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Selective sensing of Cu(II) at ng ml^{-1} level based on phosphorescence quenching of 1-bromo-2-methylnaphthalene sandwiched in sodium deoxycholate dimer

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Using sodium deoxycholate as a protective medium, the selective recognition of Cu(II) at ng ml^{-1} level is realized through dynamic phosphorescence quenching of 1-bromo-2-methylnaphthalene (BMN) without deoxygenation. The limit of detection is 4.32 ng ml^{-1}, and the relative standard deviation is 1% at 10 μM, linear up to 1 × 10^{-5} M.

Copper is an essential trace element that is widely distributed in animal and plant tissues. Besides Fe^{3+} and Zn^{2+}, it ranks the third in abundance in human among the essential heavy metals.[1] It also acts as a cofactor for a number of metalloenzymes such as catalase, peroxidases and cytochromeoxidase to facilitate enzyme function.[2] Therefore, the determination of traces of Cu(II) in water or biological samples has been an important topic in environmental and biological analysis. Numerous fluorescent chemosensors directed towards the detection and measurement of Cu(II) have been proposed.[3] In contrast, developments of the related simple systems based on room temperature phosphorescence (RTP) have been quite few.[4] The RTP method has many advantages over fluorescence, such as large Stokes shift, good signal-to-noise ratio and long triplet lifetime. Unfortunately, collision quenching by oxygen often occurs in solution due to the long lifetime of the phosphor's triplet states and paramagnetic property of molecular oxygen. And it is necessary to carry out deoxygenation procedure before RTP sensing. Considerable efforts have been made to produce RTP without deoxgenation, including using the synergetic effects of surfactants and cyclodextrin.[5] We previously reported that RTP of 1-bromo-4-bromoacetyl naphthalene could be induced by sodium deoxycholate (NaDC) in the presence of oxygen.[6] The special micellar aggregates of NaDC effectively protect the excited triplet state from quenching in solution and are therefore appear very promising for the development of new phosphorescent sensors to recognize metal ions. Herein a simple, convenient and fast approach is reported to measure Cu(II) in NaDC micelle solution. To the best of our knowledge, this is the first practical RTP signalling system for Cu(II) in aqueous solution without deoxygenation.

In the presence of 1% methanol in NaDC solution, BMN emits strong phosphorescence at 534 nm when excited at 287 nm (Fig. 1). NaDC induces the phosphor to display phosphorescence without the removal of oxygen, while no RTP emission of BMN is observed in fully aqueous solution. The results are consistent with the conclusion reported previously.[6] Namely, BMN is shielded from oxygen in the exterior environment of the NaDC aggregates. The RTP intensity increases with the increase of NaDC and reaches a maximum value when the NaDC concentration is 4 mM. Then the RTP intensity drops sharply and disappears with further increase of NaDC concentration. The results indicate that in the lower concentration range NaDC might do not exist as monomers but as dimers,[7] which tightly sandwich the phosphor and provide a relatively isolated micro-environment to avoid quenching by oxygen. With an increase in [NaDC], much larger and looser helical aggregates would occur[8] so that the phosphorescence decreases due to the less rigid interior of the NaDC aggregates.

Owing to the poor solubility of BMN in water, methanol is employed to prepare the stock solution of phosphor. The experimental results show that methanol has an insignificant effect on RTP intensity when methanol is limited within the volume proportion of 3%. So methanol is not removed prior to RTP sensing.

The effects of added metal cations on the RTP intensity of BMN at the emission maxima have been studied as shown in Fig. 2.† BMN exhibits quenching to some extent upon addition of most metal ions. Among the metals tested here, the highest sensitivity is obtained with Cu^{2+}. In fact, with just 40 μM of Cu^{2+}, the phosphorescence is completely quenched. Comparatively, other metal ions have a lesser degree of quenching and the intensity remains at of over 60% at the emission wavelength of 534 nm. Exceptionally serious interference is caused by the addition of Fe^{2+}. However, it can be eliminated by using hydrogen peroxide to oxidize Fe^{2+} to Fe^{3+}, which has no significant effect on the determination of Cu^{2+}‡. The system shows no obvious spectral changes upon the addition of various copper salts inclusive of $CuCl_2$, $Cu(NO_3)_2$, $CuSO_4$ and $Cu(OAc)_2$, indicating the effect of the anions is negligible. And thus the system witnesses a highly sensitive and selective detection method potential to future use.

The Stern–Volmer relationship is linear up to 1 × 10^{-5} M ($r^2 = 0.9912$). The detection limit is 6.79 × 10^{-8} M (4.32 ng ml^{-1}). The precision of the proposed method, evaluated as the relative standard deviation at the 1 × 10^{-5} M Cu^{2+} level is 1% (n = 7).

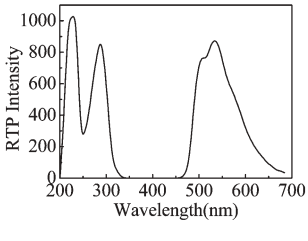

Fig. 1 RTP spectra of BMN in NaDC solution of 4 mM.

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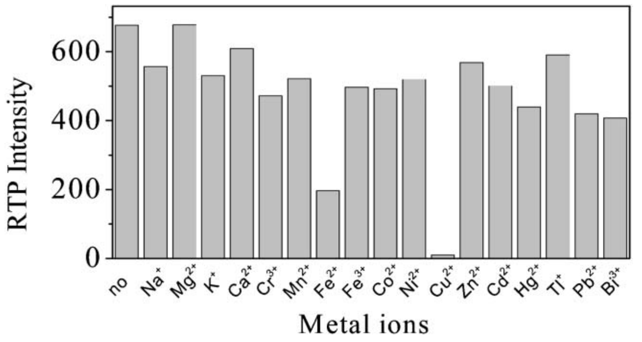

Fig. 2 Effect of various metal ions on the RTP intensity of BMN in NaDC media ([BMN] = 1×10^{-5} M, [M^{n+}] = 4×10^{-5} M, [NaDC] = 4×10^{-3} M).

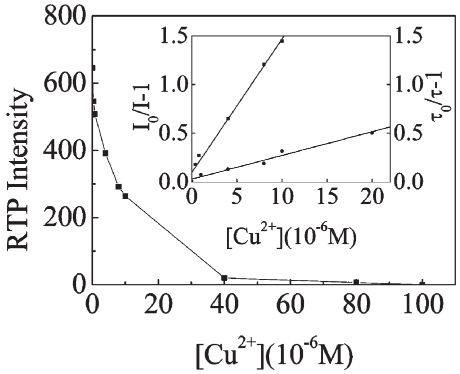

Fig. 3 Effect of copper ion on RTP intensity of BMN in NaDC media (inset is the Stern–Volmer curve during the quenching process), [BMN] = 10 μM; [NaDC] = 4 mM; [Cu^{2+}] = 0, 1, 4, 8, 10, 40, 60, 80, 100 μM.

The RTP lifetime values of BMN as a function of the Cu^{2+} concentration have also been measured and analyzed according to the equation, $\tau_0/\tau = 1 + K_q\, \tau_0\, [Q]$, where τ_0 and τ represent the liftetimes without and with quenchers, k_q the quenching rate constant, and [Q] the concentration of quenchers. The whole quenching process obeys a single exponential decay, and the linear relationship between $\tau_0/\tau - 1$ and the concentration of copper shown in Fig. 3 reflects the dynamic process. The τ_0 is 4.36 ms and the k_q value obtained from the plot of τ_0/τ *vs.* [Q] is 5.6×10^6 M^{-1} s^{-1}. Considering that NaDC can provide a rigid and hydrophobic micro-environment to protect BMN from quenchers inclusive of molecular oxygen, the effective quenching by Cu^{2+} could not be the result of simple intermolecular collision. In combination with the widely accepted quenching mechanism for Cu(II),[9] it might be an electron exchange or electron transfer process that similarly occurs between BMN and copper ions coordinating to the negatively charged carboxylate groups of NaDC micelles, and thus results in RTP quenching. However, more studies are needed to get a clearer understanding about this matter.

In conclusion, NaDC could induce BMN to emit strong phosphorescence in the presence of oxygen. The phosphor shows large RTP quenching effects with Cu(II), making this system an interesting candidate for Cu(II) measurement in aqueous solution. A limit of detection of 4.32 ng·ml^{-1} is achieved.

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Notes and references

† BMN is prepared into 1 mM of methanol solution. The salts (analytical grade) are mainly chloride, while for Tl^+, Pb^{2+} and Bi^{3+} are nitrates, and for Fe^{2+} is sulfate, all the salts solution are of 0.1 mM with doubly deionized water. The adding sequence is BMN, metal ion and NaDC. After the equilibration of 6 hrs, RTP sensing is carried out on LS-55 spectrometer (Perkin-Elmer).

‡ The newly prepared $FeSO_4$ solution is treated with hydrogen peroxide (30%) and sulfuric acid at the stoichiometric ratio, and other metal ions also see similar treatment for comparison.

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