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ARTICLE TYPE

Preparation of europium complex-conjugated carbon dots for ratiometric fluorescence detection of copper(II) ions

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In this work, by conjugating a europium complex, 4,4'-bis(1'',1'',1'',2'',2'',3'',3''-heptafluoro-4'',6''-hexanedion-6''-yl)chlorosulfo-*o*-terphenyl-Eu^{3+} (BHHCT-Eu^{3+}), onto the surface of carbon dots (C-dots), a new type of dual-fluorophore nanoparticles, C-dots-BHHCT-Eu^{3+}, has been successfully prepared for the ratiometric fluorescence detection of Cu^{2+} ions in aqueous media. The results of transmission electron microscopy (TEM) and fluorescence spectroscopy characterizations indicate that the nanoparticles are monodisperse, spherical and uniform in size (~8.6 nm in diameter), and have stable and well-resolved dual-wavelength emission properties. Under excitation at 337 nm, the composite nanoparticles of C-dots-BHHCT-Eu^{3+} exhibit two emission peaks at 410 nm and 615 nm, respectively. Upon the addition of Cu^{2+} ions, the emission intensity of the nanoparticles at 615 nm is significantly decreased, while that at 410 nm shows no response to the addition of Cu^{2+} ions. Correspondingly, the emission intensity ratio, I_{615}/I_{410}, shows a good linearity against the concentration of Cu^{2+} ions. In addition, the investigation results of fluorescence responses of the nanoparticles to different metal ions reveal that the fluorescence response of C-dots-BHHCT-Eu^{3+} to Cu^{2+} ions is highly specific without interferences of other metal ions. All of the results suggest that the new dual-fluorophore composite nanoparticles could be used as a ratiometric fluorescence probe for the detection of Cu^{2+} ions in aqueous media with high selectivity and sensitivity.

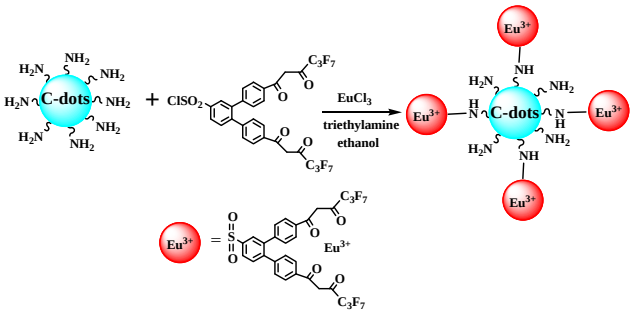
Introduction

Carbon dots (C-dots) are a new class of fluorescent nanomaterials that have drawn great attention due to their excellent properties including good photostability,[1] impressive water-solubility,[2] lack of blinking,[3,4] upcoverted fluorescence emission[5] and excellent biocompatibility.[6] They have been applied in cell and small animal bioimaging,[2,3,7] fabrication of light-emitting devices (LED),[8] inks for printing patterns,[9,10] and photocatalysis for photo-assisted catalytic reactions.[11] Moreover, C-dots have been developed to act as fluorescent probes for the detections of some anions and cations.[6,12-16] For example, Huang et al. prepared water-soluble C-dots containing surface carboxylate groups to detect phosphate in sewage by using the property of Eu^{3+} ions that exhibit higher affinity to phosphates than carboxylate groups.[12] Liu and co-workers developed a fluorescent probe for the detection of fluoride ions in toothpaste based on the competitive ligand reactions between the carboxylate groups on the C-dots and F^- ions coordinated to $Zr(H_2O)_2EDTA$.[16] Qu et al. developed C-dots to detect the content of Hg2+ ions in water by using the mechanism that Hg^{2+} ions can facilitate the non-radiative electron/hole recombination annihilation through an effective electron transfer process.[15] All of these works about the application of fluorescent C-dots to ion detections are based on the monitoring of single wavelength emission intensity changes of C-dots. More recently, Tian et al. synthesized a ratiometric fluorescence probe based on C-dots and CdSe/ZnS quantum dots (QDs) to detect Cu^{2+} ions in cells by introducing a Cu^{2+} ions sensitive ligand, N-(2-aminoethyl)-N,N,N'-tris(pyridin-2-ylmethyl) ethane-1,2-diamine (AE-TPEA) onto the nanohybrid.[7] Compared to the traditional probes, the ratiometric fluorescence probes have excellent sensitivity and selectivity with a built-in correction ability for environmental effects[17] because of employing the ratio of two emission intensities at different wavelengths as a signal.[18] To date, the exploration of C-dots as a material for preparing ratiometric fluorescence probes for selective sensing of metal ions remains in the early stage. The design and controllable synthesis of this kind of ratiometric nanoprobes by a simple and labor-saving method is still a great challenge.

On the other hand, as well-known luminescent labels/probes, Eu^{3+} complexes have been widely used for the immunofluorescence assay,[19] DNA hybridization assay,[20] selective staining of cell nucleoli,[21] singlet oxygen detection[22] and time-resolved fluorometric detections of biomarkers[23-25] because of their unique properties including long luminescence lifetimes, large Stokes shifts, and sharp emission bands. The short-lived background signal from biological samples and optical components can be effectively eliminated to achieve high sensitivity by using their long-lived luminescence through the time-resolved detection technique. A number of Eu^{3+} complexes have been synthesized and explored for the above biomedical applications.[26,27] Among them, 4,4′-bis(1″,1″,1″,2″,2″,3″,3″-

heptafluoro-4″,6″-hexanedion-6″-yl)-chlorosulfo-*o*-terphenyl-Eu^{3+} ($BHHCT\text{-}Eu^{3+}$) is a representative β-diketonate-Eu^{3+} complex with a amino-reactive group,[28] which can be directly used as a biolabel for highly sensitive bioassays. The coordination feature of $BHHCT\text{-}Eu^{3+}$ has motivated us to think that it might be also a useful material for the development of ratiometric nanoprobes for the detection of certain metal ions when it is integrated onto the fluorescent C-dots.

In this work, by conjugating $BHHCT\text{-}Eu^{3+}$ onto the surface of C-dots, we prepared the $BHHCT\text{-}Eu^{3+}$ conjugated C-dots as a ratiometric fluorescence nanoprobe for the sensitive and selective detection of Cu^{2+} ions in aqueous media. The ratiometric nanoprobe based on $BHHCT\text{-}Eu^{3+}$-conjugated C-dots for Cu^{2+} ions has several considerable features as the followings. (1) Under a single wavelength excitation, the nanoprobe exhibits dual emission peaks at 410 and 615 nm, respectively. The two emission peaks do not interfere each other because the emission peak of Eu^{3+} complex is quite sharp and the dual emission peaks have no overlap. (2) The emissions of the nanoprobe at 410 and 615 nm play two roles for the recognition and ratiometric fluorescence detection of Cu^{2+} ions. The emission at 615 nm can selectively respond to Cu^{2+} ions with the intensity changes corresponding to the variation of Cu^{2+} concentration, while that at 410 nm does not affect by Cu^{2+} ions to give a internal reference signal for the ratiometric detection. (3) The Eu^{3+} complex, $BHHCT\text{-}Eu^{3+}$, acts as not only a fluorophore, but also a fluorescence sensor for Cu^{2+} ions without the use of extra Cu^{2+} specific receptor. (4) Unlike other works that Cu^{2+} ratiometric hybrid probes were prepared with tedious synthesis steps, the synthesis procedure of the C-dots-$BHHCT\text{-}Eu^{3+}$ nanoparticles is simple, effective and labor-saving. Scheme 1 shows the synthesis procedure of the C-dots-$BHHCT\text{-}Eu^{3+}$ nanoparticles.



Scheme 1 Preparation of C-dots-$BHHCT\text{-}Eu^{3+}$.

Results and discussion

Preparation and TEM characterization of the nanoparticles. In this work, the C-dots were synthesized using amino-rich chitosan as a material with a green hydrothermal synthesis method. A main advantage of this method is that the carbonization and surface-amino-functionalization can be proceed simultaneously during the reaction, so a large amounts of primary amino groups are produced on the surface of C-dots, which is favorable for the further modification of the nanoparticles. Thus the ratiometric nanoprobe, C-dots-$BHHCT\text{-}Eu^{3+}$, were synthesized with a one-step procedure by the conjugation of $BHHCT\text{-}Eu^{3+}$ and C-dots. As shown in Scheme 1, the primary amino groups of the C-dots are able to react with the sulfonyl chloride group of $BHHCT\text{-}Eu^{3+}$ in ethanol, and the Eu^{3+} complex molecules can be easily coupled onto the surface of C-dots, affording a novel ratiometric nanoprobe, C-dot-$BHHCT\text{-}Eu^{3+}$.

The ratiometric nanoprobe, C-dots-$BHHCT\text{-}Eu^{3+}$, was first characterized with transmission electron microscopy (TEM) method. As shown in Fig.1a, the C-dots derived from chitosan are mostly of spherical and well separated from each other. The size distribution of the nanoparticles shown in Fig. 1b reveals that the size of the synthesized C-dots is in the range of 1.5-4.5 nm with an average size of ~2.6 nm in diameter. The conjugation of $BHHCT\text{-}Eu^{3+}$ with C-dots results in the increase in diameters of the nanoparticles, and the size of C-dots-$BHHCT\text{-}Eu^{3+}$ is in the range of 5-15 nm with an average size of ~8.6 nm (based on the statistical analysis of 110 nanoparticles, Fig. 1c and 1d). The increased nanoparticle size might be ascribed to the conjugation of the $BHHCT\text{-}Eu^{3+}$ complex on the surface of the C-dots, and the slight aggregation of the nanoparticles occurred.

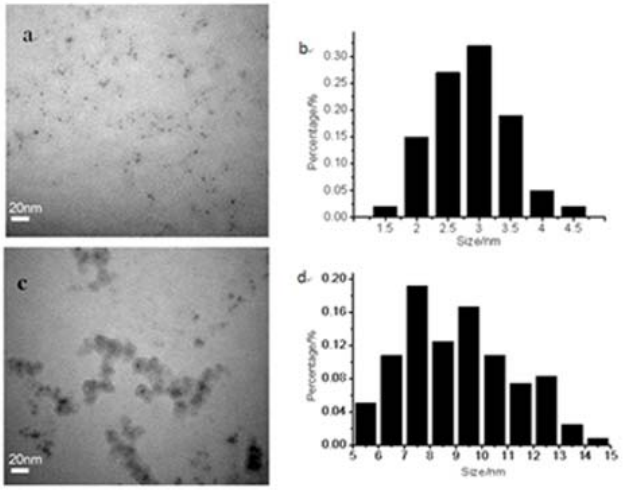


Fig. 1. TEM images and size histograms of C-dots (a, b) and C-dots-$BHHCT\text{-}Eu^{3+}$ (c, d).

UV-vis absorption and fluorescence spectra of the nanoparticles. Fig. 2 shows the UV-vis absorption and fluorescence spectra of pure C-dots, $BHHCT\text{-}Eu^{3+}$ and the C-dots-$BHHCT\text{-}Eu^{3+}$ nanoparticles, respectively. The pure C-dots derived from chitosan show a characteristic absorption peak at 288 nm (Fig. 2a), which is attributed to the typical aromatic system transition similar to the C-dots derived from ascorbic acid.[30] The Eu^{3+} complex, $BHHCT\text{-}Eu^{3+}$, exhibits two absorption peaks at 260 and 337 nm, respectively (Fig. 2b). Notably, the composite nanoparticles, C-dots-$BHHCT\text{-}Eu^{3+}$, display two pronounced absorption peaks at 268 and 337 nm (Fig. 2c), respectively. The interaction of $BHHCT\text{-}Eu^{3+}$ with C-dots results in a blue shift of the absorption peak of C-dots from 288 nm to 268 nm, and the absorption peak at 337 nm derived from $BHHCT\text{-}Eu^{3+}$ is not affected.

The fluorescence properties of the C-dots, $BHHCT\text{-}Eu^{3+}$ and the C-dots-$BHHCT\text{-}Eu^{3+}$ nanoparticles were investigated in a 50% ethanol-water (v/v) solution. As shown in Fig. 2d, the C-dots show a broad emission peak centered at 410 nm, while the C-dots-$BHHCT\text{-}Eu^{3+}$ nanoparticles display distinct dual-emission peaks at 410 nm and 615 nm upon excitation at a single wavelength of 337 nm (Fig. 2e), which are ascribed to the

combined emissions from the C-dots and BHHCT-Eu^{3+}. The strong emission at 410 nm of C-dots-BHHCT-Eu^{3+} is identical to that of C-dots, and the other sharp emission peak at 615 nm with a 3 nm red-shift compared with that of BHHCT-Eu^{3+} (Fig. 2f) is corresponded to the $^5D_0$-$^7F_2$ transition of the europium(III) ions.[25] Hence these results demonstrate that the Eu^{3+} complex, BHHCT-Eu^{3+}, has been successfully conjugated with the C-dots. In addition, the wavelength difference of the two emission peaks of C-dots-BHHCT-Eu^{3+} is as large as 205 nm, which is favorable to avoid the interference between the two emission peaks effectively, and beneficial the nanoparticles to act as a ratiometric fluorescence nanoprobe for the detection of metal ions.

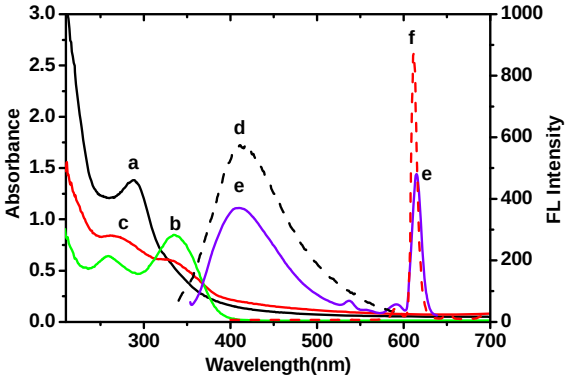


Fig. 2. UV/Vis spectra of C-dots (a), C-dots-BHHCT-Eu^{3+} (b), and BHHCT-Eu^{3+} (c) and fluorescence (FL) emission spectra of C-dots (d), C-dots-BHHCT-Eu^{3+} (e), and BHHCT-Eu^{3+} (f) at excitation wavelength of 337 nm in 50% (V/V) ethanol-water solution.

Fourier-transform infrared (FTIR) spectra of the nanoparticles. The available primary amino groups on the surface of pure C-dots make it possible that the C-dots-BHHCT-Eu^{3+} nanoparticles can be synthesized by directly reacting BHHCT-Eu^{3+} with C-dots. The presence of primary amino groups on the surface of C-dots was confirmed by the ninhydrin colorimetric assay (the inset of Fig. 3), which displays a characteristic blue color of ninhydrin reaction at the presence of C-dots. Moreover, the pure C-dots exhibit excellent water solubility with a zeta-potential of +17.5 mV in the aqueous solution before reaction. After the reaction, the conjugation of BHHCT-Eu^{3+} onto the surface of C-dots was checked by FTIR spectra. Fig. 3 shows the FTIR spectra of BHHCT, C-dots and the C-dots-BHHCT-Eu^{3+} nanoparticles, respectively. As shown in Fig. 3c. the broad peak centered at 3429 cm^{-1} might be attributed to the stretching vibration of N–H and O-H groups, the shoulder at 1226 cm^{-1} to C-F vibration and the peak at 1120 cm^{-1} to the S=O vibration. The strong peak at 1620 cm^{-1} can be observed which most likely arise from the C=O vibration, whereas the peaks at 2922 and 2851 cm^{-1} correspond to the stretching vibrations of –C-H in β-diketonate structure of BHHCT-Eu^{3+}. All of the above results reveal that BHHCT-Eu^{3+} molecules have been successfully conjugated on the surface of C-dots.

Effect of surfactant on the fluorescence intensity of C-dots-BHHCT-Eu^{3+}. The surfactant Triton X-100 often plays a vital role in enhancing the fluorescence intensity of the Eu^{3+} complex.

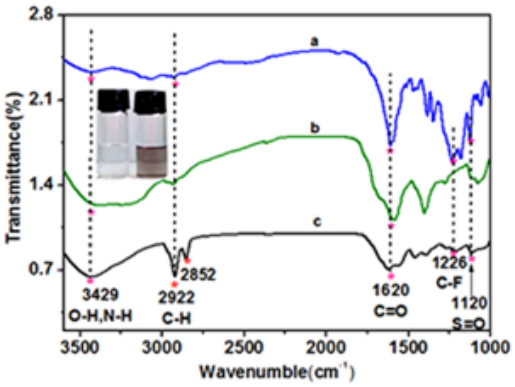


Fig. 3 FTIR spectra of BHHCT (a), C-dots (b), and C-dots-BHHCT-Eu^{3+} (c). Inset shows the characteristic blue of ninhydrin reaction (left: absence of C-dots, and right: presence of C-dots).

Fig. 4 shows the effect of Triton X-100 concentration on the fluorescence intensity of C-dots-BHHCT-Eu^{3+}. Upon additions of different concentrations of Triton X-100, the intensity of red emission at 615 nm from BHHCT-Eu^{3+} shows a continuous increase, while that of blue emission at 410 nm form C-dots remains constant. The different changes in the intensities of two emission peaks lead to visible color changes of fluorescence observed by naked eyes as displayed in the inset of Fig. 4. The enhanced Eu^{3+} emission may be attributed to the replacement of water molecules from the inner sphere of the Eu^{3+} complex by Triton X-100 molecules[31,32] and the increased solubility of C-dots-BHHCT-Eu^{3+} in the surfactant-containing solution.

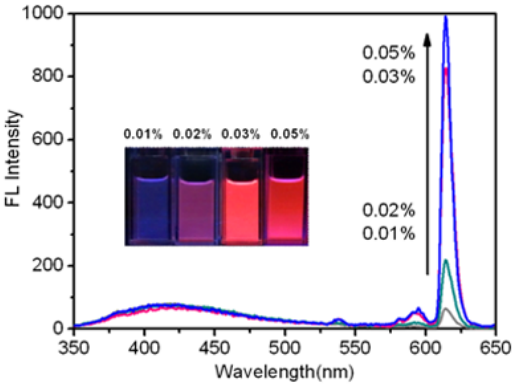


Fig. 4 Fluorescent spectra changes of C-dots-BHHCT-Eu^{3+} upon addition of different concentrations of surfactant of Triton X-100 in 0.05 M tris-HCl buffer at pH 7.4. Ex=337 nm. Inset shows the fluorescent images under UV light.

Selectivity of C-dots-BHHCT-Eu^{3+} as a ratiometric probe for the detection of metal ions. The effects of different metal ions on the fluorescence intensity of C-dots-BHHCT-Eu^{3+} were determined to investigate the potential of the new dual-emission nanoparticles as a ratiometric luminescent probe for the detection of metal ions. After the C-dots-BHHCT-Eu^{3+} nanoparticles (17 μg/mL) were reacted with different metal ions, the change of fluorescence intensity ratio of 615 nm and 410 nm, I_{615}/I_{410}, was calculated. As shown in Fig. 5, the fluorescence response of C-dots-BHHCT-Eu^{3+} shows a higher selectivity toward Cu^{2+} ions, while no change on I_{615}/I_{410} was observed in the presence of 10-fold of Fe^{2+}, Fe^{3+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Ba^{2+}, Ca^{2+}, K^{+}, Na^{+} and Hg^{2+}

ions, respectively. These results indicate that the C-dots-BHHCT-Eu^{3+} nanoparticles can be used as a ratiometric fluorescence probe for the detection of Cu^{2+} ions with high selectivity.

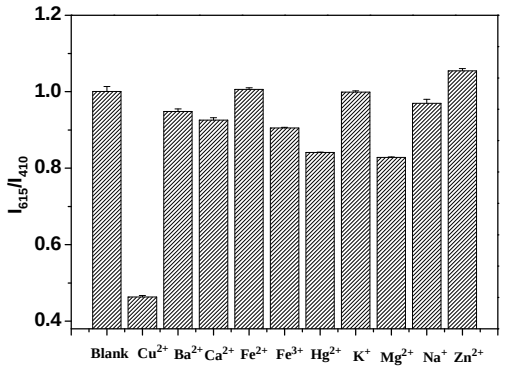


Fig. 5 Fluorescence responses of the C-dots-BHHCT-Eu^{3+} nanoparticles towards various metal ions (1.5 μM for Cu^{2+}; 15 μM for Ba^{2+}, Ca^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mg^{2+}, Na^+, and Zn^{2+}).

Performance of C-dots-BHHCT-Eu^{3+} as a ratiometric fluorescence probe for the detection of Cu^{2+} ions. To quantitatively investigate the fluorescence response of the C-dots-BHHCT-Eu^{3+} nanoparticles toward Cu^{2+} ions, the fluorescence spectra of C-dots-BHHCT-Eu^{3+} in the presence of different concentrations of Cu^{2+} ions were measured in 0.05 M borate buffer of pH 7.2. As shown in Fig. 6, upon addition of Cu^{2+}, the emission intensity of C-dots-BHHCT-Eu^{3+} at 615 nm is significantly decreased, while no fluorescence response at 410 nm can be observed. The quenching of the emission of the BHHCT-Eu^{3+} at 615 nm might be attributed to the energy transfer from the excited Eu^{3+} ions to Cu(II).[33] By plotting the emission intensity ratio of I_{615}/I_{410} against the Cu^{2+} concentration, a good linear calibration curve that can be expressed as $I_{615}/I_{410} = -0.523 [Cu^{2+}] + 1.00$ (R = 0.9995) was obtained in the Cu^{2+} concentration range of 0.1 to 1.0 μM. The detection limit, defined as the concentration corresponding to 3SD of background signal, is 4.0 nM. This result indicates that the ratiometric fluorescence detection of Cu^{2+} ions in aqueous media using C-dots-BHHCT-Eu^{3+} as a probe is highly sensitive.

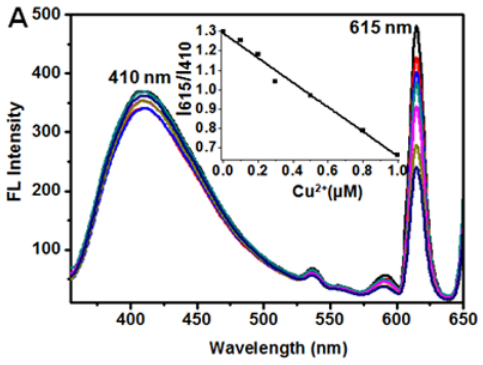


Fig. 6 Fluorescence spectra of the C-dots-BHHCT-Eu^{3+} nanoparticles in the presence of different concentrations of Cu^{2+}. The inset shows the correlation of Cu^{2+} concentration and the fluorescence intensity ratio at 615 nm and 410 nm.

To further test the practicability of the developed probe, the C-dots-BHHCT-Eu^{3+} nanoparticles were used to detect the concentrations of Cu^{2+} ions in several tap water samples. All the water samples were directly stirred with the C-dots-BHHCT-Eu^{3+} solution, and then subjected to the fluorescence measurements. As shown in Table 1, the CVs for all assays are less than 0.37%, and recoveries are in the range of 95% to 104%. These results demonstrated the good precision and accuracy of the present method for the detection of Cu^{2+} ions in aqueous samples.

Table 1 Determination of Cu^{2+} in tap water samples.

Sample	Added of Cu^{2+} (μM)	Found of Cu^{2+} (μM)	RSD (n=3,%)	Recovery (%)
1	0.75	0.73	0.22	97.33
2	0.80	0.76	0.22	95.37
3	0.85	0.87	0.24	102.11
4	0.90	0.91	0.10	101.39
5	0.95	0.98	0.37	103.16

Conclusions

In summary, a novel dual-emission fluorescence nanoprobe, C-dots-BHHCT-Eu^{3+}, has been developed by the conjugation of C-dots with a Eu^{3+} complex in this work. The C-dots-BHHCT-Eu^{3+} nanoparticles are monodispersed and spherical, and show two stable and well-resolved fluorescence emissions at 615 nm and 410 nm. In the presence of Cu^{2+} ions, the fluorescence intensities at 615 nm and 410 nm show different response behaviors, and the emission intensity ratio of I_{615}/I_{410} is linearly related to the concentration of Cu^{2+}. The results of selectivity, sentitivity and application characterizations indicate that the C-dots-BHHCT-Eu^{3+} nanoparticles are suitable to be used as a ratiometric fluorescence probe for the highly selective and sensitive detection of Cu^{2+} ions in aqueous media. In addition, the present work provides an easy strategy for the design and synthesis of nanoparticle-based ratiometric fluorescence probes for different analytes.

Experimental section

Materials and instruments. Chitosan with molecular weight of 2.5 KDa was degraded from raw material (Yuhuan Ocean Biomaterials Corporation, Zhejiang, China) in our laboratory, and BHHCT was synthesized according the literature method.[18] $CuSO_4·5H_2O$, $BaCl_2·2H_2O$, $CaCl_2$, $FeCl_2·6H_2O$, $FeCl_3·6H_2O$, $HgCl_2$, KCl, $MgCl_2·6H_2O$, NaCl, $ZnCl_2$, Triton-100 and quinoline sulfate were purchased from Aladdin. $EuCl_3·6H_2O$ was purchased from J&K company. Unless otherwise stated, all chemical materials were purchased from commercial sources and used without further purification.

Transmission electron microscopy (TEM) observations were performed on a JEM-2000 electron microscope operating at 200 kV. Nano ZS90 Zetasizer (Malvern Instruments, Malvern, UK) was used to determine the Zeta potential. The fluorescence and UV-vis absorption spectra were measured on Perkin Elmer LS 55 and Shimadzu UV-2550 spectrometers, respectively. The FTIR spectra were measured on a VECTOR 22 spectrometer with KBr pellet method.

Synthesis of C-dots-BHHCT-Eu^{3+}. The synthesis of C-dots was carried out according to a previously reported method.[29] Briefly, a solution of chitosan (0.5 g) in 2% aqueous acetic acid (20 mL) was added to a Teflon equipped stainless steel autoclave, which was then placed in a muffle furnace followed by hydrothermal treatment at 180 ^{o}C for 12 h. The obtained dark brown solution was centrifuged at a high speed (24,000 rpm) for 15 min to remove the black precipitate. The filtrate was lyophilized and the resulting C-dots were stored under vacuum for further use.

For the preparation of C-dots-BHHCT-Eu^{3+}, a solution of C-dots (82 mg), BHHCT (2 mg), and triethylamine (1.0 mL) in 100 mL of ethanol was stirred for 4 h at room temperature, then 150 μL of $EuCl_3$ (3.1 mg/mL) was added, and the mixture solution was further stirred at room temperature overnight. Ethanol and triethylamine were removed by evaporation and the resulting precipitate was thoroughly washed with water to remove the excess $EuCl_3$. Finally, the dual-emission composite nanoparticles, C-dots-BHHCT-Eu^{3+}, were obtained as a brown solid.

Fluorescence experiments. The effect of surfactant Triton X-100 on the fluorescence intensity of C-dots-BHHCT-Eu^{3+} was investigated by adding different concentrations of Triton X-100 into the solution of C-dots-BHHCT-Eu^{3+} (17 μg/mL) in 0.05 M Tris-HCl buffer at pH 7.4. The concentrations of Triton X-100 were 0.01%, 0.02%, 0.03% and 0.05% (wt/wt), respectively. The fluorescence spectra were recorded in the range of 350 nm to 650 nm using an excitation wavelength of 337 nm and a scan rate of 500 nm/min.

Detection of Cu^{2+} ions. The detection of Cu^{2+} ions was conducted in 0.05 M borate buffer of pH 7.2. The solution of C-dots-BHHCT-Eu^{3+} (17 μg/mL) was reacted with different concentrations of Cu^{2+} (0.1, 0.2, 0.3, 0.5, 0.8 and 1.0 μM), respectively. After stirring for 10 min at room temperature, the fluorescence spectra of above solutions were measured. For the selectivity experiments of metal ions, Cu^{2+} (1.5 μM) and other ions, Ba^{2+}, Ca^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^{+}, Mg^{2+}, Na^{+}, Zn^{2+} (15 μM), were added into the solution of C-dots-BHHCT-Eu^{3+} (17 μg/mL), respectively. After stirring for 10 min at room temperature, the fluorescence spectra were recorded as the above mentioned method.

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Notes and references

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