

Calixarene capped quantum dots as luminescent probes for Hg²⁺ ions

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Abstract

Luminescent and stable CdSe/ZnS core/shell quantum dots (QDs) capped with sulfur calixarene are prepared for the selective determination of mercury ions in acetonitrile with high sensitivity.

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Keywords: Quantum dots; Calixarene; Fluorescence; Probe; Mercury ions

1. Introduction

Quantum dots (QDs), a special semiconductor nanoclusters [1], have been attracting much attention owing to their new optical properties, such as a narrow, tunable, symmetric emission and photochemical stability [2]. Since the first reports using modified core–shell QDs as fluorescence labels to stain biological samples, inorganic luminescent QDs have attracted considerable attention as novel luminescence indicators of different biological processes and bio-analyses in recent years [3,4]. So far very few reports of chemical sensing of small molecules and ions with QDs via analyte-induced changes in photoluminescence have been reported. The first practical uses of CdS QDs capped with different organic ligands were employed as chemical sensor to determine zinc and copper ions in aqueous media [5]. More recently, peptide-coated CdS quantum dots were described for the determination of Cu(II) and Ag(I) [6]. Therefore, the use of QDs or nanoparticles as selective chemosensors for metal ions has been an active research field in recent years.

It is well known that the fluorescence efficiency of QDs is sensitive to the presence and nature of adsorbates at the surface QDs [7]. Therefore, it is expected that a chemical sensing system based on QDs can be developed using fluorescence changes induced by molecular recognition at the surface of QDs. Calixarenes have demonstrated outstanding complex ability towards ions, neutral molecules, *etc.*, and are considered the third best host

molecules after cyclodextrins and crown ethers [8]. Thus, a polar lower rim of calixarene composed of phenolic oxygens has been extensively modified to bind and transport metals [9]. Jin et al. prepared *p*-sulfonatocalix[4]arene-capped CdSe/ZnS for the optical detection of the neurotransmitter acetylcholine [10].

Here, we report the synthesis of CdSe/ZnS core/shell quantum dots modified with sulfur calixarene (S-Calix) and their potential application, as selective fluorescent probe for the determination of mercury ions.

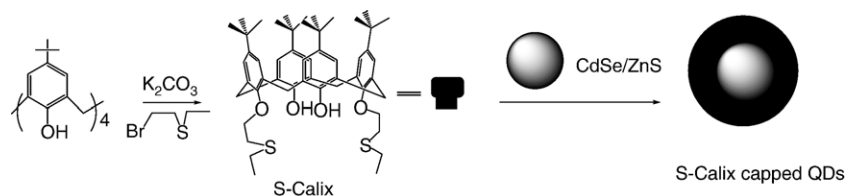
2. Experiment

CdSe quantum dots were synthesized using CdO as precursor via the procedure described by Peng's group [11], although some slight modifications were made here. Briefly, 0.03 g of CdO (0.233 mmol), 0.11 g of HPA and 3.5 g of TOPO were mixed to heat at 300–320 °C under argon flow for 15–20 min, and CdO was dissolved in HPA and TOPO. The temperature of the solution was swiftly injected and a change of solution color to red was observed. After injection, CdSe nanocrystals were left to grow for about 20 min at 250 °C. Then, the precursors prepared from (TMS)₂S and Zn(ac)₂ were added dropwise into a freshly prepared CdSe solution at 200 °C [12]. Thus, the CdSe/ZnS core/shell quantum dots were prepared in TOPO as a solvent.

For the synthesis of sulfur calix[4]arene (S-Calix), a mixture of *p*-*tert*-butylcalix[4]arene (5 mmol), bromoethoxy thioethoxy (5.5 mmol), anhydrous K₂CO₃ (50 mmol) in toluene (500 mL) was stirred and refluxed under N₂ for 24 h. All the solvent was evaporated and the residue partitioned between CH₂Cl₂ and

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Scheme 1. Formation of CdSe/ZnS coated with S-Calix.

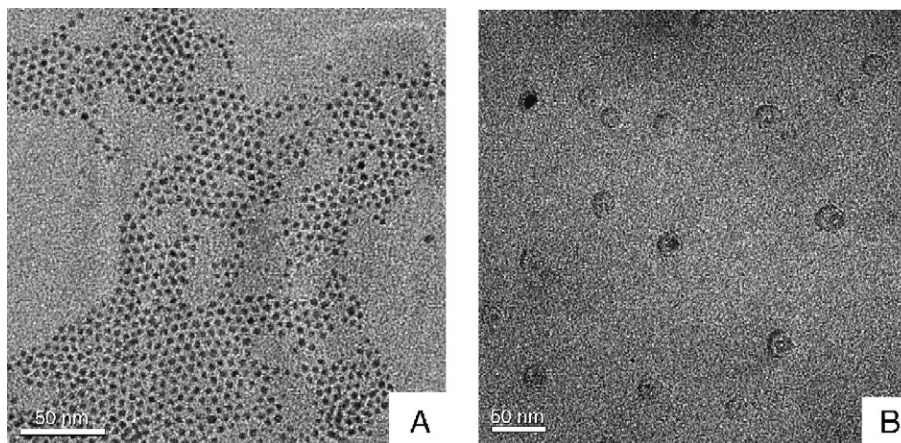


Fig. 1. TEM images of (A) original QDs and (B) QDs capped with S-Calix, scale bars are both 50 nm.

water. The organic layer was separated, dried, filtered and distilled to dryness. The remained solid was recrystallized from Pr^iOH to give white powder S-Calix in 60% yield [13].

S-Calix capped QDs were prepared by mixing the S-Calix with a dilute solution of CdSe/ZnS in acetonitrile at room temperature.

All the reagents were of analytical grade and were used without further purification. ^1H NMR spectra were recorded on Varian Mercury VX 300 instruments at ambient temperature. TMS was used as an internal standard for NMR. FAB-MS spectra were obtained from a Kratos MS80RF mass spectrometry, with *m*-nitrobenzyl alcohol as a matrix. Elemental analyses were

performed by the Analytical Laboratory of the Department of Chemistry. A JEOL-JEM 2010 TEM operated at 200 kV.

3. Results and discussion

To prepare CdSe/ZnS QDs, monodisperse CdSe QDs were first obtained according to a reported scheme [11]. Then, the CdSe core was overcoated with a ZnS shell using TOPO as a solvent based on previously published methods [12].

The synthetic route of S-Calix was depicted in Scheme 1. A mixture of *p*-*tert*-butylcalix[4]arene (5 mmol), bromoethoxy thioethoxy (5.5 mmol), anhydrous K_2CO_3 (50 mmol) in toluene (500 mL) is stirred and refluxed under N_2 for 24 h. After standard work-up, the crude product is recrystallized from CHCl_3 and petroleum ether (60–90 °C) to afford product S-Calix in 60% yield. All compounds are characterized

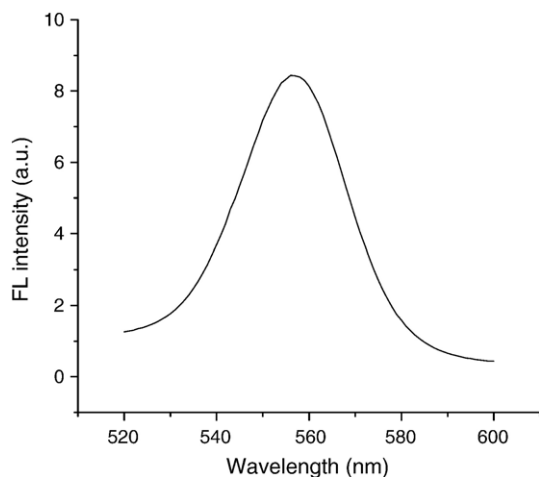


Fig. 2. FL emission spectrum of S-Calix capped QDs.

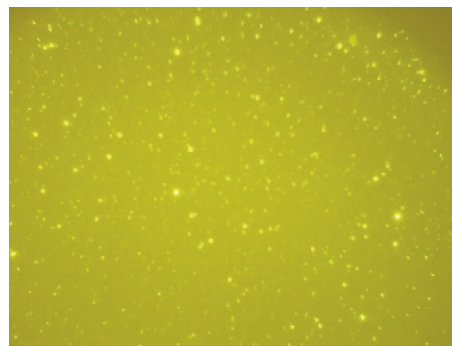


Fig. 3. FL image of S-Calix capped QDs. (The luminescence images are taken using a digital fluorescence imaging microscopy system equipped with an intensified charge coupled device camera (ICCD). The excitation wavelength is 470 nm and the magnification of the microscope was 40 \times .)

by ^1H NMR, FAB-MS and elemental analysis. The ^1H NMR spectrum of S-Calix indicates that the bridge methylene protons appear in an AB pattern, suggesting that S-Calix adapts a cone conformation [13].

S-Calix capped QDs are prepared by mixing the S-Calix with a dilute solution of CdSe/ZnS in acetonitrile at room temperature (as shown in Scheme 1). The colloidal QD solutions before and after addition of the calixarene are characterized by photon correlation spectroscopy (PCS) which provided the particle size d , which indicates that d is increased from 4 nm to around 20 nm, suggesting a layer of calixarene has been deposited on the particle surface.

As shown in TEM images (Fig. 1), the diameters of the QD particles after surface modification increase and QDs are monodisperse and uniform. Therefore, the observed increase in particle size by PCS measurement and TEM images can be attributed to a calixarene layer coated on the surface of QDs. In this experiment, S-Calix host molecules provide enhanced coordination interactions due to a cooperative, amplifying effect of multiple interaction including cation– π interaction and hydrophobic interaction *etc.*

A fluorescence (FL) spectrum of S-Calix capped QDs is shown in Fig. 2. It can be seen that the line width of the FL spectrum is narrow (with the full width at half-maximum of about 30 nm), showing that the S-Calix capped QDs are nearly monodisperse and uniform. The quantum yield determined by using rhodamine B as a criterion (QY=89%) is about 55%, which is by far higher than that of thiol-modified CdSe/ZnS QDs [14]. In Fig. 3, the FL image of S-Calix capped QDs also shows that the particles are monodisperse in CH_3CN . It proved quite stable for the colloidal suspensions of S-Calix capped QDs after photoluminescence studies over 3 months.

The fluorescence titration of S-Calix capped QDs with various metal ions is conducted to examine the selectivity. As can be seen in Fig. 4, S-Calix capped QDs towards mercury ion are rather selective. The influence of other metal ions (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cu^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+}) is very weak, even at a relatively higher concentration. Only Pb^{2+} at a higher concentration produced a measurable quenching of the luminescence of the modified QDs.

It is found that mercury ions quenched the FL intensity of S-Calix capped QDs in a concentration dependent manner (Fig. 5) that is best described by a Stern–Volmer-type equation, which can be used to develop a method for the determination of mercury ions. The linear range of the calibration curve was $0\text{--}3 \times 10^{-5}$ M. The limit of detection,

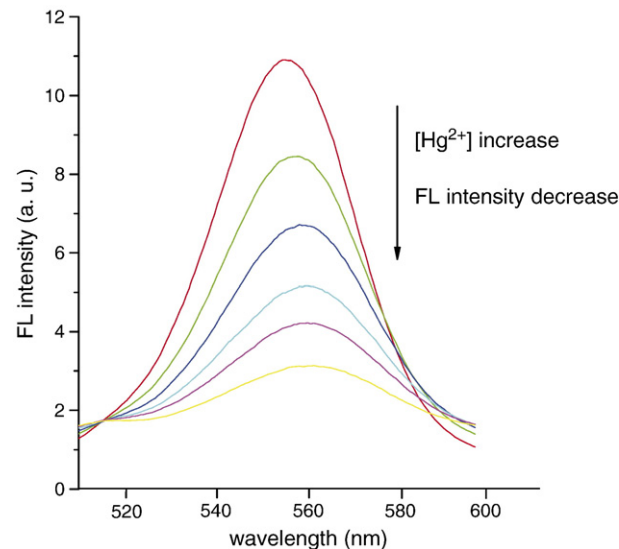


Fig. 5. Effect of Hg^{2+} concentration on FL intensity of S-Calix capped QDs.

calculated following the 3σ IUPAC criteria is 15 nM for mercury ions ($3 \mu\text{g L}^{-1}$). This may be attributed to the effective electron transfer from S-Calix to Hg^{2+} . S-Calix on the QD surface can bind Hg^{2+} selectively because for receptor molecules for the softer metal cations like mercury ions, sulfur donor atoms are preferred.

4. Conclusion

S-Calix capped CdSe/ZnS quantum dots have been successfully combined to develop a novel and highly sensitive and selective system for optical recognition and determination of mercury ions. Future study will investigate host–guest recognition of calixarene-based surface architectures of colloidal semiconductor QDs.

Acknowledgements

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References

- [1] M. Nirmal, L. Brus, *Acc. Chem. Res.* 32 (1999) 407.
- [2] W.C.W. Chan, D.J. Maxwell, X. Gao, R.E. Bailey, M. Han, S. Nie, *Curr. Opin. Biotechnol.* 13 (2002) 40.
- [3] M.J. Bruchez, M. Moronne, P. Gin, S. Weiss, A.P. Alivisatos, *Science* 281 (1998) 2013.
- [4] W.C.W. Chan, S.M. Nie, *Science* 281 (1998) 2016.
- [5] Y.F. Chen, Z. Rosenzweig, *Anal. Chem.* 74 (2002) 5132.
- [6] K.M. Gattas-Asfura, R.M. Leblanc, *Chem. Commun.* 21 (2003) 2684.
- [7] C.J. Murphy, *Anal. Chem.* 74 (2002) 520A.
- [8] a) C.D. Gutsche, *Calixarene Revisited*, The Royal Society of Chemistry, Cambridge, 1998;
b) A. Ikeda, S. Shinkai, *Chem. Rev.* 97 (1997) 1713.
- [9] Y.Y. Chen, H.B. Li, *Chem. Lett.* (2000) 1208;
Y.Y. Chen, H.B. Li, *New J. Chem.* 25 (2001) 340;
H.B. Li, Y.Y. Chen, *React. Funct. Polym.* 55 (2003) 171;
H.B. Li, Y.Y. Chen, X.L. Yang, *Chin. J. Chem.* 23 (2005) 891;
H.B. Li, Y.Y. Chen, Z.R. Zeng, C.H. Xie, X.L. Yang, *Anal. Sci.* 251 (2005) 717;

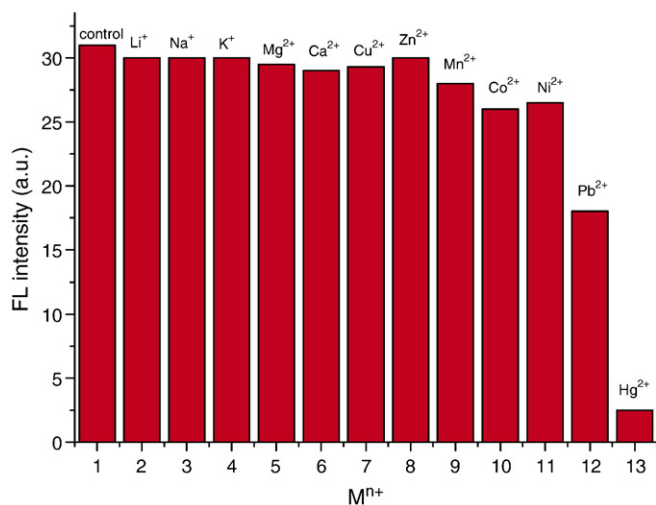


Fig. 4. Effect of different ions on the fluorescence of S-Calix capped CdSe/ZnS QDs (concentrations of Hg^{2+} in CH_3CN : 10^{-6} mol L^{-1} ; for others: 10^{-4} mol L^{-1}).

- H.B. Li, W. Xiong, Y. Yan, J.A. Liu, H.B. Xu, X.L. Yang, *Mater. Lett.* 60 (2006) 703.
- [10] T. Jin, F. Fujii, H. Sakata, M. Tamura, M. Kinjo, *Chem. Commun.* 4300 (2005).
- [11] L. Qu, X. Peng, *Chem. Soc.* 124 (2002) 49.
- [12] H.Y. Xie, J.G. Liang, Y. Liu, Z.L. Zhang, D.W. Pang, Z.K. He, *J. Nanosci. Nanotechnol.* 5 (2005) 880.
- [13] S-Calix: mp 132–134 °C ^1H NMR (300 MHz, CDCl_3) δ 0.99, 1.34 (s each, 18H each, Bu^t), 1.37 (t, 6H, SCH_2CH_3), 2.75 (q, 4H, SCH_2CH_3), 3.15 (t, 4H, OCH_2CH_2), 4.17 (t, 4H, ArOCH₂), 3.34, 4.34 (d, AB, 8H, $J=13.2$ Hz), 6.81 (s, 4H, ArH), 7.09 (s, 2H, ArOH), 7.11 (s, 4H, ArH) MS (FAB) m/z : 825 (MH^+) Anal. calc. for $\text{C}_{52}\text{H}_{72}\text{O}_4\text{S}_2$, 75.68; H, 8.79; found C, 75.64; H, 8.83.
- [14] G.P. Mitchell, C.A. Mirkin, R.L. Letsinger, *J. Am. Chem. Soc.* 121 (1999) 8122.