ABSTRACT: A new fluorescent probe LXY based on the rhodamine 6G platforms has been designed, synthesized, and characterized, which could recognize Fe\textsuperscript{3+} effectively in HEPES buffer (10 mM, pH = 7.4)/CH\textsubscript{3}CN (2:3, v/v). And the distinct color change and the rapid emergence of fluorescence emission at 550 nm achieved “naked eye” detection of Fe\textsuperscript{3+}. The interaction mode between them was achieved by Job’s plot, MS, SEM, and X-ray single-crystal diffraction. Importantly, the crystal structures proved that Fe\textsuperscript{3+} could induce the rhodamine moiety transform the closed-cycle form to the open-cycle form. But it is interesting that Fe\textsuperscript{3+} did not appear in the crystal structures. Meanwhile, the limit of detection (LOD) of LXY to Fe\textsuperscript{3+} was calculated to be 3.47 × 10\textsuperscript{-9}. In addition, the RGB experiment, test papers, and silica gel plates all indicated that the probe LXY could be used to distinguish Fe\textsuperscript{3+} quantitatively and qualitatively on-site. Moreover, the probe LXY has also been successfully applied to Fe\textsuperscript{3+} image in Caenorhabditis elegans, adult mice, and plant tissues. Thus, LXY was considered to have some potential for application in bioimaging.

INTRODUCTION

The iron industry is one of the basic industries in all industrialized countries in the world. And Fe\textsuperscript{3+} is one of the most abundant and common metal ions. Fe\textsuperscript{3+} plays an important role in the chemical industry, the environment, and living organisms, especially in the formation of red blood cells, transportation and storage of proteins, and oxygen metabolism.\textsuperscript{1–5} However, the accumulation of Fe\textsuperscript{3+} caused by industrial production has resulted in environmental pollution, such as water and soil pollution, which are greatly harmful to the human health.\textsuperscript{5,6} In addition, both deficiency and overload of Fe\textsuperscript{3+} can induce various dysfunctions of organisms as well as occurrence of certain diseases.\textsuperscript{7–10} Hence, it is important to develop rapid and sensitive methods to determine the distribution of Fe\textsuperscript{3+} to protect the human health and the ecological environment.

In the past few decades, some methods have been developed for the detection of Fe\textsuperscript{3+}, including inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (ABS). However, their disadvantages including low specificity, complicated sample preparation, and expensive instruments hindered their wide applications.\textsuperscript{11–13} Recently, increasingly more attention has been paid to the fluorescence method for the detection of Fe\textsuperscript{3+} because of its ability to detect Fe\textsuperscript{3+} rapidly, sensitively, and selectively. And it could not cause any damage to cell.\textsuperscript{14–18} To date, many fluorescent probes for Fe\textsuperscript{3+} have been synthesized successfully, which included coumarin,\textsuperscript{19,20} anthracene,\textsuperscript{21} BODIPY,\textsuperscript{22,23} cyanine,\textsuperscript{24} and rhodamines.\textsuperscript{25} Among these probes, rhodamine 6G has many advantages over other derivatives, including high extinction coefficients, high quantum yields, excellent photostability, and emission wavelengths.\textsuperscript{26–31} However, most rhodamine derivatives were obtained through C=N, but a few compounds linked by amide have been reported.\textsuperscript{32–34} It was clear that the amide-modified rhodamine 6G derivatives have more potential coordination sites to bind metal ions than C=N.\textsuperscript{35} Moreover, the interaction between rhodamine 6G and metal ions was rarely characterized by single-crystal structure, which restricted our understanding of its interaction mode between them.\textsuperscript{36,37}

In this study, we have designed, synthesized, and characterized the novel fluorescent probe LXY based on a rhodamine derivative. It was interesting that the fluorescent probe LXY achieved “naked eye” detection of Fe\textsuperscript{3+} in HEPES buffer (10 mM, pH = 7.4)/CH\textsubscript{3}CN (2:3, v/v). And other metal ions (K\textsuperscript{+}, Fe\textsuperscript{2+}, Ca\textsuperscript{2+}, Na\textsuperscript{+}, Ag\textsuperscript{+}, Cu\textsuperscript{2+}, Co\textsuperscript{2+}, Mg\textsuperscript{2+}, Cd\textsuperscript{2+}, Ni\textsuperscript{2+}, Ba\textsuperscript{2+}, Pb\textsuperscript{2+}, Al\textsuperscript{3+}, Sr\textsuperscript{2+}, Mn\textsuperscript{2+}, Zn\textsuperscript{2+}, Hg\textsuperscript{2+}, Ce\textsuperscript{3+}, and Y\textsuperscript{3+})
could not cause any interference. And the LOD of LXY to Fe$^{3+}$ is much lower than the WHO and EPA standard (Figure S14). In addition, the crystal structures of the open-ring form of LXY indicated that only Fe$^{3+}$ could induce the closed lactam ring to open. But Fe$^{3+}$ did not arise in the crystal structure. Furthermore, the RGB experiment conducted on a smartphone and using test papers showed that the probe LXY could detect Fe$^{3+}$ in water samples qualitatively and quantitatively. Finally, biological experiments indicated that the probe could achieve fluorescence imaging of Fe$^{3+}$ in Caenorhabditis elegans, adult mice, and plant tissues (Scheme 1).

**RESULTS AND DISCUSSION**

**Visual Detection.** Initially, the selectivity of probe LXY (10 μM) toward various cations was detected by visualizing color change in the solution of HEPES buffer (10 mM, pH = 7.4)/CH$_3$CN (2:3, v/v). From Figure 1, the solution mixed with Fe$^{3+}$ rather than other cations showed a color change from colorless to pink-red under visible light when the cations were added into the probe of LXY solution (Figure 1a). And fluorescence enhancement was observed significantly under UV light (Figure 1b).

**Ion Selectivity.** Before Fe$^{3+}$ was added, no absorption peaks and emission peaks were observed in the LXY solutions from 350 to 600 nm. However, the distinct absorption peak appeared at 515 nm and the strong fluorescence was observed at 550 nm once Fe$^{3+}$ was added (Figure 2). And it is found that other cations did not lead to the spectrum change except Fe$^{3+}$ (Figure S5). Therefore, the detection of LXY to Fe$^{3+}$ was not interfered by other metal ions. So, the probe of LXY might be used as the selective probe of Fe$^{3+}$.

**Effect of the pH.** It is well known that the spirolactam structure in rhodamine 6G could be transformed between the open-ring and closed-ring structures at different pH values. So, the effect of pH on LXY toward Fe$^{3+}$ was studied in the solution of HEPES buffer (10 mM, pH = 7.4)/CH$_3$CN (2:3, v/v) (Figure S6). It is obvious that pH between 6.8 and 8.0 did
not affect the selectivity of LXY toward Fe$^{3+}$. To be close to the pH of the human body, pH = 7.4 was chosen to carry out the living cell imaging.

**Sensing Mechanism.** To understand the interaction between LXY and Fe$^{3+}$, the mechanism was investigated by Job’s plots, MS, X-ray single-crystal diffraction, SEM analysis, and theoretical computations. The stoichiometric ratio of 1:1 between LXY and Fe$^{3+}$ was gained by Job’s plots (Figures 3b,d and S7). To our surprise, X-ray single-crystal diffraction showed the structure of the probe LXY from closed loop to open loop (Scheme 2), which was induced by Fe$^{3+}$. But Fe$^{3+}$ did not emerge in the single-crystal structures. And the result was also supported by mass spectral analyses because the ion peak was detected at $m/z 698.66$, which matched $[LXY + NO_3^- + H_2O]^+$ well (Figure S8). Moreover, SEM experiment was performed to study the open loop of LXY aggregation morphology. After Fe$^{3+}$ (2 equiv) was added into the LXY (1 equiv) solution, the morphology of LXY changed from

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**Figure 2.** (a) Absorption spectrum of LXY (10 μM) in the presence of various metal ions K$^+$, Na$^+$, Ag$^+$, Cu$^{2+}$, Co$^{2+}$, Ca$^{2+}$, Cd$^{2+}$, Mg$^{2+}$, Ba$^{2+}$, Pb$^{2+}$, Sr$^{2+}$, Fe$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Mn$^{2+}$, Hg$^{2+}$, Al$^{3+}$, Y$^{3+}$, Ce$^{3+}$, and Fe$^{3+}$ (30 μM) in HEPES buffer (10 mM, pH = 7.4)/CH$_3$CN (2:3, v/v). (b) Fluorescence spectrum of LXY (10 μM) in the presence of various metal ions (30 μM) in HEPES buffer (10 mM, pH = 7.4)/CH$_3$CN (2:3, v/v), ($\lambda_{ex} = 515$ nm).

**Figure 3.** (a, c) Absorption and fluorescence spectra of LXY (10 μM) in the presence of different concentrations of Fe$^{3+}$ in solution ($\lambda_{ex} = 515$ nm). (b, d) Plots of absorption and fluorescence intensities at 515 and 550 nm with Fe$^{3+}$ concentration in the range of 0.1−2.0 equiv. All measurements were taken in HEPES buffer (10 mM, pH = 7.4)/CH$_3$CN (2:3, v/v).
dendritic shape to the porous plane (Figure S9). And the orbital energy and spatial distribution levels of the “open” and “closed” loops were obtained by DFT calculation. It is clear that the electron density for the “closed” loop was mainly distributed mainly over the hippuric acid groups in the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). However, the electron density for the “open” loop changed obviously after Fe$^{3+}$ was added. The energy gaps of the “open” and “closed” loops were calculated to be 3.6843 and 2.4394 eV, respectively (Figure 4). Detection of Fe$^{3+}$ by Qualitative and Quantitative Methods. To detect Fe$^{3+}$ in water qualitatively, we prepared test papers. It is interesting that only aqueous solutions of Fe$^{3+}$ caused color changes that could be seen by the “naked eye” (Figure S10). Moreover, the smartphone attracted our attention to detect Fe$^{3+}$ on-site quantitatively. Based on the “naked eye” detection of LXY, a color assist APP of smartphone was used to determine the color changes in the RGB (red, green, blue) values and in turn find Fe$^{3+}$ concentration in solution. As shown in Figure S, a good relationship between the R/B (red/blue) ratio for LXY toward Fe$^{3+}$ ($R^2 = 0.97805$). To verify its accuracy, the experiment was conducted simultaneously by a smartphone and a UV spectrometer. The results showed that the R/B ratio was 2.237, which corresponded to a Fe$^{3+}$ concentration of 23.11 μM, and [Fe$^{3+}$] was 23.97 μM according to the absorption spectrum (Figure 5a,b). It was found that the error between the two methods was only 3.590%. Hence, it implied that LXY could effectively detect Fe$^{3+}$ in water qualitatively and quantitatively.

To further explore the application of the probe LXY, the gel plate of LXY, which was written using the Fe$^{3+}$ solution, appeared pink-red as detected by the naked eye, while the fluorescence of LXY has been enhanced under a 365 UV lamp (Figure S11). The result showed that Fe$^{3+}$ could be qualitatively detected in the solid.

**Fluorescence Imaging.** We explored the effect of LXY on the detection of Fe$^{3+}$ in plant tissues. Figure 6 shows strong green or red fluorescence once Fe$^{3+}$ was added to soybeans treated with LXY. And a similar phenomenon was also observed in the root of *Erigeron annuus* (Figure 7). Thus, it is observed that LXY had good histocompatibility and could be used for imaging plant tissues.

After the excellent imaging of LXY in plant tissues, its imaging in animals was conducted. It is evident that *C. elegans* itself did not show any fluorescence (Figure 8a). While it was incubated with LXY (10 μM, DMSO/H$_2$O = 2:8), weak green
fluorescence was observed (Figure 8b). But strong red or green fluorescence emission appeared once Fe³⁺ (20 μM, H₂O) was added and incubated with LXY (Figure 8c). After two adult mice were injected with LXY, one of them was injected with an aqueous solution containing Fe³⁺ in the same position. It is significant that the fluorescence emerged in the liver, kidney, and heart. But the other did not show any fluorescence in any organs (Figures 9, S12, and S13). The above data confirmed that LXY was biocompatible in nature and could be used to test Fe³⁺ ions in vivo.

### CONCLUSIONS

In summary, the novel LXY based on rhodamine 6G was designed, synthesized, and characterized. And LXY could distinguish Fe³⁺ from other metal ions effectively in HEPES buffer (10 mM, pH = 7.4)/CH₃CN (2:3, v/v), while the other cations did not cause interference. The recognition mode between LXY and Fe³⁺ was confirmed by common methods. However, particularly, single crystals were adopted to ascertain the interaction between them. The probe LXY could detect Fe³⁺ in water quantitatively and qualitatively by smartphone and test paper. And it is more interesting that LXY could also
be used to detect Fe$^{3+}$ in biological samples such as plant tissues, C. elegans, and adult mice. Therefore, this article provided a new way for efficient and rapid detection of Fe$^{3+}$ in the chemical industry.

**EXPERIMENTAL SECTION**

**Materials and Physical Methods.** $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker spectrometer at 400 MHz using tetramethylsilane (TMS) as an internal standard (DMSO-$d_6$ as the solvents). Mass spectrum was recorded on a Shimadzu LCMS-IT/TOF mass spectrometer. UV−vis absorption spectrum was recorded on a Shimadzu UV-1601 spectrophotometer. Fluorescence spectrum was recorded on a HORIBA FLUOROMAX-4-NIR spectrometer. The excitation wavelength is 515 nm, and the excitation slit and emission slit are both 2.5 nm. SEM images were acquired on Carl Zeiss Sigma 500. X-ray crystallographic analysis was done at the X-ray crystallography facility, Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences (CAS). Biological imaging was performed on a fluorescence inverted microscope from Research Center of Anti-aging Chinese Herbal Medicine of Anhui Province (Fuyang, China). All measurements were carried out at ambient temperature.

All reagents used were of analytical grade and used without further purification unless otherwise stated. The solution of metal ions was prepared from their nitrate salts of K$, Fe^{2+}$, Ca$^{2+}$, Na$, Ag$, Cu$^{2+}$, Co$^{2+}$, Mg$^{2+}$, Cd$^{2+}$, Ni$^{2+}$, Ba$^{2+}$, Pb$^{2+}$, Al$^{3+}$, Sr$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Hg$^{2+}$, Ce$^{3+}$, Y$^{3+}$, and Fe$^{3+}$. The ligand LXY concentration was kept constant (10 μM). The solution of the probe was prepared (10 mM, pH = 7.4)/CH$_3$CN (2:3, v/v).

**Figure 7.** Fluorescence imaging of *Erigeron annuus* root tissues. (a) Fluorescence images of E. annuus root tissues. (b) Fluorescence images of E. annuus root tissues treated with LXY (10 μM, DMSO/H$_2$O, v/v, 1:1). (c) Fluorescence images of LXY-loaded E. annuus root tissues treated with Fe$^{3+}$ (20 μM, H$_2$O). From left to right are bright field, red channel (580–650 nm), and green channel (490–550 nm).

**Figure 8.** Fluorescence imaging of C. elegans. (a) Fluorescence images of C. elegans. (b) Fluorescence images of C. elegans treated with LXY (10 μM, DMSO/H$_2$O = 2:8). (c) Fluorescence images of LXY-loaded C. elegans treated with Fe$^{3+}$ (20 μM, H$_2$O). From left to right are bright field, red channel (580–650 nm), and green channel (490–550 nm).
SEM samples (LXY, LXY after Fe³⁺ was added) were dissolved in acetonitrile, and the solution was evaporated and dried at room temperature on a silicone sheet surface. Then, they were tested followed by gold plating. Moreover, the detection limit of LXY to Fe³⁺ was calculated by the 3σ/s method.

**Preparation of Test Papers and Silica Gel Plates.** Test papers and silica plates were immersed in a solution (100 μM) and desiccated in air at room temperature. The Fe³⁺, Fe²⁺, and Hg²⁺ (100 μM) water solutions were used. Test strips were quickly immersed in the prepared solution, distilled water, and tap water. Then, they were dried at room temperature to observe the color change by the "naked eye" and a 365 UV lamp.

**Detection of Fe³⁺ by Smartphone (RGB).** The LXY concentration (10 μM) remained unchanged. Different concentrations of Fe³⁺ were added. The RGB experiment was operated on a smartphone, while UV spectrum was recorded by a spectrophotometer.

**Detection of Fe³⁺ in Biological Bodies and Plants.** The in vivo and plant experiments were conducted with the standard procedure by Research Center of Anti-aging Chinese Herbal Medicine of Anhui Province (Fuyang, China). The specific experimental operation process is given in the Supporting Information.

**Crystal Structures of LXY.** At room temperature, the probe LXY was dissolved in CH₃CN/petroleum ether (1:1) and the probe LXY and Fe(NO₃)₃·9H₂O (1:1, molar ratio) were dissolved in CH₃CN. After slow evaporation, single crystals, which were suitable for X-ray single-crystal diffraction analysis, were obtained. The crystal data are presented in the Supporting Information. CCDC 2035378 (LXY) and 2035380 (open loop of LXY) included the supplementary crystallographic data for this paper. These data could be obtained from The Cambridge Crystallographic Data Centre.

**Synthesis of the Probe LXY.** According to the reported methods, N-(rhodamine 6G) lactam-ethylenediamine (A) was synthesized and purified by recrystallization from ethanol.¹³ Then, A (460 mg, 1 mmol) and hippuric acid B (180 mg, 1 mmol) were dissolved in methylene chloride (25 mL) and also 4-dimethylaminopyridine (DMAP, 122 mg, 1 mmol) was added as a catalyst. The mixture was reacted at room temperature. After the reaction was completed, the solvent was vaporized under vacuum and the crude product was purified by silica gel chromatography (methylene chloride/methanol = 30:1) to get the probe (LXY) (Scheme 1).

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00440.

Synthesis route of N-(rhodamine 6G) lactam-ethylenediamine, ¹H NMR and ¹³C NMR spectra, pH response, competition assays, Job’s plot, mass spectrosopy analyses, detection limit, test paper and silica gel, C. elegans culture maintenance and fluorescence imaging, bioimaging application in living mice, and X-ray crystallographic data (PDF)

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Notes

The authors declare no competing financial interest.

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