Synthesis of CdTe Quantum Dots in Sol−Gel-Derived Composite Silica Spheres Coated with Calix[4]arene as Luminescent Probes for Pesticides

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Highly luminescent and stable CdTe quantum dots (QDs) in sol−gel-derived composite silica spheres coated with 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxy-26,28-dihydroxycalix[4]arene (C[4]/SiO_2/CdTe) are prepared via the sol−gel technique in aqueous media, which are characterized by transmission electron microscopy (TEM), photon correlation spectroscopy (PCS), fluorescence spectroscopy, UV−vis spectroscopy, and FT-IR spectroscopy. The synthesized nanocomposites show higher fluorescence (FL) intensity and are more stable in comparison with the SiO_2/CdTe nanoparticles (NPs). The C[4]/SiO_2/CdTe NPs allow a highly sensitive determination of methomyl via significant FL intensity enhancement. Under optimal conditions, the relative FL intensity is increased linearly with increasing methomyl concentration in the range of 0.1−50 μM with a detection limit of 0.08 μM of methomyl, while the FL intensity of C[4]/SiO_2/CdTe NPs to other pesticides including parathion-methyl, fenamithion, optunal, and acetamiprid is negligible. It is found that the enhanced luminescence intensity of the C[4]/SiO_2/CdTe NPs in a concentration of methomyl dependence is best described by a Langmuir binding isotherm equation. The possible mechanism is discussed.

Introduction

One of the current major challenges in materials chemistry is the synthesis of complex nanoscaled structures, whose properties can be manipulated by the arrangement of their constituents. Molecular recognition structures are powerful tools for organizing nanoparticles (NPs) in solution.[1] It is known that the fluorescence (FL) efficiency of quantum dots (QDs) is sensitive to surface modification of QDs.[2] Introduction of organic ligand on NPs surface affords not only the stability of these nanoentities in different solvents but also the desired surface functionality.[3] Therefore, it is expected that a chemical sensing system based on QDs can be developed using FL changes induced by molecular recognition at the surface of QDs.[4] Within this scheme, NPs modified with macrocyclic host molecules[5] are one of the interesting research topics. For example, Chen and co-workers have reported the synthesis of 15-crown-5 functionalized CdSe/ZnS QDs as well as their exploitation as a sensing unit toward K^+ in aqueous solution.[6] Liu and co-workers have reported β-cyclodextrin capped CdS and CdSe/CdS QDs used as fluorescence sensors.[7,8] Calixarenes are considered as the third host molecules after crown ethers and cyclodextrins, which have demonstrated outstanding complex ability toward ions, neutral molecules, etc.[9] Jin and co-workers have found that the surface of CdSe/ZnS QDs could be modified with amphiphilic calixarene derivatives to give water-soluble QDs.[10] Recently, we have synthesized CdSe/ZnS QDs modified with selenium calixarene and sulfur calixarene.[4,11] In the above cases of calixarene modifiers, the interfacial process is driven by the hydrophobic van der Waals interactions between the primary alkane of the stabilizing ligand like TOPO and the secondary calixarene layer, resulting in bilayer structures. It is undesirable that the loose bilayer structures based on the weak interaction of

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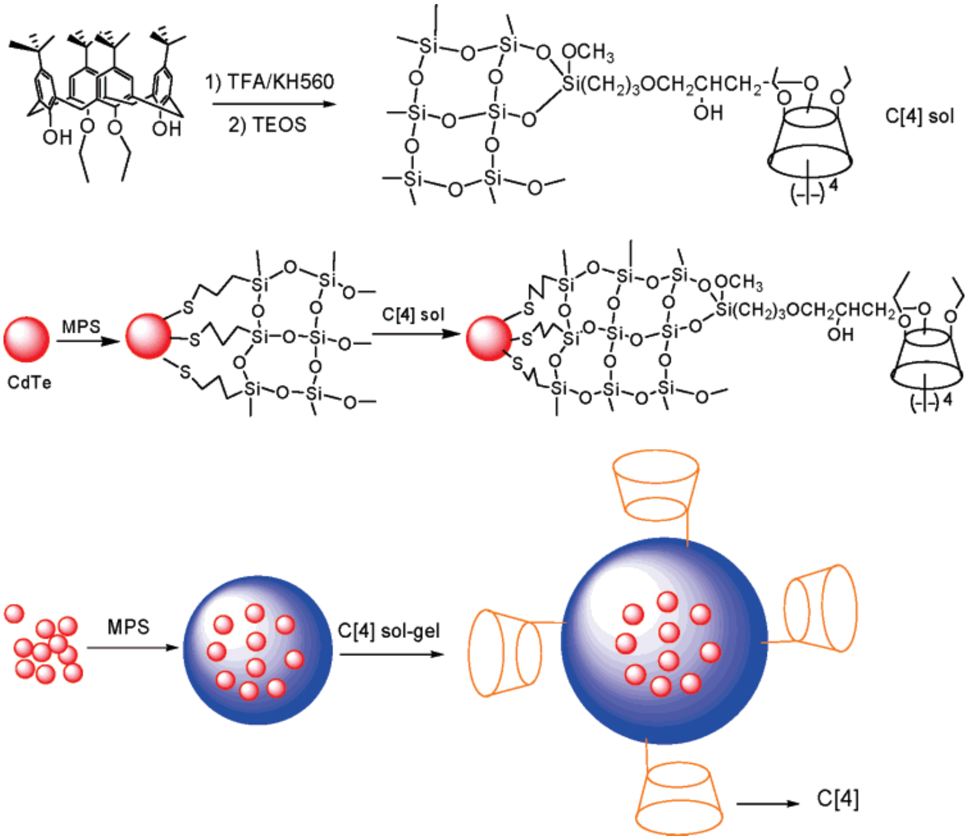
Scheme 1. Formation of C[4]/SiO_2/CdTe NPs



van der Waals are not quite stable. Therefore, it is a challenge to construct stable calixarene modified QDs.

It is known that QDs often need to be coated with inert materials to improve the chemical and photochemical stabilities, especially in aqueous systems.[12] Silica is a good option for the inert material, because not only does it impede the diffusion of charge carriers generated upon photoexcitation as well as the diffusion of oxygen from the environment,[13] but it also prevents the coated NPs from coagulating in aqueous dispersions. By using the well-known Stöber method, Liz-Marzán and co-workers have succeeded in coating aqueous CdS QDs stabilized by sodium citrate to obtain core–shell structured SiO_2/CdS particles.[13] More recently, Nann and co-workers further demonstrated that the silica coating on organic-soluble QDs by the Stöber process could also lead to well-defined structures.[14] It is reasonable to believe that the sol–gel technique in the Stöber method will be a powerful tool to introduce artificial receptor moieties onto the surface of silica sphere.

Organophosphorus (OPs) and carbamates (CBs) pesticides are widely used as insecticides in agriculture and as biocides in household products. High level exposure to OPs results in acetylcholine accumulation, which interferes with muscular responses, leading to the possibility of death.[15] Although some of them are relatively nonpersistent in the environment, they have been characterized as being highly acute. Therefore, an effective analytical method for rapid screening of OPs and CBs residues is urgently needed.[16]

In this Article, we report the synthesis of CdTe nanocystals in sol–gel-derived composite silica spheres coated with calix[4]arene and their potential application as selective fluorescent probes for the determination of pesticides.

Experimental Section

Materials and Reagents. All chemicals used were of analytical grade or of the highest purity available. All solutions were prepared with double-distilled, deionized water. Tellurium (reagent powder, 99.999%, about 200 mesh), thioglycolic acid (TGA, 99%), $CdCl_2 \cdot 2.5H_2O$ (99%), and $NaBH_4$ (96%) were purchased from Aldrich (Milwaukee, WI). C[4] (see the Supporting Information, Figure S1) was synthesized according to the reported method.[17] 3-(2-Cycloxypropoxyl)propyltrimethoxysilane (KH-560), tetraethoxysilane (TEOS), and 3-mercaptopropyltrimethoxysilane (MPS) were obtained from the Chemical Plant of Wuhan University. Trifluoroacetic acid (TFA) was purchased from Shanghai Chemical Factory, China. Pesticide standards (parathion-methyl, fenamithion, methomyl, optunal, and acetamiprid) studied were provided by the Key Laboratory of Pesticide and Chemical Biology (CCNU), Ministry of Education, China. All pesticides standards are of 98–99% purity. Parathion-methyl and optunal were dissolved in the mixture of water and ethanol, and others were dissolved in water and stored at room temperature.

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Synthesis of CdTe QDs. CdTe QDs were prepared according to the method described elsewhere.[18] The molar ratio of Cd^{2+}:TGA:HTe^- was fixed at 1:2.5:0.5. Briefly, 0.095 g of $CdCl_2 \cdot 2.5H_2O$ was dissolved in 5 mL of water, and 0.092 mL of TGA was added. Next, the solution was adjusted to pH = 11 with 1 M NaOH and deaerated with N_2 for 30 min. Next, oxygen-free NaHTe solution, which was freshly prepared from tellurium powder and $NaBH_4$ in water, was injected into the above solution under vigorous stirring. The solution was then heated at 60 °C for 2 h. Finally, CdTe QDs were obtained in aqueous media.

Preparation of SiO_2/CdTe NPs. CdTe QDs in sol−gel-derived composite silica spheres were prepared by the Stöber method.[19] 2 mL of CH_3OH was added to 5 mL of 1 mM CdTe QDs under stirring. After the mixtures were stirred for 20 min, 1 μL of MPS was added and then reacted for about 20 min at room temperature under vigorous stirring. Next, CdTe QDs in sol−gel-derived composite silica spheres were obtained in water, which was then diluted up to 25 mL at a pH of 8.0 for further experiments.

Preparation of C[4]/SiO_2/CdTe NPs. The synthesis of CdTe QDs in sol−gel-derived composite silica spheres coated with C[4] involves two steps: (1) the preparation of the C[4] sol solution; and (2) SiO_2/CdTe NPs coated with C[4] sol solution, as Scheme 1 illustrates.

The C[4] sol solution was prepared as follows: 3 mg of C[4] was dissolved in 200 μL of CH_2Cl_2, and then 50 μL of KH-560 and 38 μL of TFA were added and mixed thoroughly by ultrasonic agitation in a plastic tube for 3 min. To the resulting solution was added 100 μL of TEOS with ultrasonic agitation for another 3 min. The mixture was centrifuged at 10 000 rpm for 10 min. Finally, the C[4] sol solution with a concentration of 11 mM was obtained.[20]

SiO_2/CdTe NPs were coated with C[4] sol solution as follows: 15 μL of C[4] sol solution was added to freshly prepared 2.5 mL of SiO_2/CdTe NPs solution under vigorous stirring for 30 min, which resulted in the formation of an oil-in-water microemulsion. Evaporation of CH_2Cl_2 transfers C[4] into the aqueous phase to attach C[4] onto SiO_2/CdTe NPs by surface-bonded polymeric coating.[20,21] As Scheme 1 illustrates, C[4]/SiO_2/CdTe NPs were constructed as CdTe QDs in sol−gel-derived composite silica spheres coated with C[4].

Characterizations. UV−vis absorption spectra were acquired on a TU-1901 UV−vis spectrometer (Beijing Purkinje General Instrument Co. Ltd.). FL spectra were taken on a Fluoromax-P luminescence spectrometer (HORIBA JOBIN YVON INC.). IR spectra were measured with a NEXUS FT/IR spectrometer (Thermo Nicolet Co.).

The transmission electron micrograph (TEM) was recorded with a JEOL-JEM 2010 electron microscope operating at 200 kV. The samples were dropped onto a small copper mesh and left at room temperature so that the samples precipitated homogeneously on the carbon films among the tiny pores of the copper mesh. The average particle size (z-average size) and size distribution were measured by photon correlation spectroscopy (Nano ZS90 zetasizer, Malvern Instruments Corp., U.K.) at 25 °C under a fixed angle of 90° in disposable polystyrene cuvettes. The measurements were obtained using a He−Ne laser of 633 nm. No multi-scattering phenomenon was observed.

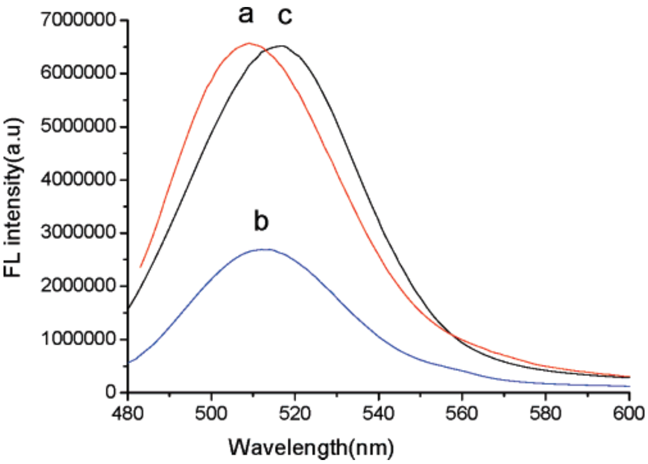

Figure 1. FL spectra of (a) CdTe QDs, (b) SiO_2/CdTe NPs, and (c) C[4]/SiO_2/CdTe NPs (ex = 460 nm).

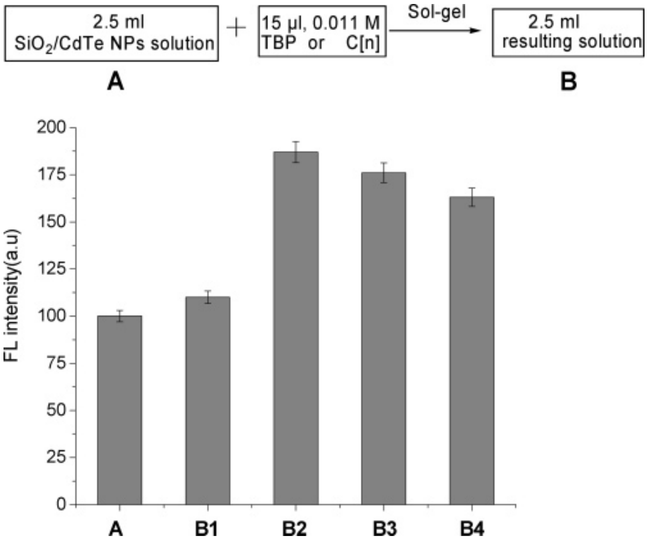

Figure 2. Effect of different coating materials on FL intensity of SiO_2/CdTe NPs (from A to B4: SiO_2/CdTe NPs, TBP/SiO_2/CdTe NPs, C[4]/SiO_2/CdTe NPs, C[6]/SiO_2/CdTe NPs, C[7]/SiO_2/CdTe NPs).

Results and Discussion

Spectra Characterizations. Figure 1 shows the FL spectra of CdTe QDs, SiO_2/CdTe NPs, and C[4]/SiO_2/CdTe NPs. It can be seen that the emission peak of C[4]/SiO_2/CdTe NPs is red shifted as compared to its precursor SiO_2/CdTe NPs, which may contribute to the increased size of NPs. It is interesting to find that the FL intensity of SiO_2/CdTe NPs is decreased in comparison with that of CdTe QDs, and when C[4] coating is attached onto the surface of SiO_2/CdTe NPs, the FL intensity of NPs is increased again. To investigate the divertive phenomena, *tert*-butylphenol (TBP), C[4], *p*-*tert*-butylcalix[6]arene (C[6]), or *p*-*tert*-butylcalix[7]arene (C[7]) are used to prepare sol solution, and 15 μL of C[4], C[6], C[7], or TBP sol (11 mM) is added to 2.5 mL of freshly prepared SiO_2/CdTe NPs solution at a pH of 8.0 under vigorous stirring for 30 min, respectively. As Figure 2 shows, under the same condition, the FL intensity is only increased by about 10% for TBP coating SiO_2/CdTe NPs. In contrast, the FL intensities are increased by about 87%, 76%, and

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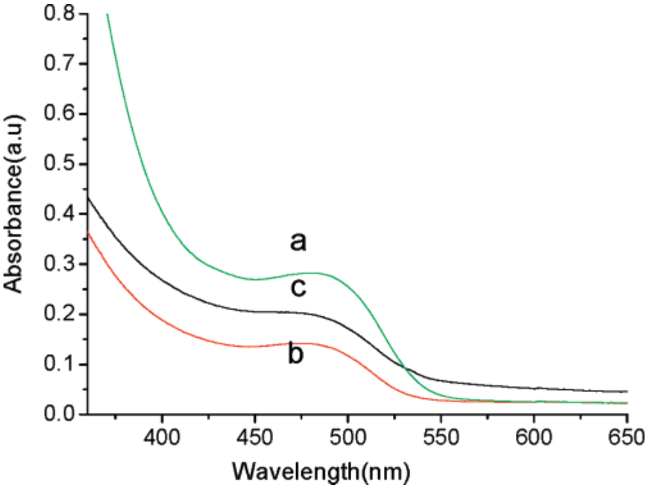

Figure 3. UV−vis spectra of (a) CdTe QDs, (b) SiO_2/CdTe NPs, and (c) C[4]/SiO_2/CdTe NPs.

63% for C[4], C[6], and C[7] coating SiO_2/CdTe NPs, respectively. It is reasonable to believe that calixarene coatings play an important role for the increasing FL intensity. The photooxidation of QDs can result in the photobleaching, which is reduced by the surface modification with calixarene. It is possible due to a cavity of calixarene composed of electron-rich benzene-π systems and a hydrophobic wall that protect the surfaces of nanoparticles well.

As can be seen from Figure 3, a distinct difference of absorption spectra of the CdTe QDs, SiO_2/CdTe NPs, and C[4]/SiO_2/CdTe NPs in the positions and peak widths is not found. It suggests that the coating process does not change the optical property of original CdTe QDs. The quantum yields (QYs) of SiO_2/CdTe NPs and C[4]/SiO_2/CdTe NPs in water are measured to be about 12% and 15%, respectively, by using Rodamine B as a criterion (QY = 89%, EtOH)[22] at room temperature. It is by far higher than that of the core−shell silica spheres of only 7% reported by Gao and co-workers.[23]

The IR spectra of SiO_2/CdTe NPs before and after coating C[4] can confirm the successful binding of C[4] to the surface of SiO_2/CdTe NPs in Figure 4. The IR data contain features identified on C[4]/SiO_2/CdTe NPs, as shown in Figure 4B: peaks in the benzene ring stretching region at 1485 cm^{-1}, the C−C stretching band at 1362 cm^{-1}, and a peak at 870 cm^{-1} for a tetra-substituted benzene ring. These results confirm the successful bonding of the C[4] onto the surface of SiO_2/CdTe NPs.

The TEM images of SiO_2/CdTe NPs and C[4]/SiO_2/CdTe NPs are shown in Figure 5B and C, respectively, which show that the modified NPs exhibit single particle features and the diameters of the SiO_2/CdTe NPs after coating with C[4] are increased. The average sizes of SiO_2/CdTe NPs and C[4]/SiO_2/CdTe NPs are measured by PCS about 70 and 100 nm, respectively (see the Supporting Information, Figure S2A and S2B). The increase in particle size by PCS measurement and TEM images can be contributed to a calixarene-SiO_2 layer coated onto the surface of SiO_2/CdTe NPs.

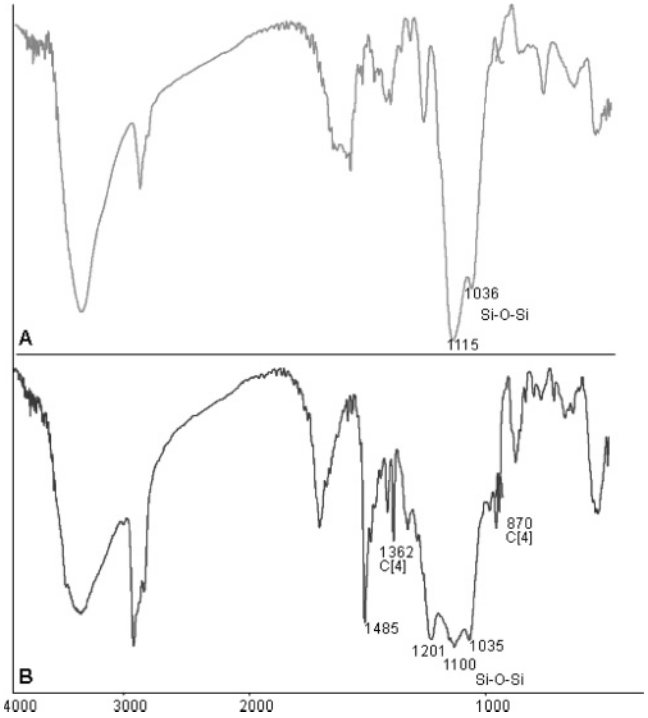

Figure 4. IR spectra of (A) SiO_2/CdTeNPs and (B) C[4]/SiO_2/CdTe NPs.

Effect of the Dosage of C[4] Sol Solution. Figure 6 shows that the dosage of C[4] sol solution has an important effect on C[4]/SiO_2/CdTe NPs. On increasing the dosage of C[4] sol solution, the FL intensity is increased dramatically with red-shift. Under optimal condition, the FL intensity is increased by 87% as compared to that of SiO_2/CdTe NPs. Yet, while the dosage of C[4] sol solution is added over 15 μL, the FL intensity of the C[4]/SiO_2/CdTe NPs is decreased quickly and appreciable precipitation is formed and visualized by the naked eye in the acting system, which is due to the large amount of hydrophobic calixarene coating decreasing the hydrophilicity of the nanocomposites. Therefore, 15 μL of C[4] sol solution is selected to prepare C[4]/SiO_2/CdTe NPs.

Stability of SiO_2/CdTeNPs and C[4]/SiO_2/CdTe NPs. The colloidal stabilities of SiO_2/CdTe NPs and C[4]/SiO_2/CdTe NPs are estimated at room temperature, as shown in Figure 7. It is found that the FL intensity of C[4]/SiO_2/CdTe NPs is increased gradually in 6 days. After that, the FL intensity is decreased in the next 9 days, and then the FL intensity is held. It is shown that the peak of SiO_2/CdTe NPs shifts to the longer wavelength quickly while the FL intensity decreases dramatically. Yet for C[4]/SiO_2/CdTe NPs, no distinct shift is observed (see the Supporting Information, Figure S3A and S3B). In the process of preparing C[4]/SiO_2/CdTe NPs, calixarene molecules are attached to SiO_2/CdTeNPs by surface-bonded polymeric coating.[20] Thus, the surface defect of SiO_2/CdTe NPs could be ulteriorly passivated, which results in C[4]/SiO_2/CdTe NPs becoming more stable.

Effect of pH on the Luminescence Response of SiO_2/CdTeNPs and C[4]/SiO_2/CdTe NPs. The effect of pH in a range between 4 and 13 is studied for CdTe QDs, SiO_2/CdTe NPs, and C[4]/SiO_2/CdTe NPs. The FL intensity of C[4]/SiO_2/CdTe NPs in the interval 5.0−11 is considerably stable

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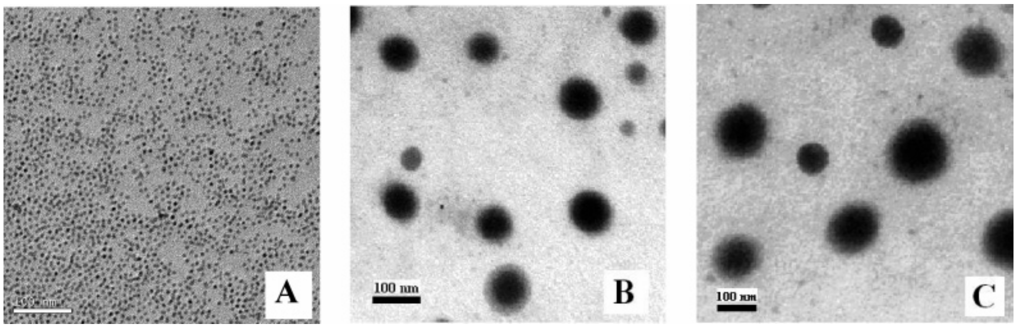

Figure 5. TEM images of (A) CdTe QDs, (B) SiO_2/CdTe NPs, and (C) C[4]/SiO_2/CdTe NPs. Scale bars are both 100 nm.

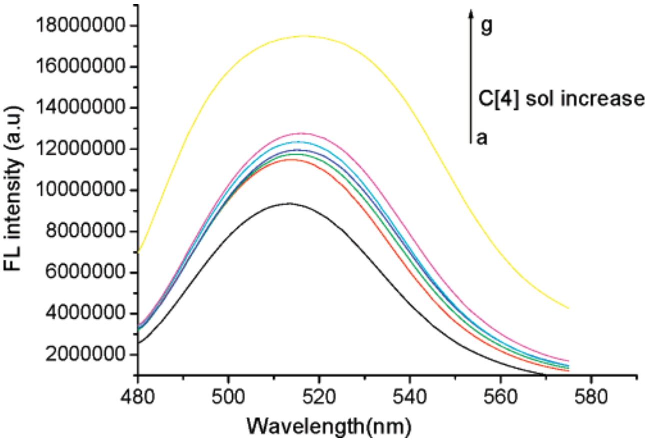

Figure 6. Effect of C[4] sol solution dosage on FL intensity of SiO_2/CdTe NPs (from a to g: 0 μL, 3 μL, 5 μL, 8 μL ,10 μL, 13 μL, 15 μL).

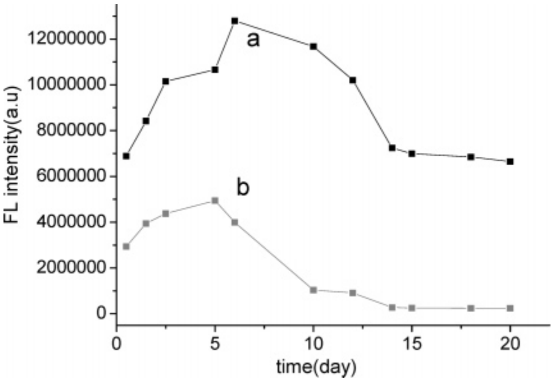

Figure 7. The photostability of (a) C[4]/SiO_2/CdTe NPs and (b) SiO_2/CdTe NPs.

(see the Supporting Information, Figure S4). However, the FL intensity is decreased quickly in acidic or strong basic media. Clearly at low pH, the surface of C[4]/SiO_2/CdTe NPs is possibly being dissolved, resulting in surface defects. At high pH, OH^- could nucleophilicly attack the surface to cleave calixarene and create surface defects. Finally, a pH of 8.0 is selected for further experiments.

Determination of Pesticides. The FL titration of SiO_2/CdTe NPs and C[4]/SiO_2/CdTe NPs with various pesticides is conducted to examine the selectivity. Figure 8 shows the effect of 10^{-5} M relevant pesticides on the FL of SiO_2/CdTe NPs and C[4]/SiO_2/CdTe NPs, including parathion-methyl, fenamithion, methomyl, optunal, and acetamiprid, which are shown in Figure 9. Only methomyl has a selective effect on the luminescence of C[4]/SiO_2/CdTe NPs over other pesticides. The FL intensity of the C[4]/SiO_2/CdTe NPs turns out to be increased sensitively in the presence of methomyl

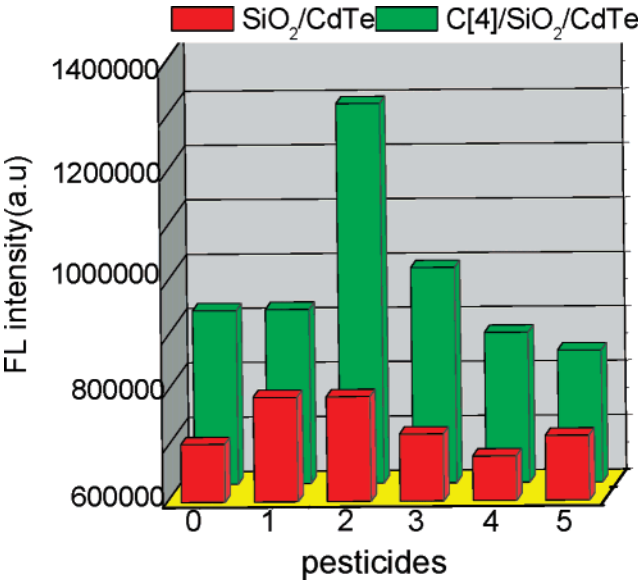

Figure 8. Effect of 10^{-5} M relevant pesticides on the FL of SiO_2/CdTe NPs and C[4]/SiO_2/CdTe NPs (from 0 to 5: control, parathion-methyl, methomyl, optunal, acetamiprid, and fenamithion).

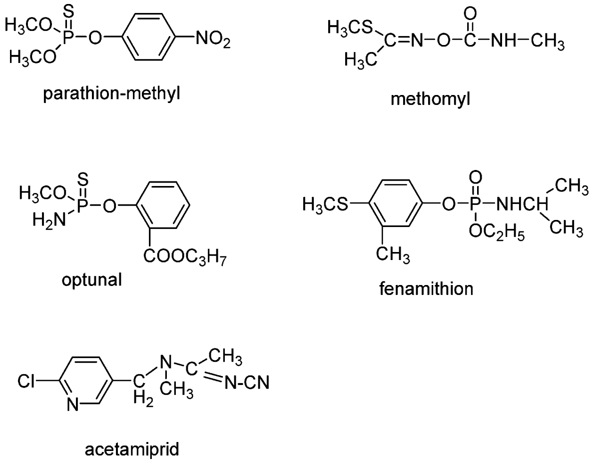

Figure 9. The chemical structures of pesticides investigated.

in water. Yet for SiO_2/CdTe NPs, all pesticides have very little effect. It is rational that C[4] plays an important role in selective luminescence response to methomyl. It is known that the well-defined structure of the calixarene cavities can be exploited for the inclusion of organic guests. However, the cavity of C[4] is not sufficiently large enough to accommodate bulk aromatic pesticides excluding a small linear molecule like methomyl, which results in the selective FL response to methomyl.[20]

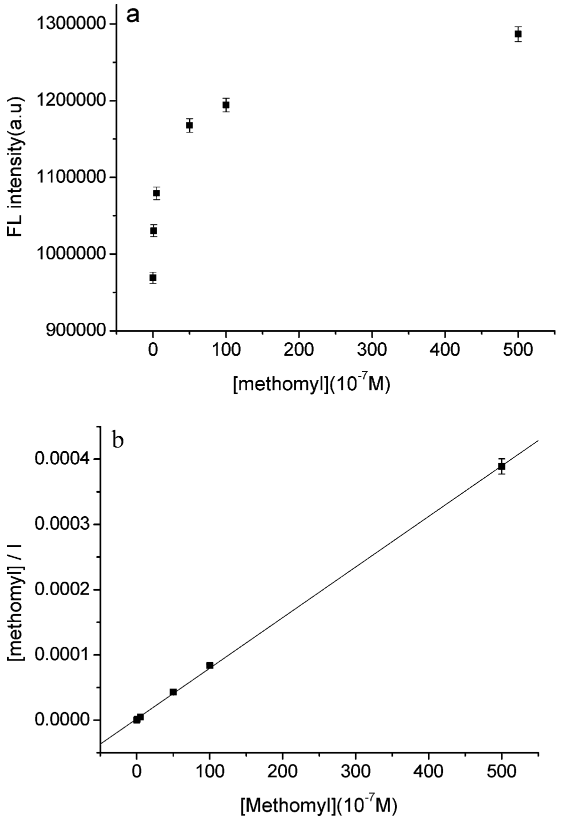

Figure 10. (a) Effect of methomyl concentration on the FL intensity of C[4]/SiO_2/CdTe NPs. (b) Langmuir binding isotherm description of the data showing a linear fit throughout the methomyl concentration range, with a binding constant of 0.41 and a correlation coefficient >0.999.

As can be seen in Figure 10, the FL emission is progressively enhanced at a concentration of 0.1−50 μM by the addition of methomyl. However, if the concentration of methomyl reaches 100 μM, the FL intensity is decreased. The detection limit, calculated following the 3σ IUPAC criteria, is 0.08 μM. The concentration dependence of FL intensity follows the binding of methomyl to the cavity of the C[4] on the surface of C[4]/SiO_2/CdTe NPs and is effectively described by a Langmuir-type binding isotherm.[24] The FL intensity is increased with increasing methomyl concentration. According to the Langmuir equation, the surface of the NPs consists of a finite number of binding sites. Each of the binding sites can absorb one pesticide from the solution.

The fraction of occupied sites is defined as θ. The rate of binding of pesticides to the surface is proportional to the pesticide concentration C in the analyte solution and to the fraction of available binding sites $1 - \theta$. The rate of binding, R_b, of pesticide to the surface is expressed as

$$R_b = K_b C(1 - \theta) \tag{1}$$

The rate of desorption of bound pesticide from the surface depends only on the fraction of occupied binding sites and is expressed as

$$R_d = K_d \theta \tag{2}$$

The rate of binding is equal to the rate of desorption at equilibrium

$$K_d \theta = K_b C(1 - \theta) \tag{3}$$

The equation can be solved for θ as a function of the ratio $B = K_b/K_d$.

$$\theta = (BC)/(1 + BC) \tag{4}$$

The fraction of occupied binding sites, θ, is related to the ratio between the signal obtained at given pesticide concentration I and the maximum intensity I_{max}.

$$\theta = I/I_{max} \tag{5}$$

Therefore, an expression that related the pesticide concentration, C, to the signal intensity can be written as

$$I/I_{max} = (BC)/(1 + BC) \tag{6}$$

This equation can be linearized to take the form

$$C/I = (1/BI_{max}) + (1/I_{max})C \tag{7}$$

Accordingly, if the Langmuir description of the binding of methomyl on the surface of the C[4]/SiO_2/CdTe NPs is correct, a plot of C/I as a function of C should be linear. The dependence of C/I as a function of C, where C is the methomyl concentration and I is the FL intensity of the C[4]/SiO_2/CdTe NPs at given methomyl concentrations, is shown in Figure 10b. A relative linearity is observed throughout the entire range of methomyl concentration. The binding constant B is found to be 0.41, and the coefficient of the linear fit is higher than 0.999. The remarkable Langmuirian fit suggests that the probability of binding more than one methomyl to the surface of an individual NPs, which is imperative for aggregation or non-Langmuir binding isotherm due to island formation, is negligible under the experiment conditions.

The observed luminescence emission enhancement at the concentration 0.1−50 μM of methomyl may be correlated to the structural changes of the calixarene-group shell surrounding the NPs core upon intercalation, which may result from the generation of a new and efficient radiative path involving the bound methomyl and/or from the suppression of a nonradiative process. When adding methomyl to the C[4]/SiO_2/CdTe NPs, the methomyl intercalation restricts the calixarene-cavity distort, which induces a uniform arrangement. Such ordered orientation and/or enhanced conformational rigidity of the surface substituents may suppress the quenching path to the medium by effective core protection and thus increase the luminescence intensity.[25] A similar mechanism might be involved in the present case. With respect to the possibility, we propose recently that the cluster emission is enhanced when the free motion (rotation) of the surface substituents is suppressed,[26] as illustrated schematically in Figure 11. However, when the concentration

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(25) For an analogous phenyl-capped CdS cluster, increase of the luminescence intensities upon lowering temperature has been reported: Herron, N.; Suna, A.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **1992**, 2329.

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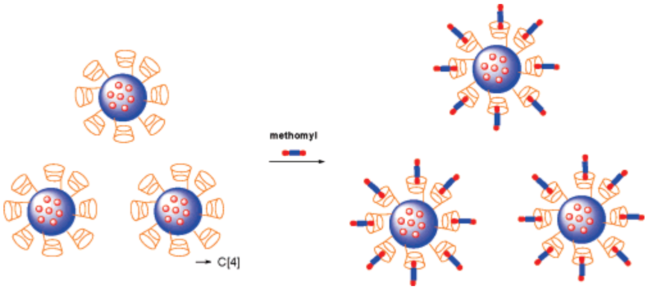

Figure 11. Schematic illustration of a possible structure of the C[4]/SiO_2/CdTe NPs-methomyl.

of methomyl reaches 100 μM, the FL intensity is decreased, which may be caused by the formation of the network structure and induced aggregation.[27]

Conclusion

Highly luminescent and stable CdTe quantum dots in sol−gel-derived composite silica spheres coated with C[4] are prepared via the sol−gel technique in aqueous media. The FL intensity of C[4]/SiO_2/CdTe is increased as compared to its precursor SiO_2/CdTe. Also, its quantum yield is up to 15%, which is higher than that of SiO_2/CdTe NPs. The synthesized NPs are employed as a novel and highly sensitive luminescence probe for optical recognition of methomyl. Enhancement of the luminescence emitted by the synthesized nanoparticles allows the determination of methomyl as low as 0.08 μM. In view of sensitivity and selectivity, they thus afford a very sensitive detection system for pesticides analysis. Furthermore, molecular recognition of calixarene modified core−shell NPs is in progress in our laboratory, which should spark a broad spectrum of interest due to its great versatility and flexibility for future applications.

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Supporting Information Available: Size distribution and photostability of SiO_2/CdTe NPs and C[4]/SiO_2/CdTe NPs. Structure of C[4] and effect of pH on luminescence response of CdTe QDs, SiO_2/CdTeNPs, and C[4]/SiO_2/CdTe NPs (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Chen, Y. F.; Rosenzweig, Z. *Anal. Chem.* **2002**, *74*, 5132.