A dansyl-based fluorescent probe for turn-off and turn-on detection of \( \text{Hg}^{2+} \) in a full water system

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Abstract

A dansyl-based fluorescent probe, 2-((5-dimethylamino)naphthalene-1-sulfonamido)acetic acid (DNSG), was synthesized from dansyl chloride and glycine. In HEPES buffer (20 mM, pH 6.7), DNSG could detect \( \text{Hg}^{2+} \) by fluorescence quenching. The maximal fluorescence intensity showed a good linear relationship with the \( \text{Hg}^{2+} \) concentration (0 ~ 80 μM). The detection limit was 0.33 μM. With the help of silk fibroin (0.076 g/L), DNSG could detect \( \text{Hg}^{2+} \) by fluorescence enhancement and blueshift. The linear concentration range for \( \text{Hg}^{2+} \) was 0 ~ 160 μM with a detection limit of 0.81 μM. DNSG could detect \( \text{Hg}^{2+} \) quickly and reversibly with excellent anti-interference ability and further could assay environmental water sample efficiently. The sensing mechanism was examined by Job’s plot, mass spectrum and \(^1\)H NMR analysis.

Graphic Abstract

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Introduction

Mercury is of concern because highly toxic mercury ions and organic mercury cause serious human health and ecological problems. It has been reported that Hg\(^{2+}\) can cause irreversible cognitive and motion disorders, even at very low concentrations [1, 2, 3]. Thus, it is necessary to develop effective analytical methods for concise and accurate detection of trace amounts of Hg\(^{2+}\) [4]. Fluorescent probes with the advantages of high sensitivity, easy operation and nondestructiveness have been particularly attractive in the detection of heavy or transition metal ions [5, 6, 7, 8, 9, 10, 11]. However, most fluorescent probes have poor water solubility, and their detection must be implemented in organic solvent-containing media. Fluorescent probes with good water solubility are urgently needed. Furthermore, one probe can usually respond to the analyte by fluorescence quenching or fluorescence enhancement. There are few fluorescent probes that can detect one analyte by both fluorescence quenching and fluorescence enhancement.

Dansyl is a significant fluorophore suitable for fluorescent probes because of its high fluorescence quantum yield and large Stokes shift [12, 13, 14, 15, 16, 17]. To date, most dansyl-based probes detect metal ions by fluorescence quenching [18, 19, 20, 21, 22], while turn-on fluorescent probes have higher sensitivity and more application fields. Therefore, developing turn-on dansyl-based fluorescent probes is of great significance. Priyanka et al. reported that the dansyl amino acid probe could detect Hg\(^{2+}\) by fluorescence enhancement after the addition of bovine serum albumin (BSA) [23], which suggests that the sensitivity of the probe to substrate can be changed by introducing some assisted components to the detection system.

Silk fibroin (SF) is the main component of silk, which is composed of 18 amino acids such as glycine, alanine, serine and tyrosine. SF is biocompatible, non-toxic and biodegradable. Therefore, it is widely used in food additives, cosmetics, biomedical materials and other fields.

Here, we attached glycine to a dansyl moiety to achieve a fluorescent probe (DNSG) with a simple structure and good water solubility. Similar to most reported dansyl-based fluorescent probes, DNSG could detect Hg\(^{2+}\) through fluorescence quenching. Then, inspired by the literature, SF prepared from the cocoons of B. mori silkworm in our laboratory was introduced to the testing system and the expected result that DNSG could detect Hg\(^{2+}\) by fluorescence enhancement achieved.

Experimental

Synthesis of the probe

Materials and apparatus can be found in Supplementary materials. As shown in Scheme 1, dansyl chloride (0.1 g, 0.37 mmol) was dissolved in acetone (10 mL), and sodium bicarbonate (0.59 g, 7.06 mmol) aqueous (10 mL) solution with glycine
(0.13 g, 1.77 mmol) was added slowly. The resulting mixture was reacted for 2 h at room temperature [24]. Then, the solvent was evaporated to dry on a rotary evaporator. HCl aqueous (1 M) was added dropwise to adjust the pH to 4.5, and ethyl acetate (15 mL × 3) was used to extract the product in aqueous solution. The organic layer was collected, and the solvent was evaporated on a rotary evaporator. The product was purified using column chromatography on silica and eluted with methanol/dichloromethane (1/10, v/v). The dansyl-based fluorescent probe DNSG was obtained as a brown solid (23 mg, 19.8%). 1H NMR (400 MHz, DMSO-d6, δ/ppm): 8.44 (d, J = 7.9 Hz, 1H, d), 8.29 (d, J = 8.8 Hz, 1H, g), 8.13 (d, J = 7.0 Hz, 1H, e), 7.59 (dd, J = 13.6, 7.9 Hz, 2H, f, c), 7.25 (d, J = 7.4 Hz, 1H, b), 3.53 (s, 2H, i), 2.82 (s, 6H, a) (Supplementary materials, Fig. S1). 13C NMR (75 MHz, DMSO-d6, δ/ppm): 171.19 (1C, m), 152.25 (1C, c), 136.92 (1C, h), 130.22 (1C, i), 130.06 (1C, e), 130.01 (1C, k), 128.88 (1C, f), 128.76 (1C, g), 124.45 (1C, j), 120.17 (1C, d), 116.04 (1C, b), 46.09 (3C, a, l) (Fig. S2). HRMS (m/z): calculated for C14H16N2O4S 308.0831, found 309.0928 [M + H]+, 331.0721 [M + Na]+ (Fig. S3). IR (KBr) cm⁻¹: 3278 (OH), 2940 (CH₃), 1700 (C = O), 1592, 1469, 1415 (ArH) (Fig. S4). Elemental analysis: calculated for C14H16N2O4S: C, 54.53, N, 9.08, H, 5.23; found: C, 54.15, N, 8.86, H, 5.61. The fluorescence quantum yield of DNSG is 0.47.

Preparation of the silk fibroin solution

The cocoons of B. mori silkworm were degummed three times in 0.05% (wt) Na₂CO₃ solution at 98 ~ 100 °C for 30 min and then washed completely with deionized (DI) water to remove the sericin proteins on the outermost surface. After drying at 60 °C for at least 6 h, the silk fibers were dissolved in LiBr solution (9.5 mol/L) in a 15:100 bath ratio (w/v) for 40 min, followed by dialysis against running DI water to remove the salts and small molecules for 3 ~ 4 d and then further purification by centrifugation to obtain the final silk fibroin (SF) solution.

UV–Vis absorption and fluorescence test

DNSG and metal salts were dissolved in DI water to form 1 and 10 mM stock solutions, respectively. When DNSG acted as a quenched probe, a stock solution of DNSG (100 μL) and one of the ion stock solutions (200 μL) were added into a 10 mL volumetric flask and diluted with HEPES buffer solution (20 mM, pH 6.7) for the selectivity study. In the titration experiment, 100 μL stock solution of DNSG was mixed with a certain amount of the Hg²⁺ stock solution and diluted to 10 mL with HEPES buffer solution (20 mM, pH 6.7). When DNSG was used as an
enhanced probe, silk fibroin (200 μL, 0.076 g/L) was added to the volumetric flask before metal ions, and the rest of the operation was the same as that of the quenched probe. The spectra of the mixed solutions were recorded after standing for 5 min. For fluorescence measurement, the excitation wavelength was 330 nm, and the slit width was 5 nm.

Real sample assay

In the real sample assay [25, 26], pond water (after filtration) or tap water from Dushu Lake Campus of Soochow University was used instead of DI water to prepare HEPES buffer solution. Then, 100 μL of a stock solution of DNSG and 60 (80 or 100) μL of a stock solution of Hg^{2+} were introduced. The mixed solution was diluted to volume with HEPES buffer solution (20 mM, pH 6.7), and the fluorescence spectra were recorded. The concentration of Hg^{2+} in real water samples was calculated from the linear relationship between the maximal fluorescence intensity of DNSG and the concentration of Hg^{2+}.

Results and discussion

DNSG as a turn-off fluorescent probe for Hg^{2+}

Selectivity of DNSG to Hg^{2+}

The UV–Vis absorption response of DNSG to various metal ions (Fig. 1) was measured first in HEPES buffer solution (20 mM, pH 6.7). Among K^+, Na^+, Mg^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Cr^{3+}, Fe^{2+}, Ca^{2+}, Pb^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+} and Cd^{2+}, most of the ions had no apparent effects on the absorption of DNSG, except that Fe^{3+} slightly strengthened the absorption. This result indicated that the UV–Vis absorption spectra of DNSG did not obviously respond to the investigated metal ions in HEPES buffer solution (20 mM, pH 6.7).
Then, the fluorescence spectra of DNSG upon the addition of metal ions were measured. As shown in Fig. 2, the fluorescent signal of DNSG was strong upon excitation at 330 nm. The addition of Hg$^{2+}$ induced a great decrease in fluorescence intensity at 552 nm accompanied by the disappearance of the yellow fluorescence and the decrease in the fluorescence quantum yield from 0.47 (DNSG) to 0.11 (DNSG/Hg$^{2+}$), while other ions caused no significant changes in the fluorescent spectra of DNSG. Therefore, the fluorescent spectrum of DNSG was highly selective and sensitive to Hg$^{2+}$. Dansyl fluorophore is sensitive to the variation in external environment and a slight variation in the medium would result in a dramatic change in its typical and strong fluorescence, attributed to intramolecular charge transfer (ICT), involving the $N,N$-dimethylamino and sulfonamide groups [23]. In DNSG/Hg$^{2+}$ system, Hg$^{2+}$ reacted with DNSG to hindrance in charge transfer from the amino to the sulfonamide unit and quenched the fluorescence.

**Fluorescence intensity of DNSG versus concentration of Hg$^{2+}$**

The titration of DNSG (10 μM) with Hg$^{2+}$ was performed. As shown in Fig. 3, upon the gradual addition of Hg$^{2+}$ (0 ~ 80 μM), the yellow fluorescence of DNSG solutions decreased. The maximum fluorescence intensity and the concentration of Hg$^{2+}$ presented a good linear relationship with a correlation coefficient of 0.9932. The
evaluated detection limit for Hg$^{2+}$ was 0.33 μM (Calculation method: see Supplementary materials). Therefore, DNSG could be used for the quantitative detection of Hg$^{2+}$ by fluorescence quenching.

**Effects of competing ions**

To examine the selectivity of the probe for Hg$^{2+}$ in a complex background with potentially competing species, the fluorescence quenching of DNSG with Hg$^{2+}$ was investigated in the presence of other metal ions. As shown in Fig. 4, the maximum fluorescence intensity of the DNSG/Hg$^{2+}$ solutions with and without one of the competing ions showed no significant differences, which indicated that the competitive ions had negligible disturbance to the detection of Hg$^{2+}$. This observation suggests that DNSG has good anti-interference ability for detecting Hg$^{2+}$.

**Time response of DNSG to Hg$^{2+}$**

The time dependence of DNSG for sensing Hg$^{2+}$ was examined. Upon addition of Hg$^{2+}$, the fluorescence intensity at 552 nm quenched at once and stayed at a very weak level during the tested time (Fig. 5). These results showed that DNSG could be a reliable, quickly responsive probe for Hg$^{2+}$.

**DNSG as a turn-on fluorescent probe for Hg$^{2+}$**

**Selectivity of DNSG to Hg$^{2+}$**

In this part, we investigated whether SF could transform DNSG from a turn-off probe to a turn-on probe. As shown in Fig. 6, adding SF (0.076 g/L) into HEPES buffer solution (20 mm, pH 6.7) of DNSG caused no variation in the UV–Vis absorption spectrum of DNSG. When metal ions were added, only Hg$^{2+}$ induced a very weak absorption peak at approximately 280 nm, and other ions caused the absorption spectra of DNSG with silk fibroin to drift up or down in the UV region.

![Fig. 4](image-url) Effects of coexisting ions on the fluorescence maxima of the DNSG/Hg$^{2+}$ solutions. Solvent: HEPES buffer (20 mM, pH 6.7); Concentration: 10 μM DNSG, 200 μM K$^+$, Na$^+$, Mg$^{2+}$, Fe$^{3+}$, Cu$^{2+}$, Zn$^{2+}$, Cr$^{3+}$, Fe$^{2+}$, Ca$^{2+}$, Pb$^{2+}$, Ni$^{2+}$, Mn$^{2+}$, Co$^{2+}$, Cd$^{2+}$ and Hg$^{2+}$; $\lambda_{ex}$: 330 nm, slit width: 5 nm
Next, we studied the fluorescent response of DNSG to various ions after the addition of SF. K⁺, Na⁺, Mg²⁺, Fe³⁺, Cu²⁺, Zn²⁺, Cr³⁺, Fe²⁺, Ca²⁺, Pb²⁺, Hg²⁺, Ni²⁺, Mn²⁺, Co²⁺ and Cd²⁺ were added to HEPES buffer solution (20 mM, pH 6.7) of DNSG with SF. As Fig. 7 shows, only Hg²⁺ strengthened the fluorescence...
by 1.4-fold, accompanied by a 52 nm blueshift and an increase in the fluorescence quantum yield from 0.47 (DNSG) to 0.66 (DNSG/SF/Hg^{2+}). The fluorescence of the DNSG, DNSG/SF and DNSG/SF/Hg^{2+} solutions changed from light yellow to yellow to blue. Other ions showed no pronounced effects on the fluorescence spectra. The results demonstrated that DNSG could detect Hg^{2+} by fluorescence enhancement and blueshift. Protein like BSA is known to generate well defined hydrophobic–hydrophilic cavities in aqueous media and the microenvironment sensitive dansyl fluorophore exhibits enhanced fluorescence in hydrophobic media [23]. Based on the similar principle, another protein SF-assisted DNSG/Hg^{2+} system exhibiting a blueshifted enhanced fluorescence.

**Fluorescence intensity of DNSG versus concentration of Hg^{2+}**

Fluorescence titration was conducted, and the results are shown in Fig. 8. The emission intensity increased gradually with increasing concentrations of Hg^{2+} (0 ~ 200 μM), and the wavelength had a 52 nm blueshift. There was a good linear relationship ($R^2 = 0.9859$) between the fluorescence intensity and Hg^{2+} concentration in the range of 0 ~ 160 μM. The detection limit was 0.81 μM.

**Effects of competing ions**

To research the influence of coexisting ions on the detection of Hg^{2+}, K^+, Na^+, Mg^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Cr^{3+}, Fe^{2+}, Ca^{2+}, Pb^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+} and Cd^{2+} were added to the DNSG/SF/Hg^{2+} solution, respectively, and fluorescence spectra were recorded. As shown in Fig. 9, the competitive ions showed negligible disturbance to the detection of Hg^{2+} by both maximal fluorescence intensity and maximal fluorescence wavelength. This observation suggested that DNSG had good anti-interference ability for detecting Hg^{2+} as a turn-on fluorescent probe.

**Fig. 8** Fluorescence spectra of DNSG (10 μM) with different concentrations of Hg^{2+} a and the relationship between the maximal fluorescence intensity and the concentration of Hg^{2+} b. Solvent: HEPES buffer (20 mM, pH 6.7); Concentration: SF: 0.076 g/L, Hg^{2+} from bottom to top: 0, 20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 μM; $λ_{ex}$: 330 nm, slit width: 5 nm
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Time response of DNSG to Hg$^{2+}$

As an important factor for evaluating the probe in practical sensing, the response time toward Hg$^{2+}$ was tested. Clearly, the addition of Hg$^{2+}$ to the HEPES buffer solution of DNSG/SF led to an immediate and obvious fluorescence enhancement and blueshift of the peaks. Moreover, the fluorescence intensity and the shift of the peaks remained constant over a relatively wide period of time. Hence, DNSG is a reliable, quickly responsive turn-on fluorescent probe for Hg$^{2+}$ (Fig. 10).

Real sample analysis

To test the practical application of DNSG, a standard addition method to determine Hg$^{2+}$ in pond water and tap water samples was applied. The Hg$^{2+}$ content in all samples was calculated by the linear equation from fluorescence titration. The results are displayed in Table 1.

From Table 1, it can be seen that the detected concentrations of Hg$^{2+}$ were all close to that of the added ones whether DNSG was a turn-off or a turn-on fluorescent probe. As a quenched probe, the recovery was between 95.5 and 98.1%. The relative standard deviation (RSD) of the three measurements was between 0.6 and 1.4%. As an enhanced probe, the recovery was between 95.3 and 100.8%. The RSDs
of the three measurements were between 0.2 and 5.3%. It is apparent that DNSG is a concise, accurate and effective fluorescent probe for Hg\(^{2+}\) that can detect Hg\(^{2+}\) in multiple ways. The performance of some reported probes and DNSG are summarized in Supplementary materials (Table S1) for comparison.

**Sensing mechanism exploration**

*DNSG as a turn-off fluorescent probe for Hg\(^{2+}\)*

The reaction mechanism of DNSG when it was a quenched probe was studied first. Job’s plot confirmed that DNSG and Hg\(^{2+}\) were 1:1 stoichiometric ratio (Fig. 11) with a binding constant of 3.63 \times 10^5 M\(^{-1}\) (Calculation method can be found in Supplementary materials).

Then, reversible experiment was performed. As shown in Fig. 12, Hg\(^{2+}\) weakened the fluorescence intensity of DNSG in HEPES buffer solution (20 mM, pH 6.7). Upon addition of EDTA to the solution of DNSG/Hg\(^{2+}\), the fluorescence spectra almost returned to the original state in the absence of Hg\(^{2+}\), and the result confirmed that the Hg\(^{2+}\) recognition process was reversible.

**Table 1** Recovery of Hg\(^{2+}\) in pond water and tap water

| Method | Sample    | Hg\(^{2+}\) added (μM) | Hg\(^{2+}\) found (μM) | Recovery (%) | RSD (n=3) (%) |
|--------|-----------|-------------------------|-------------------------|--------------|--------------|
| Turn-off | Pond water | 60                      | 57.3                    | 95.5         | 1.4          |
|         |           | 80                      | 77.7                    | 97.1         | 0.7          |
|         | Tap water  | 60                      | 58.6                    | 97.7         | 1.2          |
|         |           | 80                      | 78.5                    | 98.1         | 0.6          |
| Turn-on | Pond water | 60                      | 56.8                    | 94.7         | 0.7          |
|         |           | 100                     | 100.8                   | 100.8        | 2.6          |
|         | Tap water  | 60                      | 57.2                    | 95.3         | 5.3          |
|         |           | 100                     | 98.3                    | 98.3         | 0.2          |

![Fig. 11] Job’s plot for Hg\(^{2+}\) versus DNSG. Solvent: HEPES buffer (20 mM, pH 6.7); Concentration: total of DNSG and Hg\(^{2+}\): 50 μM; \(λ_{ex}\): 330 nm, slit width: 5 nm; \(F_0\) and \(F\): the maximal fluorescence intensity before and after addition of Hg\(^{2+}\), respectively
The mass spectrum of the DNSG/Hg$^{2+}$ solution was determined as shown in Fig. 13, where m/z 511.3212 is the molecular ion peak of [DNSG + Hg$^{2+}$ + H$^+$], and 533.3331 is the molecular ion peak of [DNSG + Hg$^{2+}$ + Na$^+$], indicating that DNSG can complex with Hg$^{2+}$ at a 1:1 ratio.

The $^1$H NMR spectrum of DNSG with Hg$^{2+}$ was measured in DMSO-$d_6$ (Fig. 14). Compared to the $^1$H NMR spectrum of DNSG, only the protons of H$_2$O were shifted from 3.33 to 3.91 ppm, which meant that H$_2$O joined the complex. The fact that the protons of the naphthalene rings (7.21 ~ 8.48 ppm) and CH$_3$ (2.82 ppm) almost remained in situ suggested that N(CH$_3$)$_2$ were not involved in the complexation.

Considering Job’s plot, reversible experiment, mass and $^1$H NMR spectra, we depicted a sensing mechanism of turn-off DNSG for Hg$^{2+}$ in Scheme 2.
The reaction mechanism of DNSG as an enhanced probe was also studied. Job’s plot experiment indicated a 1:2 stoichiometry for DNSG and Hg$^{2+}$ (Fig. 15). The binding constant was $1.10 \times 10^8 \text{ M}^{-2}$.

As shown in Fig. 16, the fluorescence intensity of DNSG in HEPES buffer solution (20 mM, pH 6.7) was weakly enhanced after the addition of SF. With the addition of Hg$^{2+}$, the fluorescence intensity increased, and the wavelength blueshifted. Upon addition of EDTA to the solution of DNSG/SF/Hg$^{2+}$, the fluorescence spectra almost returned to the original state in the absence of Hg$^{2+}$, and the result confirmed that the Hg$^{2+}$ recognition process was reversible.

$^1$H NMR spectra of DNSG, DNSG/SF and DNSG/SF/Hg$^{2+}$ were collected and compared (Fig. 17). Except widening the proton peak of H$_2$O, the addition of SF to DNSG caused no obvious changes in the proton signals of DNSG, which indicated that DNSG did not react with SF. The reason that proton signals of SF were not observed may be due to the low concentration of SF and the solvent effect of D$_2$O.

**DNSG as a turn-on fluorescent probe for Hg$^{2+}$**

The reaction mechanism of DNSG as an enhanced probe was also studied. Job’s plot experiment indicated a 1:2 stoichiometry for DNSG and Hg$^{2+}$ (Fig. 15). The binding constant was $1.10 \times 10^8 \text{ M}^{-2}$.

As shown in Fig. 16, the fluorescence intensity of DNSG in HEPES buffer solution (20 mM, pH 6.7) was weakly enhanced after the addition of SF. With the addition of Hg$^{2+}$, the fluorescence intensity increased, and the wavelength blueshifted. Upon addition of EDTA to the solution of DNSG/SF/Hg$^{2+}$, the fluorescence spectra almost returned to the original state in the absence of Hg$^{2+}$, and the result confirmed that the Hg$^{2+}$ recognition process was reversible.

$^1$H NMR spectra of DNSG, DNSG/SF and DNSG/SF/Hg$^{2+}$ were collected and compared (Fig. 17). Except widening the proton peak of H$_2$O, the addition of SF to DNSG caused no obvious changes in the proton signals of DNSG, which indicated that DNSG did not react with SF. The reason that proton signals of SF were not observed may be due to the low concentration of SF and the solvent effect of D$_2$O.
**Fig. 15** Job’s plot for Hg$^{2+}$ versus DNSG/SF. Solvent: HEPES buffer (20 mM, pH 6.7); Concentration: SF: 0.076 g/L, total of DNSG and Hg$^{2+}$: 100 μM; $\lambda_{ex}$: 330 nm, slit width: 5 nm; $F_0$ and $F$: the maximal fluorescence intensity before and after addition of Hg$^{2+}$, respectively.

**Fig. 16** Fluorescence spectra of DNSG, DNSG/SF, DNSG/SF/Hg$^{2+}$ and DNSG/SF/Hg$^{2+}$/EDTA. Solvent: HEPES buffer (20 mM, pH 6.7); Concentration: DNSG: 10 μM, SF: 0.076 g/L, Hg$^{2+}$ and EDTA: 200 μM; $\lambda_{ex}$: 330 nm, slit width: 5 nm.

**Fig. 17** $^1$H NMR spectra of DNSG, DNSG/SF and DNSG/SF/Hg$^{2+}$ in D$_2$O (400 MHz).
After adding Hg\textsuperscript{2+}, the proton peaks of the naphthalene ring (7.63 ~ 8.46 ppm) and tertiary amino N(CH\textsubscript{3})\textsubscript{2} (3.07 ppm) in the \textsuperscript{1}H NMR spectrum of DNSG/SF/Hg\textsuperscript{2+} were downfield, indicating that the nitrogen atom in N(CH\textsubscript{3})\textsubscript{2} probably coordinated with Hg\textsuperscript{2+} in the presence of SF. The peak of H\textsubscript{2}O further widened, indicating that H\textsubscript{2}O joined the complex. The peak of CH\textsubscript{2} (3.51 ppm) greatly reduced, indicating that its adjacent imino (NH) and carbonyl (C = O) groups participated in the chelation of Hg\textsuperscript{2+}.

FTIR was also performed (Fig. S5). Compared to the IR spectrum of DNSG, the most important change in the IR spectrum of DNSG/SF/Hg\textsuperscript{2+} is the appearance of a broad peak between 3618 and 2778 cm\textsuperscript{-1} which indicates H\textsubscript{2}O involved in the complexation. The same information has been suggested by the \textsuperscript{1}H NMR spectra (Fig. 17).

According to Job’s plot, reversible experiment and \textsuperscript{1}H NMR spectra, we depicted a sensing mechanism of DNSG for Hg\textsuperscript{2+} with the assistance of SF in Scheme 3.

Conclusion

In summary, we reported a fluorescent probe (DNSG) synthesized from dansyl chloride and glycine. DNSG can detect Hg\textsuperscript{2+} not only by fluorescence quenching but also by fluorescence enhancement with the help of silk fibroin. The detection can be carried out in a full water system reversibly. DNSG showed many advantages, such as simple synthesis, good water solubility, high selectivity, fast response speed and strong anti-interference ability. 1:1 and 1:2 complex formed between DNSG and Hg\textsuperscript{2+} in the turn-off and turn-on detection, respectively. Moreover, DNSG can be applied in determination of Hg\textsuperscript{2+} in environmental water samples. Thus, DNSG is a desired concise, accurate and effective multichannel fluorescent probe for Hg\textsuperscript{2+}.

Supplementary Information  The online version contains supplementary material available at https://doi.org/10.1007/s11164-022-04846-y.

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Authors contributions  Chunming Sha did most research work and wrote the first draft of the manuscript. Zhengkun Li supplemented some data. Shenzhou Lu prepared silk fibroin. Xiaolong Hu collated and
checked references. Dongmei Xu contributed ideas, supervised the work, revised and completed the manuscript.

Declarations

Conflicts of interests There are no competing interests to declare.

References

1. H.A. Spiller, Clin. Toxicol. 56, 313 (2018)
2. W.-L. Cui, Z.-H. Zhang, L. Wang, J. Qu, J.-Y. Wang, Spectrochim Acta Part A Mol. Biomol. Spectrosc. 267, 120516 (2022)
3. N. Jamasbi, G. Mohammadi Ziarani, F. Mohajer, A. Badiei, Res. Chem. Intermed. 48, 899 (2022)
4. C. Zhang, B. Gao, Q. Zhang, G. Zhang, S. Shuang, C. Dong, Talanta 154, 278 (2016)
5. D.T. Quang, J.S. Kim, Chem. Rev. 110, 6280 (2010)
6. X. Qian, Z. Xu, Chem. Soc. Rev. 44, 4487 (2015)
7. K. Xiang, Y. Liu, C. Li, B. Tian, J. Zhang, RSC Adv. 5, 52516 (2015)
8. M. Hong, X. Lu, Y. Chen, D. Xu, Sens. Actuators B Chem. 232, 28 (2016)
9. Y. Chen, T. Tang, Y. Chen, D. Xu, Res. Chem. Intermed. 44, 2379 (2018)
10. T. Tang, J. Wang, D. Xu, Res. Chem. Intermed. 46, 1425 (2020)
11. P. Li, R. Li, K. Wang, Q. Liu, B. Ren, Y. Ding, R. Guan, D. Cao, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 276, 121213 (2022)
12. W. Nasomphan, P. Tangboriboonrat, S. Smanmoo, J Flourence. 27, 2201 (2017)
13. N. Qureshi, S. Ehtisham-ul-Haque, M. Abbas, M. Yameen, M.F. Azhar, G. Mahmoudi, A. Nazir, M. Iqba, J. Mater. Res. Tech. 8, 1576 (2019)
14. E. Jeong, S. Yoon, H.S. Lee, A. Kumar, P.S. Chae, Dyes Pigments 162, 348 (2019)
15. Y. Wang, J. Zhou, L. Zhao, B. Xu, Dyes Pigments 18, 10851 (2020)
16. G. Gao, X. Wang, Z. Wang, X. Jin, L. Ou, J. Zhou, P. Xie, Talanta 215, 120008 (2020)
17. J.B. Asha, M. Karthik, P. Suresh, Mater. Adv. 2, 3107 (2021)
18. M. Yang, M. Sun, Z. Zhang, S. Wang, Talanta 105, 34 (2013)
19. S. Zhou, Z. Zhou, X. Zhao, Y. Xiao, G. Xi, J. Liu, B. Zhao, Spectrochim Acta Part A Mol. Biomol. Spectrosc. 148, 348 (2015)
20. A. Kumar, H.S. Kim, Spectrochim Acta Part A Mol. Biomol. Spectrosc. 148, 250 (2015)
21. C. Sha, S. Lu, F. Lv, D. Xu, Res. Chem. Intermed. 42, 5825 (2016)
22. Y. Liu, B. Jiang, L. Zhao, L. Zhao, Q. Wang, C. Wang, B. Xu, Spectrochim Acta Part A Mol. Biomol. Spectrosc. 261, 120009 (2021)
23. P. Srivastava, M. Shahid, A. Misra, Org. Biomol. Chem. 9, 5051 (2011)
24. P. Stefan, N. Marc, S. Thorssten, M. Hans, WO2014037394 (2014)
25. S. Xue, Z. Xie, Y. Chu, W. Shi, Y. Liu, Y. Zhao, Luminescence 37, 108 (2022)
26. U. Krishnan, S.K. Iyer, Photochem. Photobiol. 98, 843 (2022)

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