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Molecularly Imprinted Polymer Nanospheres based on Mn-doped ZnS QDs via a precipitation polymerization for room-temperature phosphorescence probing of 2,6-Dichlorophenol

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ABSTRACT

In this paper, a novel molecularly imprinted polymers (MIPs) based on Mn doped ZnS quantum dots (QDs) with molecular recognition ability was successfully synthesized by precipitation polymerization using 2,6-Dichlorophenol (2,6-DCP) as template, methacrylic acid (MAA) as the functional monomer and ethyl glycol dimethacrylate (EGDMA) as the cross-linker. The obtained materials (MIPs-ZnS:Mn QDs), which were composed of Mn doped ZnS QDs as phosphorescence signal and MIPs as molecular selective recognition sites, could sensitively and selectively recognize the template molecules by using the spectrofluorometer. After the experimental conditions were optimized, a linear relationship was obtained covering the linear range of 1.0-56 μmol L^{-1} with a correlation coefficient of 0.9994. The developed method was applicable to routine trace determination of 2,6-DCP in real examples. And this study provides a general strategy to fabricate MIPs-coated QDs with excellent performance and is desirable for chemical sensor application.

Keywords: Mn-doped ZnS quantum dots, Room Temperature Phosphorescence, Molecularly imprinted polymers, 2,6-Dichlorophenol, Selective recognition.

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1 Introduction

In recent years, quantum dots (QDs) have attracted extensive attention and application in the scientific community due to the unique optical and electronic properties, such as narrow and symmetric emission, broad excitation and excellent photostability. [1, 2] In particular, QDs have been widely used as probes for detecting different kinds of analytes including ions[3], small molecules[4], and biological macromolecule[5, 6]. To our knowledge, most of the detection methods are based on the fluorescence properties, and there are only a few studies on using of the phosphorescence properties. Room temperature phosphorescence (RTP) as an effective detection mode has become a hotspot due to its fascinating advantages over fluorescence. [7, 8] The QDs with phosphorescence have longer lifetime, which can allow an appropriate delay time and avoid the interferences from autofluorescence and scattering light. [9, 10] It is for this reason that RTP QDs detection shows very famous reliability. Therefore, the RTP detections based on QDs is a topic of great interest.

Molecular imprinting is an attractive technique for synthesizing polymer materials with specific recognition sites. The synthetic polymer materials, known as molecularly imprinted polymers (MIPs), are synthesized by the copolymerization of function monomers and a cross-linker in the presence of template molecules. After the template molecules are removed from the polymer matrixes, the binding sites with complementary size and shape of functionalities are obtained.[11] Due to their high specific selectivity and stability, MIPs have been widely used in various significant applications, such as sensors,[12] separation,[13] drug delivery,[14] and catalysis. [15] In recent years, surface molecular imprinting technique has become one of a hot research at home and abroad. Compared with the traditional method, this technique can provide a practical way to improve mass transfer, rebinding percentage and selectivity.[16] Recently, a novel kind of MIPs-based RTP materials (QDs) as efficient sensors have been reported, which integrated the merits of the excellent RTP property of QDs and high selectivity of surface molecular imprinting technology.[7, 9, 17, 18] For now, most of MIPs-based RTP QDs composites were using silica as the matrices, such as MIPs (silica)/ZnS QDs for domoic acid and MIPs (silica)/ZnS QDs for pentachlorophenol.[7, 9] Meanwhile, a report used polymer as the matrices using a surface graft copolymerization in aqueous media for proteins.[18] Therefore, more novel strategies and methods for fabricating MIPs-based RTP materials (QDs) are required.

Chlorophenols (CPs), as a group of phenolic compounds, have been widely used in pharmacy, pesticide and herbicide.[19] The presence of CPs in the environment is of particular concern due to their high toxicities and most aquatic organisms.[20] Due to its bad impact on the environment, CPs have been listed by the U.S. Environmental Protection Agency (U.S.EPA) as priority environmental pollutants.[21] Thus, the detection of CPs from complex matrix is of great importance. To date, there have been a lot of methods reported such as Gas Chromatography Mass Spectrometry (GC–MS) [22], high performance liquid chromatography (HPLC) [23], capillary electrophoresis [24], capillary electrochromatography[25] and thin-layer chromatography[26] for the determination of CPs. However, the shortcomings of these methods are: time consuming, expensive reagents and tedious sample pretreatment. Therefore, the development of simple, rapid and selective CPs detecting methods presents a challenge.

The objective of this work is to develop a new and eco-friendly type of optical composite material combining the merits of molecular technology and phosphorescence property of Mn-doped ZnS QDs for specific recognition of target 2,6-Dichlorophenol (2,6-DCP, one of CPs). The vinyl modified Mn-doped ZnS QDs was used as the optical material and the core substrate. The uniform imprinted polymers was grafted onto the surface of vinyl modified Mn-doped ZnS QDs by precipitation polymerization. This imprinting layer was obtained using 2,6-DCP as the template, methacrylic acid (MAA) as the functional monomer, 2,2'-azobisisobutyronitrile (AIBN) as the initiator and ethyl glycol dimethacrylate (EGDMA) as the cross-linker. The MIPs coated ZnS:Mn QDs were characterized by transmission electron microscope (TEM), scanning electron microscope (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The RTP quenching relationship between 2,6-DCP and MIPs-ZnS:Mn QDs was investigated. This proposed RTP artificial sensor (MIPs-ZnS:Mn QDs) aims to offer a simple, rapid and selective sensing system for detecting 2,6-DCP in real samples.

2 Experimental

2.1 Reagents and chemicals

All chemicals were of analytical grade reagents. $ZnSO_4 \cdot 7H_2O$, $MnCl_2 \cdot 4H_2O$, $Na_2S \cdot 9H_2O$, 3-(methacryloyloxy)propyl trimethoxysilane (KH-570), methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), 2,2'-azobis (2-methylpropionitrile) (AIBN), 2,6-Dichlorophenol (2,6-DCP), 2,4-Dichlorophenol (2,4-DCP), 2,4,5-Trichlorophenol (2,4,5-TCP) and 2,4,6-Trichlorophenol (2,4,6-TCP) were all purchased from Aladdin reagent Co., Ltd. (Shanghai, China). Dry toluene, methanol, ethanol and acetonitrile were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Double distilled water (DDW) was used throughout the experimental procedures.

2.2 Instrument

The morphology and structure of prepared samples were observed by transmission electron microscope (TEM, JEOL, JEM-2100) and scanning electron microscope (SEM, JEOL, JSM-7001F). Infrared spectra (4000–400 cm^{-1}) in KBr were recorded using Nicolet NEXUS-470 FTIR apparatus (USA). The X-ray diffraction (XRD) spectra were collected on a XRD-6100Lab X-ray diffractometer (Shimadzu, Japan) with Cu Kα radiation over the 2θ range of 10-80°. The phosphorescence measurements were performed on a Cary Eclipse spectrofluorometer (USA) equipped with a plotter unit and a quartz cell (1.0 cm × 1.0 cm).

2.3 Synthesis and Functionalization of Mn-Doped ZnS QDs.

Mn-Doped ZnS QDs in aqueous solution were synthesized according to previous reports with minor modification.[9, 17] In a typical synthesis, $ZnSO_4$ (6.25 mmol), $MnCl_2$ (0.5 mmol), and 20 mL of water was mixed in a three-necked flask. After stirring at room temperature for 20 min, a 5.0 mL, 6.25 mmol of Na_2S solution was injected. Then the mixture was kept stirring overnight. Finally the resultant Mn-doped ZnS QDs was obtained following centrifugation, washing with absolute ethanol and DDW three times and drying in vacuum oven at 60 ^{o}C overnight.

The surface of Mn-Doped ZnS QDs was endowed with reactive vinyl groups through modification with KH-570. Briefly, 0.5 g of the obtained Mn-Doped ZnS QDs and 2.0 mL of KH-570 were dispersed into 100 mL of dry toluene and then vigorously stirred under N_2 at 90 °C for 12 h. The products were collected and washed with toluene and ethanol several times. At last, the vinyl-modified Mn-Doped ZnS QDs (KH-570-ZnS:Mn QDs) were dried under vacuum for further use.

2.4 Molecular Imprinting of 2,6-DCP at the Surface of KH-570-ZnS:Mn QDs

The 2, 6-DCP-imprinted polymer layer on the surface of KH-570-ZnS:Mn QDs were prepared via in situ precipitation polymerization. MAA and EGDMA were used as a functional monomer and cross-linking agent, respectively. Typically, 2,6-DCP (0.1 mmol), methacrylic acid (0.4 mmol) and EGDMA (1.6 mmol) were dissolved in acetonitrile (60 mL) to self-assemble at room temperature. 50 mg of KH-570-ZnS:Mn QDs were dispersed into the above solution by ultrasonication. Then AIBN (10 mg) as the initiator was added. This mixture was purged with nitrogen for 30 min. Finally, a two-step polymerization was carried out in a constant temperature bath oscillator with the rotation rate of 200 rpm. The slow prepolymerization was first undertaken at 50 ^{o}C for 6 h, and the normal polymerization was completed at 60 ^{o}C for 24 h. After the polymerization reaction, the resulting MIPs-ZnS:Mn QDs were collected by centrifugation and washed with acetonitrile and ethanol several times to remove the unreacted monomers. The size and morphology of the MIPs-ZnS:Mn QDs were controlled by changing the amount of ZnS:Mn QDs and varying the total amount of polymeric monomers (MAA and EGDMA). The template 2,6-DCP in the MIPs was extracted with a mixture solvent of methanol and acetic acid (9 : 1, v/v). The nonimprinted polymer (NIPs-ZnS:Mn QDs) were also prepared under the same conditions but without addition of 2,6-DCP.

2.4 Measurement Procedure.

All the RTP detections were performed under the same conditions: the excitation wavelength was set at 320 nm with a recording emission range of 500-700 nm, and the slit widths of the excitation and emission were both 10 nm. The photomultiplier tube voltage was set at 670 V. MIPs-ZnS:Mn QDs and NIPs-ZnS:Mn QDs were dispersed in DDW to get the fresh-made stock solution (200 mg/L). 2,6-DCP stock solution (1 mmol/L, in DDW) was stocked at 4.0 ^{o}C. An appropriate quantity of MIPs-ZnS:Mn QDs and NIPs-ZnS:Mn QDs was added to a 5.0 mL colorimetric tube and a given concentration of analyte standard solution was added sequentially.

3 Results and discussion

3.1 Preparation and Characterization of MIPs-ZnS:Mn QDs

Figure 1 illustrates the principle to synthesize MIPs-ZnS:Mn QDs. Firstly, Mn doped ZnS QDs were synthesized via a simple and practicable method at room temperature. Then, the Mn doped ZnS QDs were functionalized with KH-570 via a simple silanization reaction to form polymerizable vinyl groups. Subsequently, the precipitation polymerization was chosen as a beneficial and appropriate route to form the structural polymers on the KH-570-ZnS:Mn QDs. As shown in Figure 1, 2,6-DCP was used as the template molecule to involve in the formation of the imprinted polymer on the surface of ZnS QDs. In the presence of functional monomer (MAA), initiator (AIBN) and cross-linking agents (EGDMA), the 2,6-DCP@MIPs-ZnS:Mn QDs were formed by a two-step polymerization via the slow prepolymerization at 50 ^{o}C and the normal polymerization at 60 ^{o}C. After the templates were removed from the imprinted polymers with solvent extraction, the MIPs-ZnS:Mn QDs were obtained and the generated recognition sites could selectively rebind the template molecules owing to the wonderful compatibility of size, shape and chemical interactions.

Figure 1 Schematic procedure for preparation of MIPs-ZnS:Mn QDs

The thickness of the imprinted polymer plays a very important role because it influences RTP intensity and removal of the templates. In this study, a common mole ratio of template/monomer/cross-linker =1:4:16 was used. On this basis, the size of MIPs-ZnS:Mn QDs could be controlled by two factors: the quantity of the ZnS QDs and the total amount of monomers. When the total amount of monomers was fixed, three kinds of RTP imprinted materials (P1-P3) differing in the quantity of the KH-570-ZnS:Mn QDs were prepared. The detailed compositions of the studied materials (P1-P3) are summarized in Table 1. The structures of the imprinted polymers were evaluated with TEM and SEM. The images of TEM and SEM were recorded to evaluate the property of the imprinted polymers. The TEM and SEM images for different imprinted polymers (P1-P3) are shown in Figure 2. As shown in Figure 2, it could be found that both of the imprinted polymers consisted of spheroidal particles. When 50 mg KH-570-ZnS:Mn QDs and 2.0 mmol polymerization precursors were used, the imprinted microsphere polymers with a diameter of 200 nm (P1) were obtained (Figure2a, b). As the amount of the KH-570-ZnS:Mn QDs increased to 150 mg, we could see from Figure 2c,d that the diameter of the imprinted polymers was about 100 nm (P2). As the amount of the KH-570-ZnS:Mn QDs increased to 250 mg, as shown in Figure 2e, f, the diameter of the imprinted polymers was about 60 nm (P3). The sizes are listed in Table S1 in detail. As far as we know, if the imprinted polymer was too thick, the removal of templates would become difficult.[26] Therefore, P3 was selected as the optimized imprinted polymers for the further experiments. In addition, the NIPs-ZnS:Mn QDs were the same as the MIPs-ZnS:Mn QDs in size and morphology.

Table 1 Chemical composition of the studied MIPs and NIPs.

Figure 2 TEM images of different MIPs-ZnS:Mn QDs (P1:a, P2:c, P3: e) and SEM images of different MIPs-ZnS:Mn QDs (P1:b, P2:d, P3: f)

The formation of Mn-doped ZnS QDs could be confirmed by wide angle X-ray diffraction characterization. Figure 3a showed the X-ray diffraction patterns of the Mn-doped ZnS QDs (curve 1), KH-570-ZnS:Mn QDs (curve 2) and MIPs-ZnS:Mn QDs (curve 3). The crystal structures of the three samples exhibited cubic zinc blende with peaks indexed as (111), (220), and (311) planes. The XRD pattern of KH-570-ZnS:Mn QDs and MIPs-ZnS:Mn QDs was similar to that of Mn-doped ZnS QDs, indicating that the surface modification and coating of polymer layer did not change the crystalline structure of Mn-doped ZnS QDs. The intensities of the (111), (220), and (311) diffraction peaks of MIPs-ZnS:Mn QDs were weaker than that of KH-570-ZnS:Mn QDs and Mn-doped ZnS QDs due to the imprinted polymer shell coated the quantum dots.

Figure 3 X-ray diffraction patterns (a) of ZnS:Mn QDs (1), KH-570-ZnS:Mn QDs (2) and MIPs-ZnS:Mn QDs (3), and FT-IR spectra (b) of ZnS:Mn QDs (1), KH-570-ZnS: Mn QDs (2), MIPs-ZnS:Mn QDs (3) and NIPs-ZnS:Mn QDs (4).

The FT-IR spectra of Mn-doped ZnS QDs (curve 1), KH-570-ZnS:Mn QDs (curve 2), MIPs-ZnS:Mn QDs (curve 3) and NIPs-ZnS:Mn QDs (curve 4) were shown in Figure 3b. To our knowledge, the peak at 620 cm^{-1} belonged to the ZnS QDs corresponding to sulfuret and the width peak between 3000 and 3700 cm^{-1} and the characteristic peak at 1614 cm^{-1} are observed due to O–H vibration of water.[9, 28] After the modification of KH570, as shown in Figure 5(curve 2), there came new absorptions at 1617 cm^{-1}, 1718 cm^{-1} and 550-850 cm^{-1}, which might attribute to C=C stretching mode, C=O stretching vibration and C-Cl vibration of KH570 respectively.[29] This phenomenon indicated that the surface of the Mn-doped ZnS QDs was successfully endowed with reactive vinyl groups through modification with KH570. As shown in Figure 5(curve 3 and curve 4), the MIPs-ZnS:Mn QDs and NIPs-ZnS:Mn QDs showed similar locations and appearance of the major bands. The peak around 2968 cm^{-1} was C–H band, and the absorption band at 3440 cm^{-1} (O–H stretching) of the polymers could be attributed to MAA molecules. The two characteristic peaks at 1730 cm^{-1} (C=O stretching) and 1100-1200 cm^{-1} (C−O−C stretching) confirmed the presence of EGDMA in the polymers.[30] All those bands showed that the MIPs was grafted on the surface of the ZnS QDs.

3.2 Addition of MIPs-ZnS:Mn QDs

The addition of MIPs-ZnS:Mn QDs from 6.0 mg/L to 18 mg/L was used to investigate the effects on the 2,6-DCP detection system. Both linear range and detection sensitivity were important for the analyze method of the RTP detection system. The change rate of RTP intensity [$(P_0 - P)/P_0$] (P_0 and P represent for the RTP intensity before and after adding 2,6-DCP into the system) determined the analysis sensitivity; meanwhile, high RTP intensity of MIPs-ZnS:Mn QDs could obtain wide linear range.[31] As shown in Figure 4, when the concentration of MIPs-ZnS:Mn QDs was low, a little amount of 2,6-DCP could lead to obvious phosphorescence quenching, and high sensitivity could be obtained with a narrow linear range; when the MIPs-ZnS:Mn QDs was in higher levels, RTP intensity was increased, while the phosphorescence quenching rate was relatively small. As a result, a concentration of 12 mg/L was chosen for the detection of 2,6-DCP.

Figure 4 Effects of the addition of MIPs-ZnS:Mn QDs on RTP intensity. Curve a: the function of variation rate of RTP intensity of detection system (containing MIPs-ZnS:Mn QDs + 16 µmol/L 2,6-DCP) vs. addition of MIPs-ZnS:Mn QDs; Curve b: the function of relative RTP intensity vs. addition of MIPs-ZnS:Mn QDs

3.3 Stabilities

The RTP stability of MIPs-ZnS:Mn QDs was estimated by RTP intensity as a function of time at room temperature. As shown in Figure 5a, the RTP stability of MIPs-ZnS:Mn QDs was stable for 7.0 times measurements within 1.0 h. The maintained RTP intensity within 1.0 h may well be because the ZnS:Mn QDs were well protected by the polymer shell of the MIPs and the composite had an excellent stability.

3.4 Detection time

In order to determine the optimal detection time of the RTP quenching procedure, a certain amount of 2, 6-DCP (16 μmol L^{-1}) was mixed with MIPs-ZnS:Mn QDs (12 mg L^{-1}). The RTP intensities were recorded at different interval time and the results were shown in Figure 5b. It was found that the RTP intensity decreased at the initial beginning, when time was up to 50 min, the RTP intensity was almost the same. As a result, the MIPs-ZnS:Mn QDs had a good and steady response rate for 2, 6-DCP, and 50 min was selected as the optimal detection time for the following experiments.

Figure 5 Stabilities of MIPs-ZnS:Mn QDs (a) and effect of time on RTP intensity (Experiment condition: MIPs-ZnS:Mn QDs, 12 mg L^{-1}; 2, 6-DCP, 16 μmol L^{-1}) (b).

3.5 MIPs-ZnS:Mn QDs and NIPs-ZnS:Mn QDs with template 2,6-DCP of different concentrations.

Under the optimal conditions, this research used MIPs-ZnS:Mn QDs as the optical material to detect 2,6-DCP based on the RTP quenching between ZnS:Mn QDs and the target molecule. The test was implemented in a colorimetric tube with water after incubation target 2,6-DCP with MIPs-ZnS:Mn QDs for 50 min at room temperature, and NIPs-ZnS:Mn QDs were used as a contrast. Figure 6a and 6b showed the spectral response of MIPs-ZnS:Mn QDs and NIPs-ZnS:Mn QDs with template 2,6-DCP at different concentrations, respectively. The RTP quenching followed the Stern-Volmer equation[32, 33]:

$$P_0/P=1+K_{sv}[c] \qquad (1)$$

P and P_0 are the RTP intensities of the MIPs-ZnS:Mn QDs and NIPs-ZnS:Mn QDs in the absence and presence of the template 2,6-DCP, respectively. K_{SV} is the Stern-Volmer constant, and [c] is the concentration of 2,6-DCP. The equation was applied to quantify the different quenching constants in this study, and the ratio of $K_{SV,MIP}$ to $K_{SV,NIP}$ was defined as the imprinting factor (IF). It was found from Figure

6c and 6d that the RTP intensities of the MIPs-ZnS:Mn QDs and NIPs-ZnS:Mn QDs decreased linearly with the increase of the concentrations of 2,6-DCP. As shown in Figure 6c, the $K_{SV,MIP}$ was found to be 46560 M^{-1} and the linear range of the calibration curve was 1.0-56 μmol L^{-1} with a correlation coefficient of 0.9994. On the other hand, it could be found from Figure 9d that the $K_{SV,NIP}$ was 7380 M^{-1}, the linear range of 2,6-DCP was also 1.0-56 μmol L^{-1} but with a correlation coefficient of 0.9983. Under this condition, the imprinting factor was 6.309, indicating that the MIPs-ZnS:Mn QDs had a better selectivity than the NIPs-ZnS:Mn QDs. In addition, the detection limit (3σ/k) was 0.23 μmol/L, in which k is the slope of the calibration line and σ is the standard deviation of blank measurements (n = 10).

Figure 6 RTP emission spectra of MIPs-ZnS:Mn QDs (a)and NIPs-ZnS:Mn QDs (b) (12 mg/L) with addition of the indicated concentrations of 2,6-DCP in water solution and the Stern−Volmer plots for MIPs-ZnS:Mn QDs (c)and NIPs-ZnS:Mn QDs (d).

Much excellent work about MIPs-ZnS:Mn QDs has been reported and some were summarized and compared with this present work, with the characteristics and conclusions are listed in Table 2. It can be found that most common route for MIPs-ZnS:Mn QDs is a sol-gel reaction that employs 3-aminopropyltriethoxysilane (APTES) as the functional monomer and tetraethoxysilane (TEOS) as the cross-linker. The step-growth polymerization of TEOS with APTES could anchor the QDs to the silica monoliths and interact with template molecules to form the imprinted cavities. The surface graft copolymerization was also used to prepare MIPs-ZnS:Mn QDs for proteins in aqueous media. Compared with these reported literatures, a two-step precipitation polymerization method was used to prepare MIPs-ZnS:Mn QDs in this work. The proposed methodology possesses the same superior detection limit and linear range. In addition, the obtained MIPs-ZnS:Mn QDs integrated the advantages of the excellent RTP property of the ZnS QDs and high selectivity of the molecular imprinted polymers.

Table 2 Comparison between present method and literature

3.6 Selectivity.

Several kinds of phenols structurally related to 2,6-DCP (namely, 2,4-DCP, 2,4,5-TCP and 2,4,6-TCP) were involved to evaluate the selectivity of the MIPs-ZnS:Mn QDs. As shown in Figure 7, MIPs-ZnS:Mn QDs had a strong response to 2,6-DCP, which caused a significant change of RTP intensity with a high quenching amount. And the changes in RTP intensity of the MIPs based on ZnS QDs for 2,6-DCP were more obvious than other phenols. By calculation, the difference in the quench amount ($P_0/P-1$) of MIPs-ZnS:Mn QDs and NIPs-ZnS:Mn QDs were 2.2079, 0.3885, 0.15127, 0.069 at 56 μmol L^{-1} for 2,6-DCP, 2,4-DCP, 2,4,5-TCP and 2,4,6-TCP, respectively. The results suggested that MIPs-ZnS:Mn QDs were specific to 2,6-DCP but nonspecific to other phenols and there was no selective recognition sites in the NIPs-ZnS:Mn QDs. This result can be reasonably explained as follows: In the process of synthesis of the MIPs-ZnS:Mn QDs, many specific imprinted cavities with the memory of the template 2,6-DCP were generated and the template could be bound strongly to the imprinted particles and cause changes in the RTP intensity.

Figure 7 Quenching amount of MIPs-ZnS:Mn QDs and NIPs-ZnS:Mn QDs by different kinds of 56 μmol L^{-1} chlorophenols (2,6-DCP, 2,4-DCP, 2,4,5-TCP, 2,4,6-TCP).

3.7 Analytical applications in Yangtze River sample

To demonstrate the applicability of this proposed method, MIPs-ZnS:Mn QDs were utilized for 2,6-DCP detection in water samples which were collected from Yangtze River. The samples were filtered through 0.45 μm Supor filters and stored in precleaned glass bottles. As no phenols in Yangtze River samples were detectable, a recovery study was carried out by using two methods: one is the RTP analysis, the other is ultraviolet analysis as a reference method. The experiment results are shown in Table 3. It was found that the detect results of RTP quenching method were more sensitivity and accurate than that of UV method, but the stability was less. The results showed a good accordance between the two methods. The values determined by the MIPs-ZnS:Mn QDs show the optical and selective recognition ability to provide accurate measures of 2,6-DCP concentrations on unknown environmental samples. Therefore, the MIPs-ZnS:Mn QDs could be regarded as an optional scheme for the direct analysis of relevant real samples.

. Table 3 Recovery of 2,6-DCP in Yangtze River sample with 2,6-DCP solution at different concentration levels (n= 5)

4 Conclusion

In summary, a facile and versatile strategy was explored for the preparation of the MIPs-ZnS:Mn QDs that possessed Mn doped ZnS QDs as the phosphorescence species for selective recognition of a target phenol (2,6-DCP). The MIPs-ZnS:Mn QDs integrated the advantages of the excellent RTP property of the ZnS QDs and high selectivity of the molecular imprinted polymers. Under optical conditions, the MIPs-ZnS:Mn QDs had a strong response to 2,6-DCP, which caused a significant change of RTP intensity with a high quenching amount. And the results indicated that the MIPs-ZnS:Mn QDs had good selectivity for template 2,6-DCP over other phenols. Furthermore, the proposed RTP analyze method with MIPs-ZnS:Mn QDs can successfully provide a simple, direct and selective detection of 2,6-DCP in real simples.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of

China (No. 21107037, No. 21176107, No. 21174057, No. 21277063, No. 21407057 and No. 21407064), National Basic Research Program of China (973 Program, 2012CB821500), Natural Science Foundation of Jiangsu Province (No. BK20140535), Ph.D. Innovation Programs Foundation of Jiangsu Province (No. KYLX_1032), National Postdoctoral Science Foundation (No. 2014M561595), Postdoctoral Science Foundation funded Project of Jiangsu Province (No. 1401108C)

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Tables

Table 1 Chemical composition of the studied MIPs and NIPs.

Table 2 Comparison between present method and literature

Table 3 Recovery of 2,6-DCP in Yangtze River sample with 2,6-DCP solution at different concentration levels (n= 5)

Table 1 Chemical composition of the studied MIPs and NIPs.

polymers	KH-570-ZnS:Mn QDs (mg)	Template (mmol)	MAA (mmol)	EGDMA (mmol)	AIBN (mg)
P_1	50	0.1	0.4	1.6	10
P_2	150	0.1	0.4	1.6	10
P_3	250	0.1	0.4	1.6	10

Table 2 Comparison between present method and literature

synthetic methods	target object	Response mode	Linear range	LOD	Reference
sol-gel reaction	domoic acid	RTP enhancement	0.25−3.5μM	67 nM	7
sol-gel reaction	pentachlorophenol	RTP quenching	0.2–19.1μM	86 nM	9
sol-gel reaction	2,4,5-trichlorophenol	RTP quenching	5.0–50 μM	–	17
surface graft copolymerization	bovine hemoglobin	RTP quenching	0.1–5.0 μM	38 nM	18
precipitation polymerization	2,6-dichlorophenol	RTP quenching	1.0-56 μM	230 nM	This work

Table 3 Recovery of 2,6-DCP in Yangtze River sample with 2,6-DCP solution at different concentration levels (n= 5)

sample	Concentration taken(μmol/L)	Found (μmol/L)		Recovery (%)		RSD (%)	
		FL	UV	FL	UV	FL	UV
1	10	10.35	10.43	103.5	104.3	5.2	3.6
2	20	20.32	20.48	101.6	102.4	3.8	2.7
3	40	40.2	40.52	100.5	101.3	3.4	2.3

Figures

Figure 1 Schematic procedure for preparation of MIPs-ZnS:Mn QDs

Figure 2 TEM images of different MIPs-ZnS:Mn QDs (P1:a, P2:c, P3: e) and SEM images of different MIPs-ZnS:Mn QDs (P1:b, P2:d, P3: f)

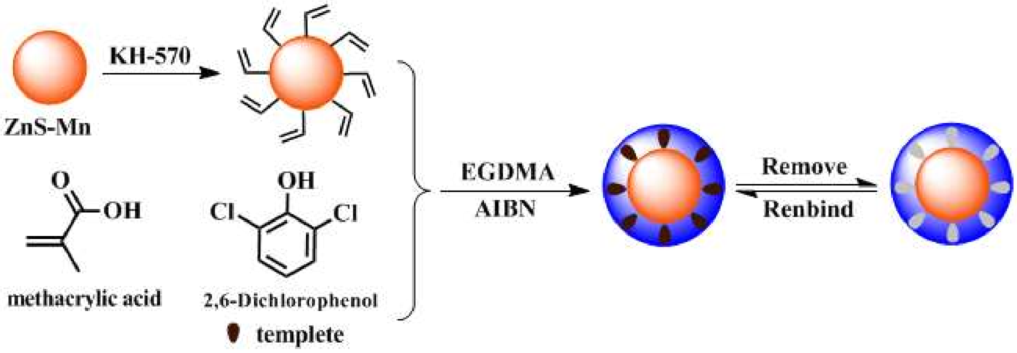
Figure 3 X-ray diffraction patterns (a) of ZnS:Mn QDs (1), KH-570-ZnS:Mn QDs (2) and MIPs-ZnS:Mn QDs (3), and FT-IR spectra (b) of ZnS:Mn QDs (1), KH-570-ZnS: Mn QDs (2), MIPs-ZnS:Mn QDs (3) and NIPs-ZnS:Mn QDs (4).

Figure 4 Effects of the addition of MIPs-ZnS:Mn QDs on RTP intensity. Curve a: the function of variation rate of RTP intensity of detection system (containing MIPs-ZnS:Mn QDs + 16 μmol/L 2,6-DCP) vs. addition of MIPs-ZnS:Mn QDs; Curve b: the function of relative RTP intensity vs. addition of MIPs-ZnS:Mn QDs

Figure 5 Stabilities of MIPs-ZnS:Mn QDs (a) and effect of time on RTP intensity (Experiment condition: MIPs-ZnS:Mn QDs, 12 mg L^{-1}; 2, 6-DCP, 16 μmol L^{-1}) (b).

Figure 6 RTP emission spectra of MIPs-ZnS:Mn QDs (a)and NIPs-ZnS:Mn QDs (b) (12 mg/L) with addition of the indicated concentrations of 2,6-DCP in water solution and the Stern−Volmer plots for MIPs-ZnS:Mn QDs (c)and NIPs-ZnS:Mn QDs (d).

Figure 7 Quenching amount of MIPs-ZnS:Mn QDs and NIPs-ZnS:Mn QDs by different kinds of 56 μmol L^{-1} chlorophenols (2,6-DCP, 2,4-DCP, 2,4,5-TCP, 2,4,6-TCP).



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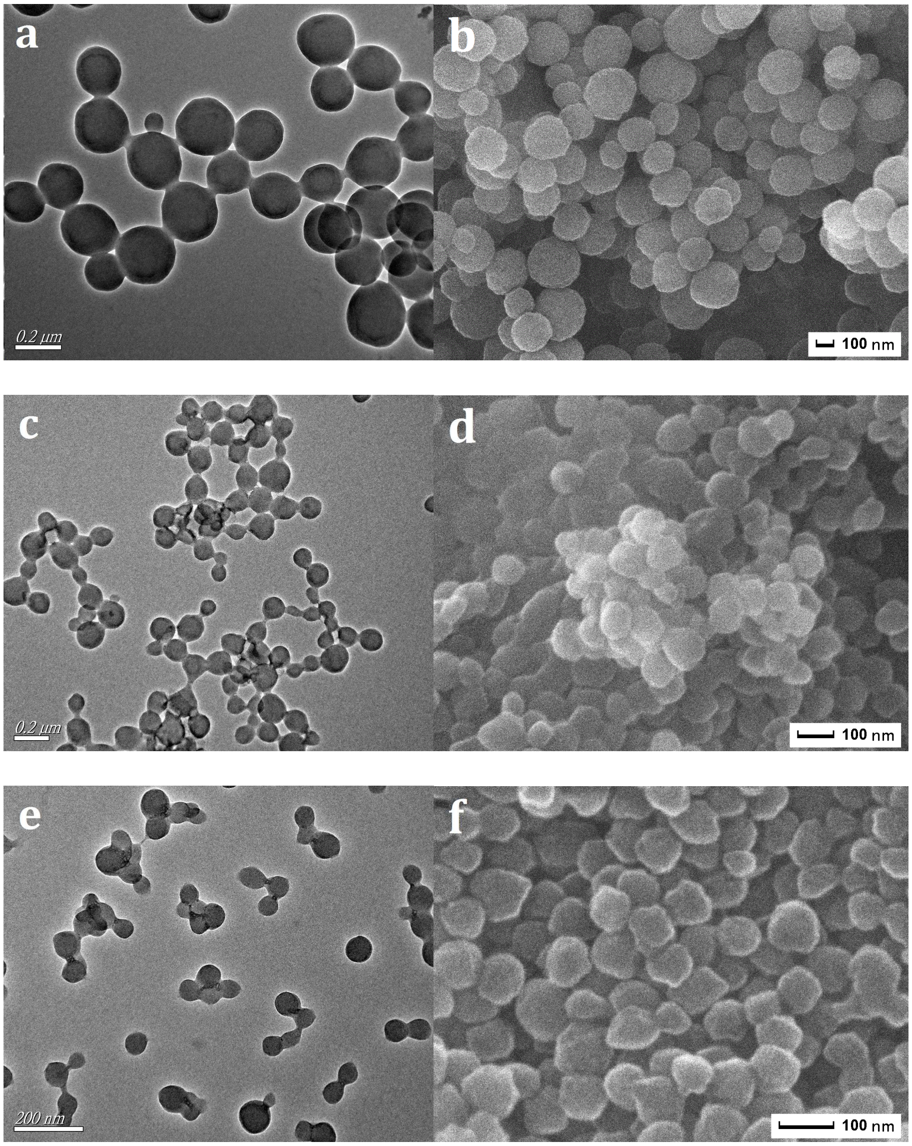

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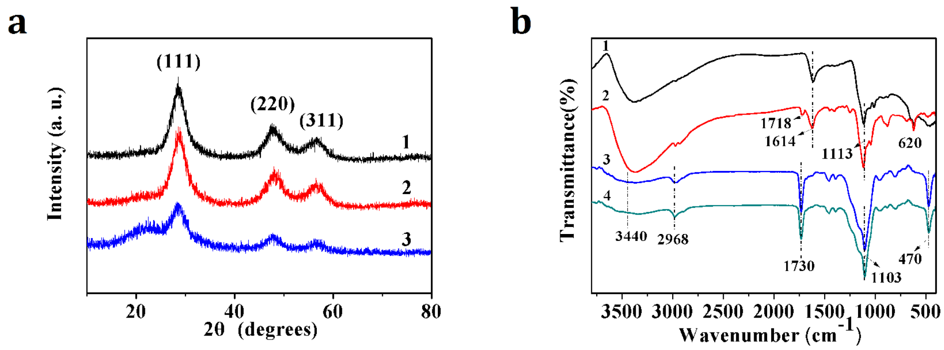

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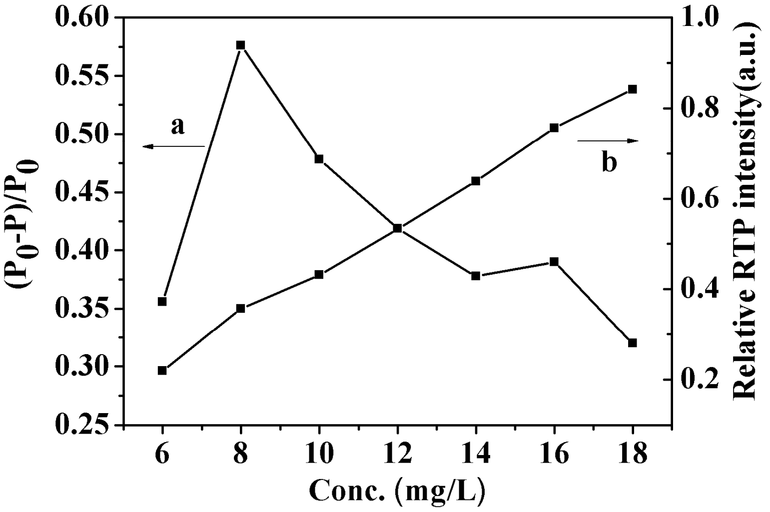

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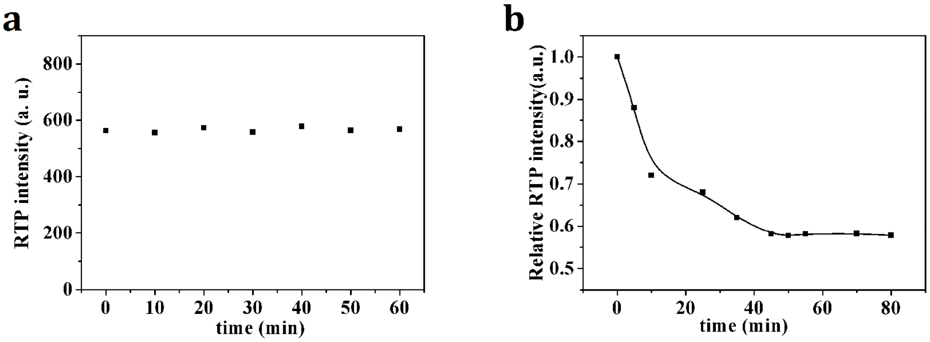

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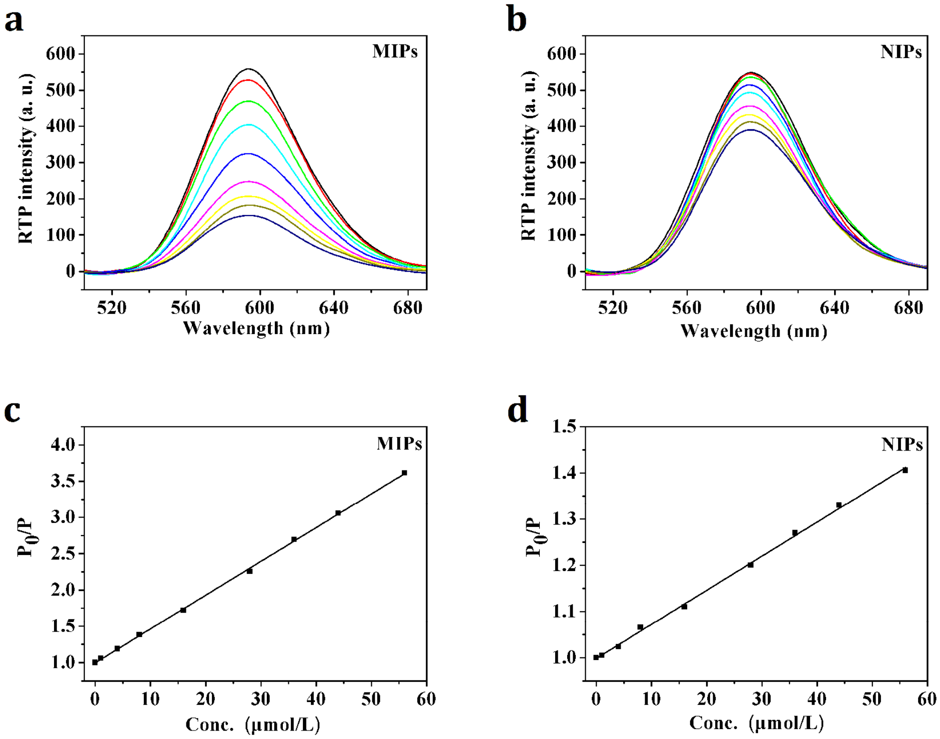

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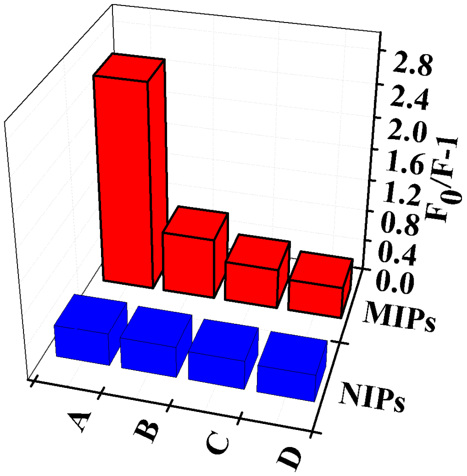

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