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A simple approach based on transmetalation for the selective and sensitive colorimetric/fluorometric detection of copper(II) ions in drinking water†

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The search for feasible and efficient methods for sensing cations in the environment is a challenge of current scientific interest. Among the colorimetric and fluorometric methods, those that enable the direct and rapid detection of the analytes are highly desirable. Here a simple approach based on the transmetalation of a Zn(II) Schiff-base complex for the selective and sensitive colorimetric and fluorometric detection of Cu²⁺ ions in aqueous solution is reported. This method offers the advantages of being direct, fast, and not requiring any treatment of the sample. A detection limit down to 0.60 μM is obtained from the spectrophotometric data. The method is demonstrated to be efficient for the quantitation of Cu²⁺ ions in drinking water.

Introduction

The colorimetric and fluorometric sensing of cations is an area of intense current interest. Various review contributions based on conventional organic chemosensors through metal coordination,^{1–3} including Schiff-bases,^{4,5} host–guest supramolecular chemistry,⁶ including macrocycles as ion-pair receptors⁷ and calixarenes,⁸ aggregation-induced emission,⁹ luminescent coordination polymers,¹⁰ metal–organic frameworks,¹¹ metal nanoparticles,^{12,13} quantum dots,¹³ and sensing arrays,¹⁴ or involving a chemodosimetric approach,^{15,16} have been reported in the recent literature (regarding the last decade). This huge amount of research activity highlights the breadth and interest of this research field. In this context, sensing of copper(II) ions is doubtless one of the most investigated topics.^{1–19}

Besides these methods, a further approach for detecting cations is represented by transmetalation or metal exchange.^{20,21} Thus, starting from a metal complex, sensing can be achieved *via* a cation-exchange mechanism exploiting optical spectroscopic changes, often fluorescence enhancement or quenching, upon transmetalation. This can offer further advantages with respect to the above sensing methods in terms of greater selectivity and straightforward application. However, sensing data based on transmetalation are limited compared with the other methods. Regarding the sensing of copper(II) ions, few examples based on

transmetalation have been reported in the literature,^{22–30} and only some of them include quantitative detection data.^{27–30}

Copper plays an important role in biology as an essential trace element that is fundamental to the proper functioning of enzymes, such as superoxide dismutase, cytochrome oxidase, or metallothionein.³¹ Moreover, it is involved in neurobiology and in neurodegenerative disorders.^{32–34} Both a deficiency and an excessive copper intake produce adverse health effects.³⁵ Copper is widely used for producing wires, pipes, and various manufactures, as well as in agriculture as a antimycotic agent. Sources for copper contamination include agriculture, industrial waste, mining, and photovoltaics.^{36–38} Therefore, copper pollution represents an emerging issue for environmental and human health.^{39,40}

As the main sources of human copper intake are food and water, the European Union has established a limit of 2 mg L^{−1} (corresponding approximatively to 30 μM) for the concentration of copper(II) in drinking water,⁴¹ as recommended by the World Health Organization (WHO) guidelines for water quality.^{42,43}

Lewis acidic zinc(II) complexes of tetradentate Schiff-base ligands have recently emerged for their aggregation and sensing properties.^{44–46} In particular, derivatives of 2,3-diaminomaleonitrile, Zn(salmal), are characterized *via* their relevant optical spectroscopic changes in relation to the nature of the aggregate species or monomeric adducts.^{47–53} We have demonstrated that in a solution of weak coordinating solvents a 5-*tert*-butyl-substituted Zn(salmal) complex (1) forms relatively stable adducts, which easily transmetalate with divalent ions of the first transition series, but at different rates.⁵⁴ In particular, transmetalation with Cu²⁺ ions is faster than that with other cations, regardless of the nature of the counteranion. These results stimulated us to further explore the selective and sensitive

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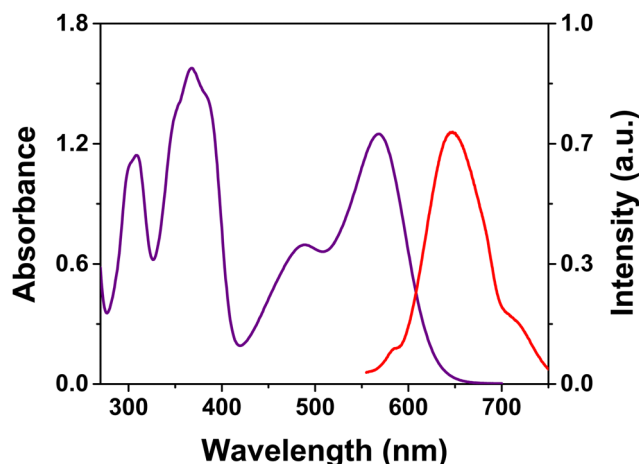
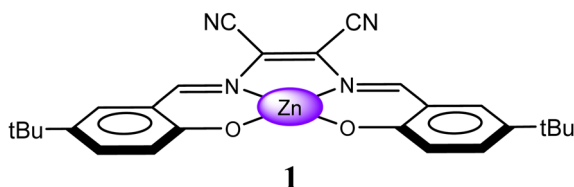


Fig. 1 UV/Vis optical absorption and fluorescence ($\lambda_{\text{exc}} = 535$ nm) spectra of **1** (40 μM solution in MeCN).

detection of Cu^{2+} ions using this simple and straightforward approach.

In this paper we report on the selective, sensitive, colorimetric and fluorometric detection of Cu^{2+} ions in aqueous solution based on transmetalation of the $\text{Zn}(\text{II})$ Schiff-base complex **1**, highlighting the simple feasibility of this efficient method.



Results and discussion

The absorption spectrum of **1** in acetonitrile (MeCN) solution in the visible region is characterized by an absorption band centred at 489 nm, followed by a more intense band at 568 nm, both of which are responsible for the violet colour of the solution. Moreover, **1** shows a weak red fluorescence emission ($\phi \leq 0.01$) centred at 645 nm that is independent of the excitation wavelength (Fig. 1). MeCN solutions of **1** are stable over time at room temperature.

Starting from a 40 μM solution of **1** in MeCN, upon the addition of up to 2.0 equiv. of aqueous solutions of various metal cations, as nitrates or perchlorates, including Na^+ , Mg^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , and Pb^{2+} , the optical absorption and fluorescence emission spectra remain almost unchanged. Instead, the addition of 2.0 equiv. of an aqueous solution of Cu^{2+} salts leads to an immediate and substantial change in the optical absorption spectrum in the visible region, with the disappearance of the band at 568 nm and the formation of a new broad band centred at 530 nm, accompanied by a colour change of the solution from violet to magenta, and a complete quenching of the fluorescence (Fig. 2). It is well known that $\text{Cu}(\text{II})$ complexes are characterized by fluorescence turn-off of the organic chromophores, owing to the paramagnetic quenching effect.⁵⁵

These data are consistent with the fast and complete transmetalation of the Zn^{2+} ion with the Cu^{2+} ion (Scheme 1). In fact, identical results, in terms of the optical absorption spectra without any fluorescence emission, are obtained by comparing the spectra of **1** in MeCN upon the addition of 2.0 equiv. of aqueous solutions of Cu^{2+} salts with those recorded by dissolving the $\text{Cu}(\text{salma})$ complex in MeCN.⁵⁴

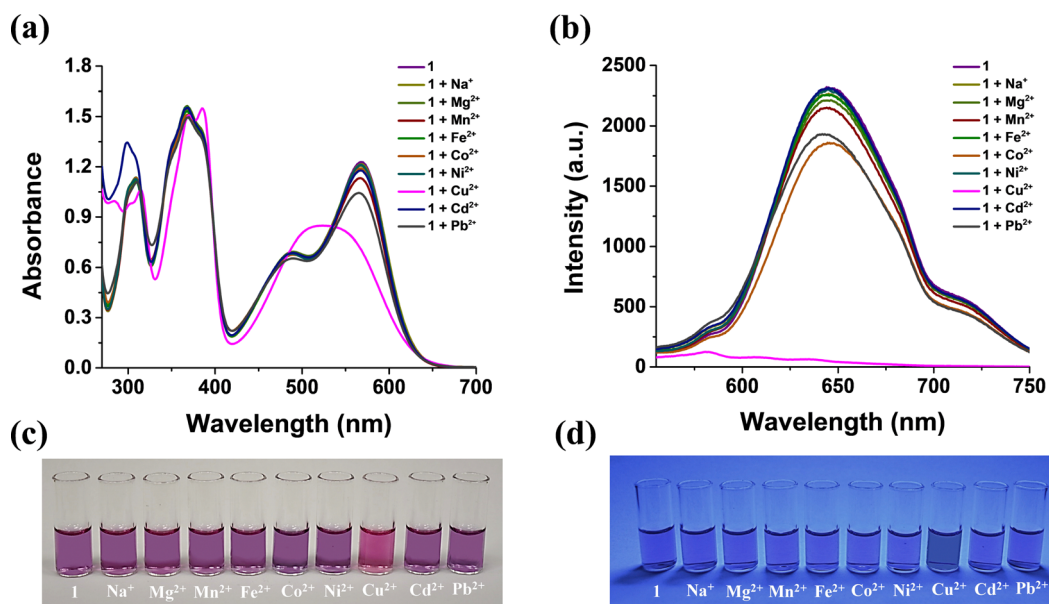
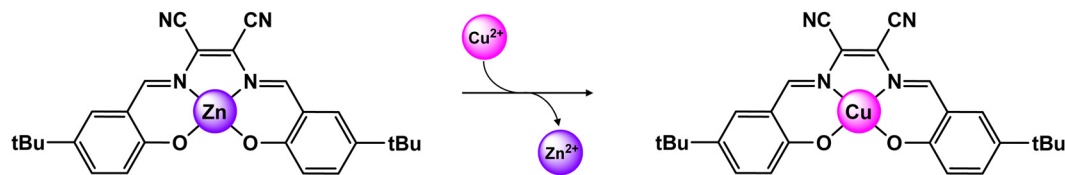


Fig. 2 (a) Optical absorption and (b) fluorescence emission ($\lambda_{\text{exc}} = 535$ nm) spectra of **1** (40 μM solution in MeCN) and after the addition of 2.0 equiv. of various metal cations (as aqueous solutions of nitrate or perchlorate salts). Photographs under natural light (c) and under 365 nm light (d) after the addition of 2.0 equiv. of various metal cations.





Scheme 1 Mechanism of sensing of Cu^{2+} by transmetalation.

These findings suggest that **1** can be involved in the selective sensing of Cu^{2+} ions in aqueous solution. To assess the sensing performance, various spectrophotometric titrations were carried out with the concentration of **1** being varied in the range of 10–40 μM . The comparison of three different titrations (Fig. S1, ESI†) shows that the best performance, in terms of providing a larger linear dynamic range, is obtained with a concentration of 40 μM . Therefore, spectrophotometric and spectrofluorometric titrations were performed using this concentration.

Spectrophotometric titrations indicate that the progressive addition of Cu^{2+} ions implies a parallel decrease in the optical absorption band intensity centred at 568 nm, and the formation of the new broad band centred at 530 nm, which is associated with the formation of the $\text{Cu}(\text{salmal})$ complex (Fig. 3). The formation of multiple isosbestic points further supports the formation of a new species upon transmetalation. Saturation is reached after the addition of 1.5 equiv. of Cu^{2+} . It is noteworthy that the titration data clearly indicate a linear relationship between the absorbance at 568 nm and the concentration of Cu^{2+} added over the entire 0–60 μM titration range (Fig. S2, ESI†). The binding constant for the formation of the $\text{Cu}(\text{salmal})$ complex upon transmetalation, obtained from the Benesi–Hildebrand plot⁵⁶ of $1/(A - A_0)$ versus $1/[\text{Cu}^{2+}]$, was found to be 6.7×10^3 . Moreover, the Benesi–Hildebrand plot (Fig. 4a) shows excellent linearity, supporting a transmetalation ratio of 1:1. This was confirmed by the Job plot analysis (Fig. 4b). According to the IUPAC definition,^{57,58} the limit of

detection (LOD) of **1** towards Cu^{2+} was determined to be 0.60 μM , which is much lower than the allowed maximum level of Cu^{2+} (30 μM) in drinking water.^{41–43}

Analogously, spectrofluorometric titrations upon the progressive addition of Cu^{2+} show a decrease in the band emission at 645 nm, until complete quenching of the fluorescence after the addition of 1.5 equiv. of Cu^{2+} , with a linear dependence between the intensity of the fluorescence and the concentration of the Cu^{2+} added (Fig. 5). Moreover, the related estimated binding constant ($K = 2.3 \times 10^3$; Fig. S3, ESI†) and LOD (0.90 μM ; Fig. S4, ESI†) are comparable to those derived from the spectrophotometric data.

Therefore, overall these data suggest that **1** can potentially be employed for the quantitative detection of Cu^{2+} , *via* colorimetric/fluorometric dual mode, by transmetalation. These results favourably compare with the few quantitative data reported in the literature for the detection of Cu^{2+} by transmetalation,^{27–30} with the advantage that in our case the cation salts are dissolved in water, without any pretreatment of the sample.

The selectivity of **1** towards Cu^{2+} ions was further proven through competitive experiments (Fig. 6). Specifically, the optical absorption/fluorescence emission response of **1** was evaluated in the presence of other cations. In this regard, some common cations (Na^+ , Mg^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , and Pb^{2+}) were considered as potential interferents. Cations that give acidic hydrolysis in aqueous solution (*e.g.*, Al^{3+} , Fe^{3+}) were

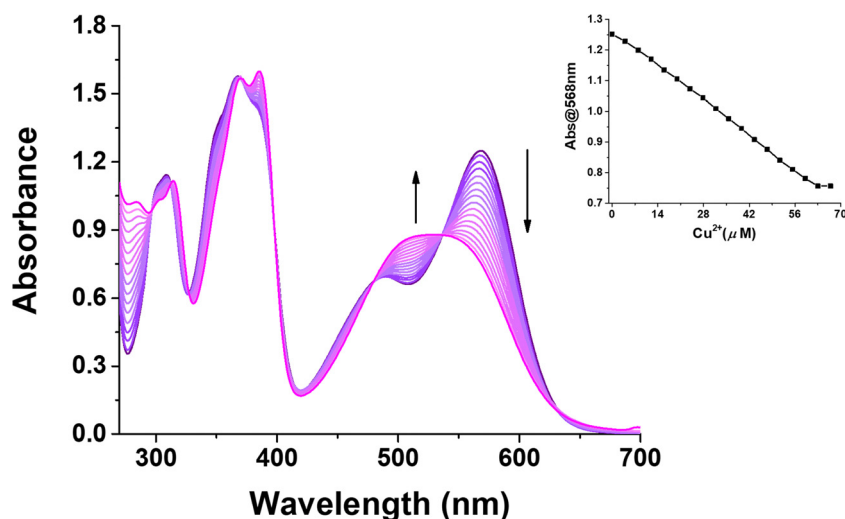


Fig. 3 Optical absorption titration curves of **1** (40 μM solution in MeCN) with the addition of Cu^{2+} (as an aqueous solution of the perchlorate salt). The concentration of Cu^{2+} added varied from 0 to 70 μM . Inset: Variation of the absorbance at 568 nm as a function of the concentration of Cu^{2+} added.



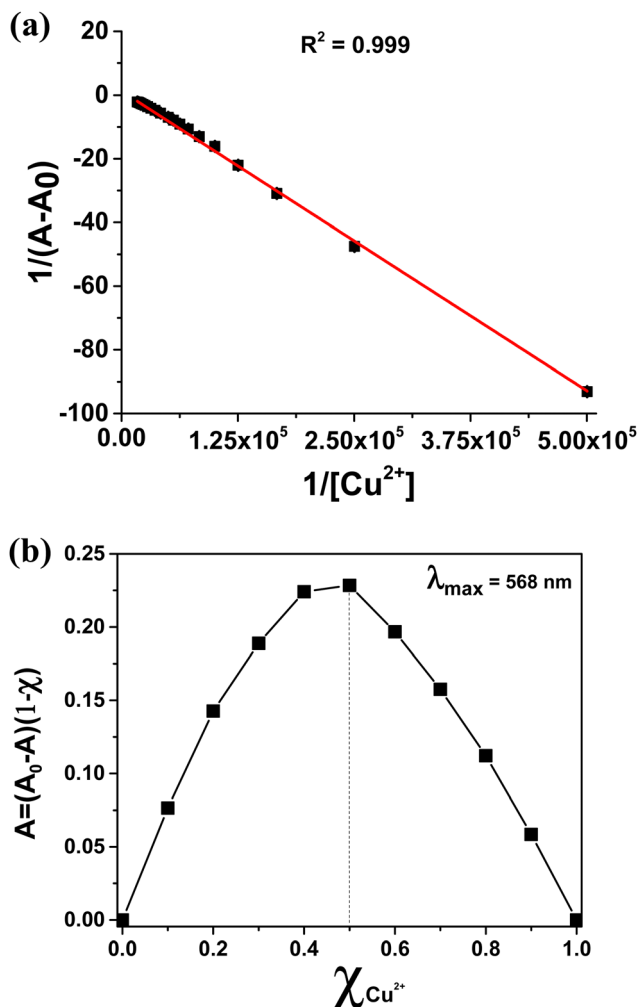


Fig. 4 (a) Benesi-Hildebrand plot (absorbance at 568 nm) for calculation of the binding constant of **1** (40 μM solution in MeCN) with Cu^{2+} (weight given by data error bars). (b) Job plot for the transmetalation of **1** with Cu^{2+} in MeCN. The total concentration of **1** and Cu^{2+} is 40 μM .

not considered because these species lead to the demetalation of **1**. We made this choice because all colorimetric/fluorometric measurements involving **1** in MeCN solution and aqueous solutions of cations, including Cu^{2+} , were carried out without pH adjustment. The optical absorption/fluorescence response of **1** in the presence of Cu^{2+} ions is very similar to that obtained after the addition of Cu^{2+} ions mixed with each potential interfering cation (Fig. 6). This demonstrates the selectivity of **1** for Cu^{2+} ions, even in the presence of other cations.

Given the good sensing performance of **1**, our method was tested using real water samples, obtained as laboratory tap water and supermarket spring water. Blank experiments using known amounts of the water samples added to the MeCN solution of **1** always indicated negligible changes in the absorption/fluorescence. Therefore, **1** was tested for spiking/recovery experiments, adding different concentrations of Cu^{2+} ions to samples of water. Data were analysed using changes in the absorption spectra and the calibration line from spectrophotometric titrations (Fig. S2, ESI[†]). As shown in Table 1, every

sample shows a good recovery rate and a low relative standard deviation (RSD). Therefore, complex **1** is suitable for practical applications.

Conclusions

The search for simple and efficient methods for the sensing of cations in the environment is a challenge of current scientific interest. Here, we have presented a straightforward approach, based on transmetalation, for the colorimetric/fluorometric sensing of Cu^{2+} ions in aqueous solution. This method offers the advantages of being simple, direct, and fast, without the need for any treatment of the sample, for the selective and sensitive detection of Cu^{2+} ions in drinking water. Moreover, it may represent a general method for the sensing of Cu^{2+} or other cations in various environments through optimization of the subtle relationships between the structure and stability of Zn(II) salen-type complexes, and transmetalation.

Experimental

Materials and general procedures

Complex **1** was synthesized, purified, and characterized as previously reported.⁵⁴ Chemicals were purchased from Sigma-Aldrich and used as received. Ultrapure water purified using the Milli-Q purification system was used to prepare the aqueous solutions of nitrate or perchlorate salts. Stock solutions of **1** in MeCN were prepared by dissolving a known amount of the complex in the solvent using a volumetric flask. MeCN solutions of **1** used for spectrophotometric/spectrofluorometric measurements were prepared by diluting the stock solution.

Measurements

Optical absorption spectra were recorded at room temperature using an Agilent Cary 60 spectrophotometer. Fluorescence spectra were recorded at room temperature using a JASCO FP-8200 spectrofluorometer (JASCO Europe). All measurements were recorded immediately after the addition of the aqueous solutions of the cations to the MeCN solutions of **1**. Identical results were obtained even when recording the measurements after some time (10, 20, 30, or 60 min later). Spectrophotometric and fluorometric titrations were performed using a 1 cm path cell. Titrations were performed by adding increasing amounts of a 5.0 mM aqueous solution of copper perchlorate to 3 ml of a 40 μM solution of **1**, using Rainin (Mettler Toledo) positive displacement pipettes. The excitation wavelength for fluorometric titrations was chosen to be at an isosbestic point. The addition of defined amounts of distilled water or various samples of tap water or spring water to MeCN solutions of **1** does not involve any change in the optical absorption or ^1H NMR spectra, indicating that no demetalation/decomposition occurs. Spiking and recovery experiments were performed by directly adding a known amount of copper perchlorate to the spring water or tap water. The spiked solution was then added to the 40 μM solution of **1** in MeCN and the recovered



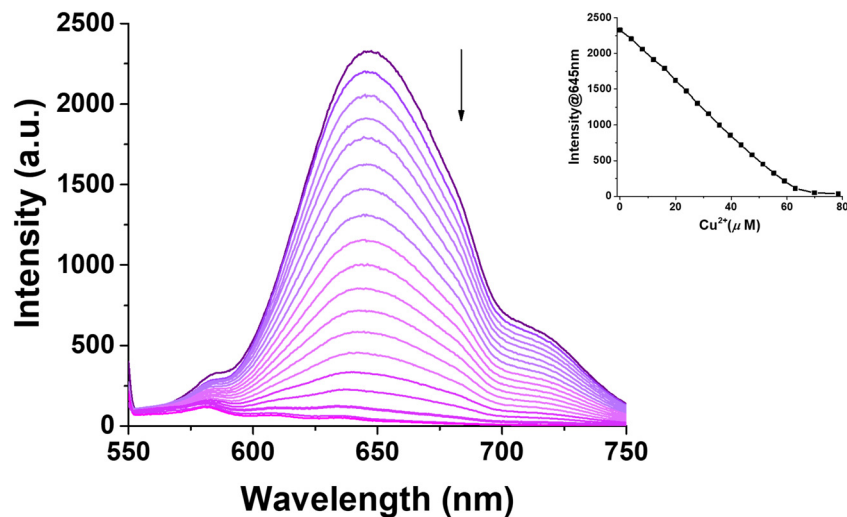


Fig. 5 Fluorescence titration curves of **1** (40 μM solution in MeCN; $\lambda_{\text{exc}} = 536 \text{ nm}$) with the addition of Cu^{2+} (as an aqueous solution of the perchlorate salt). The concentration of Cu^{2+} added varied from 0 to 80 μM . Inset: Variation of the fluorescence at 645 nm as a function of the concentration of Cu^{2+} added.

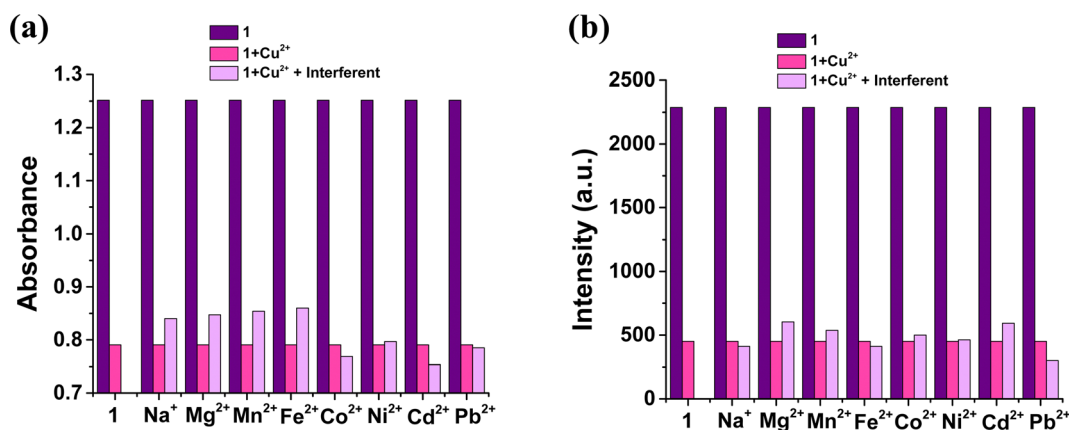


Fig. 6 Change in (a) the absorbance of **1** at 568 nm (40 μM solution in MeCN) and (b) the fluorescence emission intensity of **1** at 645 nm (40 μM solution in MeCN, $\lambda_{\text{exc}} = 536 \text{ nm}$; purple bars), and upon the addition of 1.25 equiv. of Cu^{2+} (as an aqueous solution of the perchlorate salt; magenta bars), as well as upon the addition of 1.25 equiv. of Cu^{2+} in the presence of 1.25 equiv. of the interferent (light blue bars).

Table 1 Recovery results of Cu^{2+} in different water samples ($n = 3$)

| Sample | Cu^{2+} added (μM) | Found (μM) | Recovered \pm RSD (%) |
|--------------|--|-------------------------|-------------------------|
| Tap water | 10.0 | 9.20 | 92.0 ± 2.9 |
| | 20.0 | 18.6 | 93.0 ± 4.3 |
| | 40.0 | 39.3 | 98.3 ± 4.6 |
| Spring water | 10.0 | 9.30 | 93.0 ± 3.2 |
| | 20.0 | 19.1 | 95.5 ± 1.9 |
| | 40.0 | 38.8 | 97.0 ± 2.1 |

percentage was calculated using the equation of the calibration line from the spectrophotometric titration data. The fluorescence quantum yield for **1** in MeCN was determined with respect to that of the 4-alkoxy-substituted Zn(salmal) derivative ($\phi = 0.24$ in THF).⁴⁷

Calculation of the binding constant and limit of detection

The binding constant for the formation of the Cu(salmal) complex upon transmetalation was calculated *via* the Benesi-Hildebrand plot⁵⁶ from spectrophotometric (eqn (1)) or spectrofluorometric (eqn (2)) data:

$$1/(A - A_0) = 1/\{K(A - A_0)[\text{Cu}^{2+}]\} + 1/[A - A_0] \quad (1)$$

$$1/(F - F_0) = 1/\{K(F - F_0)[\text{Cu}^{2+}]\} + 1/[F - F_0] \quad (2)$$

where A_0 (F_0) is the absorbance (fluorescence) of **1**, and A (F) is the absorbance (fluorescence) that was recorded upon the addition of progressive amounts of Cu^{2+} . The binding constant value was calculated from the ratio of the intercept to the slope of the linear regression fit of $1/(A - A_0)$ or $1/(F - F_0)$ against $1/[\text{Cu}^{2+}]$. Each point was obtained from at least three replicate titrations.



The limit of detection was calculated according to the IUPAC recommendation,^{57,58} from both the optical absorption and fluorescence data (eqn (3)):

$$\text{LOD} = 3\sigma/k \quad (3)$$

where σ is the standard deviation of the blank, and k is the slope of the calibration line from the spectrophotometric or spectrofluorometric titration data. Fifteen blank replicates were considered. The calibration lines were obtained from plots of the absorbance or fluorescence intensity of **1** versus the concentration of Cu^{2+} added. Each point is related to the mean value obtained from at least three replicate measurements.

Conflicts of interest

There are no conflicts to declare.

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