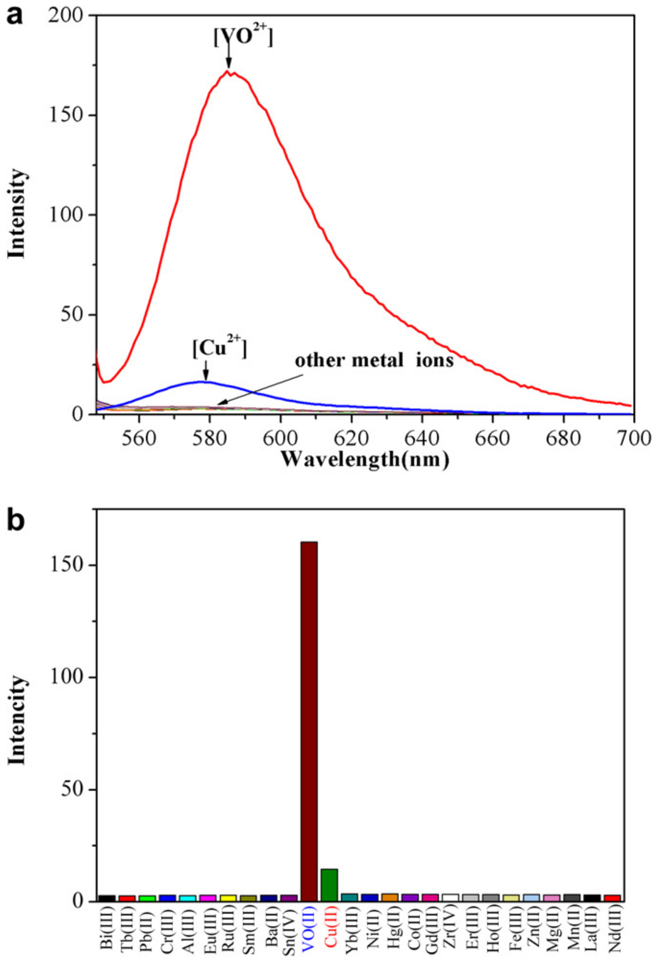

Fig. 6. (a) Fluorescence spectra of CSR (200 nM) with various metal ions (100 μM except VO^{2+} that is 2 μM) in methanol–HEPES (1:1, v/v, pH 7.0) solution ($\lambda_{ex} = 530$ nm, $\lambda_{em} = 583$ nm, slit: 10 nm/10 nm); (b) The fluorescence intensity at 583 nm of CSR (200 nM) upon addition of various metal ions (100 μM except VO^{2+} that is 2 μM). Each spectrum is acquired 10 min after metal ions addition.

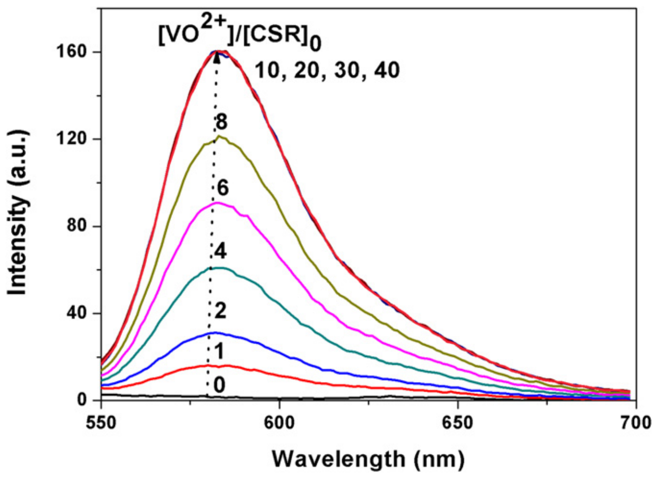

Fig. 7. Fluorescence spectra of CSR (200 nM) in the presence of different concentrations of VO^{2+} (0, 0.2, 0.4, 0.8, 1.2, 1.6, 2.0, 4.0, 6.0, 8.0 μM) in methanol–HEPES (1:1, v/v, pH 7.0) solution ($\lambda_{ex} = 530$ nm, $\lambda_{em} = 583$ nm, slit: 10 nm/10 nm). Each spectrum is acquired 10 min after VO^{2+} addition.

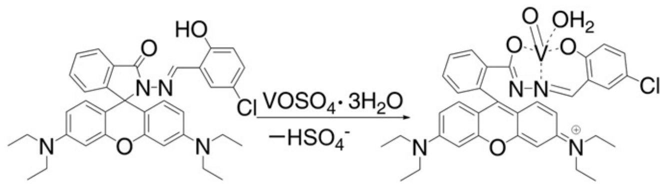

Fig. 8. The proposed mechanism for fluorescence response of CSR to VO^{2+} basis of ESI-MS data which afforded a peak at m/z 678.3 assigned for $[CSR + VO + H_2O-H]^+$ ion (calcd. 678.2).

of CSR binding with VO^{2+} ions was determined by fluorescence titration with VO^{2+} in the same solvent (Fig. 7). As the concentration of VO^{2+} ions increased, the CSR fluorescence increased significantly until at 10 equiv VO^{2+} the fluorescence intensity did not change. The significant fluorescence enhancement may be due to the V=O double bond, which increased the degree of conjugation for the whole rhodamine molecule (Fig. 8). Electrospray ionization mass (ESI-MS) provided direct evidence for the above proposed mechanism by a peak at m/z 678.3 (calcd for 678.2, $[CSR + VO + H_2O-H]^+$), which indicated the formation of the complex of CSR and VO^{2+}.

Interestingly, both the CSR-Cu^{2+} and the CSR-VO^{2+} ensembles exhibited the excellent selectivity towards pyrophosphate anion ($P_2O_7^{4-}$, PPi) in UV–vis spectra (Fig. 9) and in fluorescence spectrum

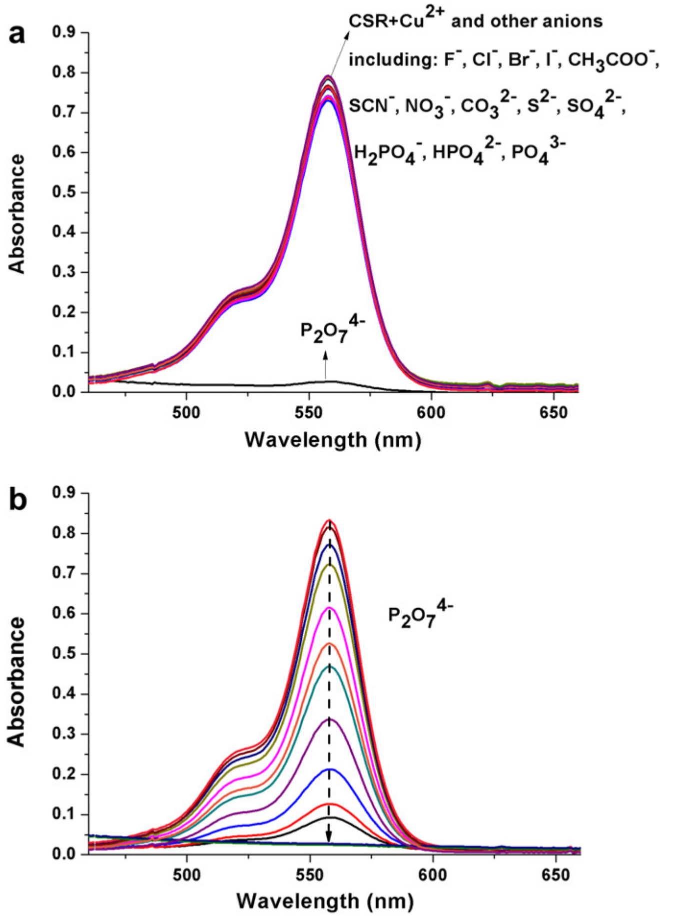

Fig. 9. (a) UV–vis spectra of the [CSR-Cu^{2+}] ensemble (20 μM in methanol–HEPES (1:1, v/v, pH 7.0)) was added with various foreign anions (1000 μM) including F^-, Cl^-, Br^-, I^-, AcO^-, SCN^-, NO_3^-, CO_3^{2-}, S^{2-}, SO_4^{2-}, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} and $P_2O_7^{4-}$ (PPi, 400 μM); (b) UV–vis spectra: with addition of $[P_2O_7^{4-}]$ = 0, 40, 80, 160, 200, 240, 280, 360, 400 μM to methanol–HEPES (10 mM, 1:1, v/v, pH 7.0) buffer, the [CSR-Cu^{2+}] = 20 μM.

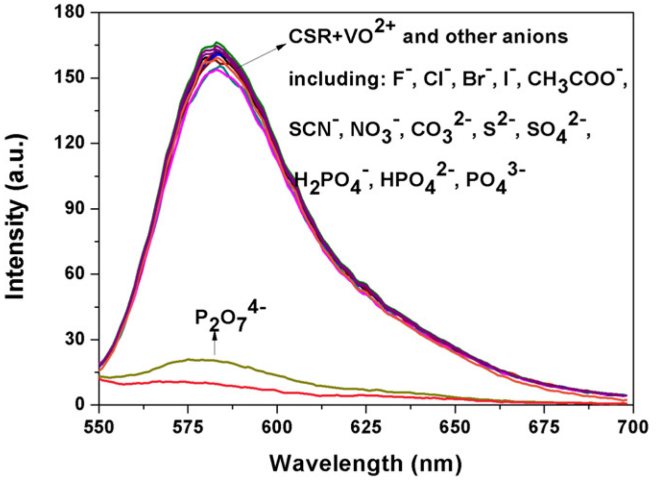

Fig. 10. Fluorescence spectra ($\lambda_{ex/em} = 530/583$ nm; slit: 10 nm/10 nm) of the [CSR-VO^{2+}] (200 nM) with various anions (100 μM) including F^-, Cl^-, Br^-, I^-, AcO^-, SCN^-, NO_3^-, CO_3^{2-}, S^{2-}, SO_4^{2-}, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} and $P_2O_7^{4-}$ (PPi, 2 μM).

(Fig. 10) respectively over other common anions including fluoride (F^-), chloride (Cl^-), bromide (Br^-), iodide (I^-), acetate (AcO^-), thiocyanate (SCN^-), nitrate (NO_3^-), carbonate (CO_3^{2-}), sulfite (S^{2-}), sulfate (SO_4^{2-}), dihydrogen phosphate ($H_2PO_4^-$), hydrogen phosphate (HPO_4^{2-}), phosphate (PO_4^{3-}). These suggest CSR can be applied to sensor PPi anions by employing an indirect trick to be cooperated with Cu^{2+} or VO^{2+} ions. This is similar detection of PPi with the one developed by Tian's group [54].

4. Conclusions

A new rhodamine-based derivative (CSR) was prepared and characterized by ^1H NMR and ^{13}C NMR and X-ray crystallography. CSR exhibited different selectivity at micromolar levels for Cu^{2+} in UV–visible spectroscopy and at nanomolar levels for VO^{2+} in fluorescence spectra. This is, to the best of our knowledge, the first reported example of a dual detecting rhodamine derivative capable of detecting both Cu^{2+} and VO^{2+}. CSR displayed Cu^{2+}-selective chromogenic behavior and turned from colourless to purple red, which allowed naked-eye detection of Cu^{2+} ions in aqueous 50% CH_3OH solution. The OFF–ON type fluorescence changes of the spirolactam moiety could conveniently detect VO^{2+}. To date, there have been very few the rhodamine-based dual chemosensors reported [36]. We believe a dual rhodamine-based chemosensor such as that developed here, could be a new approach for many rhodamine derivatives and might be great interest in developing multifunctional sensors for heavy- and transition-metal cations. In addition, CSR-M^{2+} (M = Cu or VO) ensembles can play chemosensor to sense PPi anions like dicyano dyes developed by Tian's group [54,55].

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