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Fluorescent and colorimetric detection of Cu^{2+} with enhanced sensitivity using adduct of Ag⁺-coordination-polymers with a binding compound

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ABSTRACT

Enrichment strategy based on the carrier covered with multiply binding groups is an effective way for improving sensing performance in terms of sensitivity and selectivity. However, the majority of reported carriers built through covalent chemistry are time- and cost-consuming because of the additional synthesis and characterization loads. Therefore, one key to the success of this strategy lies in the building of the carriers in a feasible manner. Supramolecular chemistry offers an ideal way to construct functional carriers. However, the reported supramolecular carriers established *via* hydrophobic effects and electrostatic interactions lack stability during the sensing process. Thus, another key would be to develop a supramolecular carrier of suitable stability. In this study, we reported a proof-of-the-concept supramolecular system for sensing Cu^{2+} , the adduct of dye Alizarin Red S (ARS) with Ag⁺-thiol coordination polymer, *via* an indicator displacement assay, in which ARS is the indicator. A sensing system for Cu^{2+} was established with LODs of 2.1×10^{-8} M and 9.8×10^{-8} M, respectively, using fluorescence intensity and RGB values as the sensing index. The sensitivity and selectivity towards Cu^{2+} were greatly enhanced by the polymeric structure of the polymer-ARS adduct, comparing to those of the monomeric adduct, monomer-ARS. The structural stability of the polymeric sensing system was evaluated by DLS, TEM and CD investigations. The proposed new strategy approves to be feasible and holds promise for rational design for other target species.

1. Introduction

Enrichment strategy offers an excellent sensing performance in terms of the sensitivity and selectivity, and it has been widely applied in the sensing system that uses the indicator displacement assays (IDA) [1,2]. A key feature of this strategy is the polymeric or aggregated structure of the sensing receptor that is covered by multiple binding sites for target analytes. Variety of sensing materials, including nanoparticles [3–5], dendrimers [6] and carbon dots [7] have been developed and used as carriers to enrich binding sites/molecules for sensing analytes. However, the building of those materials requires elaborate design and complex synthetic procedures, being therefore time- and cost-taking. Self-assembled aggregates, built from a simple molecule *via* noncovalent weak interactions, can effectively decrease synthetic loads. For example, micelles [8–10] and vesicles [11–13] have been widely established and incorporated with binding groups or components. However, the

formation of those aggregates was driven by hydrophobic effects and electrostatic interactions, leading to a drawback of low stability to confront practical environmental factors, such as temperature, pH and charged species. Therefore, a key success in enrichment strategy roots in designing a stable polymeric structure for enriching functional groups by choosing a proper weak interaction or combination of them.

Recently, coordination polymers of Ag^+ with a cysteine-based thiol ligand, supported by argentophilic interactions, have been widely investigated [14–18]. The binding constant of Ag^+ with a thiol ligand (R-SH) is *ca.* 10^{13} M⁻¹, which guarantees the rapid generation and structural stability of the Ag^+ -SR coordination polymers. More importantly, silver ions and S atoms are arranged in one-dimensional chain-liked structure that holds R moiety together, potentially to increase the local concentration of the binding groups incorporated within it or binding to it and result in signal amplification [14]. Taking advantage of the polymeric structure of the Ag^+ -SR chain, highly effective chiral

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Scheme 1. (a) Previously reported carriers for enriching binding groups [3–13]. (b) Schematic illustration of Cu^{2+} detection with the *in situ* formed polymer-ARS adduct from Ag⁺, L-PBA and ARS based on fluorescence and RGB signals. (c) Cu^{2+} detection with monomer-ARS adducts. The dashed red lines in polymeric backbone represent Ag⁺...Ag⁺ interactions.

recognition [18] and chiral amplification of glucose [19] have been achieved. Recent research showed that this polymeric structure of Ag^+ -SR chain contributes to the high activity of catalyst modified on it [20]. We therefore assumed that a well-designed coordination polymer of Ag^+ is an ideal candidate as the carrier to load on binding groups, affording improved analytical performance in sensing events.

Inspired by these pioneering works performed on aggregated carriers [3-13] (Scheme 1a), as a proof-of-concept, in this research, we choose in situ generated coordination polymers of Ag⁺ with a L-cysteine derivative of phenylboronic acid (L-PBA, monomer), as such carrier (polymer) to enrich the ARS dye through a boronic ester formation, for the sensing of a model analyte, Cu²⁺ that coordinates to ARS, via IDA (Scheme 1b), in which cysteine residues supply -SH groups to coordinate with Ag⁺, while its chiral center provides an additional way of looking into the formation process of the polymeric structure. It was expected that the polymeric structure of Ag⁺-L-PBA, stabilized by the Ag⁺...Ag⁺ interactions, holds ARS dyes close to each other, thereby its local concentration was increased to improve the sensitivity towards Cu²⁺. Whereas, as the control system, the L-PBA-ARS adduct (monomer-ARS) shows low sensitivity and selectivity to Cu^{2+} (Scheme 1c). In the proposed sensing strategy, fluorescence emission of ARS is turned on by reacting with boronic acid group and then switched off by Cu^{2+} that disrupts the boronate bonds of ARS with the boronic acid moiety in the thiol ligand, by competitively coordinating with ARS. It deserves to point out that the on-off fluorescence is accompanied with a solution color change from orange to purple, which motivated us to further evaluate Cu²⁺ using the RGB values extracted from the color pictures.

Moreover, in order to improve the accuracy of the results, a RGB picker software that can give the average R, G and B values of random chosen region on the picture, different from the commonly reported works that only analyze one pixel point per time, was developed by our group. Therefore, a dual-mode fluorescent and colorimetric detection of Cu²⁺ with enhanced sensitivity and selectivity was developed by the use of a polymeric framework of coordination polymers of Ag⁺ that bind dye ARS indicators. Taking Ag⁺-L-PBA coordination polymers as the carrier for binding ARS dye for Cu²⁺ detection features the following unique advantages. (i) The high binding affinity between Ag⁺ and thiol ligands guarantees its stability in sensing process, comparing to these carriers built on hydrophobic effects or electrostatic interactions. (ii) The preparation of polymer-ARS is simple enough, which could be in situ prepared from Ag⁺, L-PBA ligand and ARS through a mixing operation, avoiding complex synthesis steps. (iii) Particularly, the polymeric structure increases the local concentration of bind compounds, offering enhanced selectivity and sensitivity towards Cu^{2+} .

2. Methods

2.1. Materials

L-Cysteine ethyl ester and 4-carboxyphenylboronic acid were purchased from Energy Chemical Reagent Co. Ltd (Shanghai, China). AgNO₃ was obtained from Chemical Reagent Company (Beijing, China). ARS was obtained from Bio Basic Inc. (Beijing, China). All metal salts of chloride or nitrate salts were purchased from Sinopharm (Beijing,



Fig. 1. (a) Absorption, (b) CD spectra, (c) DLS data and (d, e) TEM images of L-PBA in the absence and presence of 1.0 eq Ag⁺, and (f) ¹H NMR signals of phenyl –CHs of L-PBA in the absence and presence of 0.5 and 1.0 eq Ag⁺ in 0.05 M pH 6.7 PBS buffer. [L-PBA] = 20μ M.

China). All the chemicals were of analytical grade and used without further purification. Phosphate buffer solutions (PBS) of pH 4.5–8.5 were prepared by mixing NaH₂PO₄ (50 mM) and Na₂HPO₄ (50 mM) at different volume ratios. Buffers of pH 9.0–10.0 were similarly prepared by mixing NaHCO₃ (50 mM) and Na₂CO₃ (50 mM). The pH values of the buffer solutions were adjusted and monitored with a pH meter (Mettler Toledo Five Easy Plus) at 25 °C. Purefied water used in all experiments brought from Wahaha company (Hangzhou, China).

2.2. Apparatus

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV500 and 850 NMR spectrometer in dimethyl sulfoxide (DMSO- d_6). Tetramethylsilane ($\delta = 0$ ppm) was utilized as a reference. Circular dichroism (CD) spectra were recorded on JASCO J-810CD Chiroptical Spectrometer. Absorption spectra were recorded on a Varian Cary 300 UV–Vis spectrophotometer. Fluorescence spectra were recorded on Horiba Fluorolog fluorescence spectrophotometer. Dynamic light scatter (DLS) experiments were performed on Malvern Nano S90 mastersize at a scattering angle of 90°. Transmission electron microscopy (TEM) images were taken on a JEM 1400 microscope.

2.3. General procedures

2.3.1. Synthesis of L-PBA

The synthesis and detailed ¹H NMR and ¹³C NMR and HRMS characterization of L-PBA are supplied in Scheme S1 (Fig. S1-3).

2.3.2. Preparation of Ag⁺-L-PBA coordination polymer

The polymer was prepared by separately adding 8.0 μ L of 5 mM L-PBA stock solution and 4.0 μ L of 10 mM AgNO₃ stock solution into buffer solutions to give a final concentration of L-PBA and Ag⁺ of both 20 μ M.

2.3.3. Preparation of polymer-ARS

To the solution of the prepared polymer, ARS of concentration of 10 mM was subsequently added, until the final concentrations of L-PBA, Ag^+ and ARS all of 20 μ M.

2.3.4. Fluorescence sensing of Cu^{2+}

Fluorescence measurements were performed at an excitation wavelength of 495 nm. To the above made solution of the polymer-ARS adduct, a series of Cu^{2+} stock solution (10 mM) was added, followed by recording fluorescence spectra every time, until the emission signal levels off.



Fig. 2. (a) Fluorescence spectra of the polymer in the presence of ARS of increasing concentration from 0 to 150 μ M in 0.05 M pH 6.7 PBS buffer and (b) absorption spectra of ARS and polymer-ARS adduct. Inset in Fig. 2a represents the intensity titration profile. [L-PBA] = [Ag⁺] = 50 μ M.

2.3.5. Colorimetric sensing of Cu^{2+}

Different volumes of Cu^{2+} (10 mM) solution ranging from 0 to 8 µL were added into an aqueous buffer solution of 2.0 mL at pH 6.8 containing polymer-ARS adduct of 20 µM. 2 min later those samples were placed in a 20 × 20 × 20 cm airtight box that is equipped with a LED strip inside and the graphs of the sample were recorded on the camera of a smartphone and analyzed by a RGB picker software developed by us.

3. Results and discussion

3.1. Preparation of Ag⁺-L-PBA coordination polymers

To verify the successful construction of Ag^+ -L-PBA coordination polymers, we examined the absorption and CD spectra of L-PBA in 50 mM pH 6.7 PBS buffer in the presence of Ag^+ of increasing concentration. Fig. 1a shows that a new and enhancing absorption band appears at 348 nm with the addition of Ag^+ , which is assigned to the ligand-tometal-metal charge transfer (LMMCT) [14,21] transition. Meanwhile, monomeric L-PBA was CD silent, while as the addition of Ag^+ , the chirality of the L-cysteine residue in L-PBA was successfully transferred to the *in situ* formed chromophores relating to the Ag^+ ... Ag^+ interactions along the polymeric backbone, from which corresponding CD signal is turned on around 350 nm (Fig. 1b). Both the changes in absorption and CD spectral profiles indicate the successful construction of the coordination polymers of Ag^+ with L-PBA, facilitated by argentophilic interactions. Titration results of the absorption and CD spectra of L-PBA by Ag^+ are given in Fig. S4a and S4b that the characteristic CD signals at



Fig. 3. (a) Fluorescence spectra of polymer-ARS with Cu^{2+} of increasing concentration of in 0.05 M pH 6.7 PBS buffer, the inset of (a) shows the photo of polymer-ARS sensing solution in the absence (left) and presence (right) of Cu^{2+} , and (b) plots of intensity versus Cu^{2+} concentrations, and the inset shows the fitted linear relationships. [L-PBA] = $[Ag^+] = 20 \ \mu\text{M}$, $[Cu^{2+}] = 0$ –20 μM .

292 nm (Fig. S4c) and absorbance at 350 nm (Fig. S4d) as a function of $[Ag^+]$ confirm the 1:1 stoichiometry between Ag^+ and L-PBA ligand. The polymeric structure of coordination polymer was confirmed by its DLS diameters of around 450 nm (Fig. 1c), accompanied by the observation of chain-like morphology in TEM images (Fig. 1e), while that of L-PBA in the absence of Ag^+ was about 1.5 nm (Fig. 1c) and no aggregated species were found in its TEM image, in agreement with its monomeric form (Fig. 1d). Moreover, ¹H NMR signals of phenyl group of L-PBA are gradually weakened and disappeared at 1 eq Ag^+ , further confirming the binding of Ag^+ with L-PBA to form coordination polymers (Fig. 1f).

3.2. Preparation of polymer-ARS adduct

It is known that the fluorescence of ARS could be turned on when its excited state proton transfer from phenol hydroxyl to ketone oxygen is blocked by forming boronate ester with a boronic acid group [22–27]. Firstly, we investigated the response of polymer to ARS. Results shown in Fig. 2 show that the Ag⁺-L-PBA coordination polymer itself is at fluorescent off state over 500–700 nm, and it is turned on at 583 nm upon introducing ARS (Fig. 2a). This fluorescence emission originates from the reversible boronate easter bond formation between *cis*-1,2-diol moiety of ARS and the boronic acid group in the thiol ligand of the Ag⁺-L-PBA coordination polymers, suggesting that ARS as an indicator is

successfully anchored on the polymeric backbone via boronate formation. The fluorescence intensity of the polymer-ARS as a function of storing time indicated that the sensing system has stability for 48 h (Fig. S5). The stability and fast preparation of the sensing system offers its possibility for practical applications. Fluorescence titration levels off at 1.0 eq ARS, meaning the best interaction ratio of polymer with ARS (inset in Fig. 2a). Finally, this 1:1 ratio was taken to prepare polymer-ARS adduct for the detection of Cu^{2+} in the following experiments. Moreover, the absorption of ARS itself at 515 nm, is blue-shifted by 14 nm with an isosbestic point at 510 nm, during its interaction with the polymer, further supporting the successful formation of the polymer-ARS adduct (Fig. 2b). Similar CD spectral profile of the polymer-ARS adduct to that of the polymer was observed (Fig. S6a), suggesting the loading of ARS dye has no influence on the supramolecular structure of polymers. DLS data indicate a small increase in the diameter by 16 nm of the polymer upon binding ARS (Fig. S6b), while the TEM morphology remains almost unchanged (Fig. S6c). All of the above results demonstrate that the loading of ARS has not destructed the polymeric framework.

3.3. Detection of Cu^{2+} using fluorescence signal

The influence of solution pH ranging from 4.5 to 10.0 on Cu²⁺ detection using fluorescence of the polymer-ARS adduct was examined. The $(I_0 - I)/I_0$ value of the sensing system increases in the pH ranging from 4.5 to 6.7 and drops at higher pH, in which I₀ and I refer to the fluorescence intensity of the polymer-ARS adduct in the absence and presence of Cu^{2+} , respectively (Fig. S7). Therefore, a pH value of 6.7 was chosen for detecting Cu^{2+} . Optimization of reaction time shows that the fluorescence intensity of sensing system decreased quickly within 0.5 min after the addition of Cu²⁺ (Fig. S8), demonstrating a rapid detection to Cu²⁺. Fluorescence of the polymer-ARS adduct at 548 nm was found quenched upon the addition of Cu^{2+} (Fig. 3a), accompanied with solution color changes from orange to purple (inset in Fig. 3a). Plots of fluorescence intensity against Cu²⁺ concentration show a plateau at 1.3 μ M Cu²⁺, which means the highest release of ARS from the polymeric backbone led by Cu^{2+} (Fig. 3b). Meanwhile, the absorbance at 501 nm increases together with a red-shift of 6 nm of the polymer-ARS adduct in the presence of 1.4 μ M Cu²⁺ (Fig. S9). Job plots confirm a 1:1 stoichiometry between the polymer-ARS adduct and Cu^{2+} (Fig. S10), which is in accordance with that reported by Minami [25]. To confirm the repeatability of Cu²⁺ detection by polymer-ARS, the detection experiments of each concentration were repeated three times, through of which the relative standard deviation (RSD) were calculated to be with average value of 3.6 %, exhibiting a good reproducibility and potential possibility for real application. Inset in Fig. 3 shows a good linear relationship ($R^2 = 0.991$) of the changes in fluorescence intensity of the polymer-ARS adduct with the concentration of Cu²⁺ over the range of $0.5-1.3 \mu$ M. The linear regression equation is y = 4.576-1.769x, and the limit of detection (LOD) is of 2.1 \times 10^{-8} M that is much lower than the level allowed in drinking water, for example, ca. 20 µM set by the U.S. Environ mental Protection Agency, USEPA. Table S1 exhibits the previously reported sensors for Cu^{2+} detection that also rely on coordination effect with Cu²⁺. Obviously, our proposed sensing strategy has a considerable or even more sensitive response to Cu²⁺, and its preparation involves in only the condensation reaction, effectively avoiding time- and cost-consuming, comparing to the reported chemosensors that were synthesized with multi-step reactions.

To demonstrate the superiority of the polymeric structure in the sensing platform, the monomeric molecule-based sensor, the L-PBA/ARS adduct was also examined as a control system for Cu^{2+} detection under its optimal pH of 0.05 M PBS buffer of pH 7.0 (Fig. S7). Based on a similar sensing mechanism, the fluorescence intensity of monomer-ARS adduct (Fig. S12) decreases with Cu^{2+} , from which a linear working concentration range is found from 0 to 7.7 μ M with a LOD of 2.5 $\times 10^{-7}$ M (Fig. S11). The LOD is 12-fold lower in the polymer-ARS adduct



Fig. 4. (a) Histogram graphs of changes in fluorescence intensity of the polymer-ARS adduct versus Cu²⁺ and other metal ions, and (b) Histogram graphs of changes in fluorescence intensity of the polymer-ARS adduct in the presence of Cu²⁺ together with other metal ions in 0.05 M pH 6.7 PBS buffer, other metal ions including Mg²⁺, Al³⁺, Co²⁺, Ca²⁺, K⁺, Mn²⁺, Ni²⁺, Zn²⁺, Ag⁺, Cd²⁺, Hg²⁺, and Pb²⁺. [L-PBA] = [Ag⁺] = [ARS] = 20 \mu M, [Cu²⁺] = 5 \mu M. [other metal ions] = 25 \mu M. The inset represents the color of polymer-ARS in the presence of various metal ions.

sensing system than that of the monomer-ARS adduct. One factor assumed to contribute to the higher sensitivity of the polymer-ARS adduct is the high local concentration of ARS enriched by the multiple binding on the polymeric backbone. The result confirms the high performance in sensitivity of the proposed strategy that uses receptor with highly concentrated binding sites as carriers for enriching indicator molecules as sensing elements.

3.4. Selectivity

To test the selectivity of the sensing using polymer-ARS adduct, we investigated its fluorescence response to representative metal ions including K⁺, Ag⁺, Ca²⁺, Mg²⁺, Zn²⁺, Pb²⁺, Cd²⁺, Co²⁺, Ni²⁺, Hg²⁺ and Al^{3+} at the concentration of 25 $\mu M,$ which is 5 times that of $Cu^{2+}.$ The result indicates that those tested ions do not alter the change in the fluorescence of the polymer-ARS adduct (Fig. 4a), except for Zn^{2+} that makes the emission of ARS red-shifted from 585 nm to 595 nm (Fig. S12a). The result was also reflected in an obvious solution color change that 5 μM of ${\rm Cu}^{2+}$ makes the solution color change from orange to purple, whereas the tested other metal ions do not, even at a concentration 5-fold that of Cu^{2+} (inset in Fig. 4a). Although other metal ions, including Ca^{2+} , Mg^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Hg^{2+} , and Al^{3+} could form complex with ARS by coordinating with O atom of ARS, their binding affinity exhibits subtle differences according to the hardsoft acid-base principle and that could be regulated by solution pH. The excellent selectivity towards Cu^{2+} is attributed to the multiply binding sites on the polymeric backbone that effectively magnifies the minor differences in the binding of ARS with Cu²⁺ over other metal ions, at optimal pH [13,28]. Indeed, the control experiment does indicate that the monomeric adduct, ARS-L-PBA exhibits no selectivity towards Cu²⁺ detection (Fig. S12b and S13). Moreover, previously reported sensors that are constructed from single phenylboronic acid molecule and catechol dye also lack selectivity towards Cu²⁺ detection as summarized in Table S2. Our proposed sensing strategy, taking polymeric Ag⁺-L-PBA as the carrier to increase the local concentration of ARS, exhibits superior sensitivity that contributes to the enhanced selectivity for Cu^{2+} , comparing with the adducts of single PBA with catechol dye. Meanwhile, we found that there is a difference in the optimal pH values of the polymer-ARS from the monomer-ARS adduct for detecting Cu^{2+} , again indicating that the polymeric structure has a significant enhancement of

Table 1

Recovery of Cu^{2+} spiked in real tap water samples.

Cu^{2+} added (µM) Cu^{2+} detected (µM) Recovery (%)		
0.30	0.32 ± 0.05	106 ± 16.5
0.40	0.39 ± 0.02	97.5 ± 5.1
0.50	0.51 ± 0.06	102 ± 12.8
0.60	0.59 ± 0.01	98 ± 1.6
0.70	0.73 ± 0.02	104 ± 3.7
0.80	0.81 ± 0.03	101 ± 3.7

the interaction of ARS with Cu^{2+} . As an excellent sensor, its response should not be interfered by other co-existing species. Therefore, an interference experiment was performed. Fig. 4b shows that the fluorescence of the polymer-ARS adduct is significantly quenched by Cu^{2+} in the presence of the competitive metal ions, exhibiting the good selectivity of the polymer-ARS adduct in sensing Cu^{2+} over the tested other metal ions.

3.5. Detection of Cu^{2+} in tap water

A much more challenging goal is to detect Cu^{2+} in a complicated real sample. To evaluate the practicality of the proposed sensor, we detected the concentration of Cu^{2+} in tap water filtered through 0.22 µm membrane. The addition of the water samples spiked with Cu^{2+} led to a significant decrease in the fluorescence intensity of the sensor. The recoveries of these measurements are in the range of 97.5–106%, respectively, for tap water (Table 1), which confirms the reliability of our sensor for Cu^{2+} determination in environmental samples.

3.6. Detection of Cu^{2+} based on RGB analysis

In view of the obvious colour change of the sensor solution in the presence of Cu^{2+} , a rapid and intelligent sensing platform for on-site Cu^{2+} detection was developed by taking RGB value as the output signal, as shown in Fig. 5a. It should be noted that the RGB values displayed in image are fluctuant due to the interference from the intensity and direction of light that affect the distribution of light and shade in the photograph, resulting in the inaccuracy of the result when using a conventional RGB analysis software that only gives the RGB value of one

point [29–31]. To minimize this error, a RGB picker software that could directly give the average R, G, and B values of random region on the image, was developed by us for color extraction. Meanwhile, in order to decrease the influence of the natural light differences on the solution color when taking pictures using a smartphone, we prepared a closed box equipped with a LED strip inside for placing samples. The R - B value was adopted to establish the relationship with Cu^{2+} concentration, in which R and B values represent the average value of the chosen region containing 200 \times 200 pixel points on the image. As shown in Fig. 5b, a linear relationship of y = 39.38-51.93x was observed in the range of 0–1.7 μM Cu^{2+} with a LOD of 9.8 \times 10^{-8} M. Moreover, the solution color experiences an obvious change from orange to light red, light purple and purple at Cu²⁺ concentration of 0.4–0.6 μ M, 0.8–1.0 μ M and 1.1–1.7 μ M, respectively, affording the possibility of visual detection of Cu^{2+} by naked eyes. This result supplies an intelligent tool for Cu^{2+} detection by using a smartphone equipped with a RGB picker, which is simple, costefficient and portable compared to traditional laboratory equipment.

4. Conclusions

In summary, a sensitive and selective fluorescence sensing system with a polymeric structure was developed to detect Cu^{2+} . The sensory system taking Ag⁺ coordination polymer as the carrier to load and increase the local concentration of dye ARS that coordinates to Cu^{2+} , exhibits a much higher sensitivity and selectivity than that of the monomeric L-PBA-ARS adduct. Fluorescence of the polymer-ARS adduct is quenched by Cu^{2+} , together with a change in solution color from orange to purple, allowing actually fluorescent and colorimetric dualmode detection of Cu^{2+} with excellent LODs of 2.1×10^{-8} M and 9.8 $imes 10^{-8}$ M, respectively. The greatly enhanced sensing performance of the polymeric sensing system is attributed to the multiple binding sites supplied by the polymeric framework of the coordination polymers of Ag⁺ of the thiol ligand that bears a boronic acid group that interacts with dye ARS, resulting in a substantially higher local concentration of the dye that binds to Cu²⁺. In principle, this strategy could be extended to other target analyte by choosing a suitable binding dye to be loaded on the polymeric backbone of the coordination polymers of Ag⁺.



Fig. 5. (a) Scheme of on-site visual quantitative colorimetric process with polymer-ARS adduct using a smartphone-assisted RGB picker software, (b) average RGB values of polymer-ARS adduct at different Cu^{2+} concentration and the corresponding linear relationship of R – B value versus Cu^{2+} concentration. The inset images show solution colors of the polymer-ARS adduct at Cu^{2+} concentrations of 0–1.7 μ M.

CRediT authorship contribution statement

Su-Li Dong: Writing – original draft, Resources, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Yan Xu:** Validation, Formal analysis, Data curation. **Yun-Bao Jiang:** Writing – review & editing, Supervision, Resources, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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Data availability

Data will be made available on request.

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