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COMMUNICATION

An effective Cu(II) quenching fluorescence sensor in aqueous solution and 1D chain coordination polymer framework†

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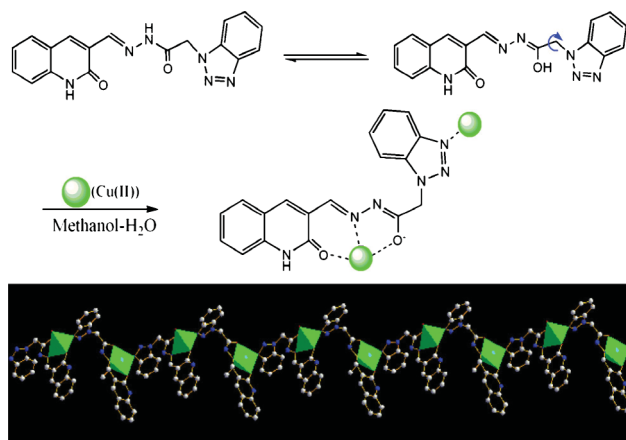**In the article, a novel fluorescent probe for the copper cation based on fluorescence quenching mechanism was designed. It exhibited high selectivity for Cu(II) over other common metal ions in aqueous media. Furthermore the coordination between Cu(II) and the organic molecule sensor fabricated an interesting 1D chain coordination polymer framework.**

In the present years, the development of highly selective and sensitive fluorescent probes toward metal ions has attracted considerable interest. A large number of fluorescent chemosensors based on an off–on mechanism have been designed.[1] Among the fluorescent probes toward metal ions, the study of chemosensors for Cu(II) is a very meaningful and challenging work. The copper ion is the third in abundance after iron and zinc ions among the essential heavy metal ions in organisms, for example many enzymes and proteins, and it plays a vital role in several biological processes. The inadequate and excessive uptake of Cu(II) in biological systems can cause oxidation and disorders associated with neurodegenerative diseases, such as Alzheimer's disease, Menke's disease and Wilson's disease.[2] Moreover, in the natural environment, copper is also considered as a significant pollutant owing to its high toxicity.[3] So it is very necessary to synthesize new fluorescent chemosensors to detect copper in biological systems and the environment. On the other hand, upon binding of target ions with organic molecules, different sensing mechanisms including photo-induced electron transfer (PET), internal charge transfer (ICT) and fluorescence resonance energy transfer (FRET) have been researched for Cu(II) fluorescent probes.[4] These turn-on fluorescent chemosensors, which can enhance effectively the fluorescence intensity of sensors upon binding Cu(II), have been reported extensively.[5] However, effective fluorescent probes based on the photo-induced electron transfer fluorescence quenching mechanism (PET) are relatively rare.[6] Herein, we report a highly

selective quenching fluorescent probe toward Cu(II) in aqueous media, which acts by way of a photo-induced electron transfer (PET) mechanism.

On account of their excellent luminescence properties, quinoline derivatives have been widely used as fluorophores in fluorescence chemosensors. In recent years, many fluorescent chemosensors based on quinoline derivatives have been reported.[7] In addition, acyl hydrazone groups have also been developed due to their powerful chelating activities.[8] In the present work, the quenching fluorescent chemosensor for Cu(II) is 3-formylquinoline-2(1H)one, bearing 1H-benzotriazol-1-acetic acid hydrazide (L). The procedure used for its synthesis is shown in Scheme S1†, and is also described in the ESI.† The structure was determined by ¹H-NMR (ESI†). According to our original design, the organic molecule could chelate metal ions *via* two carbonyl O atoms and one imino N atom, but by X-ray crystal structure analysis, the coordination of L with Cu(II) exhibited an interesting 1D chain polymer framework ([CuL]$_n$). By analyzing the crystal structure, one nitrogen atom from 1H-benzotriazol-1-acetic acid hydrazide acted as a bridge to connect with Cu(II), which coordinated with two carbonyl O and one imino N from the other ligand (Fig. 1). To characterize [CuL]$_n$ more intensively, its ESI-MS was analyzed. As shown in Fig. S1,† the peaks at 409.2, 754.3, 815.2, 1162.9 and 1225.0 were assigned as the fragment ion peaks of ([Cu(II) + L], [Cu(II) + L + Cu(II)], [Cu(II) + L + Cu(II) +L], [Cu(II) + L + Cu(II) +

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Fig. 1 The coordination mechanism and 1D chain coordination polymer framework ([CuL]$_n$) of sensor L with Cu(II).

L + Cu(II)] and [Cu(II) + L + Cu(II) + L+ Cu(II) + L]) from [CuL]$_n$, indicating apparently the formation of [CuL]$_n$ in MeOH–H$_2$O media. Moreover, the elemental analysis and IR spectra (Fig. S2†) were also tested to characterize [CuL]$_n$. The elemental analysis data (anal. calcd (%): C, 44.81; H, 3.25; N, 19.77. Found (%): C, 44.25; H, 3.58; N, 19.21) suggested that the empirical formula was Cu(II)$_2$·L$_2$·H$_2$O·CH$_3$OH·(NO$_3^-$)$_2$ without free solvent molecules. In the FT-IR spectrum of L, the observed IR bands at 1681.25 cm^{-1} and 1648.52 cm^{-1} were attributed to the carbonyl stretching vibrations from quinoline-2(1H)one and 1H-benzotriazol-1-acetic acid hydrazide, respectively. Analysizing the IR spectrum of [CuL]$_n$, the band at 1681.25 cm^{-1} had been replaced by the characteristic band at 1640.94 cm^{-1}, and that the characteristic band of carbonyl at 1648.52 cm^{-1} from 1H-benzotriazol-1-acetic acid hydrazide had disappeared, which was a convincing proof of an enolic carbonyl. Simultaneously, the vibration band at 1603.28 cm^{-1} for L was assigned to the v (C=N) stretch, which shifted to 1588.35 cm^{-1} upon coordination of nitrogen atom. Compared with the nitrogen–nitrogen vibration (589.75 cm^{-1}) from the benzotriazol section of L, the IR band of [CuL]$_n$ exhibited an apparent change (to 563.11 cm^{-1}). Additionally, the intense absorption band in the IR spectrum associated with the asymmetric stretching appeared at 1383.95 cm^{-1}, clearly establishing that there are free nitrate groups (C_{2v}) in [CuL]$_n$. All the results confirmed completely that the structure was [CuL]$_n$.

The electronic absorption spectrum (UV-vis spectrum, Fig. 2) of sensor L in MeOH–H$_2$O media exhibited a strong band at 385 nm. Addition of Cu(II) (0.2 µM) to L resulted in a red-shift of 4 nm to 389 nm in the absorption spectrum, then the absorption band intensity at 389 nm dropped gradually with increased Cu(II) concentration, which implied a typical PET process. In the fluorescence quenching system based on a PET process, the receptor is the Cu(II) chelating domain, the fluorescence motifs are the quinoline-2(1H)one and the 1H-benzotriazol fluorophores from the sensor. The very effective fluorescence quenching phenomenon really happened when the receptor (Cu(II) chelating domain) integrated into the fluorescence motifs.

The photophysical properties of L were investigated by examining its fluorescence behavior upon addition of several ions such as K(I), Na(I), Mg(II), Ca(II), Zn(II), Cd(II), Hg(II), Al(III), Pb(II),
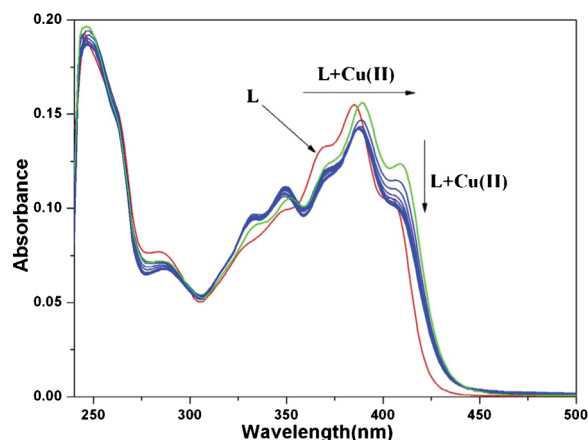

Fig. 2 The electronic absorption spectrum of L (10 µM) upon addition of Cu(II) (0–2 equivalent) in MeOH–H$_2$O (9 : 1) solution.

Cr(III), Ni(II), Mn(II), Co(II), Fe(III) and Cu(II) in MeOH–H$_2$O solution (Fig. 3). It was observed that the metal ions such as Zn(II), Cd(II), Hg(II) and Mg(II) could enhance weakly the fluorescence of L. K(I), Na(I), Ca(II), Al(III) and Pb(II) did not interfere with the fluorescence of L. However, d^{10} transition metal ions Ni(II), Mn(II), Co(II), Fe(III) and Cu(II) quench the emission intensity of L. Interestingly, Cu(II) exhibited very distinct quenching activity over other metal ions, as it could quench the fluorescence of L completely. Thus L could be used as a highly selective fluorescence probe for Cu(II) in the presence of most metal ions.

The fluorescence titration spectrum of L (10 µM) in MeOH–H$_2$O solution was also investigated (Fig. 4). L showed a strong emission band at 460 nm when excited at 380 nm. Upon addition of Cu(II) ion (0–20 µM), remarkable fluorescence quenching of L was observed. Moreover, through fitting the fluorescence titration curve, the 1 : 1 stoichiometry between L and Cu(II) was estimated, which was in accordance with the result from the X-ray crystal structure analysis. Furthermore, the association constant for Cu(II) was estimated to be 4.31×10^4 M^{-1} in MeOH–H$_2$O solution by the linear Benesi–Hildebrand expression $I_0/(I - I_0) = I_0/[L] + I_0/[L] \times K_s \times [M]$.[9] I is the change in the fluorescence intensity at 460 nm, K_s is the stability constant, and [L] and
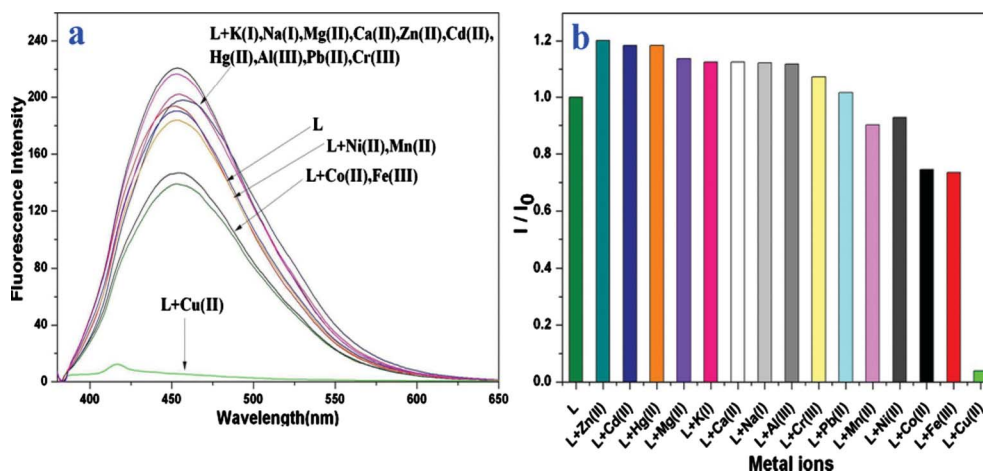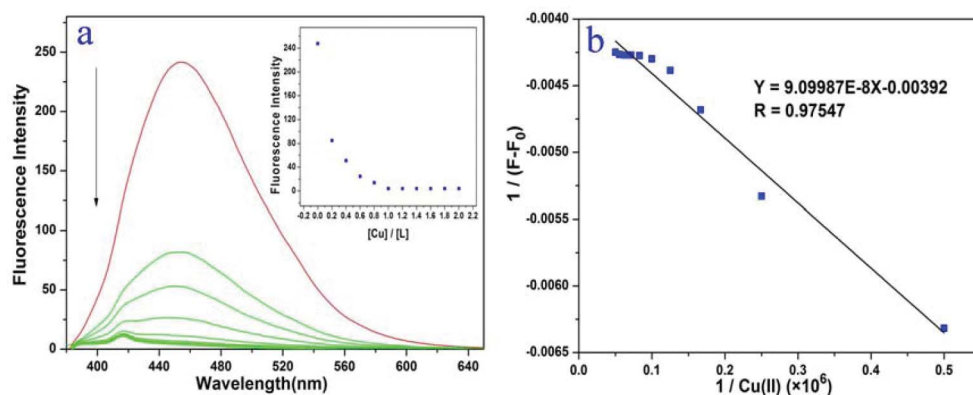

Fig. 3 a. Fluorescence spectrum of L (10 µM) upon addition of K(I), Na(I), Mg(II), Ca(II), Zn(II), Cd(II), Hg(II), Al(III), Pb(II), Cr(III), Ni(II), Mn(II), Co(II), Fe(III) and Cu(II) (10 µM) in MeOH–H$_2$O (9 : 1) solution. b. Histogram of fluorescence selectivity experiment.

Fig. 4 a. Fluorescence titration of L (10 μM) upon addition of Cu(II) (0–2 equivalents) in MeOH–H$_2$O (9 : 1) solution. Inset: the fluorescence intensity curve of L at 460 nm. b. Benesi–Hildebrand expression fitting of fluorescence titration curve of L in MeOH–H$_2$O (9 : 1) solution.
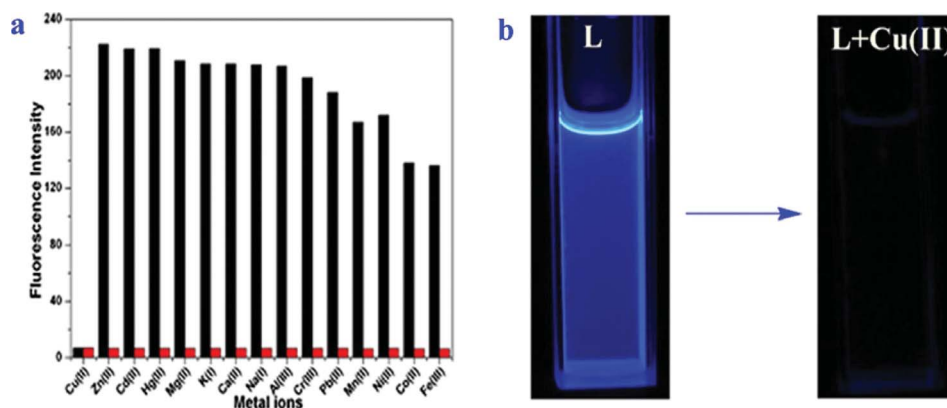
Fig. 5 a. Fluorescence intensity of L (10 μM) upon addition of various metal ions in MeOH–H$_2$O (9 : 1) solution. Black bars represent the fluorescence response of L to the various metal ions (10 μM). Red bars represent the addition of Cu(II) (10 μM) to the solution. b. The fluorescence images of L and L with addition of Cu(II) under UV light in MeOH–H$_2$O (9 : 1) solution.

[M] are the concentration of L and Cu(II), respectively. I_0 is the fluorescence intensity of L in the absence of Cu(II). On the basis of the plot of 1/[I] *versus* 1/[Cu], the stability constant can be obtained.

To validate the practical selectivity of sensor L with Cu(II) over other competitive metal ions, the fluorescence competitive experiment was tested. As shown in Fig. 5a, while Cu(II) elicited a prominent fluorescence quenching of L, the addition of other metal ions did not cause any discernible changes. All the results indicated that the fluorescence probe exhibited higher selectivity over other metal ions. Moreover, a more complex real sample was simulated to demonstrate the high selectivity of L with Cu(II). Fig. S3† illustrated the complex system; it was clear that the coexistence metal ions system (10 μM) did not effectively quench the fluorescence of senor L, nevertheless an apparent fluorescence quenching phenomenon occurred with addition of Cu(II) (10 μM), which further indicated the excellent selectivity of L with Cu(II) in MeOH–H$_2$O solution. Additionally, to evaluate visually the high selectivity for Cu(II), the fluorescence images of L (1 mM) and L (1 mM) upon addition of Cu(II) (1 mM) was also investigated (Fig. 5b), indicating the blue fluorescence of L could be quenched effectively upon addition of 1 equivalent Cu(II) in MeOH–H$_2$O solution. The sensitivity of senor L with Cu(II) in MeOH–H$_2$O solution was also tested. The fluorescence titration profile of sensor L (10^{-6} M) with Cu(II) (Fig. S4†) demonstrated the detection of Cu(II) is at the 0.1 parts per million level. Under the conditions, the fluorescence intensity of the solution of sensor L was still proportional to the amount of added Cu(II) (Fig. S5†).

In summary, we have developed a novel Cu(II) fluorescent chemosensor based on a photo-induced electron transfer (PET) mechanism. It exhibits high selectivity and sensitivity toward Cu(II) over other metal ions in MeOH–H$_2$O media. The fluorescence emission of L can be effectively quenched upon addition of Cu(II) in MeOH–H$_2$O solution. Moreover, according to the theory investigation and X-ray crystal diffraction, a 1 : 1 stoichiometry between L and Cu(II) is formed, and they construct an interesting 1D chain coordination polymer framework ([CuL]$_n$). The excellent selectivity and sensitivity of sensor L for Cu(II) in aqueous media indicates its potential application value in the biological monitoring and tracking of copper.

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