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Original article

The specific detection of Cu(II) using an AIE-active alanine ester

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ABSTRACT

Cu(II) detection is important because it plays crucial role in several biological processes and ecological systems. Fluorescent techniques have attracted more and more attention in Cu(II) detection. In this report, we contribute a novel strategy to use fluorescence spectroscopy for Cu(II) specific detection. The specificity relies on the fact that, of the many metal cations, only Cu(II) can catalyze the hydrolyzation of α-amino acid ester. The novelty originates from the unique aggregation-induced emission (AIE) property of the fluorescent label. We designed a model α-amino acid ester (TPE-Ala) constructed with alanine and tetraphenylethene-functionalized methanol (TPE-methanol). In comparison with the precursor TPE-Ala, TPE-methanol has lower solubility and is easy to form aggregates in water, thereby displaying a higher fluorescent response. Thus, the Cu(II) catalyzed hydrolyzation can be monitored by recording the fluorescence enhancement and fluorescent detection Cu(II) is rationally achieved.

1. Introduction

Copper is an essential element in the ecosphere and the third abundant element after ferrum and zinc in our bodies. The divalent copper cation, *i.e.* Cu(II), participates a series of biological processes and the change in Cu(II) concentration can be considered as a clue of degenerated diseases, such as Menkes syndrome, Alzheimer's disease, Prion disease and amyotrophic lateralizing sclerosis [1–5]. As a result, the detection of Cu(II) is important in both fields of fundamental research and practical application.

Due to the high sensitivity, ease of manipulation, and visual observation, fluorescent detection has become an attractive technique with many instructive research reports on the fluorescent detection of Cu(II) [6–14]. Most fluorescent detection methods take advantage of the coordination capacity of Cu(II) to amino and/or oxygen moieties. The coordination may result in the variation of fluorescence features including emission intensity, color and life time, thus the fluorescent detection of Cu(II) is achieved.

Aggregation-induced emission (AIE) is a unique fluorescent phenomenon [15] and it has been found versatile applications in chemical and biological detections [16–19]. According to AIE mechanism [16,19,20], the fluorescence turn-on/turn-off process can be observed if the reaction between the substrate and the resultant molecules can alter the aggregation behavior (solubility) of the fluorescent species. These observations triggered the attempt of using AIE luminogens as fluorescent probes to detect cysteine (Cys) and homocysteine (Hcy). For example, we used aldehyde functionalized silole, tetraphenylethene (TPE) and carbazole derivatization to detect Cys over other amino acids and glucose [21–23]. The specially designed probe can selectively react with Cys and Hcy to form thiazinane and thiazolidine derivatives in the presence of diverse amino acids to protect Cys, and glucose. The discrimination relies on the reaction-dependent fluorophore aggregation, or the solubility of adducts of the probe molecule and analytes. This strategy is intrinsically a fluorescent titration, which combines the high sensitivity of fluorescence spectroscopy and the reliability of precipitate titration methodology.

Herein, we report our efforts to expand this strategy to Cu(II) detection. It was found that Cu(II) could catalyze the hydrolyzing of α-amino acid ester in aqueous solution at room temperature to produce α-amino acid and corresponding alcohol [24,25]. This commonplace, but simple reaction, triggered the idea of adapting the AIE mechanism to detect Cu(II). The basic concept is shown in Scheme 1. Given that the solubility of the AIE-labeled α-amino acid ester is higher than that of AIE-labeled aliphatic alcohol (hydrolyzed resultant), the Cu(II)-catalyzed hydrolyzing process must be accompanied by the increase of fluorescence intensity, thus Cu(II) can be detected by fluorescence change.

2. Experimental

2.1. Materials and instruments

Protected α-alanine, 4,6-dimethyl-2-aminopyridine (DMAP), piperidine, *N*,*N*′-dicyclohexylcarbodiene (DCC), *N*,*N*′-dicyclohexylcarbodiene were purchased from Aldrich Chemical Co.

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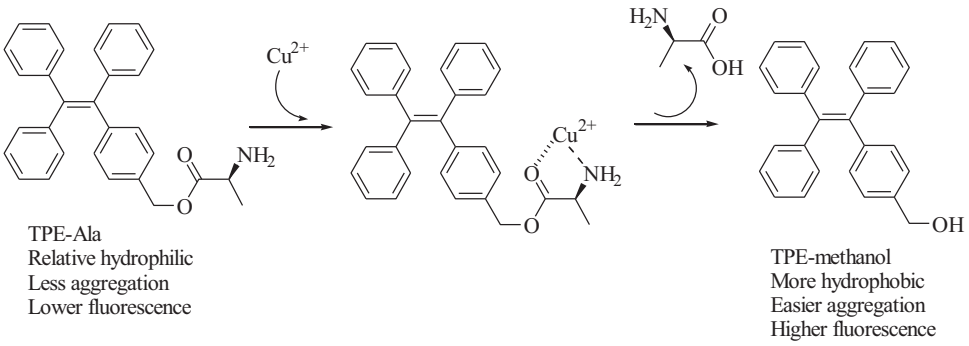


Scheme 1. Cu(II) catalyzed hydrolyzation of an AIE-labeled α-amino acid ester and expected fluorescence change.

Dichloromethane, ethyl acetate, and petroleum ether (60–90 °C) were purchased from Huadong Medicine Co., Ltd. Copper nitrate, sodium nitrate, potassium nitrate, calcium nitrate, ferric nitrate, cobalt nitrate, magnesium nitrate, nickel nitrate, zinc nitrate, and chromium nitrate were purchased obtained from Sinopharm Chemical Reagent Co., Ltd. They were all analytical grade reagents and used as received. All other chemicals and regents were commercially available and used without further purification. Tris–HCl buffer solutions were prepared as standard procedure. UV–visible (UV–vis) absorption spectra were measured on a Varian CARY 100 Bio UV–vis spectrophotometer. Fluorescence spectra were recorded on a Perkin–Elmer LS 55 spectrofluorometer. The ^{1}H NMR data were measured on a Mercury plus 300 MHz NMR spectrometer using tetramethylsilane (TMS) as internal standard.

2.2. Synthesis of the protected TPE-labeled α-amino acid ester

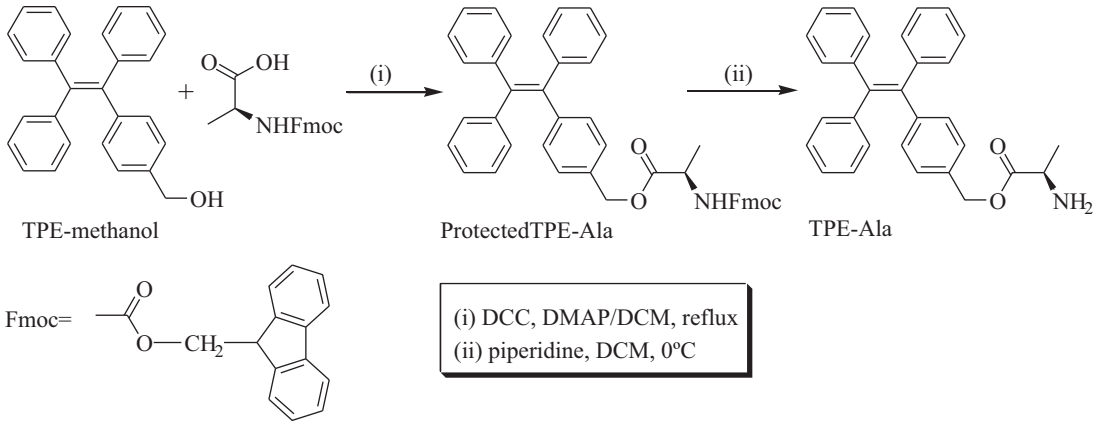
The synthetic route to the target molecule is shown in Scheme 2. α-Alanine was chosen to be the prototype of α-amino acids due to the simplicity in its chemical structure. TPE was used as the AIE label for its easiness in preparation and functionalization. The synthesis of TPE-functionalized methanol was reported elsewhere and we used it directly as reported in this work [26]. Into a baked 50 mL double-necked flask was added 300 mg (0.83 mmol) of TPE-functionalized methanol, protected alanine (310 mg, 0.99 mmol), DCC (340 mg, 1.66 mmol), 4,6-dimethylaminopyridine (DMAP) (200 mg, 1.66 mmol), and DCM (15 mL). The mixture was stirring at room temperature for 12 h. The resultants were filtered and the filtrate was rotatory-evaporated. The residual solid was purified on a silica gel column with ethyl acetate/petroleum (1:1, v/v) as eluent. The resultant was recrystallized using absolute alcohol as solvent and the protected TPE-labeled α-amino acid ester was obtained in a yield of about 70%. Characterization data: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80–7.68 (d, 2H, J = 6.4 Hz), 7.60 (d, 2H, J = 6.2 Hz), 7.40 (m, 2H), 7.31 (m, 2H), 7.15–6.92 (m, 19H), 5.42 (d, 1H, J = 9.1 Hz), 5.10 (m, 2H), 4.40 (m, 3H), 4.23 (m, 1H), 1.42 (d, 3H, J = 5.2 Hz). The ^{1}H NMR spectrum can be found in the Supporting information as Fig. S1. Elementary analysis, calculated for $C_{45}H_{35}NO_4$ (%): C 82.70, H 5.36, N 2.14; found (%): C 81.96, H 5.89, N 2.22.

2.3. Synthesis of the target TPE-labeled α-amino acid ester (TPE-Ala)

Into a baked 20 mL double-necked flask was added 200 mg (0.30 mmol) of the protected TPE-functionalized methanol and 8 mL of dichloromethane. The solution was cooled with an ice bath to 0–5 °C, and 2 mL piperidine was introduced into the cooled solution under stirring. The mixture was kept at 0–5 °C and stirred for 2 h then stirred at room temperature for 2 h. The solvent was removed by rotatory evaporation and the residual was extracted twice with ethyl acetate and water. The obtained solid was recrystallized with absolute alcohol and the target resultant TPE-Ala was obtained in a yield of 83%. Characterization data (see Fig. S2 in Supporting information): ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.78–8.62 (s, 2H), 7.20–6.93 (m, 19H), 5.14–5.11 (s, 2H), 4.10–4.02 (m, 1H), 1.43–1.38 (d, 3H, J = 5.5 Hz). Elementary analysis, calculated for $C_{30}H_{26}NO_2$ (%): C 83.33, H 6.02, N 3.24; found (%): C 82.89, H 6.41, N 3.21.

2.4. Fluorescent detection of Cu(II) and other cations

The appropriate amount of copper nitrate was dissolved in 4 mL pure water or 10 mmol/L Tris–HCl buffer solution with proper pH value, then a suitable amount of TPE-Ala was added under vigorous



Scheme 2. Synthetic route to the target TPE-labeled α-amino acid ester (TPE-Ala).

stirring to dissolve TPE-Ala in the aqueous solution as soon as possible. The upper limit of the solubility of TPE-Ala in pure water is about 4 μmol/L and this concentration was determined as an optimized concentration in order to get better fluorescent responses. The mixture was stirred at room temperature for 2 h in the presence of 100 μmol/L Cu(II) cations and underwent the necessary fluorescent measurement. Other metal nitrates were similarly treated and the fluorescent measurement procedures were identical to the case of copper nitrate. The purpose of using relative high concentration of metal cations is to achieve faster fluorescent detection. As revealed by Fig. S3 (in Supporting information), at low Cu(II) concentration, the fluorescence enhancement requires a longer time, which is unfavorable for practical detection.

3. Results and discussion

It can be seen from Scheme 1 that TPE-Ala ester is constructed by a hydrophobic TPE moiety and a hydrophilic alanine moiety. Upon Cu(II) catalyzed hydrolyzation, the hydrophilic alanine and the hydrophobic TPE moieties separate from each other, with the resulted TPE-methanol having a higher hydrophobicity than TPE-Ala. As a result, TPE-methanol molecules are easier to form aggregates in aqueous solution and exhibit stronger fluorescence. Based on the fluorescence enhancement, the presence of Cu(II) in the aqueous solution is confirmed. Since TPE-methanol and TPE-Ala have the identical fluorophore (TPE) and the emission peak appears at around 460 nm, the change in fluorescence intensity depends on the relative solubility of TPE-methanol and TPE-Ala. Due to the large hydrophobic TPE group, TPE-Ala has a low solubility in water. When the concentration is higher than 4 μmol/L, aggregates of TPE-Ala will form in aqueous solution at room temperature. Fortunately, TPE-methanol is insoluble in water. Thus we can observe the fluorescence enhancement. As shown in Fig. 1, when 100 μmol/L Cu(II) (from copper nitrate) was added to a 4 μmol/L TPE-Ala aqueous solution, an observed fluorescence increase was recorded after 2 h. Without the addition of copper nitrate, the fluorescence intensity of TPE-Ala aqueous solution remained unchanged. It is noted that extending the reaction time can lead to higher fluorescence intensity, but for the ultimate application of fluorescent detection, the prolonged response time is inappropriate. Therefore, we use 2 h as a unified time in all detection experiments.

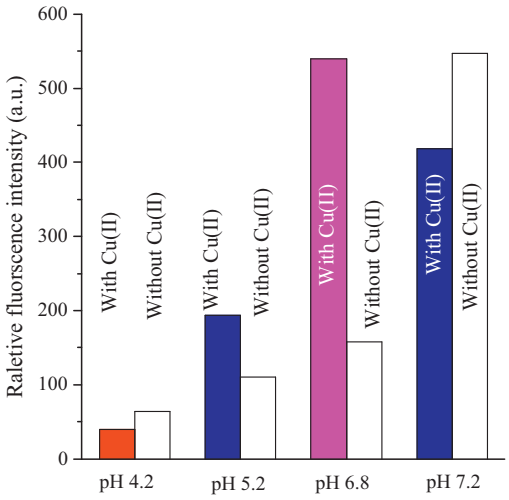


Fig. 2. Variation of fluorescence intensity of 4 μmol/L TPE-Ala aqueous solution with (filled column) and without Cu(II) (open column) in Tris–HCl (0.01 mol/L) buffer at different pH values. λ_{ex} = 321 nm; concentration Cu(II) = 100 μmol/L.

According to the literature, Cu(II) can effectively catalyze the hydrolyzation reaction of α-amino acid esters at a proper pH window [25]. To explore the pH value at which Cu(II) can properly catalyze the hydrolyzation of TPE-Ala, we tried the fluorescence responses of TPE-Ala to Cu(II) at different pH values, which were tuned by using Tris–HCl buffer solution. Considering that Tris–HCl has efficient pH tuning capacity in the pH region of 3 to 9, we selected four typical pH values of 4.2, 5.2, 6.8, and 7.2. The experimental data are summarized in Fig. S4. The data of peak fluorescence intensity (at 460 nm) are extracted to organize the histogram in Fig. 2. At pH 4.2, TPE-Ala itself shows weak fluorescence. When the pH is adjusted to 5.2, the solubility of TPE-Ala in buffer solution decreases and the solution exhibits stronger fluorescence than at pH 4.2. Addition of Cu(II) to the solution leads to an observed increase in fluorescence intensity. Further increasing the pH value to 6.8, the fluorescence intensity of the TPE-Ala aqueous solution becomes even stronger in comparison with the case of pH 5.2. After addition of Cu(II) to the solution, an over 200% enhancement in fluorescence intensity was recorded.

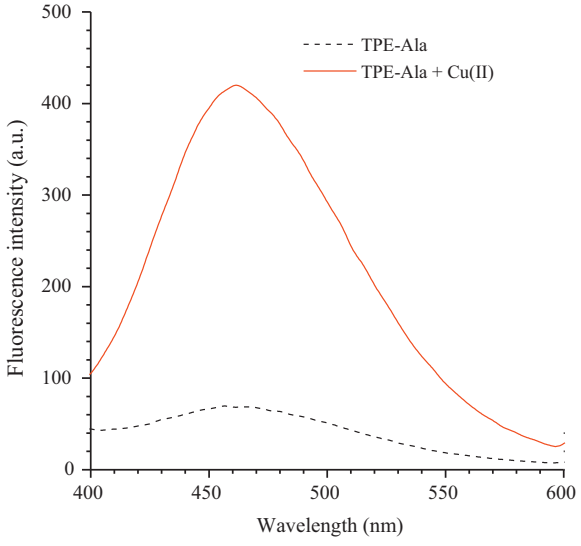


Fig. 1. Fluorescent spectra of 4 μmol/L TPE-Ala aqueous solution and its mixture containing 100 μmol/L Cu^{2+} (after stirring for 2 h; reaction temperature = 25 °C; excitation wavelength (λ_{ex}) = 321 nm).

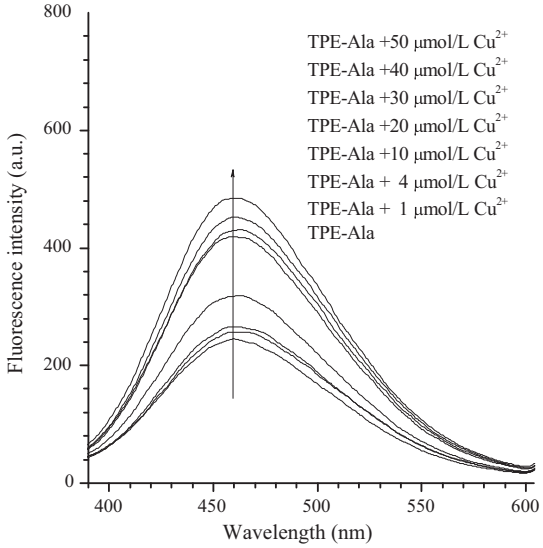


Fig. 3. Effect of Cu(II) concentration on the fluorescent intensity change of 4 μ mol/L TPE-Ala aqueous solution. Solution pH = 6.8, λ_{ex} = 321 nm.

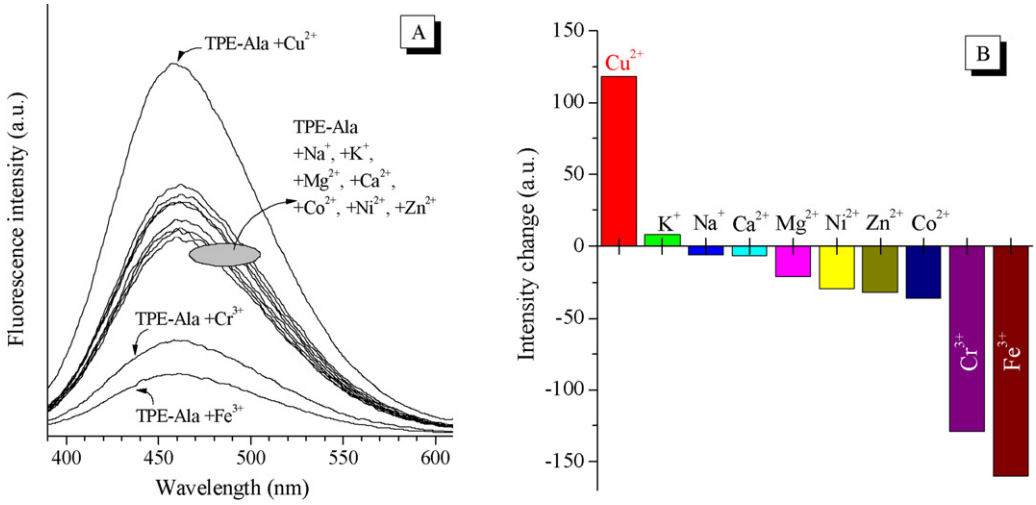


Fig. 4. (A) Fluorescence responses of 4 μmol/L TPE-Ala to 100 μmol/L different metal cations. (B) The relative change of fluorescence in the presence of different metal cations in comparison with the control sample (without any metal ion, used as baseline). Fluorescence measurements were carried out in pH 6.8 Tris–HCl buffer solution at room temperature and λ_{ex} = 321 nm.

The observed pH dependent fluorescence change can be ascribed to the protonation effect of the amino group. At lower pH, the protonation increased the solubility of TPE-Ala in aqueous solution, which reduced the fluorescence emission. Meanwhile, the protonation reduced the affinity of amino group to Cu(II), thus weakened the Cu(II) catalyzed hydrolyzation of TPE-Ala, thus addition of Cu(II) into the buffer solution at pH 4.2 showed limited fluorescence enhancement. At low pH, the addition of Cu(II) to the solution has a weak negative effect on the fluorescence change, since Cu(II) has some fluorescence quenching effect.

To clarify the origin of the observed fluorescence enhancement, thin layer chromatograph (TLC) was used to monitor the process of the reaction. In the resultant mixtures of TPE-Ala and Cu(II) at pH 5.2 and 6.8, we found that a component has the same R_f value as the standard TPE-methanol when hexane, hexane/acetic ether mixture and dichloromethane were used as developing solvents. Therefore, we conclude that the fluorescence enhancement is associated with the production of TPE-methanol. At pH 7.2, the fluorescence intensity of the TPE-Ala aqueous solution is higher than in aqueous acid solutions because the solubility of TPE-Ala becomes lower in neutral and basic aqueous solutions. We did not try the fluorescent response in higher pH values considering that at basic conditions the ester can be hydrolyzed directly by hydroxyl group and it is impossible to clearly demonstrate the catalyzing effect of Cu(II).

Based on the above experimental results, we established 6.8 as the optimized pH value to do the successive fluorescent detection experiments. The effect of Cu(II) concentration on the fluorescent intensity of 4 μmol/L TPE-Ala aqueous solution (pH 6.8) is shown in Fig. 3. It should be pointed out that there is fluctuation of fluorescence intensity between different patches. The fluctuation comes from the fact that the hydrolyzation resultant TPE-methanol is easy to form aggregates, and the size and number of the aggregates are influential on the fluorescence intensity. The data in Fig. 3, which are extracted from a typical patch of fluorescent detection indicate that the fluorescence enhancement is proportional to Cu(II) concentration. At around 100 μmol/L Cu(II), the fluorescence enhancement shows a decreasing trend (see Fig. S5), which may be associated with the fluorescent quenching effect of high concentration Cu(II), thus we set 100 μmol/L as the maximum Cu(II) concentration.

The specification is one of the crucial factors of practical fluorescence detection. Accordingly, we studied the influence of a series of metal cations (concentration: 100 μmol/L) on the fluorescence response of TPE-Ala in pH 6.8 buffer solution with the experimental results summarized in Fig. 4A and 4B. If the peak fluorescence intensity of 4 μmol/L TPE-Ala in pH 6.8 buffer solution is set as the base, the data in Fig. 4B clearly exhibit the following trends. Firstly, at the concentration of 100 μmol/L, metal cations in IA and IIA groups, such as Na(I), K(I), Mg(II), and Ca(II), show very weak influence on the fluorescence of TPE-Ala. Secondly, the divalent transition metal cations in the same period as copper, including Co(II), Ni(II) and Zn(II), also have little effect on the fluorescence change. Thirdly, it is found that the trivalent metal cations, such as Fe(III) and Cr(III), display a negative effect on the fluorescence intensity. This effect can be explained as following: both Fe(III) and Cr(III) have strong hydrolyzation capacities and 100 μmol/L Fe(III) and Cr(III) can lead to the acidification of the aqueous solutions. As a result, the intrinsic pH value of 100 μmol/L Fe(III) and Cr(III) aqueous solutions is evidently lower than 6.8, and the decrease of fluorescence intensity is expected, just as the situation observed in Fig. 2. As a pertinent proof, we recently took the advantage of their pronounced hydrolyzation properties to specifically detect trivalent cations by monitoring the fluorescent changes of the pyridinyl-functionalized TPE derivative [27]. Finally and most importantly, among all the tested metal cations, TPE-Ala shows a large and positive fluorescent response only with Cu(II). This result provides a solid support of the specific detection of Cu(II) by fluorescent methodology.

4. Conclusion

We have explored the feasibility of detecting Cu(II) in aqueous media by a fluorescent technique by using an α-amino acid ester as a model compound (TPE-Ala). The hydrolyzation of TPE-Ala in aqueous solution can be catalyzed by Cu(II) at room temperature and TPE-methanol is derived. The more hydrophobic TPE-methanol shows higher ability to form aggregates in aqueous media. Thanks to the unique AIE activity of TPE moiety, the aggregation of the generated TPE-methanol molecules can be monitored as evident by the fluorescence enhancement of the system. Thus in the presence of Cu(II), the reaction solution is validated. A concentration of 4 μmol/L TPE-Ala, pH 6.8 in aqueous solution, and 2 h reaction time are the optimized detection condition. Under these conditions, the fluorescence enhancement is proportional to Cu(II) concentration from 1 μmol/L to 100 μmol/L. At the concentration of 100 μmol/L, or the upper limit concentration for Cu(II), metal cations including

Na(I), K(I), Mg(II), Ca(II), Co(II), Ni(II), and Zn(II) demonstrate little effect on the change of fluorescence intensity, while Fe(III) and Cr(III) display a negative effect on the change of fluorescence intensity. Therefore, TPE-Ala can be used as a fluorescent probe to specifically detect Cu(II) in aqueous solution. The present concept-proven work lays the foundation of using AIE-active molecular probe to detect Cu(II) based on the solubility differences between the reactant and resultant and permitted the development AIE-active fluorescent probes for the detection of other metal cations.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cclet.2013.05.014.

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